

# MERCURY STABILIZATION USING THIOSULFATE AND THIOSELENATE

by

Mohammad Barkat Ullah

B.Sc., Bangladesh University of Engineering and Technology (BUET), Dhaka,

Bangladesh, 2008

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF  
MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies  
(Materials Engineering)

**THE UNIVERSITY OF BRITISH COLUMBIA**

(Vancouver)

April, 2012

© Mohammad Barkat Ullah, 2012

## ABSTRACT

Mercury is commonly present with gold in nature. As a result it has a tendency to follow gold through the cyanide recovery circuit and ends up in the electro-winning cell as elemental mercury. The laws on the sale and international transport of this mercury are changing. Ultimately, it appears that it will be necessary to stabilize and dispose in a stable form. Mercury sulfide (HgS) and mercury selenide (HgSe) have significantly lower solubilities. The concept of using a thiosulfate dissolution/precipitation method to stabilize mercury as mercury sulfide has been investigated. Comparing the solubilities of mercury sulfide and mercury selenide, mercury selenide is much less soluble. For this reason, the second idea in this thesis is to use sodium thioselenate as a source of selenium in mercury solution to produce mercury selenide.

To pursue this project, mercury analysis, mercury leaching and mercury precipitation tests were performed at different temperatures and solution conditions. The resulting solutions were analyzed by Atomic Absorption Spectroscopy (AAS) and the solid precipitates were analyzed by X-ray Diffraction. The EDTA titration method for mercury analysis is effective for a simple mercury nitrate solution. If sodium thiosulfate was added in the solution, thiosulfate interfered with the solution and the titration method was not effective. As a result the AAS method was adopted.

Red mercury sulfide can be precipitated by simple aging of mercury thiosulfate solution. Parameters such as temperature, pH and thiosulfate concentration have an effect on the rate and extent of mercury sulfide precipitation. With an increase of temperature, thiosulfate concentration and at lower pH, the mercury precipitation rate increases. However at very high temperature such as 70°C and 80°C mercury precipitates as a mixture of red and black mercury sulfide.

Thioselenate synthesis was attempted from a mixture of sodium sulfite and selenium powder. The reaction between sulfite and elemental selenium was too slow to be useful.

The environmental stability of the mercury sulfide precipitates produced from thiosulfate solutions was investigated. Solid Waste Disposal Characterization (SWDC) tests were done to

check the precipitation limit for land disposal and Resource Conservation and Recovery Act (RCRA).

## TABLE OF CONTENTS

<b>ABSTRACT</b> .....	<b>ii</b>
<b>TABLE OF CONTENTS</b> .....	<b>iv</b>
<b>LIST OF TABLES</b> .....	<b>vii</b>
<b>LIST OF FIGURES</b> .....	<b>viii</b>
<b>ACKNOWLEDGEMENTS</b> .....	<b>ix</b>
<b>DEDICATION</b> .....	<b>x</b>
<b>1 INTRODUCTION</b> .....	<b>1</b>
<b>2 LITERATURE REVIEW</b> .....	<b>3</b>
2.1 Mercury Emission Sources .....	3
2.2 Legislative Changes for Mercury .....	4
2.2.1 U.S. Regulations .....	4
2.2.1.1 Air Emissions.....	4
2.2.1.2 Land Disposals .....	5
2.2.1.3 U.S. Mercury Export Ban and Its Implications .....	7
2.2.2 European Regulations .....	8
2.2.3 Canadian Regulations.....	8
2.3 Mercury Stabilization Processes .....	9
2.3.1 Stabilization as Mercury Sulfide.....	9
2.3.2 Stabilization by Amalgams .....	10
2.3.3 Stabilization in an Insoluble Matrix.....	10
2.4 An Overview of Different Stabilization Processes.....	11
2.4.1 Mercury Stabilization as Mercury Sulfide (Bethlehem Apparatus).....	11
2.4.2 Process for Stabilization of Metallic Mercury (DELA, Germany) .....	12
2.4.3 Stabilization of Metallic Mercury Using Sulfur (STMI, Gif sur Yvettes, France) .....	12
2.4.4 Wet Process to Synthesize Mercury Sulfide .....	13
2.4.5 Sulfur Polymer Cement Stabilization and Solidification (SPSS) .....	13
2.4.6 Process for Stabilization of Mercury (ADA Technologies).....	14
2.4.7 Chemically Bonded Phosphate Ceramic Encapsulation .....	14
2.4.8 DeHgTM- Process - Nuclear Fuel Services, Inc. (NFS) .....	15
2.4.9 Amalgamation with Zinc or Copper .....	15
2.5 Mercury –Thiosulfate Chemistry .....	17
2.5.1 Thiosulfate Chemistry .....	17
2.5.2 Mercury Sulfide Chemistry .....	19

2.5.2.1 Introduction .....	19
2.5.2.2 Thermodynamic Data for Mercury Sulfide .....	19
2.5.2.3 Formation of Mercury Sulfide .....	21
2.5.2.4 Conversion between Forms of Mercury Sulfide .....	23
2.5.2.5 Stability of Mercury Sulfide .....	23
2.6 Thioselenate Chemistry .....	24
2.7 Research Objectives.....	25
<b>3 EXPERIMENTAL METHODS .....</b>	<b>26</b>
3.1 Materials .....	26
3.1.1 Mercury and Selenium Samples.....	26
3.1.2 Reagents .....	26
3.2 Experimental Apparatus.....	26
3.3 Experimental Procedures.....	28
3.3.1 Preliminary Test Work .....	28
3.3.2 Mercury Precipitation Test (at Controlled pH).....	29
3.3.3 Selenium Dissolution Test .....	30
3.4 Mercury Analysis .....	30
3.5 Solid Waste Disposal Characterization (SWDC).....	31
<b>4 RESULTS AND DISCUSSIONS.....</b>	<b>32</b>
4.1 Preliminary Experiments.....	32
4.1.1 Mercury Analysis Tests .....	32
4.1.2 Mercury Leaching Tests .....	34
4.1.3 Mercury Precipitation Tests (at Uncontrolled pH).....	35
4.2 Mercury Precipitation Tests (at Controlled pH) .....	41
4.2.1 Effect of Temperature and pH .....	41
4.2.3 Effect of Thiosulfate Concentration .....	45
4.3 Selenium Dissolution Tests .....	50
4.4 Solid Waste Disposal Characterization.....	51
<b>5 CONCLUSIONS .....</b>	<b>52</b>
<b>6 FUTURE WORKS.....</b>	<b>54</b>
<b>REFERENCES.....</b>	<b>55</b>
<b>APPENDIX .....</b>	<b>59</b>
A.1 Procedure .....	59

<i>A.2 Data Assessment and Quality Control Measures</i> .....	62
<i>A.3 Waste Management</i> .....	63

## LIST OF TABLES

Table 2.1: An Overview of Different Mercury Stabilization and Encapsulation Technologies .....	16
Table 2.2: Thermodynamics of Mercury Sulfide Formation .....	22
Table 2.3: Selenium Solubility in 1.0 M Na <sub>2</sub> SO <sub>3</sub> at Various Temperatures and Selenosulfate Formation Constants, K. ....	24
Table 3.1: Overview of Experiments with Sodium Sulfite and Selenium Powder .....	30
Table 4.1: Mercury Titration Tests at Different Conditions .....	33
Table 4.2: Observation Data for Mercury Leaching Test.....	34
Table 4.3: Overall Data for pH Changes with Time in Mercury Precipitation Tests .....	36
Table 4.4: Overall Data of Mercury Concentration with Time .....	37
Table 4.5: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Uncontrolled pH): (wt. %) .....	38
Table 4.6: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Controlled pH): (wt. %).....	44
Table 4.7: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Controlled pH): (wt. %).....	47
Table 4.8: Results of Selenium Dissolution Tests in Different Conditions .....	50
Table 4.9: Results of SWDC Tests for Mercury Precipitation .....	51
Table A.1: Lists the Limits for Universal Treatment Standards and RCRA .....	63

## LIST OF FIGURES

Figure 2.1: Eh-pH Diagram for the Aqueous Sulfur System (1M Sulfur, 25°C).....	17
Figure 2.2: Eh-pH Diagram for the Metastable Aqueous Sulfur System (1M Sulfur, 25°C) .....	18
Figure 2.3: Structure of the Thiosulfate Ion.....	18
Figure 2.4: Eh-pH Diagram for the Hg-S-H <sub>2</sub> O System at 298 K. Activities of Dissolved Hg .....	20
Figure 2.5: Metastable Eh-pH Diagram for the Hg-S-H <sub>2</sub> O System at 298 K with Activities of Dissolved Mercury and Sulfur of 0.1 and 1 Respectively .....	21
Figure 3.1: Schematic Diagram of the Experimental Setup.....	27
Figure 3.2: Diagram of the Controlled pH Experimental Setup .....	28
Figure 4.1: Mercury Leaching and Precipitation Data with Time .....	35
Figure 4.2: Rietveld Refinement Plots of Sample (a) pH 5, (b) pH 6, (c) pH 8 and (d) pH 10 .....	40
Figure 4.3: Mercury Precipitation with Time at 40°C, 50°C and 60°C for (a) pH 5 and (b) pH 6 .....	42
Figure 4.4: Mercury Precipitation with Time at 70°C and 80°C for (a) pH 5 and (b) pH 6 .....	43
Figure 4.5: Rietveld Refinement Plots of Sample (a) pH 5- 80°C, (b) pH 6- 80°C.....	45
Figure 4.6: Mercury Precipitation with Time for Different Thiosulfate Concentration at (a) pH 5 and (b) pH 6 ....	46
Figure 4.7: Rietveld Refinement Plots of Sample at 0.1M Thiosulfate (a) pH 5- 80°C, (b) pH 6- 80°C .....	48
Figure 4.8: Rietveld Refinement Plots of Sample at 0.25M Thiosulfate (a) pH 5- 80°C, (b) pH 6- 80°C .....	49

## **ACKNOWLEDGEMENTS**

I am heartily thankful to my supervisor, Dave Dreisinger, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding and appreciation of this project.

Thanks to hydro group, especially Berend Wassink and all the material engineering staff who made life easier for me. Also this work would not have been possible without the financial support of Newmont Mining Corporation.

I owe my most sincere gratitude to my parents and family for their endless support, my wife Tahmina Akter for her understanding and inspiration, and for all the loving care. Lastly, I offer my regards and blessings to all of my friends who supported me during the completion of the project.

## **DEDICATION**

‘To my parents’

## 1 INTRODUCTION

Mercury is a naturally occurring metal, and the only metallic element that is a liquid at ambient temperatures, having the appearance of a silver shiny metal. Mercury is 13.5 times heavier than water, although it is relatively volatile in the metallic state [1]. Mercury is geologically concentrated in regions associated with volcanic activity, high heat flow, and plate tectonic boundaries, and is commonly found associated with gold deposits [2]. Mercury undergoes extensive biological cycling in sediments to toxic and biologically available methylated forms and back to stable and less available sulfide complexes [3]. Mercury has long been associated with gold mining, and releases of mercury into the environment remain a concern due to its health effects on humans and other organisms [2]. It also has a tendency to follow gold through the cyanide leaching circuit, and comes up in the electrowinning cells as elemental mercury.

The management of mercury in gold mining operations falls in three categories: 1) By product production captured for sale, 2) Atmospheric emissions, and 3) Wastes deposited on site, primarily as a minor component of waste rock. The laws on the sale and international transport of this mercury are changing [4]. Ultimately, it appears that it will be necessary to stabilize and dispose (or store) in a stable form.

The stabilization of mercury from various routes has been thoroughly reviewed in the literature. Some methods are suitable for elemental mercury, while others have only been recommended or tested for mercury containing material, sometimes at very low levels (e.g. in soils). Based on an extensive literature survey, three existing stabilization approaches could be identified: conversion to sulfide / selenide, amalgamation, and stabilization within an insoluble mineral matrix [5]. In most of these cases elemental mercury and sulfur was used to precipitate a stable form of mercury sulfide. For each of these approaches a number of technological implementations were found which are described in detail in literature review.

The main problem in using mercury sulfide as a method of stabilizing mercury is the problem of reacting the mercury with the sulfur to form stable (preferably red cinnabar) mercury sulfide. Another problem is the ultimate stability of the mercury sulfide. Mercury sulfide becomes leachable at high pH (higher than about pH 11, depending on conditions) or in the presence of excess sulfide or elemental sulfur [6].

For these reason a new idea has been proposed in this research. In this case, sodium thiosulfate is used instead of elemental sulfur as a source of sulfur. And as source of mercury, elemental mercury and mercury oxide is used. In this concept, thiosulfate forms a complex with mercury and with the passing of time this breaks down and mercury sulfide is precipitated. As a further extension of this idea, the use of thioselenate as a precipitating agent for mercury was also proposed.

This thesis contains six chapters. The second chapter gives a review of existing literature on the mercury-thiosulfate system and a brief background on thioselenate. The experimental methods are described in chapter three, followed by a discussion of the experimental results in chapter four. The conclusions are presented in chapter five, followed by the recommendations in the final chapter.

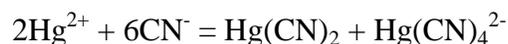
## 2 LITERATURE REVIEW

### 2.1 Mercury Emission Sources

Mercury is commonly observed in gold mining areas and concentrations of mercury vary substantially depending on each site. The concentrations of mercury in gold ore can range from undetectable to over 0.01% by weight [4].

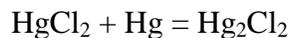
Because metallic mercury is a relatively volatile liquid, it can escape to the atmosphere, in any thermal process. In gold operations, several mercury emission points exist, and include: roasting or autoclaving, regeneration of carbon used to capture gold cyanide, retorting of mercury during refining, electrowinning cells, and, finally volatilization from waste rock and other mine residue. The amount released to the atmosphere at each point can vary dramatically depending on the ore concentration, the specific process utilized and the effectiveness of the mercury control measures [2].

In addition, mercury has a tendency to follow gold through the circuit, and ends up in the electrowinning cells as elemental mercury. In gold operation, cyanide solution is commonly used in the extraction of gold from its ore. Cyanide, in the presence of oxygen, reacts with elemental gold and converts it to water soluble gold cyanide complex. These process fluids are then passed over activated carbon, which captures the gold cyanide complex, and is thus removed from the aqueous solution. Mercury closely follows the chemistry and mechanism of capture of gold cyanide. In the presence of cyanide, mercury is converted to a highly water soluble di- or tetra-cyano mercury complex.



Mercury cyanide complexes are then captured with gold cyanide on activated charcoal and can ultimately be collected via retorts as liquid metallic mercury [4]. Additional mercury can be collected from roasters or autoclaves using air pollution control processes. In this case, mercury is recovered from roasters in a process which sprays mercuric chloride droplets in a scrubber cell

for the roaster. Mercuric chloride reacts with elemental mercury and forms mercurous chloride (calomel), which is not volatile.



The calomel is captured as a precipitate and is transferred to a mercury recycler who presumably converts it to elemental mercury [2].

## **2.2 Legislative Changes for Mercury**

An overview of the legislation related to mercury air emissions and land disposal is given below with specific focus on U.S. regulations and a brief discussion on Canadian and European action.

### **2.2.1 U.S. Regulations**

#### **2.2.1.1 Air Emissions**

According to the Clean Air Act, as revised in 1990, there are 188 air toxics, known as ‘hazardous air pollutants.’ In that list, mercury is listed as a toxic pollutant. In the Clean Air Act, technology-based standards for certain sources that emits these air toxics above specified emission thresholds will be established by the environmental protection agency (EPA). The standards are known to as ‘maximum achievable control technology’ (MACT). Additionally, ‘major’ sources should require obtaining operating permits for the purpose of ensuring compliance with all applicable requirements including emission standards [7].

The state of Nevada passed a mercury control program known as ‘Nevada Mercury Air Emissions Control Program’ (NMCP) in March of 2006. The NMCP is designed to build on an earlier voluntary program to reduce mercury emissions. This program regulates all precious metal mining facilities in Nevada and ensures that the mercury emissions data being reported is accurate and verifiable. The main goal of this program is to develop a process for establishing Nevada MACT (NvMACT) to emit mercury. In some cases, existing technologies will likely be determined to be NvMACT [8].

### **2.2.1.2 Land Disposals**

The Resource Conservation and Recovery Act (RCRA) require the safe management of hazardous mercury wastes, from the time they are produced, through storage and transportation, to their final treatment and disposal. The EPA has established standards for the treatment and recycling of mercury waste that must be fulfilled before these wastes can be land disposed. Certain mercury wastes, including mercury-containing household hazardous waste and waste generated in very small quantities are exempt from some RCRA hazardous waste requirements.

If the quantity, concentration, physical, chemical or infectious characteristics of solid wastes that may cause an increase in mortality or serious illness or pose a substantial threat to human health or the environment known as hazardous wastes under the rules by RCRA. There are four characteristics of hazardous waste considered by EPA. The characteristics are toxicity, reactivity, corrosivity and ignitability. If the solid waste exhibits any of these characteristics by applying the tests given by EPA, will be considered as hazardous wastes Elemental mercury generated at gold mining operations is likely to exhibit the characteristic of toxicity. The toxicity of a waste is determined by the Toxic Characteristic Leach Procedure (TCLP) test and occasionally by a constant pH leaching test [9]

The TCLP test is a standard test designed to determine the mobility of organics and metals present in the waste. For solid wastes, the particle size is reduced to 9.5 mm and the sample is extracted at a 20:1 liquid to solid ratio for 16 to 20 hours using either extraction fluid 1 (glacial acetic acid, water and sodium hydroxide) or extraction fluid 2 (glacial acetic acid) depending on the pH of the original sample. The extract is then analyzed and if it contains mercury at levels of at least 0.2 mg/L, the waste is considered hazardous. Occasionally a more stringent leachate level of 0.025 mg/L Hg (the Universal Treatment Standard or UTS) is used.

The constant pH leaching procedure is used as a check for the chemical integrity of the waste. In the constant pH test, wastes are kept for a 14 day exposure to pH values of 2, 4, 6, 8, 10 and 12 with constant agitation. 0.1 M nitric acid and 0.1 M sodium hydroxide are used as lixiviants rather than glacial acetic acid that are used in the TCLP analysis. The Universal Treatment Standard of 0.025 mg/L Hg is used to assess leachability in this test.

The RCRA Land Disposal Restrictions (LDR) program establishes hazardous waste treatment standards that minimize environmental threats resulting from land disposal. LDR treatment standards are set to ‘substantially diminish’ the toxicity of the wastes.

There are various mercury contaminated wastes and each of them has different treatment process determined by EPA. Different types of mercury contaminated wastes and these treatment processes are described below:

- High mercury waste: High mercury wastes are defined as hazardous wastes that contain more than 260 mg/kg of total mercury. These wastes must undergo a thermal treatment such as retorting or incineration that is capable of volatilizing mercury and subsequently condensing the mercury for recovery. The residue from the retorting process must then meet the low mercury waste standards.
- Low mercury waste: Low mercury wastes are defined as hazardous wastes containing less than 260 mg/kg of total mercury. Low mercury wastes that exceed a TCLP mercury concentration of 0.2 mg/L must be treated to meet the universal treatment standard (UTS) limit of 0.025 mg/L. Mercury residues from retorting or incineration have to meet only the 0.2 mg/L.
- Elemental mercury: There is no standard treatment process for elemental mercury determined by EPA. When EPA determined standards for mercury-contaminated wastes, it did so assuming that any elemental mercury in hazardous wastes would be recovered and sold for incorporation into various products. Elemental mercury was not (and is not) commonly disposed as a waste.

But in the upcoming U.S. elemental mercury export ban of 2013, elemental mercury will likely have to be managed as hazardous waste, but it is unclear whether EPA will adopt a suitable treatment standard for the disposal of such wastes before the export ban becomes effective. If a treatment technology is considered, it is expected that as a minimum, the TCLP limit of 0.2 mg/L would be required, but the standard could be more stringent. If by suitable treatment the toxicity characteristic is removed, a hazardous waste can be disposed in a non-hazardous landfill. Otherwise, disposal in a permitted facility would be necessary even after treatment to meet the land disposal restrictions [10, 11].

### **2.2.1.3 U.S. Mercury Export Ban and Its Implications**

In September 2008, The United States Congress passed the Mercury Export Ban Act. According to this act all the selling, conveying or distributing of elemental mercury by a federal agency to any other federal, state or local agency or any other private individual or entity are banned. The only exception is the transfer between federal agencies to facilitate storage. From January 1, 2013, the export of elemental mercury from the United States will be prohibited [12].

According to this act the Department of Energy will have to provide a long-term management and storage option for elemental mercury generated by the private sector. It also described that the EPA has to report to Congress on mercury-related compounds such as mercuric chloride, mercurous chloride or calomel, mercuric oxide, and other mercury compounds used in significant quantities in products or processes. The report will be used to determine if the ban should include the export of mercury compounds as well. The main focus of the report is believed to be:

- The sources of the mercury compounds imported into or manufactured in U.S.
- The purpose for which each of the mercury compounds is used domestically and the amounts consumed annually for each purpose.
- The sources and amounts of each mercury compound exported annually in the last three years.

The export ban is aimed to control the flow of mercury into the commodity market from the U.S. to the developing countries where mercury is often used in mining [13].

EPA had done a lot of research to treat elemental mercury for final disposal; however, none of the methods were adequate for waste that was going to be landfilled with other waste because the treated mercury is very sensitive to pH and salinity. They also concluded that the conditions had to be just right to meet the universal treatment standard (UTS) of 0.025 mg/L in a standard leach test, huge amounts of stabilizing material were needed and that the technologies work only for site-specific conditions [9].

### **2.2.2 European Regulations**

The European Union is also enacting an export ban for mercury and mercury compounds as of March 15, 2011. Along with metallic mercury the ban will also include mercury compounds such as cinnabar ore, mercury chloride and mercury oxide with an aim to examine by January 2010 the need to include other mercury compounds and mercury products in an effort to eliminate any loopholes. The main reason behind this export ban is similar to that of the U.S. export ban aiming to control the use of mercury in the developing countries.

The regulation calls for the storage of mercury waste either in salt mines, in deep, underground, hard rock formations or in safe above ground facilities. It is also expected that by January 2010, the Commission will establish a report evaluating whether solidification of metallic mercury is a safe disposal option.

In particular, Sweden has imposed that any waste containing at least 1% mercury should be stabilized in the form of mercury sulfide and stored in deep bed rock repositories. The design and the storage responsibilities lie with the generators of mercury waste. Mercury sulfide stored in such deep bedrock repositories aim to isolate the mercury from the biosphere for a very long time, preferably more than 1000 years. The Swedish EPA also directs that any leaching of mercury from a repository must produce concentrations in well water of less than 0.001 mg/L as administered by the National Food Administration for drinking water.

### **2.2.3 Canadian Regulations**

In the Canadian Environmental Protection Act (CEPA) mercury is declared as a 'toxic' substance with long term harmful effects on the environment and which constitutes a danger to human health. Also, Canada-wide standards have been developed to control mercury emissions from specific sectors such as the base metal smelting, the chlor-alkali and coal power plants. For existing copper, lead and zinc facilities mercury emissions should be controlled to 2g Hg/tonne total production of finished metals. New and expanding zinc, nickel and lead facilities have a guideline of 0.2 g Hg/tonne of finished metals and for copper facilities, 1g Hg/tonne of finished copper. Under the 'Export and Import of Hazardous Wastes Regulations' mercury and its compounds are subject to transportation regulations [9].

## 2.3 Mercury Stabilization Processes

In the past decades a number of mercury stabilization processes have been developed. Some of them are suitable for elemental mercury and some of them are for mercury contaminated waste.

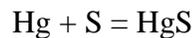
The way these processes are placed can be divided into three groups such as:

1. Stabilization as mercury sulfide.
2. Stabilization as amalgam.
3. Stabilization with the components of an insoluble matrix (cement, phosphate ceramic, magnesia binder).

The processes described in this section are one or a combination of one or two groups. In each case elemental mercury and/or an oxidized form of mercury react with some sort of chemical agents that can form a less soluble and a less volatile chemical compound of mercury.

### 2.3.1 Stabilization as Mercury Sulfide

In the first approach, mercury sulfide can be formed by using elemental sulfur and elemental mercury or with other sulfur containing substances such as sodium or potassium sulfides:

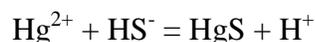


The conversion of mercury to mercury sulfide can be obtained by dissolving mercury in the liquid sulfur, by mixing solid sulfur with liquid mercury or in a gas phase reaction between gaseous mercury and gaseous sulfur. In each case high temperature is used. At room temperature mercury sulfide can exist in either these two forms or a mixture of these two:

- A red cinnabar ( $\alpha$ -HgS) and
- A black metacinnabar ( $\beta$ -HgS).

The black metacinnabar is less thermodynamically stable but it is the main product in the laboratory based experiments.

But if mercury is present in an oxidized form in the contaminated waste such as  $\text{Hg}^{2+}$ , a sulfide containing chemical agent such as hydrogen sulfide ( $\text{H}_2\text{S}$ ), alkali sulfides (like  $\text{Na}_2\text{S}$ ) is used to convert this mercury to mercury sulfide:



In some processes elemental mercury is first oxidized by strong oxidizing acids like nitric acid ( $\text{HNO}_3$ ) to aqueous  $\text{Hg}^{2+}$  and then precipitated as mercury sulfide.

### **2.3.2 Stabilization by Amalgams**

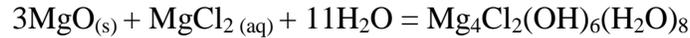
Mercury is the only metal that is liquid at room temperature and it is the only one that readily forms alloys by bringing it into contact with other metals like lead, copper, zinc, nickel or cobalt (except iron which allows storing of mercury in iron flasks). Alloy formation with mercury are called amalgams. They are solid but sometimes quite soft or paste-like materials. In some processes amalgamation is used as mercury stabilization technique. In this technique mercury or the mercury-containing waste is mixed with a metal powder (mostly zinc or copper) to give the solid amalgam, such as



### **2.3.3 Stabilization in an Insoluble Matrix**

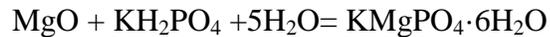
The principle idea behind this technique is to create a media in which mercury forms less soluble compounds. Here, mercury doesn't form any compound or alloy. A common technique that is used in many hazardous wastes is stabilization/solidification with Portland cement based materials. In Portland cement, there are several chemical substances and minerals like Portlandit (calcium hydroxide,  $\text{Ca(OH)}_2$ ), calcium silicates and aluminates that after mixing with water first form a slurry that hardens after a period of time due to the formation of a three-dimensional network of interlinked calcium silicate hydrates (CSH). At the same time, an alkaline or at least near neutral media is maintained in the remaining pore water. Most heavy metals form quite insoluble hydroxides under such conditions. Some metals are even incorporated into the CSH-matrix.

The same principle is used in magnesia cement. In this case, magnesium oxide reacts with a magnesium chloride solution (or other soluble magnesium compounds) magnesium hydroxide chlorides are formed such as



The resulting pore water has a near neutral pH and ensures a low solubility for many heavy metals.

Other type of material that is used in this stabilization technique is phosphates. If magnesium oxide is mixed with an aqueous solution of hydrogen phosphates (or phosphoric acid), a solid magnesium phosphate is formed:



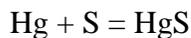
Heavy metals like lead  $\text{Pb}^{2+}$  or mercury  $\text{Hg}^{2+}$  form insoluble phosphates that are embedded in an impermeable matrix of magnesium phosphates [5].

## **2.4 An Overview of Different Stabilization Processes**

### **2.4.1 Mercury Stabilization as Mercury Sulfide (Bethlehem Apparatus)**

Liquid mercury can be stabilized as mercury sulfide by using elemental mercury and elemental sulfur in the vapour phase followed by encapsulation of mercury sulfide in a polymer matrix. This process was investigated by Bethlehem Apparatus Co. Inc. in Hellertown, Pennsylvania. In this process high temperature pressure vessels are used. At first these vessels are evacuated using vacuum pump and then backfilled with nitrogen so that mercury cannot react with oxygen and produce mercury oxide. After that sulfur is loaded into vessel and heated to 482°C (900°F) at a pressure of 20 psi and mercury is injected into this sulfur rich environment. The mercury vaporises and reacts with sulfur vapour to form mercury sulfide [9].

The stabilization technique between elemental sulfur and elemental mercury follows the reaction below:



The sulfur added to the mercury in an S:Hg ratio of at least 1:1 but the preferable ratio is 3:1. In the second step, the mercury sulfide is fed through an extruder to create pellets with polymers such as HDPE or LDPE and is finally formed into the size 7 x 7 mm [14]. X-ray diffraction analysis of the product by Lehigh University confirmed that the product has the same hexagonal crystal structure as cinnabar or red mercury sulfide which is determined by using X-ray diffraction analysis. A tomography scan showed that the produced mercury sulfide had no trace of elemental mercury and a head space analysis confirmed the absence of mercury in the gas phase [9].

#### **2.4.2 Process for Stabilization of Metallic Mercury (DELA, Germany)**

The mechanism of this process is almost similar to the previous process. In this process elemental mercury and elemental sulfur reacts in the vapour phase to produce mercury sulfide. Here a vacuum mixer is utilized; at first it is flooded with nitrogen to replace any oxygen that can oxidize any mercury or sulfur. A vacuum (<0.9 bar) is applied and then exact amount of sulfur is added. The mixer is heated higher than the boiling temperature of mercury (> 580°C). Then mercury is injected into the vacuum mixer. Due to high temperature environment within several seconds' mercury reacts with the gaseous sulfur to form mercury sulfide and it can be condensed down by cooling down the gas phase. This process can be used as a batch as well as a continuous process [5]. The final product using this process is a mixture of black metacinnabar ( $\beta$ -HgS) and a red cinnabar ( $\alpha$ -HgS) [15].

#### **2.4.3 Stabilization of Metallic Mercury Using Sulfur (STMI, Gif sur Yvettes, France)**

This stirring process is used to stabilize the radioactively contaminated elemental mercury by using elemental sulfur in a glass apparatus at higher temperature. In this process the molar ratio of Hg:S is 1:1 to 1:3. Both mercury and sulfur is taken into a round-bottom flask of an apparatus containing a motor, an axial glass pipe and a rotatable axial flask. By rotating the flask at 50 rpm

for 2 hours at 20°C, the reaction takes place. But the reaction is faster at temperature 60-80°C. If mercury sample contains some volatile contaminations, these can be purified at 90-110°C. If mercury itself needs purification, even higher temperature such as 360°C can be applied in the same apparatus. The product obtained by this process is identified as mixture of black metacinnabar and sulfur [16].

#### **2.4.4 Wet Process to Synthesize Mercury Sulfide**

This is a classical route to synthesize mercury sulfide. In this process mercury is initially dissolved in a strong oxidizing acid such as nitric acid, HNO<sub>3</sub> or contain a strongly complexing agent like chloride such as hydrochloric acid, HCl in order to overcome the noble characteristics of mercury. Then in this aqueous solution sodium or potassium sulfide is used to precipitate black metacinnabar [17].

#### **2.4.5 Sulfur Polymer Cement Stabilization and Solidification (SPSS)**

In this method powdered mercury, sulfur and polymerizing additives are mixed at room temperature and then heated until the mixture melts. The product is mercury sulfide encapsulated in a sulfur polymer matrix. The method was developed for treating mercury containing radioactive waste but it can also be applicable for elemental mercury [18].

Here, at first mercury containing waste is mixed with powdered sulfur polymer cement (SPC which contain 95% sulfur and 5% organic modifiers) under an inert atmosphere [19]. This mixing process takes place at elevated temperature and is continued for 4-8 hours. Sometimes a chemical stabilizer such as sodium sulfide is added to convert soluble mercury chloride. The mixture is then heated to 120 - 150°C to form a molten product. Additional SPC is added to ensure complete conversion of mercury into mercury sulfide. It also improves the viscosity of the molten product. The molten product can be cast in any desirable form, preferably in containers ready for final disposal [5].

In the final product, mercury sulfides (cinnabar, metacinnabar) were found by XRD and it also shows lower mercury solubility and vapour pressure [20].

#### **2.4.6 Process for Stabilization of Mercury (ADA Technologies)**

ADA's treatment process for elemental mercury consists of reacting liquid mercury with a proprietary sulfur mixture in a commercially available paddle mixer to produce mercuric sulfide. The mercury sulfide passes the TCLP limit and UTS standards for leachable mercury although in some cases the leachability is not consistent. The process can handle high and low concentrations of speciated mercury such as mercury oxide and water soluble mercury compounds such as mercuric chloride and elemental mercury [21].

In this method, the first step is to pre-treat the waste in a way that oxidized forms of mercury are reduced to elemental mercury. Then powdered sulfur (10 - 500 micrometers) is added to an (open) pug mill with a set of counter-rotating blades. After starting the mixing blades mercury is then poured in. Then the mixing is continued for 5 - 10 minutes when a bulking material (typically sand) is added to the mixture and mixing pursued for additional 10 - 30 minutes. Then a polysulfide (calcium, sodium or any other alkali or earth alkali compounds) is added that acts as an activator for the reaction between mercury compounds and the sulfur reagent. The end of the reaction is signalled by an end of heat generation as the reaction between mercury and sulfur is exothermal. In this technique no heating is required [35].

#### **2.4.7 Chemically Bonded Phosphate Ceramic Encapsulation**

Chemically bonded phosphate ceramics (CBPCs) are well suited for encapsulation because of the solidification of this material occurs at low temperatures and over a wide range of pH. Phosphate ceramics are formed by reaction between magnesium oxide (MgO) and mono potassium phosphate ( $\text{KH}_2\text{PO}_4$ ) in solution.

The magnesium potassium phosphate hydrate formed is a hard, dense ceramic and acts as a crystalline host matrix for the waste. CBPC waste stabilization is done by slowly stirring a mixture of the waste, about 0.5% of sodium sulfide, MgO and  $\text{KH}_2\text{PO}_4$  in water. Dissolution of  $\text{KH}_2\text{PO}_4$  yields potassium phosphates and hydronium ions. The increase in acidity increases the solubilities of MgO and Hg compounds and leads to the release of  $\text{Mg}^{2+}$  and  $\text{Hg}^{2+}$  ions. The released Hg is then converted to HgS. However, in the presence of excess sulfides Hg could

reduce to  $\text{Hg}_2\text{SO}_4$ , which is more soluble than  $\text{HgS}$  and hence not a desirable form for disposal [23].

The mixing step ensures that the waste particles are completely encapsulated or coated with binder [24]. CBPCs can treat both solid and liquid wastes. For treating solid waste materials, the material is crushed to a particle size of 4 to 75  $\mu\text{m}$  [25].

#### **2.4.8 DeHg<sup>TM</sup>- Process - Nuclear Fuel Services, Inc. (NFS)**

In the DeHg<sup>TM</sup>- Process mercury is amalgamated with a proprietary mixture of reagents. Oxidized species are solidified by another group of unspecified agents. It is capable of treating wastes containing elemental mercury and/or oxidized forms of mercury.

In the DeHg process, the process is operated at ambient temperature in a ventilated hood. Reactions take place in a reactor. It consists of two parts. In the first one (amalgamation) elemental mercury content is reacted with amalgamating agents (unspecified), in the second part (stabilization, if necessary) oxidized mercury species and complexes are broken up using a proprietary reagent and removed from the waste as an insoluble precipitate [26], [27].

The final product is a press cake. If the material passes TCLP tests it is ready for disposal, otherwise it will be reprocessed. This implies that in some cases the process fails to meet regulatory standards.

#### **2.4.9 Amalgamation with Zinc or Copper**

In the copper amalgam process, fine copper powder (325 mesh) is washed with nitric acid and then milled in a laboratory shaker with stainless steel balls [17]. Elemental mercury is added so that the mixture contains 65 wt % mercury. The mixture is milled for 45 minutes, the resulting paste stirred and, milled for 45 minutes. It is then allowed to harden and later crushed into a powder, if necessary.

In the zinc amalgam process, fine zinc powder (325 mesh) is washed with nitric acid and then milled in a laboratory shaker with stainless steel balls [17]. Elemental mercury is added so that the mixture contains 45 wt % mercury. The mixture is milled for 2h.

Headspace analysis showed that the vapour pressures of mercury above zinc and copper amalgams were nearly the same as those above pure elemental mercury [28].

**Table 2.1: An Overview of Different Mercury Stabilization and Encapsulation Technologies**

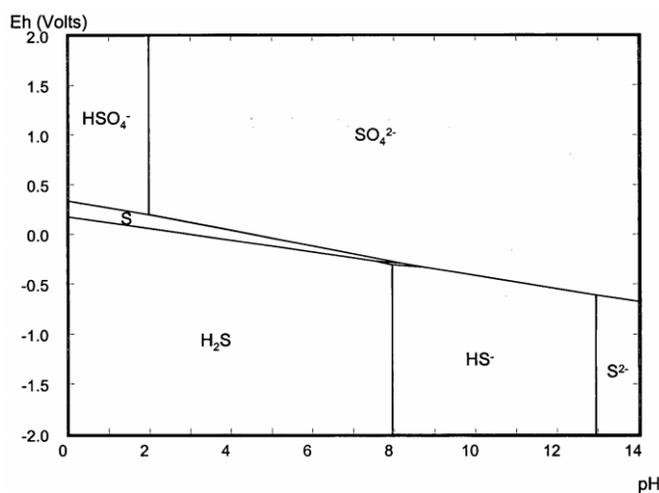
<b>Process</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Applicability</b>
<b>Bethlehem Apparatus</b> <b>(Mercury sulfide process)</b>	Final product is cinnabar, homogenous product	Mercury mobilisation at high pH, small company may not have the resources.	Elemental mercury
<b>Della Germany</b> <b>(metallic mercury)</b>	Used as a batch as well as continuous process.	The product is a mixture of red and black mercury sulfide.	Elemental mercury.
<b>STMI, Gif sur Yvettes, France</b> <b>(metallic mercury)</b>	Low temperature is used.	Product is a mixture of black mercury sulfide and sulfur.	Elemental mercury.
<b>SPSS</b>	High resistance to corrosive environment, high mechanical strength.	Residual sulfur and mercury observed, developed an excess void, inconsistent result.	Elemental mercury and soluble mercury compounds.
<b>ADA Technologies</b>	Reaction starts at ambient temperature, conventional equipment, passes the TCLP test.	Inconsistent leachability, forms metacinnabar	Elemental mercury and soluble mercury compounds.

Process	Advantages	Disadvantages	Applicability
<b>DeHg<sup>TM</sup> - Process</b>	Ambient conditions,	Generate large amount of hydrogen gas, some time passes UTS standards.	Soil like material and elemental mercury.

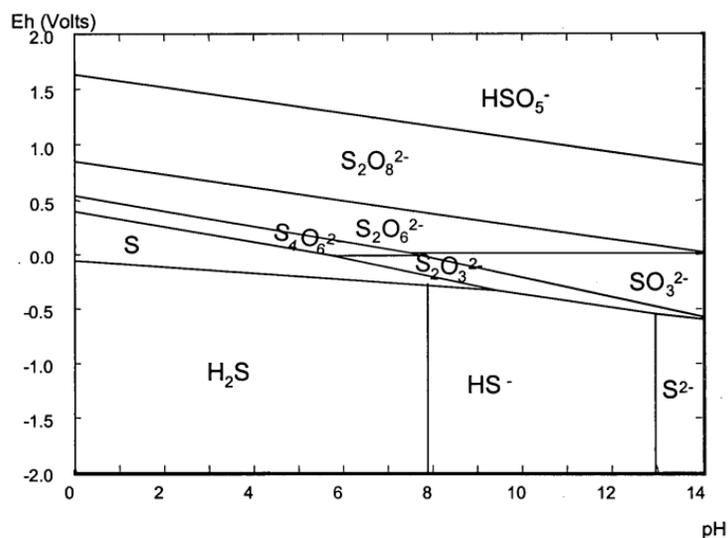
## 2.5 Mercury –Thiosulfate Chemistry

### 2.5.1 Thiosulfate Chemistry

Thermodynamically, thiosulfate is a metastable ion. Like other metastable sulfur oxyanions, thiosulfate needs to lose or gain electrons to reach sulfate or sulfide which are stable [29]. For that reason in a typical Eh- pH diagram of the sulfur-water system thiosulfate has no dominant region in aqueous solution (figure 2.1). Thiosulfate will have dominant region only when sulfate formation is omitted in the construction of the Eh- pH diagram for the sulfur-water system, that the metastable sulfur species appear (figure 2.2).

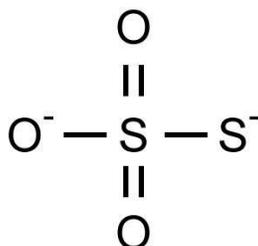


**Figure 2.1: Eh-pH Diagram for the Aqueous Sulfur System (1M Sulfur, 25°C)**



**Figure 2.2: Eh-pH Diagram for the Metastable Aqueous Sulfur System (1M Sulfur, 25°C)**

Thiosulfate compounds containing the group  $S_2O_3^{2-}$  which is like sulfate ion with one oxygen atom having been replaced by a sulfur atom. The two sulfur atoms are not equivalent in chemical characteristics (figure 2.3).



**Figure 2.3: Structure of the Thiosulfate Ion**

The unique chemistry of the thiosulfate ion,  $S_2O_3^{2-}$  OR  $SSO_3^{2-}$ , is mainly due to the sulfide like sulfur atom which is responsible for the complexing abilities with metals and for the reducing properties [30].

Chemical properties of thiosulfate include:

- It has a tendency to hydrolyse at  $\text{pH} < 5.5$ 
  1. To  $S^0$  and  $\text{HSO}_3^{2-}$  at mildly acidic pH.
  2. To more complex structures in strong acid.
- It has a tendency to be oxidized (by  $\text{O}^{2-}$ ,  $\text{Cu}^{2+}$  etc.)

- Relative hydrolytic stability in the basic solution.
- Thiosulfate forms metal sulfides with copper, silver, mercury etc.
- Thiosulfate can form complex ions with a number of metals such as gold, silver, copper, mercury etc.

The two most important salts of thiosulfate are sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$  or  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and ammonium thiosulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  [31]. Sodium thiosulfate was used in this research.

## 2.5.2 Mercury Sulfide Chemistry

### 2.5.2.1 Introduction

Mercury, a toxic element, is the only metal that is a liquid (m.p.  $-39^\circ\text{C}$ ) at room temperature and has a significant vapour pressure (0.01 mm mercury) [32]. It has a low solubility of  $56 \mu\text{g/L}$  in water at room temperature and has a molar mass of  $200.6 \text{ g/mol}$ . The toxicity and volatility of mercury in the atmosphere, land and water and the fact that it can be found in the environment not only as a simple inorganic and organic compounds but also as complex compounds and in its methylated form it is easily absorbed into living organisms, especially fish where it bio-accumulates, makes it an element of concern [33].

Many mercury compounds such as mercury chloride ( $\text{HgCl}_2$ ), mercury sulfate ( $\text{HgSO}_4$ ), mercury oxide ( $\text{HgO}$ ) are significantly soluble. But mercury sulfide ( $\text{HgS}$ ) and mercury selenide ( $\text{HgSe}$ ) have significantly lower solubilities.

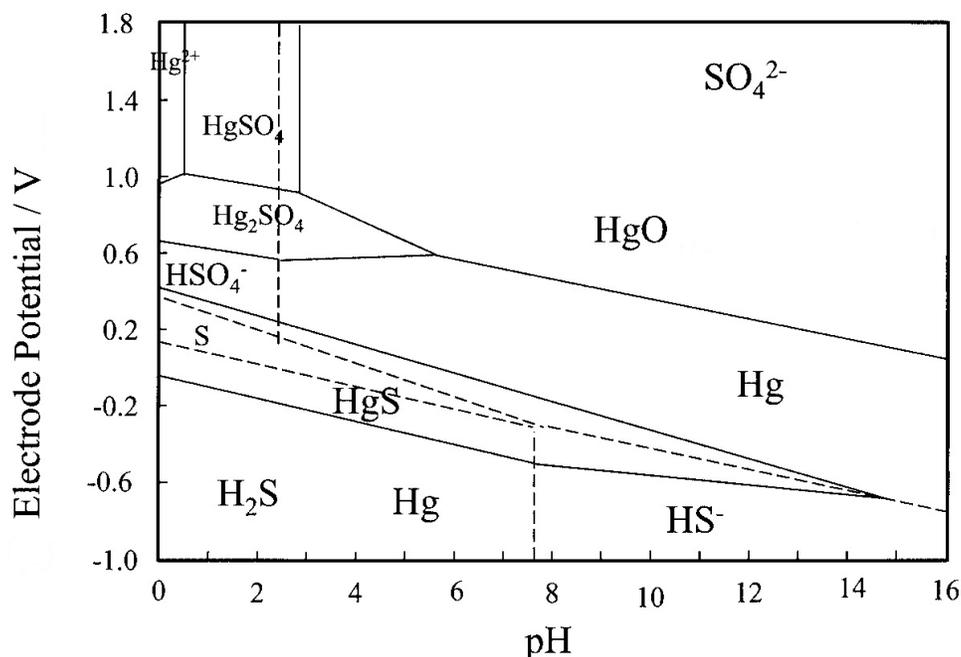
Mercury sulfide exists in two forms in nature such as

- $\text{HgS}$  red (hexagonal form) found in nature as cinnabar ( $\alpha\text{-HgS}$ ), and
- $\text{HgS}$  black (cubic tetrahedral form or amorphous) or metacinnabar ( $\beta\text{-HgS}$ ) [9].

The chemistry of mercury sulfide is discussed further in the sections below.

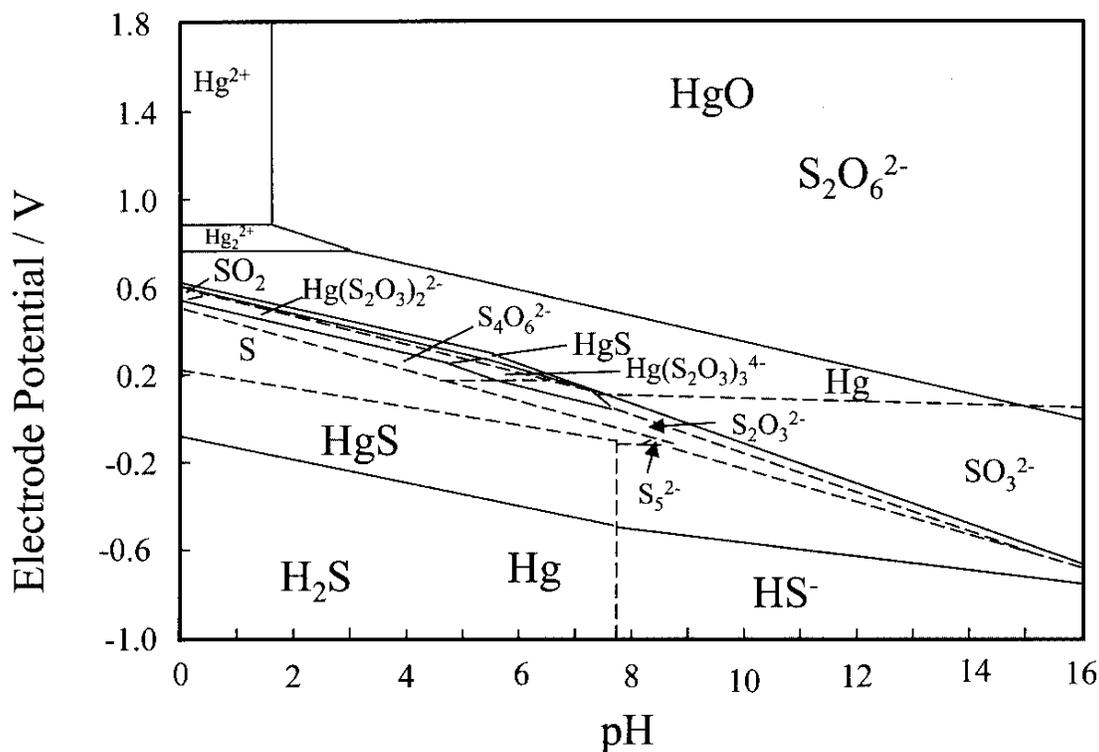
### 2.5.2.2 Thermodynamic Data for Mercury Sulfide

In a simple Eh-pH diagram (figure 2.4) for mercury and sulfur, oxidation of  $\text{HgS}$  to  $\text{S(VI)}$  and elemental  $\text{Hg}$  is predicted thermodynamically. At low potentials,  $\text{HgS}$  reduction is predicted to produce elemental mercury and  $\text{H}_2\text{S}$  ( $\text{pH} < 7$ ) OR  $\text{HS}^-$  ions ( $\text{pH} > 7$ ).



**Figure 2.4: Eh-pH Diagram for the Hg-S-H<sub>2</sub>O System at 298 K. Activities of Dissolved Hg = 0.1, sulfur = 1, in Equilibrium with HgS and HgO**

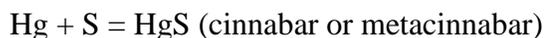
But in reality oxidation of HgS to S(VI) and elemental Hg is not possible in kinetic experiments due to the strong interaction of sulfur with mercury, and the large activation energy involved. Therefore a metastable Eh-ph diagram for mercury and sulfur is given below (figure 2.5). In this metastable diagram, excluding S(VI) species to expose areas of predominance of  $\text{Hg}(\text{S}_2\text{O}_3)_x^{y-}$  and  $\text{Hg}(\text{SO}_3)_n^{m-}$  complexes is shown. The former species are formed when Hg is oxidized in thiosulfate-containing solutions. HgS is predicted to be oxidized to elemental Hg and sulfur oxyanions at  $\text{pH} > 7$ , but when the dissolved mercury activity is decreased, HgS oxidation to elemental Hg becomes restricted to pH values above about 9 [9].



**Figure 2.5: Metastable Eh–pH Diagram for the Hg-S-H<sub>2</sub>O System at 298 K with Activities of Dissolved Mercury and Sulfur of 0.1 and 1 Respectively**

### 2.5.2.3 Formation of Mercury Sulfide

Based on the thermodynamics data, it is feasible to produce mercury sulfide by using elemental sulfur and liquid mercury and mercury oxide. Iron sulfides can be used to form mercury sulfides. During the reaction to form HgS from elemental mercury and elemental sulfur, reactions which may occur include:



The oxidation of sulfur is more thermodynamically feasible than oxidation of elemental mercury. For the reaction between elemental mercury and sulfur, the high density and surface tension of mercury severely inhibits the mixing of sulfur and mercury that is required for maximum interaction. Vigorous stirring is needed to disperse the sulfur in the mercury to initiate room temperature blending interactions. While the stoichiometric molar ratio of sulfur to mercury is 1, the preferred ratio in practice is >1.25 [34]. Thermodynamic data for the formation of mercury

sulfide from elemental mercury, mercuric oxide and various forms of sulfur are shown in Table 2.2

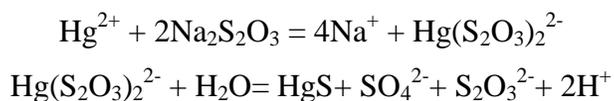
**Table 2.2: Thermodynamics of Mercury Sulfide Formation**

Reagent	Reaction	Gibbs free energy, $\Delta G^\circ$ (kJ/mol)
$S^\circ$	$S + Hg^\circ = HgS_{(s)}$	-46
	$S + HgO = HgS + \frac{1}{2} O_2$	10
	$4S + 3HgO + H_2O = 3HgS + SO_4^{2-} + 2H^+$	-477
FeS	$FeS + Hg^\circ + 2H^+ + \frac{1}{2} O_2 = HgS + Fe^{2+} + H_2O$	-266
FeS <sub>2</sub>	$FeS_2 + 2Hg^\circ + 2H^+ + \frac{1}{2} O_2 = 2HgS + Fe^{2+} + H_2O$	-245

Mercury sulfide can be formed from a mercury thiosulfate solution. The formation of mercury sulfide from thiosulfate is thermodynamically feasible. The thermodynamic data for the formation of mercury sulfide is given below



In this case, mercury is initially dissolved as a thiosulfate complex. However upon aging, the thiosulfate breaks down to form sulfur and sulfate. The sulfur precipitates as mercury sulfide and the sulfate remains in solution.



#### 2.5.2.4 Conversion between Forms of Mercury Sulfide

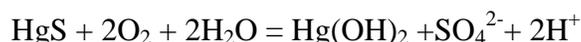
The conversion of black ( $\beta$ ) to red ( $\alpha$ ) cinnabar is an exothermic process with a transition temperature given in different literature sources as 315°C, 345°C or 386°C and heat of transformation of 371.13 kJ/mol [35].

Although metacinnabar should readily transform to cinnabar at ambient temperature, metacinnabar has been found to be the most common form in laboratory precipitation experiments and in natural environments [36]. It is possible to convert from red to black cinnabar using aqueous ammonium sulfide. Red cinnabar reacts with a solution of ammonium sulfide in liquid ammonia forming  $(\text{NH}_4)_2\text{S}\cdot\text{HgS}$ . This compound is unstable in the presence of moisture, losing  $\text{H}_2\text{S}$  and  $\text{NH}_3$  to produce metacinnabar [9].

Formation of metacinnabar at low temperatures is attributed to a nonstoichiometric arrangement of Hg and S and the presence of impurities in HgS. Impure forms of metacinnabar can be stabilized at ambient temperature by Zn, Fe and Se. Cinnabar is a non-stoichiometric solid where mercury vacancies are coupled with interstitial sulfur substitution. It has been suggested that the stoichiometry of stable cinnabar can range from  $\text{Hg}_1\text{S}$  to  $\text{Hg}_{0.9673}\text{S}$  at 298K. One consequence of this non-stoichiometry is that cinnabar of stoichiometry  $\text{Hg}_{<0.9}\text{S}$  can lose the red colour that exists because of its reflectivity at wavelengths  $>575$  nm and appear black. Colour alone is not a reliable diagnostic tool of the form of HgS [9].

#### 2.5.2.5 Stability of Mercury Sulfide

Mercury sulfide is one of the most stable mercury compounds, and can be generated from elemental mercury as well as other mercury compounds. It is one of the least soluble of the metal sulfides ( $K_{\text{SP}}= 10^{-52}$  for metacinnabar and  $10^{-56}$  for cinnabar), [37] and is the thermodynamically favoured species under reducing conditions. However, even under oxidizing conditions, HgS is very resistant to weathering. The oxidation reaction in the equation below is very slow.



The low solubility and inert redox character of HgS shows a particularly stable Hg phase. However, there has been some experimental work showing conditions under which the solubility is enhanced such as in the presence of excess sulfide or at very high pH, high chloride concentrations may also increase mercury sulfide dissolution [38].

## 2.6 Thioselenate Chemistry

Early work showed that elemental selenium could be reacted with sulfite to form selenosulfate ion,  $\text{SeSO}_3^{2-}$ , was stable, but the formation of thioselenate,  $\text{SeSO}_3^{2-}$ , from sulfur and selenite has been controversial. Elemental selenium dissolves in sulfite solution to form selenosulfate ion:  $\text{Se} + \text{SO}_3^{2-} = \text{SeSO}_3^{2-}$ . The formation constants for this equilibrium at temperatures from 0 to 35°C are reported. The isomeric thioselenate anion,  $\text{SSeO}_3^{2-}$ , is not, however, produced by the reaction of sulfur with selenite.

Sulfite and selenosulfate are in equilibrium according to



The values of K at various temperatures are given in Table. The results given in Table show that the solubility of selenium in sulfite solution increases with temperature.

**Table 2.3: Selenium Solubility in 1.0 M  $\text{Na}_2\text{SO}_3$  at Various Temperatures and Selenosulfate Formation Constants, K.**

Temperature (°C)	Se solubility (mol/L)	K
0	0.203	0.255
13	0.268	0.366
20	0.300	0.430
25	0.340	0.440
35	0.379	0.610

Sulfur and selenium powder may be used directly in the solution to produce selenosulfate. Potassium selenosulfate was prepared by dissolving 24 g of analyzed  $\text{K}_2\text{SO}_3$  (82.4%) and 5.9 g

BaCl<sub>2</sub>, 2H<sub>2</sub>O in 10 mL water, removing the BaSO<sub>4</sub>, by filtration, and then saturating with Se (3.1 g) over 2 h at ca 60°C, filtering through a glass fibre filter paper to remove any excess Se, and leaving standing at 0°C, protected from oxygen, overnight. The colorless solution produces white crystals, which analyze as K<sub>2</sub>SeSO<sub>3</sub>·3.5H<sub>2</sub>O [39].

## 2.7 Research Objectives

From the literature review section it can be said that it is thermodynamically possible to form stable mercury product by using mercury containing thiosulfate solution. So the objectives of this research are at first;

- To form a stable mercury product from a mercury containing thiosulfate solution.
- Testing of the leaching and precipitation of mercury using a thiosulfate bath. Specific testing will include studies on;
  - a) Effect of temperature
  - b) Effect of pH
  - c) Effect of thiosulfate concentration
  - d) Stability of mercury in solution with time
- Testing of the formation of thioselenate and using this thioselenate in similar procedures and variations on the experimental conditions.

### **3 EXPERIMENTAL METHODS**

This section covers the materials and reagents used for testing, followed by a description of the experimental apparatus and an overview of performed testwork. This chapter concludes with a description of the analytical method used in this work.

#### **3.1 Materials**

##### **3.1.1 Mercury and Selenium Samples**

To study the behaviour of mercury in sodium thiosulfate solution, at first pure elemental mercury was used. After that mercuric oxide (HgO) (213357-ACS reagent,  $\geq 99.0\%$ ) was used as a source of mercury in the mercury thiosulfate solution.

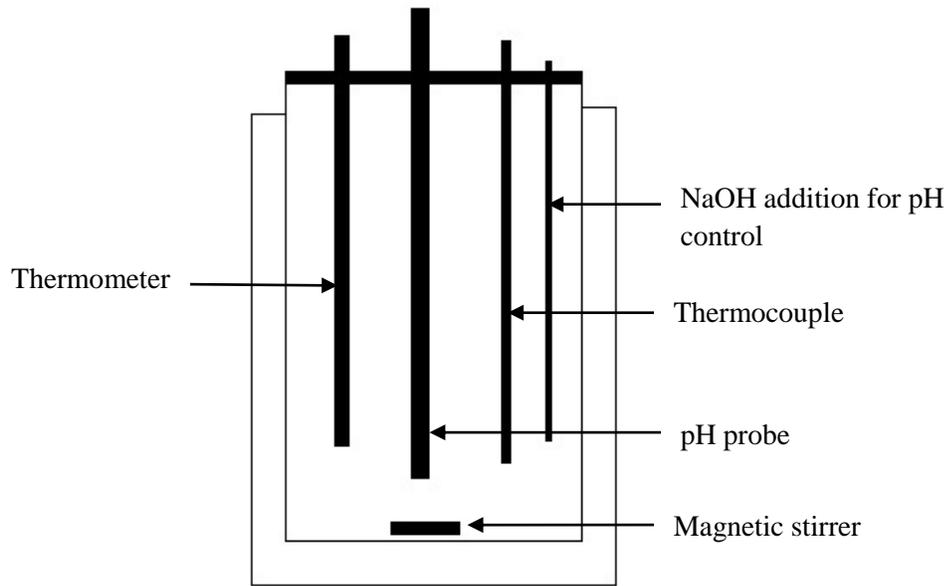
In the selenium dissolution test, selenium powder (209651-ACS Reagent-100 mesh, 99.5%) was used.

##### **3.1.2 Reagents**

- In the titration method for mercury analysis, 0.05M nitric acid (HNO<sub>3</sub>) was used to make mercury nitrate solution. Hexamine solution was used to adjust the solution pH. Xylenol orange was used as an indicator and Ethylenediaminetetraacetic acid (EDTA) was used for titration.
- In mercury leaching and precipitation test, sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was used.
- In mercury precipitation test (at controlled pH), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was used in solution and sodium hydroxide (NaOH) was used to adjust the pH of the solution.
- In the selenium dissolution test, sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) was used to dissolve selenium powder to produce sodium thioselenate.

#### **3.2 Experimental Apparatus**

A schematic diagram of the experimental setup used for the batch precipitation test is given in Figure 3.1. The experiments were carried out in two 500 mL cylindrical glass vessel with a removable rubber lids. The solution was stirred by magnetic stirrer.



**Figure 3.1: Schematic Diagram of the Experimental Setup**

In case of high temperature, the glass vessels were attached to a water bath heated by an immersion heater. A thermocouple was placed in the reactor to provide temperature control. A thermometer was used to check the processing temperature.

Controlled pH experiments were performed by addition of sodium hydroxide and sulfuric acid. Two valves were connected to two pH controller, regulated the flow of the sodium hydroxide solution from two volumetric flasks. The pH was controlled in a range of  $\pm 0.10$  pH. A photograph of the controlled pH experiment is given in figure 3.2.



**Figure 3.2: Diagram of the Controlled pH Experimental Setup**

In these experiments, two pumps were used to regulate the sodium hydroxide flow from the flask to the glass vessels by using rubber wire. Two computers were used to collect data for sodium hydroxide addition.

### **3.3 Experimental Procedures**

Three sets of experiments were performed in this study:

1. Preliminary test work.
  - a. Mercury analysis test
  - b. Mercury leaching test
  - c. Mercury precipitation test.
2. Mercury precipitation test (at controlled pH)
  - a. In different temperature.
  - b. In different thiosulfate concentration.
3. Selenium dissolve test.

#### **3.3.1 Preliminary Test Work**

The preliminary testwork involved mercury analysis test, mercury leaching test and mercury precipitation test. The first question arrived in this study is to determine the mercury content in

the solution. To determine the mercury content at first a mercury titration method was used. In this method mercury oxide was added to 0.05M HNO<sub>3</sub> solution to make 0.01M 200 mL mercury nitrate solution. Then the pH of this acidic solution was adjusted to 5-5.5 with hexamine solution. Several drops of xylenol orange were used as an indicator. Then the solution was titrated with 0.01M EDTA. When the solution color was changed from red to yellow the method was stopped and EDTA volume was recorded to determine the mercury content in the solution. But in our study, sodium thiosulfate was used to precipitate mercury sulfide. For this reason in this titration method, sodium thiosulfate was used in the mercury nitrate solution. The rest of the titration method was the same as described earlier.

At first, to precipitate mercury sulfide, a mercury leaching test was adopted. In the mercury leaching test, 0.1 g mercury metal was leached by using 100 mL of 0.2 M sodium thiosulfate solution. This test was done at different pH such as 5,6,7,8,9,10 and 12. In all cases the temperature was constant at room temperature. All experiments were continued for 9 days, in each day sample solution was taken by the syringe and filtered by using 0.25µm nylon filter and taken for analysis.

After that mercury precipitation tests were done by using 10g/L mercury from mercury oxide dissolved in 0.25M sodium thiosulfate solution. The tests were done at uncontrolled pH 5, 6, 8 and 10. In uncontrolled pH tests, the pH was allowed to drift. In these tests a water bath was used to control the room temperature (25°C). All experiments were continued for 9 days. In each day sample solution was taken by the syringe and filtered by using 0.25µm nylon filter and was taken for the analysis. After 9 days, the solid residue was filtered and dried at the room temperature for 3 days and then taken for the XRD analysis.

### **3.3.2 Mercury Precipitation Test (at Controlled pH)**

After the preliminary testwork, some adjustments were taken to improve the mercury precipitation test. As above the experiments were done by using 10g/L mercury from mercury oxide dissolved in 0.25M sodium thiosulfate solution. But in this case solution pH was controlled by constant supply of sodium hydroxide using a pH controller which was connected with a pump. The temperatures used in this pH controlled test were 40°C, 50°C,60°C, 70°C and 80°C and tests were done at pH 5 and 6. To control the temperature a water bath was used in each test.

The tests at temperature 40°C, 50°C and 60°C were done for seven days but the tests at temperature 70°C and 80°C were done for only 40 hours.

After that another set of mercury precipitation test were done at different thiosulfate concentration such as 0.05M, 0.1M, 0.25M, 0.5M, 0.75M and 1M. But in this case only 1g/L mercury from mercury oxide was used. The temperature used in this pH controlled test was 70°C and tests were done at pH 5 and 6. These experiments were continued for 30 hours. Liquid samples were taken after 1hr, 2hr, 4hr, 8hr, 12hr, 24hr and 30hr by using a syringe and filtered by using 0.25µm nylon filter and were taken for analysis. The solid residue was filtered and dried at room temperature for 3 days and then taken for the XRD analysis.

### 3.3.3 Selenium Dissolution Test

To study the effect of sodium thioselenate on mercury, at first experiments were done to prepare sodium thioselenate in the laboratory. In these experiments, selenium powder and sodium sulfite was mixed. The tests were done at different sodium sulfite concentration, temperature and time which shown in the table below:

**Table 3.1: Overview of Experiments with Sodium Sulfite and Selenium Powder**

$\text{Na}_2\text{SO}_3$ (g)	Se(g)	Time(hrs)	Temp (°C)
1	0.05	4	50
1	0.05	8	50
1	0.05	24	60
1	0.01	24	70
1.5	0.05	24	60
2	0.1	48	60

### 3.4 Mercury Analysis

To determine the content of mercury in the liquid sample at first the traditional titration method was used. In this method sodium thiosulfate and potassium persulfate was added into mercury nitrate solution. The mercury nitrate solution was prepared by using mercury oxide and nitric

acid solution. Then the pH of this solution was carefully adjusted to 5-5.5 by using hexamine solution. Several drops of xylenol orange were used as an indicator. Then the solution was titrated with 0.01M EDTA. After the solution color changes; the titration method was stopped and EDTA volume was recorded. This method was not successful as thiosulfate interfered with titration. For this reason atomic absorption spectroscopy (AAS) was used for mercury analysis.

For the AAS method the liquid mercury samples were taken from the experimental solution in different times by using syringe. Then the solution was filtered by 0.25 $\mu$ m nylon filter and after that only 2ml was taken by using pipette. The solution volume was then adjusted to known volume (200ml) by adding distilled water and the mercury content was measured by AAS.

The solid residues of the mercury samples were analyzed by using the Rietveld method and X-ray power diffraction data and were performed by Dept. of Earth & Ocean Sciences in UBC. The samples were ground into fine powder with a corundum mortar and smeared on to a glass slide with ethanol. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2 $\theta$  with CoK $\alpha$  radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

### **3.5 Solid Waste Disposal Characterization (SWDC)**

The SWDC test is to reflect the interaction of the leachant and buffering capacity of the waste. It is applicable for single batch extractions only. It does not apply to organic substances, volatile matter or biologically active samples. This test is similar to EPA TCLP test but is informational only and not intended for regulated purposes.

The description of this method is given in Appendix section. However, in this research instead of using 10g sample only 2 g sample was used. And the test was done for the sample at pH 5 70°C and for sample pH 5 80°C. After the test was done, the result of mercury concentration in extraction fluid was compared with the data of Universal Treatment Standards for land disposal and RCRA limits for hazardous/non-hazardous determination.

## **4 RESULTS AND DISCUSSIONS**

The experimental results are presented and discussed in this chapter. As mentioned in Chapter 3, three sets of experiments were conducted for this research: preliminary test works, mercury precipitation tests (at controlled pH) and selenium dissolution tests. The experimental results are presented and discussed accordingly.

### **4.1 Preliminary Experiments**

The preliminary experiments were done to obtain an understanding of the behavior of mercury in thiosulfate solution. Three sets of preliminary tests were done in this research: Mercury analysis tests, mercury leaching tests and mercury precipitation tests (at uncontrolled pH). The results of these experiments were used to determine the experimental conditions and analysis of mercury for future testwork.

#### **4.1.1 Mercury Analysis Tests**

As described in section 3.3.1 mercury analysis tests were done with the mercury nitrate solution. At first the theoretical mercury titration tests were performed and after that the titration method were performed by using sodium thiosulfate in the mercury nitrate solution. The results for mercury analysis tests are shown in table 4.1.

**Table 4.1: Mercury Titration Tests at Different Conditions**

<b>pH</b>	<b>Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, g</b>	<b>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, g</b>	<b>Heating</b>	<b>EDTA volume (theoretical), mL</b>	<b>EDTA volume (titration), mL</b>	<b>Result</b>
5-5.5	0	0	none	4.5	4.4	Working
5-5.5	0.016	0.013	none	4.5	8.7	Not working
5-5.5	0.016	0.06	none	4.5	8.9	Not working
5-5.5	0.016	0.1	none	4.5	8.6	Not working
5-5.5	0.016	0.06	80°C	4.5	8.3	Not working

From Table 4.1, it clearly showed that under simple conditions, titration method for mercury analysis was working. But whenever sodium thiosulfate was used in that mercury nitrate solution, titration of mercury was not working. Almost double EDTA was required for titration of mercury. When sodium thiosulfate was used in mercury nitrate solution there might be a thiosulfate complex was formed which might not be break during titration. That's why almost double quantity of EDTA was required for titration. To break this thiosulfate complex, potassium persulfate was introduced in the solution prior to titration. Three quantity of potassium persulfate were used. But unfortunately these were not enough to all for the accurate titration of mercury. After that 80°C heat was applied in the solution. But that was also not enough and the titration method was not working. After performing all these titration tests, it was decided that mercury cannot be analyzed by the titration method and Atomic Absorption Spectroscopy (AAS) method was adopted.

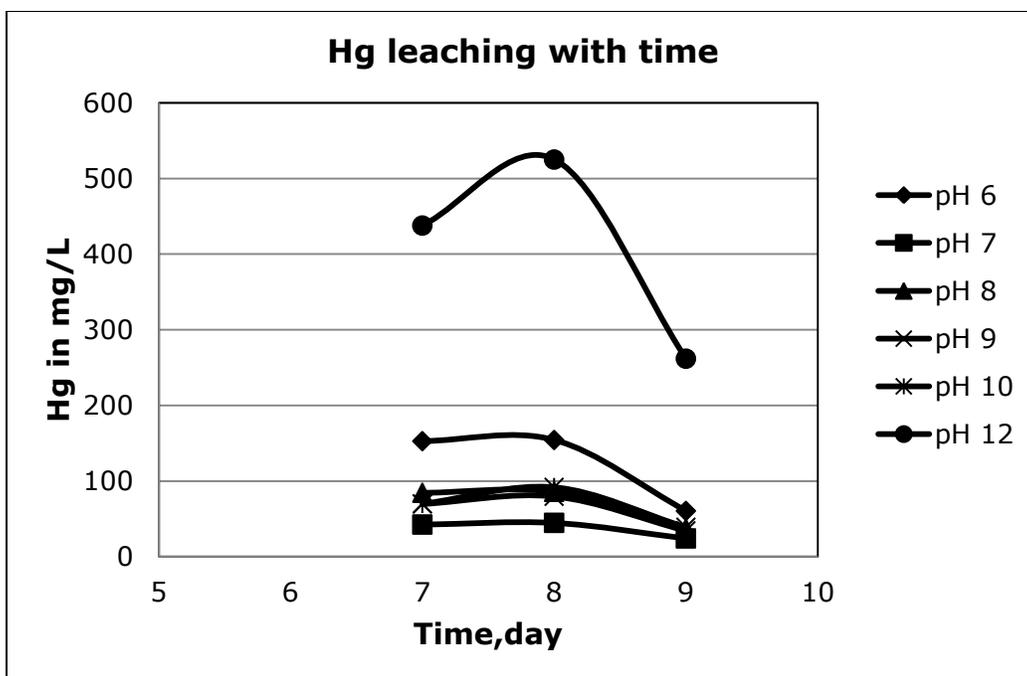
### 4.1.2 Mercury Leaching Tests

As described in section 3.1.1 mercury leaching tests were performed by using elemental mercury and sodium thiosulfate solution. In these leaching tests, elemental mercury was leached by using sodium thiosulfate solution at different pH and tests were 9 days long. In all cases temperature was kept constant at room temperature. The leaching solution of elemental mercury and sodium thiosulfate was kept in observation in each day to watch any change occurs. Table 4.2 showed the observation data in this test:

**Table 4.2: Observation Data for Mercury Leaching Test**

pH	Observation (after day 9)
6	Clear solution, No ppt.
7	Clear solution, No ppt.
8	Clear solution, No ppt.
9	Clear solution, No ppt.
10	Clear solution, No ppt.
12	Black ppt. Dark solution.

The observation data table is the visible indication of loss of mercury in thiosulfate solution. And from that it is clear in those conditions such as different pH and temperature it was very hard to dissolve elemental mercury in sodium thiosulfate solution. At pH 6 to 10 the solution (after day 9) was almost the same as day 1. But significant change occurs at pH 12; the solution went darker day by day. To find out what is happening in the solution, after day 9, the solutions were taken for the AAS analysis. Figure 4.1 shows AAS results at different pH.



**Figure 4.1: Mercury Leaching and Precipitation Data with Time**

The initial mercury content in the solution was 1000 mg/L. The leaching of mercury at pH 6 to 10 was very slow. Only 10-15% mercury was leached after 9 days. But among them at pH 6 the leaching rate was higher but the rate was decreased at higher pH. This is because at lower pH thiosulfate is not stable but at basic or higher pH thiosulfate stability increases in solution. At pH 12, 50% mercury was leached after 8 days. Then mercury leaching rate was going slowly and changes to only 250 mg/L. This is probably due to; black mercury sulfide was precipitated in the surface of elemental mercury which inhibits the leaching of mercury by thiosulfate solution. These two processes were simultaneous and therefore leaching rate was going to slow after 9 day in each condition. For this reason, elemental mercury cannot be leached in thiosulfate solution and mercury precipitation tests using mercury oxide were performed.

#### 4.1.3 Mercury Precipitation Tests (at Uncontrolled pH)

After the mercury leaching tests mercury precipitation tests were performed by using mercury oxide as a source of mercury and sodium thiosulfate solutions. These tests were done at different pH and the pH was allowed to drift throughout the test. A waterbath was used to control the temperature and all tests were continued for 9 days. The changes at pH in each day are given in table 4.3 below:

**Table 4.3: Overall Data for pH Changes with Time in Mercury Precipitation Tests**

pH							
Initial	Day 1	Day 2	Day 3	Day 5	Day 7	Day 8	Day 9
5	4.97	4.29	3.85	3.46	3.24	3.23	3.21
6	6.12	6.32	4.88	3.78	3.34	3.29	3.25
8	8.38	8.4	6.32	6.8	6.71	6.67	6.62
10	9.29	8.54	6.78	6.78	6.84	6.83	6.77

From the table 4.3, it can be said that, with the time increases the pH decreases. The main reason for decreasing pH is due to the formation of hydrogen ion as shown in the following reaction, which is described in detail in the literature.



In each day sample solution was taken by the syringe and filtered by using 0.25 $\mu\text{m}$  nylon filter and was taken for the analysis. The content of mercury in each solution in each day is given in table 4.4 below

**Table 4.4: Overall Data of Mercury Concentration with Time**

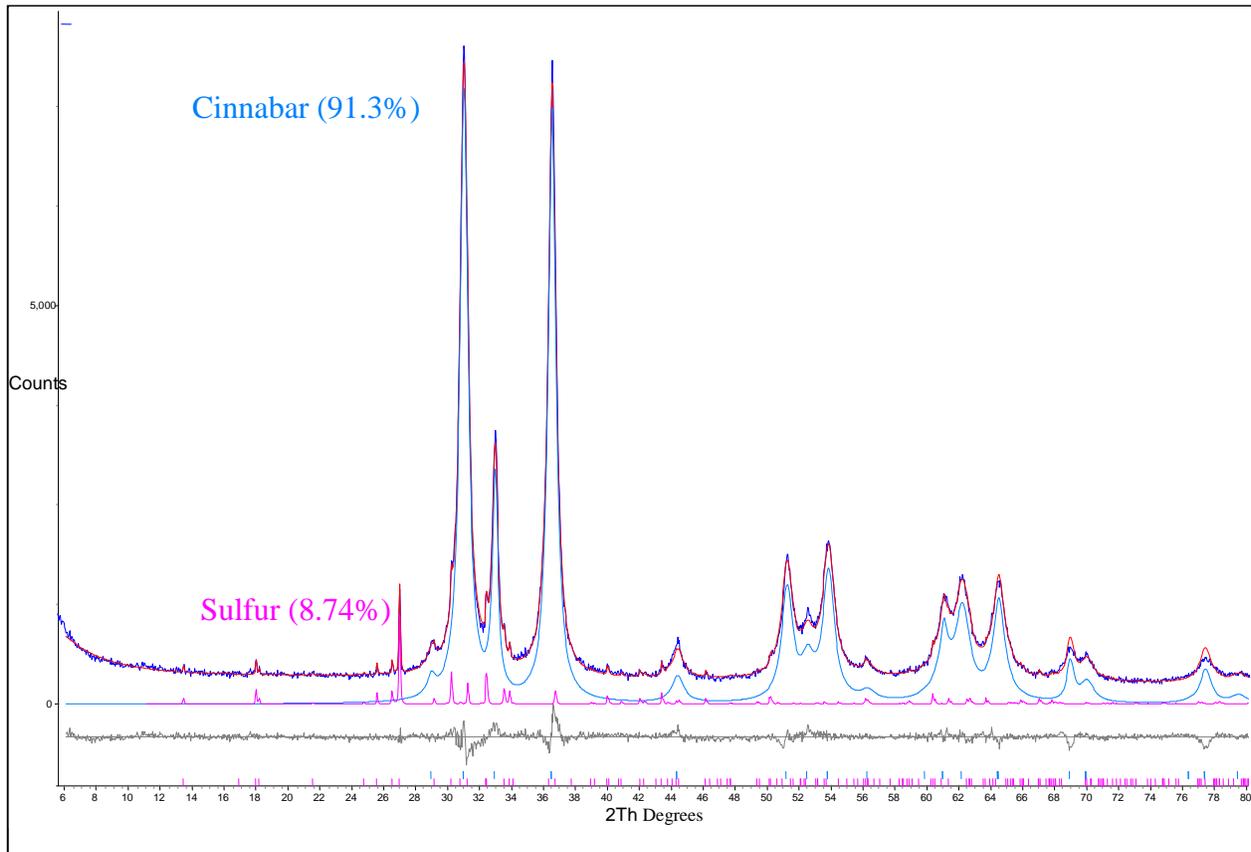
Hg (mg/L)								
pH	Initial	Day 1	Day 2	Day 3	Day 5	Day 7	Day 8	Day 9
5	9980	9540	7910	3970	3350	1080	830	340
6	9950	9710	9010	8860	8530	2750	1020	850
8	9950	9700	9620	9430	9320	8320	8220	7520
10	9960	9680	9430	9260	9390	8280	8200	7440

From the table 4.4, in each case mercury was precipitated as red powder. But at pH 5 mercury precipitation rate was very high almost 97% mercury was precipitated in this condition after 9 days. After that, at pH 6 almost 91% mercury was precipitated in the same time. But at pH 8 and 10 mercury precipitation rates were very slow. Only ~24% mercury was precipitated in those conditions.

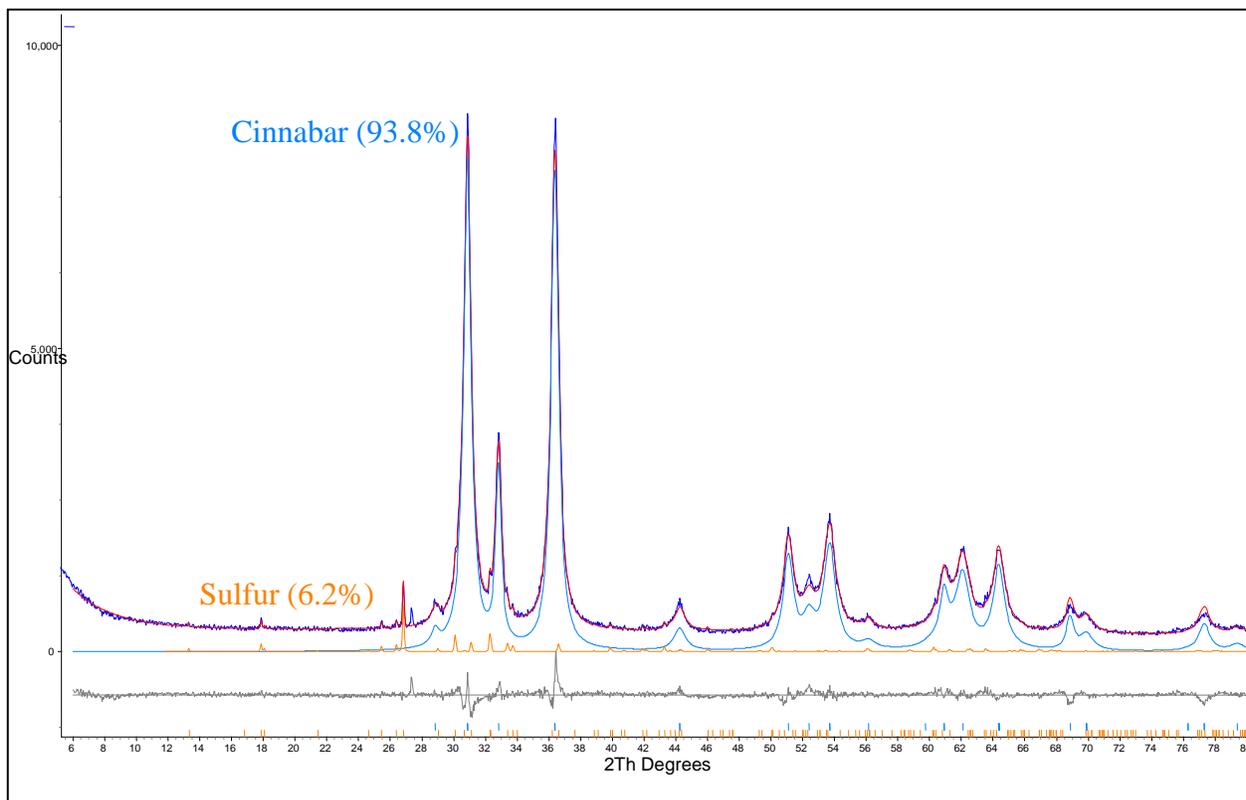
After 9 days, the solid residue was filtered and dried in the room temperature for 3 days and then taken for the XRD analysis. The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Siemens (Bruker). The X-ray powder-diffraction data were refined with Rietveld program Topas 4.2 (Bruker AXS) .The results of quantitative phase analysis by Rietveld refinements are given in Table 4.5. These amounts represent the relative amounts of crystalline phases normalized to 100%. The Rietveld refinement plots are shown in Figures 4.2.

**Table 4.5: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Uncontrolled pH): (wt. %)**

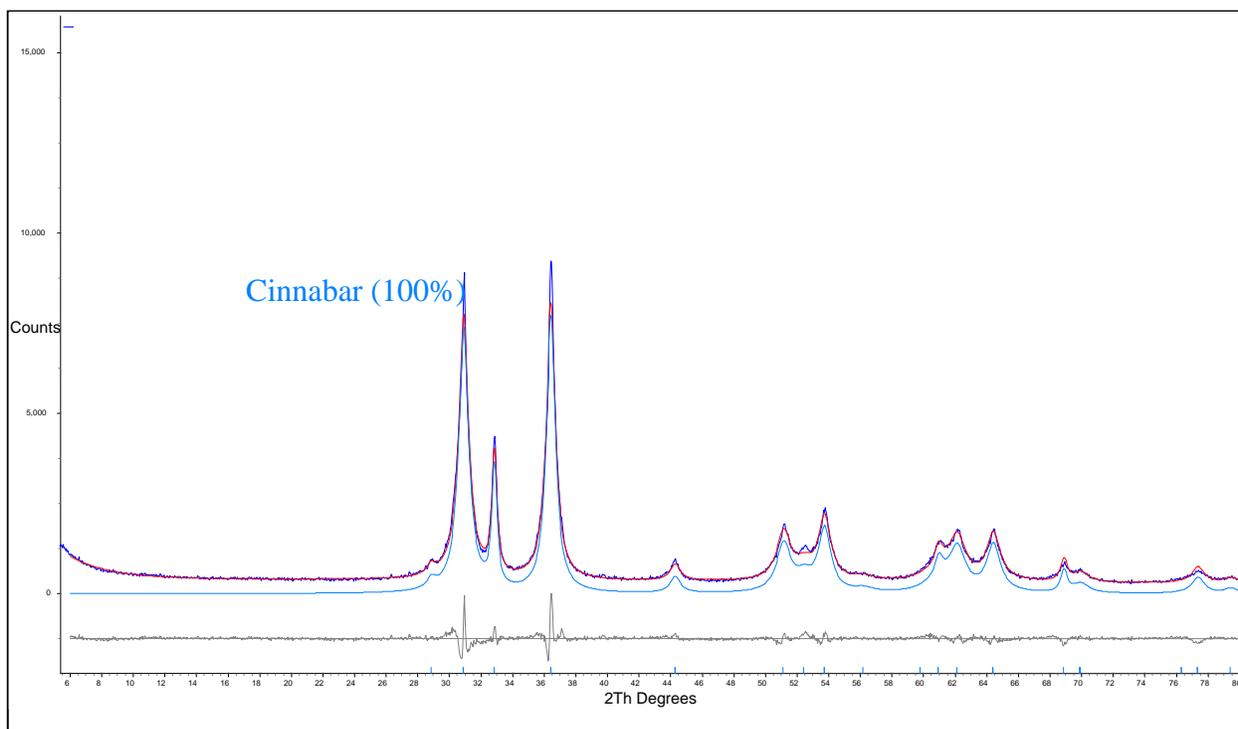
Mineral	Ideal Formula	pH-5	pH-6	pH-8	pH-10
Cinnabar	HgS	91.3	93.8	100.0	100.0
Sulfur	S	8.7	6.2		
Total		100.0	100.0	100.0	100.0



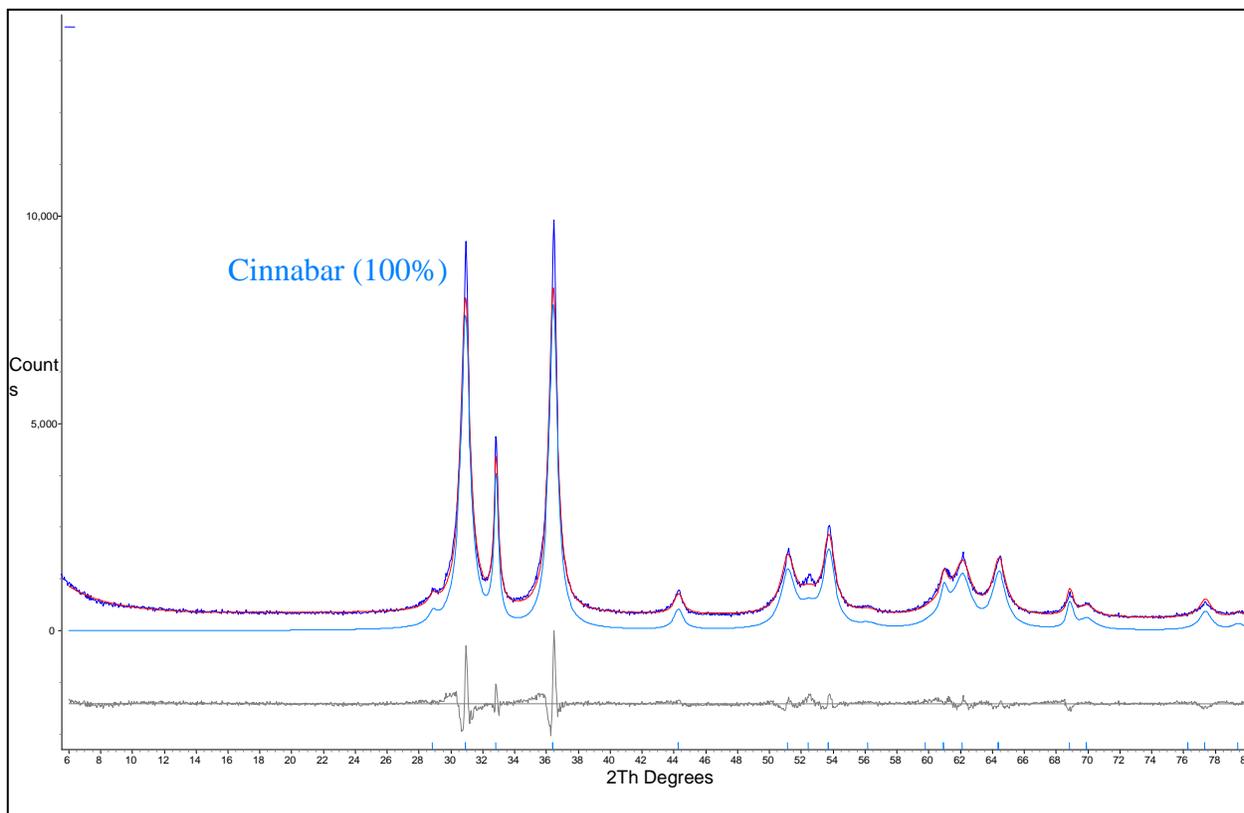
(a) pH 5



(b) pH 6



(c) pH 8



(d) pH 10

**Figure 4.2: Rietveld Refinement Plots of Sample (a) pH 5, (b) pH 6, (c) pH 8 and (d) pH 10**

From the above table and figure, the red mercury precipitate was identified as red mercury sulfide. But at pH 5 and 6 with red mercury sulfide, small amount of sulfur was precipitated. The reason for sulfur precipitation is that when the pH drops, thiosulfate breaks down to elemental sulfur and sulfite. Elemental sulfur will co-exists with mercury sulfide.

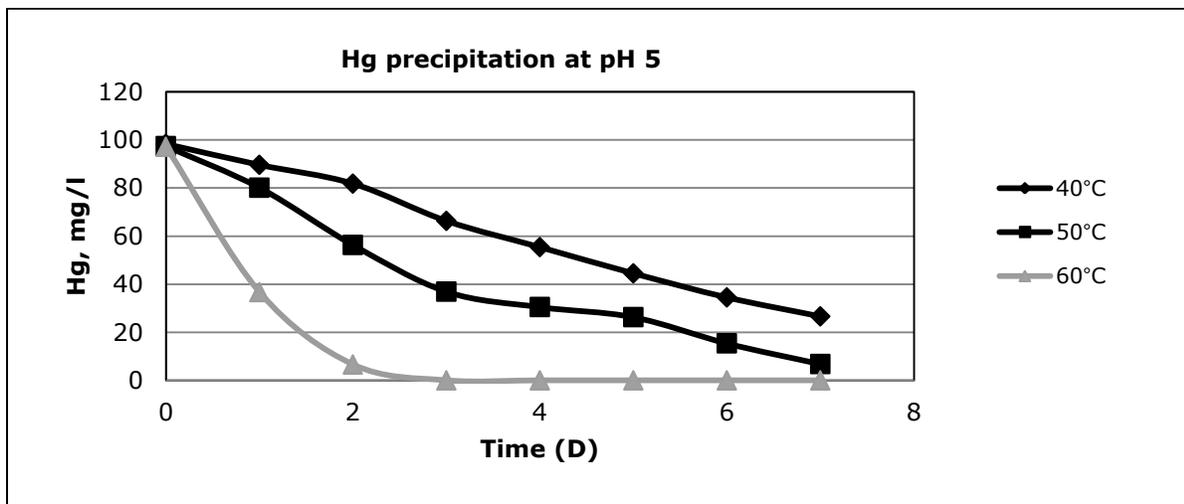
From these tests, it can be concluded that mercury sulfide can be precipitated by using mercury oxide and sodium thiosulfate solution. But at lower pH with mercury sulfide, some sulfur can be precipitated. For this reason future tests were performed at controlled pH.

## 4.2 Mercury Precipitation Tests (at Controlled pH)

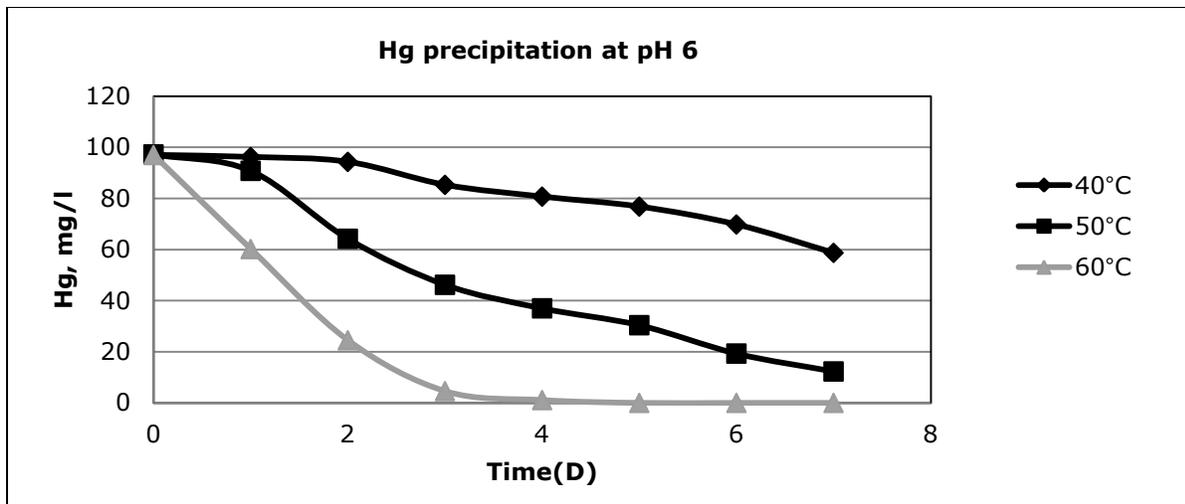
In these experiments mercury oxide (as a source of mercury) dissolved in sodium thiosulfate solution. In this case solution pH was controlled by a constant supply of sodium hydroxide solution using a pH controller. The tests were performed at different temperatures and pH to study the effect of temperature and pH.

### 4.2.1 Effect of Temperature and pH

The temperatures used in pH controlled precipitation tests were 40°C, 50°C, 60°C, 70°C and 80°C. The tests where 40°C, 50°C and 60°C temperature were used were continued for 7 days. But in other cases such as temperatures at 70°C and 80°C the tests were continued for only 35 hrs. All the tests were performed at pH 5 and 6. Figure 4.3 and 4.4 show the effect of temperature and pH on mercury precipitation:

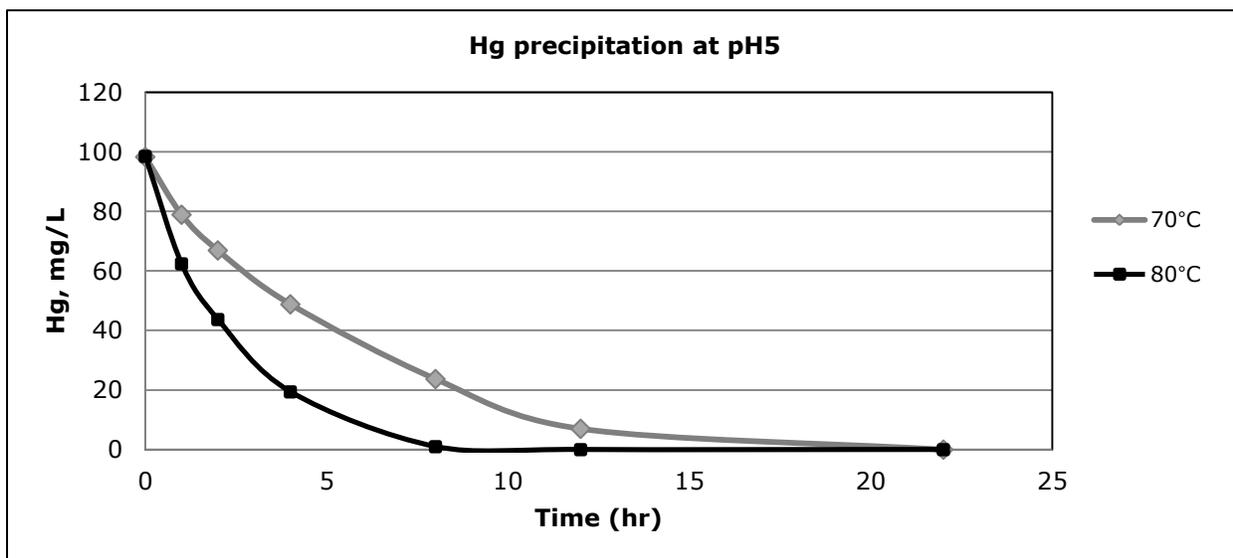


(a)

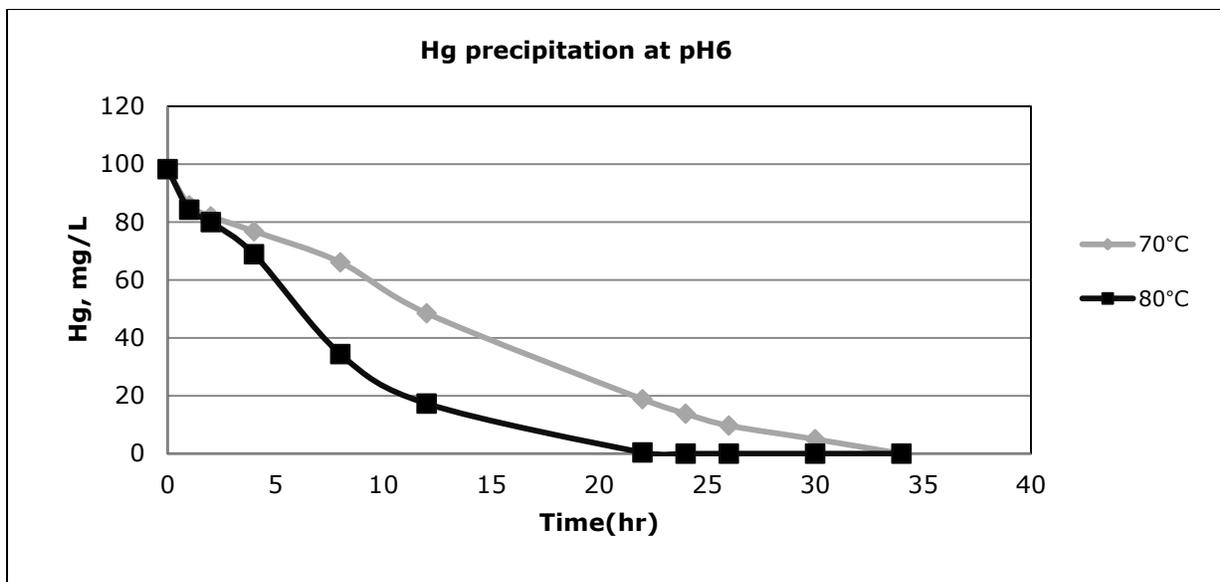


(b)

**Figure 4.3: Mercury Precipitation with Time at 40°C, 50°C and 60°C for (a) pH 5 and (b) pH 6**



(a)



(b)

**Figure 4.4: Mercury Precipitation with Time at 70°C and 80°C for (a) pH 5 and (b) pH 6**

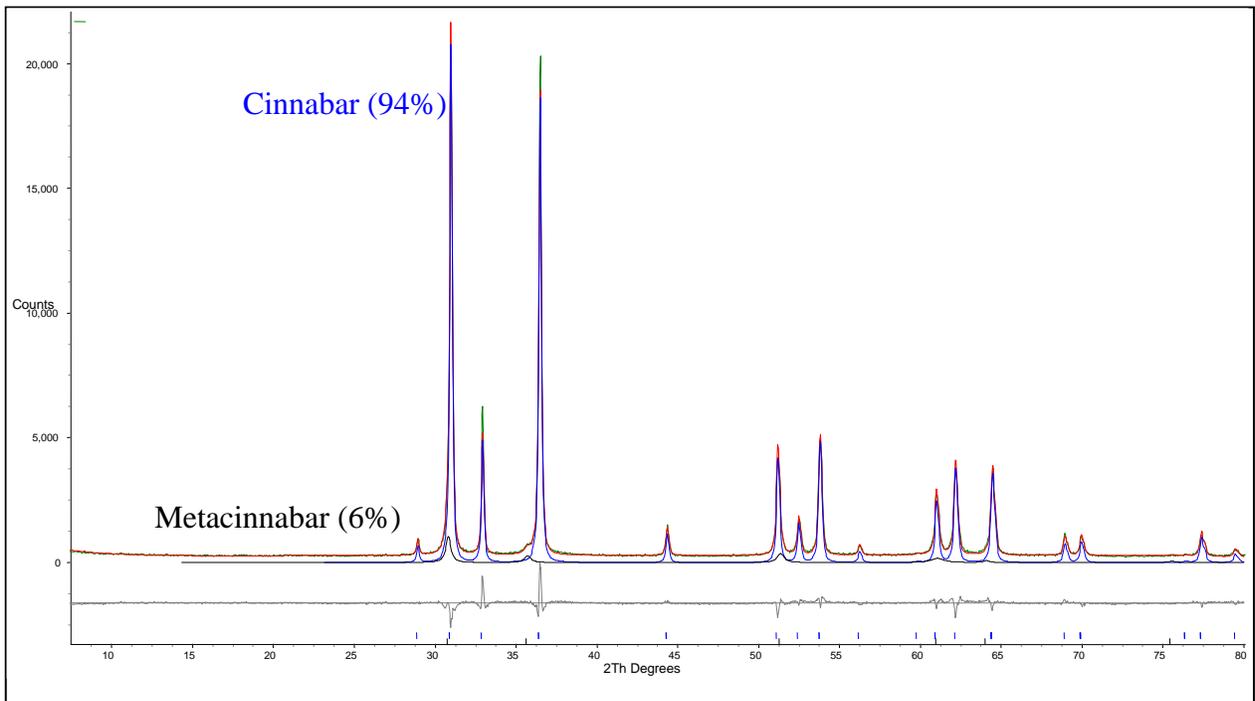
In all cases with the increase of temperature the mercury precipitation rate increases. For pH 5 and 6, at 40°C and 50°C, the mercury precipitation rate was slow and all the mercury was not precipitated after 7 days. But at 60°C, the precipitation rate increases at a level that all the mercury was precipitated within 2 days. For the 70°C and 80°C tests were performed until all the mercury was precipitated. In these cases, the mercury precipitation rate was so high that all the mercury was precipitated within 35 hours at both pH 5 and pH 6.

Mercury precipitation is more rapid at pH 5 than at pH 6 for all temperatures. As seen in the Eh-pH diagram of mercury and sulfur, it is clear that mercury sulfide region dominates at lower pH.

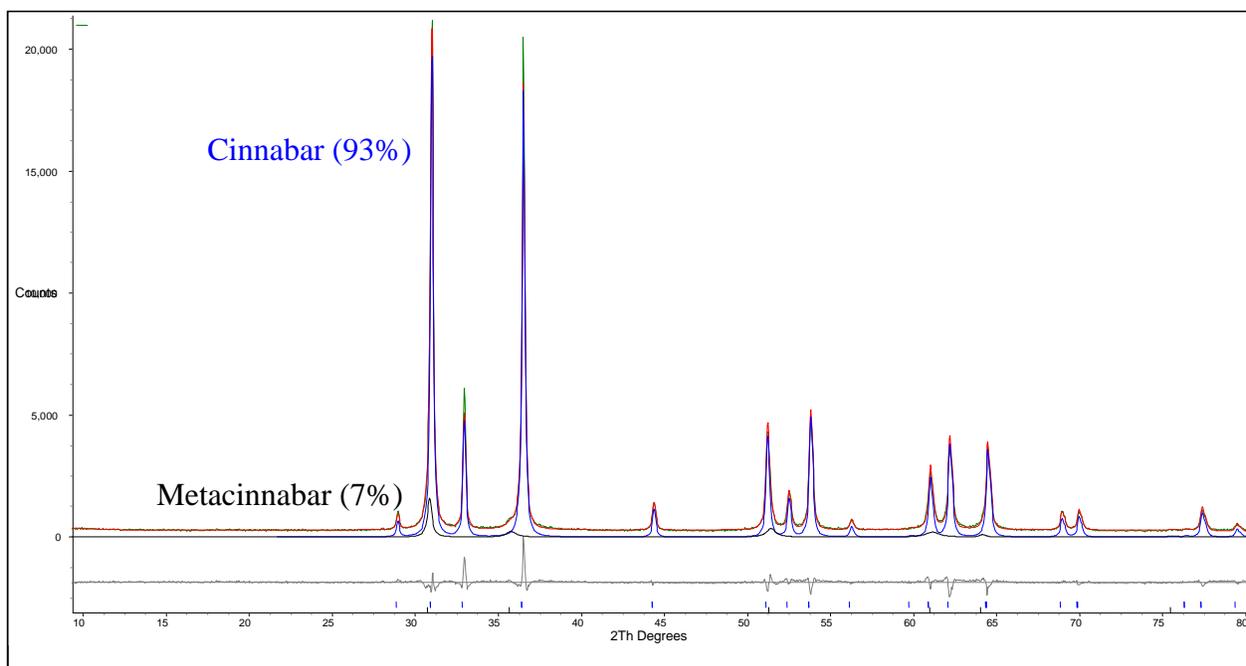
At 40°C, 50°C and 60°C, the color of mercury sulfide precipitation was red. But at 70°C and 80°C tests, the color is a mixture of red and black. So at these tests, some black mercury sulfide was produced. This is because for the 70°C and 80°C tests; the precipitation rate was so high that, crystalline mercury sulfide (red) cannot be precipitated. After that, the solid residue was filtered and dried in the room temperature for 3 days and then taken for the XRD analysis. The results of quantitative phase analysis by Rietveld refinements are given in Table 4.6. These amounts represent the relative amounts of crystalline phases normalized to 100%. The Rietveld refinement plots are shown in Figure 4.4.

**Table 4.6: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Controlled pH): (wt. %)**

Mineral	Ideal Formula	pH5 - 80°C	pH6 - 80°C
Cinnabar	HgS	94.0	93.0
Metacinnabar	HgS	6.0	7.0
Total		100.0	100.0



**(a) pH5 - 80°C**

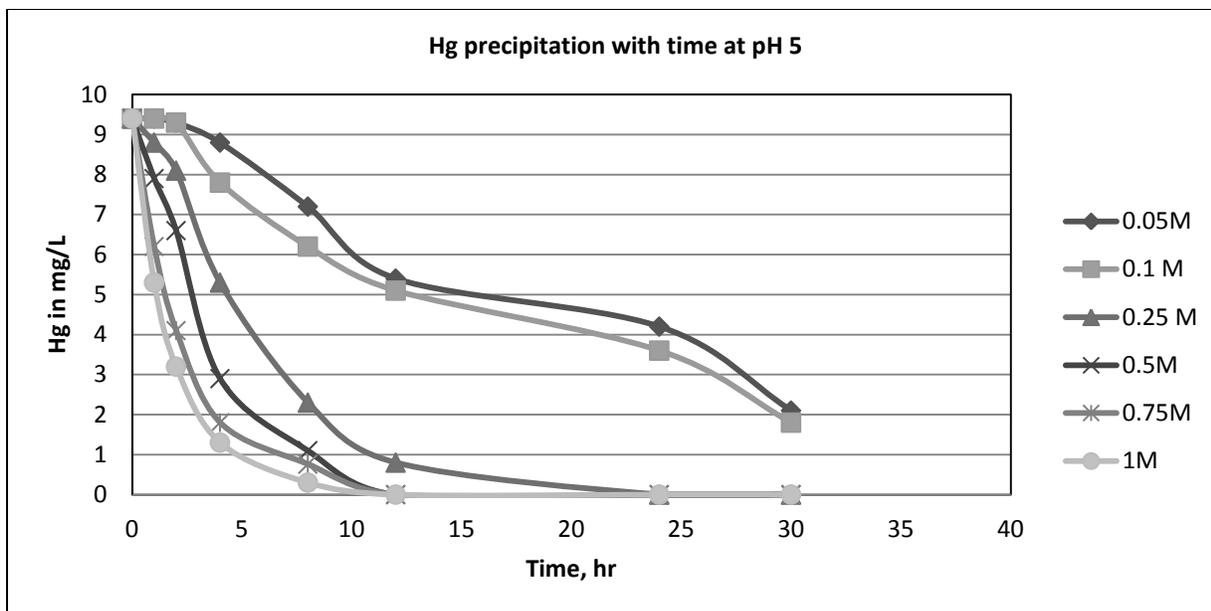


(b) pH6 - 80°C

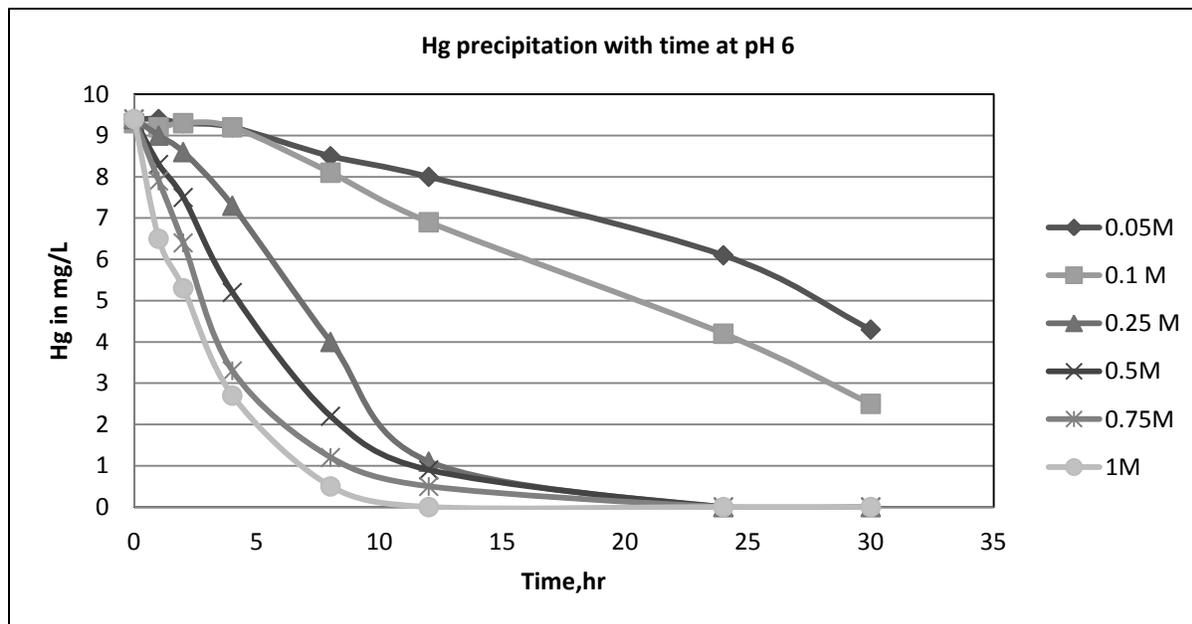
**Figure 4.5: Rietveld Refinement Plots of Sample (a) pH 5- 80°C, (b) pH 6- 80°C**

#### 4.2.3 Effect of Thiosulfate Concentration

To find the effect of thiosulfate concentration, another set of mercury precipitation tests were done at different thiosulfate concentration such as 0.05M, 0.1M, 0.25M, 0.5M, 0.75M and 1M. But in this case only 1g/L mercury from mercury oxide was used. The temperature used in this pH controlled test was 70°C and tests were done at pH 5 and 6. These experiments were continued for 30 hours.



(a)



(b)

**Figure 4.6: Mercury Precipitation with Time for Different Thiosulfate Concentration at (a) pH 5 and (b) pH 6**

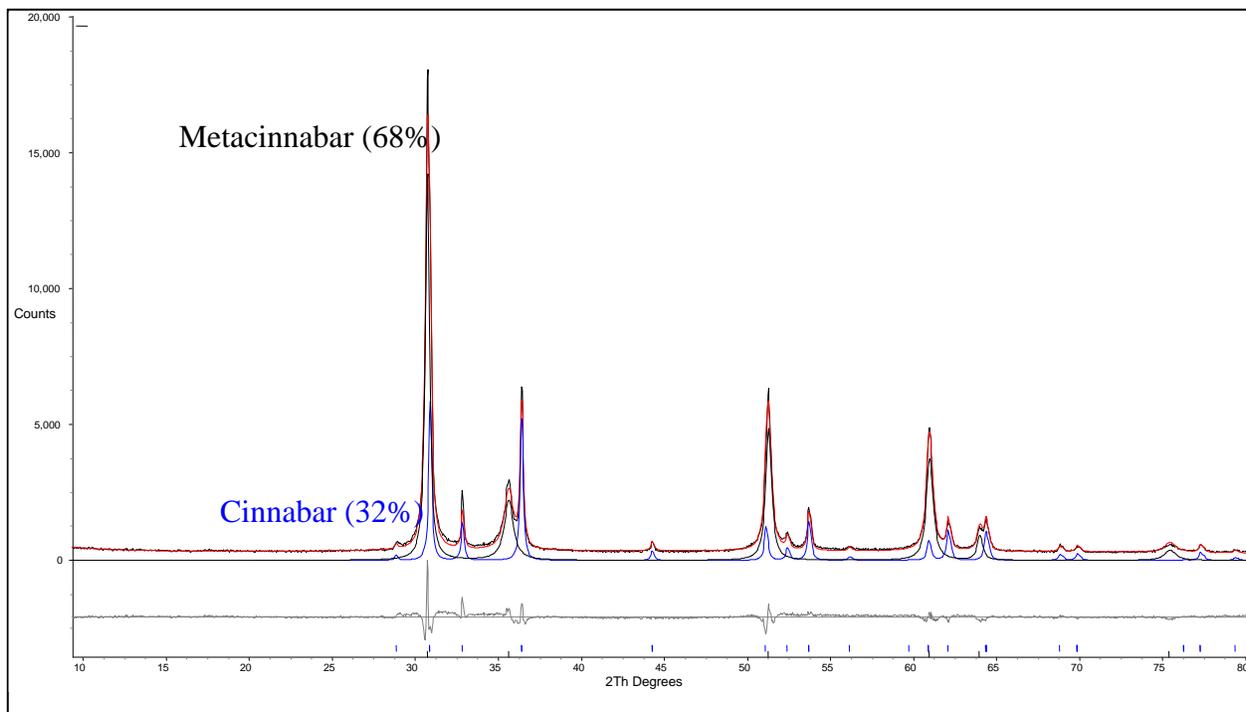
From figure 4.8, at very low thiosulfate concentration such as 0.05M and 0.1M, mercury precipitation rate is very slow and all the mercury in the solution is not precipitated within 30

hours. But the increase of thiosulfate concentration increases mercury precipitation rate and at very high thiosulfate concentration such as 0.75M and 1M, mercury precipitation rate is so high that all the mercury has been precipitated within 20 hours. The main reason for this behavior is that at low thiosulfate concentration and at low mercury content, there was an induction period for the reaction to start but with the increase of thiosulfate concentration this problem is no longer valid, a lot of thiosulfate in the solution to make a complex with mercury and that's why precipitation rate also increases.

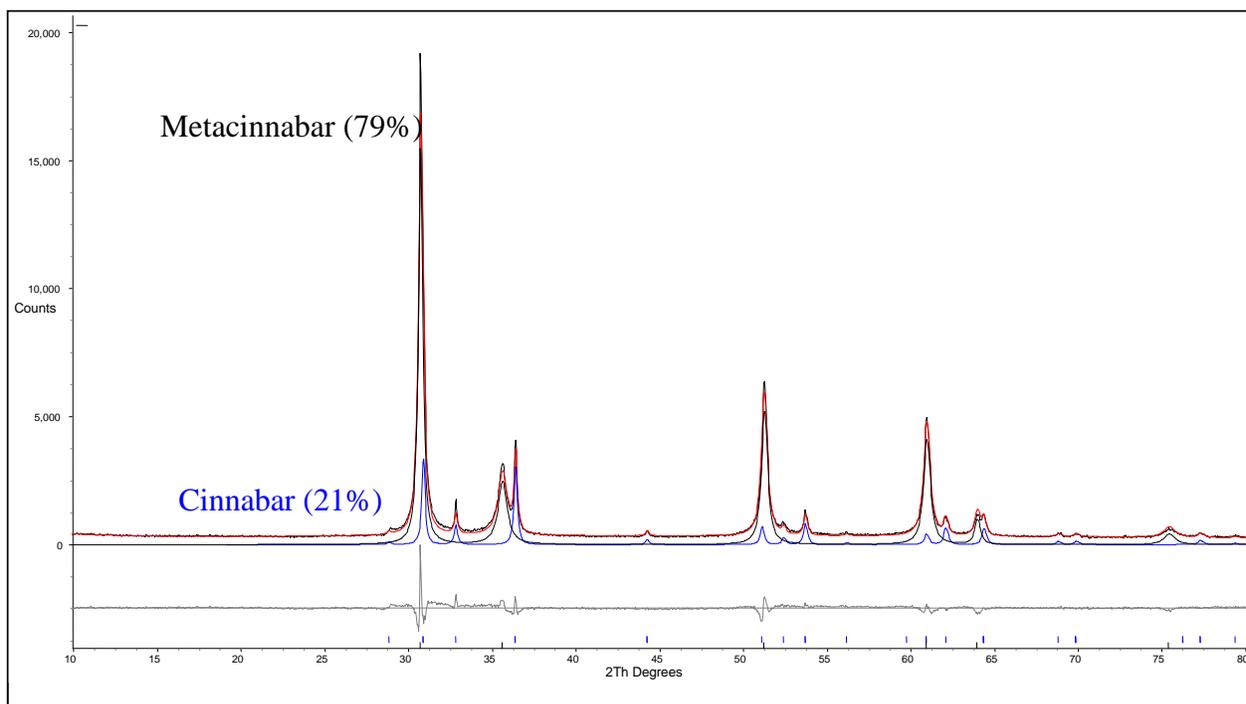
In these sets of experiment, the color of mercury precipitation is black. For that reason, the solid residue was filtered and dried in the room temperature for 3 days and then taken for the XRD analysis. The results of quantitative phase analysis by Rietveld refinements are given in Table 4.7. These amounts represent the relative amounts of crystalline phases normalized to 100%. The Rietveld refinement plots are shown in Figures 4.9 and 4.10.

**Table 4.7: Results of Quantitative Phase Analysis for Mercury Precipitation Tests (at Controlled pH): (wt. %)**

<b>Mineral</b>	<b>Ideal Formula</b>	<b>pH5 – 0.1M</b>	<b>pH6 – 0.1M</b>	<b>pH5 – 0.25M</b>	<b>pH6 – 0.25M</b>
Cinnabar	HgS	32.0	21.0	70.0	67.0
Metacinnabar	HgS	68.0	79.0	30.0	33.0
Total		100.0	100.0	100.0	100.0

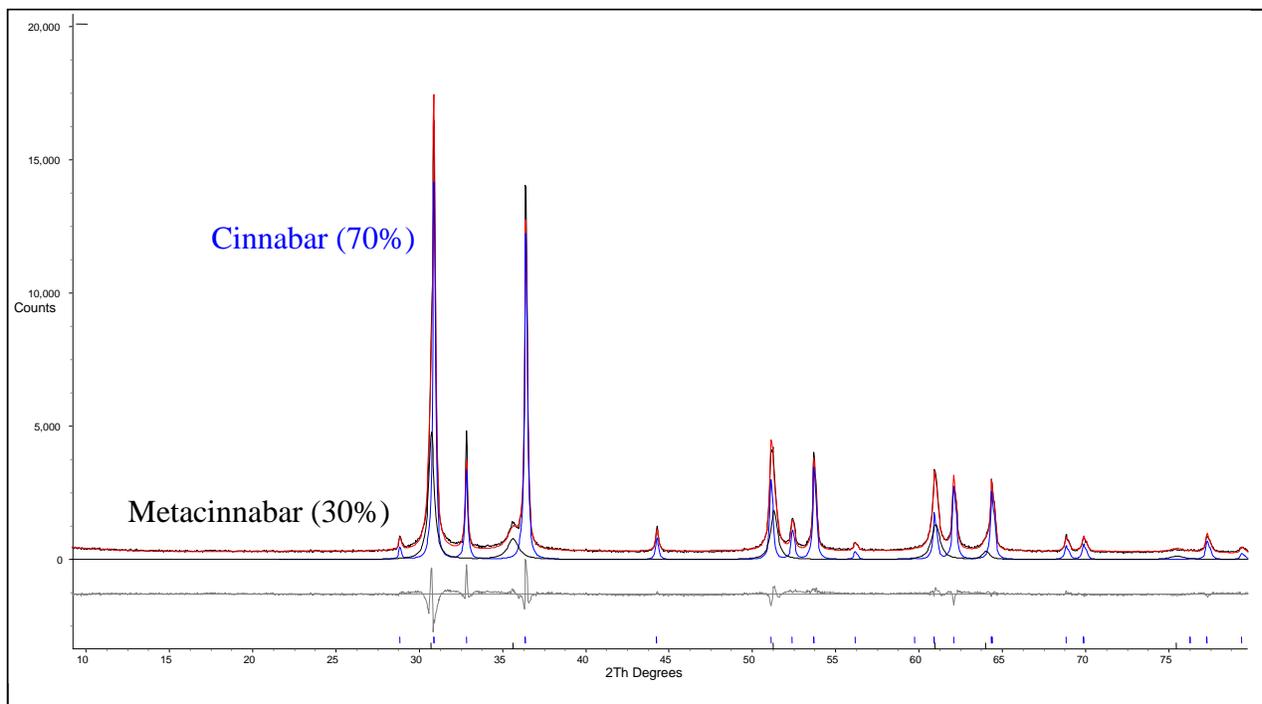


(a) pH 5- 80°C



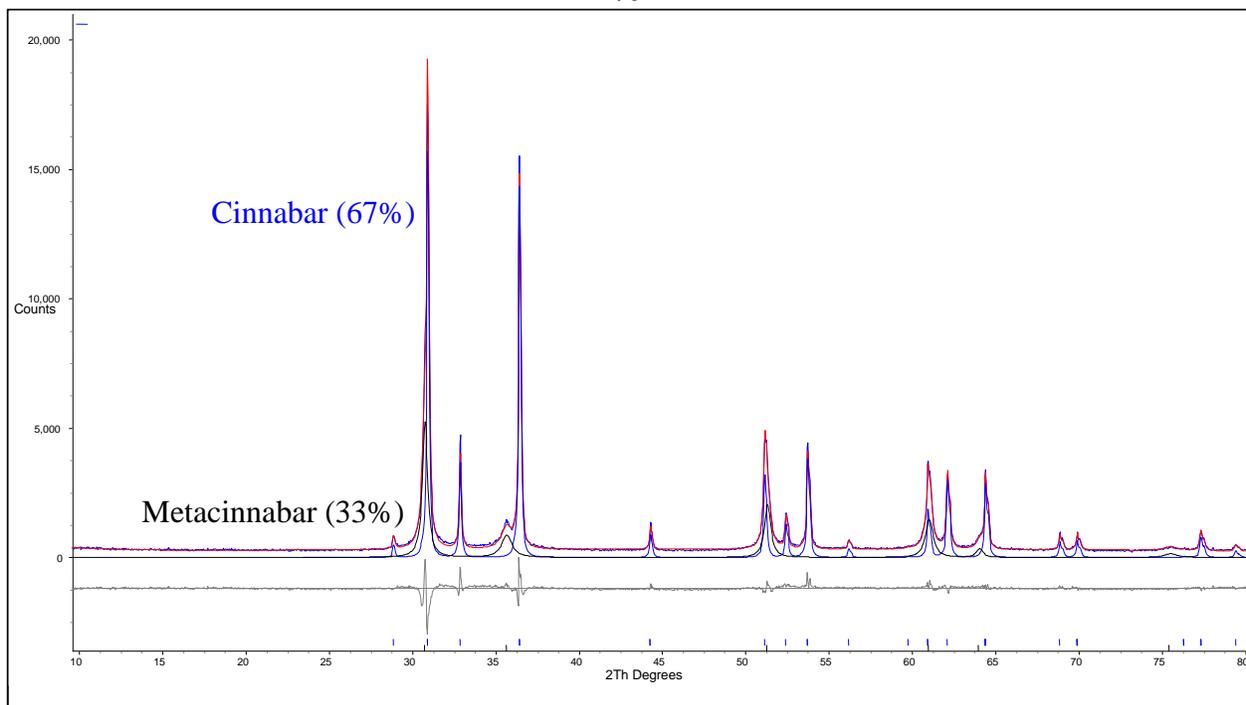
(b) pH 6- 80°C

**Figure 4.7: Rietveld Refinement Plots of Sample at 0.1M Thiosulfate (a) pH 5- 80°C, (b) pH 6- 80°C**



(a) pH 5

%



(b) pH 6

**Figure 4.8: Rietveld Refinement Plots of Sample at 0.25M Thiosulfate (a) pH 5- 80°C, (b) pH 6- 80°C**

From the table and figure, the black solid residue which was precipitated in these tests contains significant metacinnabar. At low thiosulfate concentration the percentage metacinnabar is very high in the residue. At pH 5 and 0.1M thiosulfate concentration, the percent of metacinnabar in the solid is 68 and at pH 6 and in same concentration, the percent has increased up to 79. But with the increase of thiosulfate concentration, metacinnabar percent in the solid residue decreases. The reason of this behavior might be at low concentration mercury does not have enough sulfur to formed pure mercury sulfide and also the temperature of these experiments was 70°C. In that temperature the precipitation rate was so high that red cinnabar cannot form.

### 4.3 Selenium Dissolution Tests

To prepare sodium thioselenate in the laboratory, selenium powder was mixed to dissolve in sodium sulfite solution. The tests were done at different sulfite concentration, temperature and time. The result of these experiments is given in table 4.8

**Table 4.8: Results of Selenium Dissolution Tests in Different Conditions**

<b>Na<sub>2</sub>SO<sub>3</sub> (g)</b>	<b>Se(g)</b>	<b>Time(hrs)</b>	<b>Temp (°C)</b>	<b>Se dissolution result</b>
1	0.05	4	50	40%
1	0.05	8	50	45%
1	0.05	24	60	70%
1	0.01	24	70	68%
1.5	0.05	24	60	62%
2	0.1	48	60	60%

From the table, selenium powder is very hard to dissolve in sodium sulfite solution. With the increase of time and temperature the selenium dissolution percentage increases. At 24 hours and

60°C, almost 70% selenium dissolves in thiosulfate solution. But with the increase of sodium sulfite and selenium in the solution, the dissolution percentage is decreasing.

#### 4.4 Solid Waste Disposal Characterization

The solid waste disposal characterization (SWDC) test was done to determine the Universal Treatment Standards for land disposal and RCRA limits for hazardous solid mercury sulfide residue. In this test only 2g mercury sulfide (solid residue) from 70°C and 80°C temperature test for pH 5 was used. These samples were taken because of at these conditions; the precipitation was a mixture of red and black mercury sulfide. The results from the SWDC test is given below in table 4.9:

**Table 4.9: Results of SWDC Tests for Mercury Precipitation**

<b>Solid residue</b>	<b>Hg (mg/L)</b>
Hg ppt at 70 °C and pH 5	0.09
Hg ppt at 80 °C and pH 5	0.15

From the table, the mercury content in solution is 0.09 mg/L and 0.15 mg/L respectively. If we compare the data with data for the Universal Treatment Standards for land disposal and RCRA limits for hazardous solid mercury sulfide residue (Appendix A) it can be said that mercury sulfide residue passes the RCRA limits for hazardous mercury which is 0.20 mg/L. These two solid residue, are a mixture of cinnabar and metacinnabar. This might be the reason for not passing the UTS for land disposal for mercury which is 0.025 mg/L.

## 5 CONCLUSIONS

The main objective of this study was to stabilize mercury as HgS (cinnabar) & HgSe by precipitation from thiosulfate and thioselenate solution. The following conclusions can be offered from this work:

1. The EDTA titration method for mercury analysis is effective for mercury nitrate solution but with use of sodium thiosulfate in the solution; the method is not working. As an alternative atomic absorption spectroscopy (AAS) was adopted for soluble mercury analysis.
2. Complete leaching of elemental mercury is not possible in thiosulfate solution under the conditions studied. Mercury metal is very hard to dissolve in thiosulfate solution and its leaching rate is very slow at both acidic and basic pH conditions. Leaching of mercury and precipitation of mercury sulfide occurs simultaneously which prevents further leaching of mercury in the solution.
3. Stable mercury sulfide (HgS) can be formed by using laboratory based mercury oxide (HgO) and sodium thiosulfate solution by simple aging of the mercury thiosulfate solution.
4. With the increase of temperature mercury precipitation rate increases. At low temperature such as 40°C and 50°C, mercury precipitation rate is so slow that all the mercury is not precipitated after seven days at both pH 5 and 6. But, at high temperature such as 70°C 80°C, mercury precipitation rate is so high that all the mercury is precipitated within 35 hours at both pH 5 and 6.
5. At lower pH, mercury precipitation rate is high. If the pH is allowed to decrease elemental sulfur form as a part of the precipitation.

6. At 40°C, 50°C and 60°C, the color of mercury sulfide precipitate is red. But at 70°C and 80°C tests, the color is a mixture of red and black. So at these tests, some black mercury sulfide is precipitated. Black mercury sulfide indicates the presence of metacinnabar.
7. With the increase of thiosulfate concentration, the mercury precipitation rate increases. In these cases, lower mercury content was studied and the temperature was kept constant at 70°C. At very low thiosulfate concentration such as 0.05M and 0.1M mercury precipitation rate is so slow that all the mercury is not precipitated. But at very high concentration such as 0.75 and 1M, the precipitation rate is so high that all the mercury is precipitated within 20 hours.
8. In low mercury content tests, black mercury sulfide (metacinnabar) is the dominant specie in the solid residue. But with the increase of thiosulfate concentration, the precipitation of metacinnabar decreases.
9. To prepare sodium thioselenate, selenium powder was mixed with sodium sulfite solution. But selenium powder is very hard to dissolve in sodium sulfite solution. The best result is 70% selenium powder is dissolved at 60°C temperature and in 24 hours.
10. From the SWDC tests, the mercury sulfide precipitate (tests at 70°C and 80°C at pH 5) has passed the barrier for RCRA limit for hazardous material. But unfortunately the precipitate does not pass the UTS for land disposal.

## 6 FUTURE WORKS

This work investigated the stabilization of mercury by using thiosulfate and thioselenate. From the previous chapter it can be concluded that mercury can be stabilized by thiosulfate by precipitation of mercury sulfide. However, more research should be conducted in the following areas:

- With the increase of temperature the precipitation rate increases but with the same time formation of metacinnabar increases. And also at lower mercury content formation of metacinnabar increases. Additional experiments can be done to optimize the formation of cinnabar. Factors to be studied to optimize the formation of cinnabar are mercury concentration and temperature.
- Additional experiments can be done to determine the thiosulfate and sulfate concentration in the liquid residue.
- Additional experiments should be done to form sodium thioselenate in the laboratory and then experiment should be done to precipitate mercury selenide by using mercury and sodium thioselenate.
- Due to the lack of sample SWDC tests could not be done with pure cinnabar. Additional SWDC test should be done with pure cinnabar.

## REFERENCES

1. CRC, 'Handbook of Chemistry and Physics', Chemical Rubber Company, Cleveland, OH (1969).
2. Greg Jones, Glenn Miller, 'Mercury and Modern Gold Mining in Nevada', University of Nevada, Reno, NV 89557 (2003).
3. Gustin, Mae. S., J. A. Ericksen, D. E. Schorran, D.W. Johnson, S.E. Lindberg and J.S. Coleman, "Application of Controlled Mesocosms for Understanding Mercury Air-Soil-Plant Exchange" Environ. Sci. Technol., 38:6044-6050, (2004).
4. Van Zyl, D.J.A. and G. M. Eurick, 'The Management of Mercury in the Modern Gold Mining Industry' EPA Conference Proceedings on Mercury in the Environment, (2001).
5. Sven Hagemann, 'Technologies for the stabilization of elemental mercury and mercury-containing wastes', GRS – 252, ISBN 978-3-939355-27-4,(2009).
6. Paquette, K., and G. Helz. 'Solubility of Cinnabar (Red HgS) and implications for mercury speciation in sulfidic waters.' Water, Air and Soil Pollution 80:1053-056, (1995).
7. 'Clean Air Act.' U.S. Environmental Protection Agency. <<http://www.epa.gov/air/caa/>>.
8. 'Nevada Mercury Control Program.' Bureau of Air Quality Planning. State of Nevada Division of Environmental Protection.
9. Padma Mahadevan, Noelene Ahern, 'A Review of Mercury Management in the Gold Processing Industry' Barrick Technology Centre, Vancouver, BC, (2008).
10. 'Bevill Amendment Questions' U.S. Environmental Protection Agency, <<http://www.epa.gov/oecaerth/assistance/sectors/minerals/processing/bevillquestions.html>>
11. 'Bevill Amendment Issues Training' <<http://www.epa.gov/oecaerth/assistance/sectors/minerals/processing/bevilltraining.html>>
12. GovTrack.us. H.R. 1534--110th Congress (2007): Mercury Export Ban Act of 2007, GovTrack.us (database of federal legislation) <<http://www.govtrack.us/congress/bill.xpd?bill=h110-1534&tab=summary>>
13. 'Mercury Export Ban.' 1 Nov. 2007. Chemical & Engineering News. <<http://pubs.acs.org/cen/news/85/i45/8545news5.html>>.

14. 'Bethlehem Apparatus (undated). Mercury Retirement / Stabilization'.  
<<http://www.bethlehemapparatus.com/mercury-retirement.html>>
15. Ortheil, M. 'Mercury stabilization - A new option for final disposal', presentation provided by DELA GmbH, (2009).
16. Riviere-Huc, C., Huc, V., Bosse, E. 'Method for stabilization of metallic mercury using sulfur', US Patent 2008/0019900, (2008).
17. Gorin, A. H., Leckey, J. H., Nilf, L. E., 'Final disposal options for mercury/ uranium mixed wastes from the oak ridge reservation', Oak Ridge Y-12 Plant, TN (United States), Report Y/DZ-1106, (1994).
18. Kalb, P. D., Spence, R. D., Shi, C., 'Stabilization and solidification of hazardous, radioactive, and mixed wastes', CRC Press, Boca Raton, 121-130, (2005).
19. Kalb, P. D., Adams, J. W., Milian, L. W., 'Sulfur Polymer Stabilization/ Solidification (SPSS) Treatment of Mixed-Waste Mercury Recovered from Environmental Restoration Activities at BNL', BNL Report 52614, (2001).
20. Kalb, P. D., Melamed, D., Patel, B. R., Fuhrmann, M., 'Treatment of mercury containing waste', US Patent 6 399 849, (2002).
21. John, Litz E., Thomas Broderick, and Robin M. Stewart., 'Method and apparatus for stabilizing liquid elemental mercury', ADA Technologies, Inc. (CO), assignee. Patent 6,403,044, (2002).
22. Litz, J. E., Broderick, T., Steward, R. M., 'Method and apparatus for stabilizing liquid elemental mercury'. US Patent 6 403 044.a, (2002).
23. Chattopadhyay, Sandip, 'Evaluation of chemically bonded phosphate ceramics for mercury stabilisation of mixed synthetic wastes', U.S. Environmental Protection Agency, (2003).
24. Wagh, Arun S., Dileep Singh, Seung-Young Jeong, 'Chemically bonded phosphate ceramics for stabilisation and solidification of mixed waste', Argonne National Laboratory.
25. Singh, Dileep, Arun S. Wagh, and Kartikey D. Patel, 'Polymer coating for immobilizing soluble ions in a pHospHate ceramic product'.The United States of America as represented by the United States Department of Energy (Washington, DC), assignee. Patent U.S. 6,153,809, (2002).

26. US DOE , ‘Mercury contamination – amalgamate (contract with NFS and ADA)’, Demonstration of DeHg<sup>SM</sup> process, DOE/EM-0471, (1999).
27. Morris, M. I., Hulet, G. A., ‘Development and selection of technologies for mercury management on U.S. Department of Energy sites: the mer01–mer04 and mercury speciation demonstrations’, WM’03 Conference, Tucson, AZ, (2003).
28. Mattus, C. H., ‘Measurements of mercury released from amalgams and sulfide compounds’, ORNLITM-13728, (1999).
29. Noelene Ahern, ‘Thiosulfate degradation during gold leaching in ammoniacal thiosulfate solutions: a focus on trithionate’, (2005).
30. Kirk Othmer, ‘Encyclopaedia of chemical technology, 3<sup>rd</sup> edition, John Wiley and Sons, New York, Vol. 22, pp 974-988, (1983).
31. Ellen Molleman, ‘The treatment of copper-gold ores by ammonium thiosulfate leaching’, (1998).
32. Asim B. Ray, Ariamalar S., ‘Laboratory studies on the remediation of mercury contaminated salts’, John Wiley and Sons, (2000).
33. Chiriki, Suresh. ‘Disposal Strategy for proton irradiated mercury’, Institute for safety research and reactor technology, Germany.
34. Svensson, Margareta, Bert Allard, and Anders Duker, ‘Formation of HgS-mizing HgO or elemental Hg with S, FeS or FeS<sub>2</sub>’, Science of Total Environment 368 : 418-23, (2006).
35. Svensson, Margareta. ‘Mercury Immobilization - A Requirement for Permanent disposal of mercury waste in Sweden.’ Thesis. Orebro University, Sweden, (2006).
36. Ravichandran, M., G. R.Aiken, J. N Ryan., and M. M Reddy. ‘Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades.’ Environmental Science and Technology 33:1418-423, (1999).
37. Bandon, N. P., P. A. Francis, J. Jeffrey, G. H. Kelsall, and Q. Yin. ‘Thermodynamics and Electrochemical behaviour of Hg-S-Cl-H<sub>2</sub>O systems.’ Journal of Electroanalytical Chemistry 497:18-32, (2001).
38. Ravichandran, M., G. R.Aiken, J. N Ryan., and M. M Reddy. ‘Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades.’ Environmental Science and Technology 32: 3305-3311, (1998).

39. Sheila Ball and John Milne, 'Studies on the interaction of selenite and selenium with sulfur donors. Part 3. Sulfite', University of Ottawa, Ottawa, ON, KIN 6N5, Canada, *Can. J. Chem.* 73: 716-724 (1995).

## **APPENDIX**

### **Solid Waste Disposal Characterization: (Newmont Mining Corporation, Newmont Metallurgical Services)**

The SWDC test is to reflect the interaction of the leachant and buffering capacity of the waste. It is applicable for single batch extractions only. It does not apply to organic substances, volatile matter or biologically active samples. This test is similar to EPA TCLP test but is informational only and not intended for regulated purposes.

This test method calls for the shaking of a known weight of mining waste with extraction fluid of a specified composition, followed by the separation of the liquid phase for analysis. The final pH of the extraction fluid is measured, and preserved aliquots measured for specific inorganic constituents.

This method involves concentrated acids and mechanical hazards. Concentrated nitric acid is highly corrosive and a strong oxidizer. Anhydrous acetic acid is highly corrosive. Ensure that the sample containers are secure and will not catch on the internal workings of the sample agitator to avoid burning out the motor, creating a possible fire hazard while the samples are left overnight. All processes should be carried out wearing safety glasses, protective gloves and a lab coat. As with all tests, the primary responsibility for safety lies with the analyst. Please consult the appropriate MSDS and the Newmont Chemical Hygiene plan for further details.

#### **A.1 Procedure**

1. Sample Pan
2. Desiccator
3. Laboratory Oven
4. 500mL beaker
5. Watch glass
6. 2L Nalgene FLPE Sample Container
7. 1000mL Filter Flask
8. Large Sintered Glass Frit
9. Filter Funnel
10. Frit Clamp

11. 142mm Ø, 0.7µm porosity borosilicate TCLP Filter Paper
12. Mettler DH-12 pH Meter with pH Electrode
13. 25mL Polypropylene Bottle
14. 50ml polypropylene “Digitube”
15. Stopwatch with countdown
16. Thermometer in °C

There are six types of Reagents and standards are used in this test

1. pH 4.0 Standardized Buffer Solution
2. pH 7.0 Standardized Buffer Solution
3. 1N (1M) Hydrochloric Acid (HCl) Solution

Put 500mL DI water into a 1000mL volumetric flask. Slowly add 82.64mL concentrated (12.1M) hydrochloric acid and swirl to mix. Allow the solution to equilibrate to room temperature and bring to volume with DI water.

4. Extraction Fluid #1

Add 500mL DI water to a 1000mL volumetric flask. Add 5.7mL anhydrous (glacial) acetic acid and 64.3mL 1.00M sodium hydroxide solution. Bring to volume with DI water and mix thoroughly. When prepared properly, the pH should be  $4.93 \pm 0.05$ .

5. Extraction Fluid #2

Add 500mL DI water to a 1000mL volumetric flask. Add 5.7mL anhydrous (glacial) acetic acid. Bring to volume with DI water and mix thoroughly. When prepared properly the pH should be  $2.88 \pm 0.05$ .

6. High Purity, Concentrated (15M) Nitric Acid (HNO<sub>3</sub>)

To adequately simulate the natural leaching processes at work in the ore, the sample should be leached as it is received. Samples typically range in size from 3/8 inch to 150 mesh.

A reagent blank should be carried throughout this procedure. At least 2 appropriate QC samples should be carried throughout this procedure.

Determine the solid weight fraction of two separate portions of the sample:

- Dry to constant weight at 104<sup>o</sup>C using two pans to hold sample. Cool in a desiccator and record weight to  $\pm 0.1$  g.
- Place 50 g of sample to be tested into each pan and record weight to  $\pm 0.1$  g.
- Dry at 104<sup>o</sup>C for 16-20 hours recording the drying duration. Record final weight.
- Repeat steps (1-3) if necessary to obtain constant weight.

Calculate the solids weight fraction (S) as shown in calculations for both splits and average the measurements.

- Weigh 5g of sample into a 400mL beaker. Sample should be 1mm or less in diameter.
- Add 96.5mL of DI H<sub>2</sub>O to the beaker and cover with a watch glass. Stir 5 min with a magnetic stirrer.
- Check the pH of the sample. If pH<5 then use extraction fluid #1. If pH>5 proceed to next step.
- Add 3.5mL of 1N HCl to sample, slurry briefly and heat at 50<sup>o</sup>C for 10 min on a hotplate.
- Let solution cool and record the pH. If pH<5 then use extraction fluid #1, if pH>5 use extraction fluid #2.
- Add at least 10 $\pm$ 0.1 g of test sample on dry weight basis to extraction vessel. Calculate the minimum amount of as-received waste, the dry test sample weight, mass of water in test sample and the mass of the extraction fluid.
- Use the mass of the extraction fluid to determine the volume of fluid (1g = 1mL @ room temp.) and add this amount to the vessel containing the sample. This should provide a 1:20 solid-to-liquid-ratio.
- The vessel is then placed into the extractor (agitation device) and is rotated at 30 rpm for 18.00 $\pm$ 0.25 hours. Record the time agitation was begun.
- Set up a vacuum filtration device with enough capacity to filter extraction fluid in two consecutive fills. Use a Borosilicate microfiber TCLP filter with a pore size of 0.7 $\mu$ m.
- Measure the pH of the extract immediately and record.

- Preserve 50-mL with 0.5mL of High-Purity HNO<sub>3</sub> for metals analysis
- Submit samples for SWDC\_METALS and SWDC\_HGCV

Calculation of the solids weight fraction (S):

$$S = A/B$$

A = mass after drying

B = original mass

Calculation of Minimum amount of as-received waste (M):

$$M = 100/S$$

Calculation of dry test sample weight (M<sub>d</sub>):

$$M_d = MS$$

Calculation of mass of water in sample (M<sub>w</sub>):

$$M_w = M - M_d$$

Calculation of mass of extraction fluid (M<sub>e</sub>):

$$M_e = 20M_d - M_w$$

## **A.2 Data Assessment and Quality Control Measures**

This procedure depends upon a precise leach time. Analytical results may be affected by the type of filter used. A filter of with pore size larger than 0.8 μm may require the extraction fluid to be digested prior to metals analysis. The filter should also be washed prior to filtration to eliminate any contamination of the filtrate.

Assessment of Data: Following analysis of solution, results are compared to Table A.1 which lists the limits from 40 CFR parts 268.48 with respect to Universal Treatment Standards for land disposal and RCRA limits for hazardous/non-hazardous determination.

**Table A.1: Lists the Limits for Universal Treatment Standards and RCRA**

<b>Analyte</b>	<b>UTS limits (mg/L)</b>	<b>RCRA limits (mg/L)</b>
Arsenic	5.0	5.0
Barium	21	100
Cadmium	0.11	1
Chromium	0.60	5
Lead	0.75	5
Mercury	0.025	0.20
Selenium	5.7	1
Silver	0.14	5

### **A.3 Waste Management**

For solid waste management, used filter paper and leached sample residue should be disposed of in the labeled bucket near the sample agitator.

And for any liquid waste may be disposed of down a laboratory sink drain, diluted with tap water.