

Stabilization and Testing of Mercury Containing Wastes: Borden Catalyst

by

Linda A. Rieser, Paul Bishop, Makram T. Suidan,
Haishan Piao, Renee A. Fauche, and Jian Zhang
Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221-0071

Contract No. 68-C7-0057
Task Order #20

Task Order Manager

Paul Randall
Land Remediation and Pollution Control Division
National Risk Management Research Laboratory
Cincinnati, Ohio 45268

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Notice

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed the research described here under contract number 68-C7-0057, Task Order #20 to the University of Cincinnati. It has been subjected to the U.S. EPA's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

This report was submitted by the University of Cincinnati (UC) in fulfillment of Contract No. 68-C7-0057 under the sponsorship of the U.S. Environmental Protection Agency (EPA). This report covers a period from June 1999 through July 2000; laboratory work was completed as of July 2000. This report evaluates the chemical stability of spent mercuric chloride catalyst in an aqueous environment before and after treatment with stabilizing agents. The stabilizing agents evaluated in this study are sulfide and phosphate.

Samples obtained by UC and EPA personnel at the Borden Chemicals and Plastics (BCP) plant on June 10, 1999 were characterized for total mercury content, pH, and acidity prior to performing the leaching tests on untreated waste. Leaching tests and analytical work performed by UC and their contract laboratories included the toxicity characteristic leaching procedure (TCLP), solid stability in water, and leaching at constant and variable pH values.

After completing the baseline tests on untreated waste, the spent mercuric chloride catalyst was treated with sulfide and phosphate binders to evaluate the effectiveness of these additives on reducing the concentration of mercury in the leachate. The mercuric chloride waste was crushed and combined with the binders at various molar ratios and pH ranges prior to performing the identical leaching tests noted above.

Measured mercury concentrations in the generated leachates indicate that sulfide treatment lowers the aqueous mercury concentration, while phosphate treatment has little effect on decreasing the mercury concentration. Analytical results for individual leaching methods carried out over a pH range of 2 to 12 do not define a consistent trend for mercury concentrations as a function of pH. However, samples treated with moderate to large amounts of sulfide (i.e., a S/Hg molar ratio greater than 3) released less mercury.

Table of Contents

Foreword	iii
Abstract	iv
1.0 Background	1
1.1 Waste Characterization	1
1.2 Leaching Tests	1
1.3 Treatment Reagents	1
2.0 Characterization of BCP Catalyst	2
3.0 Leaching Tests	2
3.1 Solid Stability in Water for Untreated Catalyst	2
3.1.1 Introduction	2
3.1.2 Procedure	3
3.1.3 Results	3
3.1.4 Data Quality Discussion	4
3.2 Acidity of Untreated Catalyst	4
3.2.1 Introduction	4
3.2.2 Procedure	5
3.2.3 Results	5
3.2.4 Data Quality Discussion	6
3.3 Toxicity Characteristic Leaching Procedure	6
3.3.1 Introduction	6
3.3.2 Procedure	6
3.3.3 Results	7
3.3.4 Data Quality Discussion	7
3.4 UC Constant pH Leaching Test	8
3.4.1 Introduction	8
3.4.2 Procedure	8
3.4.3 Results	8
3.5 RU-SR002.1 (Solubility and Release as a Function of pH)	9
3.5.1 Introduction	9
3.5.2 Procedure	9
3.5.3 Results	10

Table of Contents, Continued

4.0	Stabilization Treatments	11
4.1	Stabilization of BCP Catalyst by Sulfide	11
4.1.1	Introduction	11
4.1.2	Procedure	11
4.1.3	Results	12
4.1.4	Discussion	18
4.2	Stabilization of BCP Catalyst by Phosphate	19
4.2.1	Introduction	19
4.2.2	Procedure	20
4.2.3	Results	20
4.2.4	Discussion	23
5.0	Data Quality	24
5.1	Background Characterization	24
5.2	Leaching Tests	24
5.3	Acidity	27
5.4	Treatment Reagents	27
6.0	Conclusions	33

Appendices

A	Analytical Data - Environmental Enterprises Inc. - Provided upon request, Paul Randall, USEPA, Cincinnati, OH, 513 569-7673 or email Randall.Paul@epa.gov	
---	---	--

List of Tables

2.1	Chemical Characterization of Untreated BCP Catalyst	2
3.1	Solid Stability in Water for Untreated Spent Catalyst	4
3.2	Acidity Results	5
3.3	TCLP Results for Untreated Catalyst	7
3.4	Constant pH Leaching Results for Untreated Catalyst	9
3.5	RU-SR002.1 Leaching Results for Untreated Catalyst	10
4.1	Sample Test Matrix	12
4.2	Mercury Results for Sulfide Stabilization	13
4.3	Stabilization Efficiency (%)	15
4.4	TCLP Mercury Results (mg/L) for Sulfide Stabilization	16
4.5	Stabilization Efficiency for TCLP Data	17
4.6	Mercury Results for Phosphate Stabilization	21
4.7	TCLP Mercury Results (mg/L) for Phosphate Stabilization	23
5.1	Laboratory QC Data for EEI Total & TCLP Mercury Results Background Data	25
5.2	Laboratory QC Data for EEI Total Mercury Results Solid Stability in Water	26
5.3	Laboratory QC Data for EEI Total Mercury Results University of Cincinnati pH Test	26
5.4	Laboratory QC Data for EEI Total Mercury Results Rutgers University pH Test	27
5.5	Laboratory QC Data for EEI Total Mercury Results Sulfide and Phosphate Stabilization	29
5.6	Laboratory QC Data for EEI TCLP Mercury Results Sulfide and Phosphate Stabilization	31
5.7	Experimental QC Data for Test Duplicates Sulfide and Phosphate Stabilization	32

List of Figures

3.1	Acidity of Untreated Catalyst vs. Sample Solid	6
4.1	Mercury Results for Sulfide Stabilization as a Function of pH	14
4.2	Stabilization Efficiency(%)	15
4.3	TCLP Mercury Results for Sulfide Stabilization	16
4.4	Stabilization Efficiency for TCLP Data	17
4.5	Distribution of the Various Hg-H-S Species as a Function of pH	19
4.6	Mercury Results for Phosphate Stabilization	21
4.7	TCLP Mercury (mg/L) Results for Phosphate Stabilization	22

1.0 Background

The Borden Chemicals and Plastics plant (BCP) in Geismar, Louisiana produces, among other chemicals, vinyl chloride. The vinyl chloride synthesis employs a mercuric chloride catalyst, which is the subject of this study.

1.1 Waste Characterization

Spent mercuric chloride catalyst samples collected at the BCP plant were characterized for total mercury content, pH and acidity by UC and a contract laboratory prior to initiating the leaching tests. A summary of this information is provided in Section 2.0.

1.2 Leaching Tests

A variety of leaching tests were carried out with the untreated and treated mercuric chloride waste to evaluate the physiochemical controls on mercury mobility (e.g., dissolution, diffusion and/or solubility). The liquid/solid mass ratio was varied from 20 to 200 to investigate diffusion gradients, TCLP tests were used to evaluate the suitability of disposing of untreated and treated waste in landfills, and constant and variable pH tests were used to examine the leaching behavior of mercury over the pH range of 2 to 12. Section 3.0 presents the procedures and results for all test sequences.

1.3 Treatment Reagents

Treatment reagents applied to the spent catalyst consisted of sodium sulfide and sodium phosphate. The treated waste forms were prepared at various molar ratios (e.g., S/Hg = 1, 3, 5 and 7) and then leached at pH values that were initially set at 2, 4, 6, 8 and 10. Results are provided in Section 4.0.

2.0 Characterization of BCP Catalyst

On June 10, 1999 UC and EPA personnel collected samples of spent mercuric chloride catalyst from 55-gallon drums staged at the Geismar, Louisiana BCP plant. Approximately 10 kilograms (kg) of waste was collected and homogenized prior to performing the baseline characterization. The waste was homogenized by tumbling in a five gallon container for 24 hours before sampling. Observations of the homogenized waste detected no visual heterogeneity. The samples were analyzed for total mercury, pH and acidity (Table 2.1) to establish baseline conditions for the waste prior to initiating the leaching tests. Laboratory QC data associated with the reported mercury results are presented and discussed in Section 5.1.

Table 2.1 Chemical Characterization of Untreated BCP Catalyst

Chemical Parameter	Concentration	Method of Analysis
Total Mercury (2 grab samples)	20,800 mg/kg	SW-846-7470A ¹
	22,300 mg/kg	SW-846-7470A ¹
pH	2.10	pH electrode ²
Acidity	0.54 mg CaCO ₃ /g	Standard Methods ²

(1) Analysis performed by Environmental Enterprises Incorporated, Cincinnati, Ohio

(2) Analysis performed by University of Cincinnati, Cincinnati, Ohio

3.0 Leaching Tests

3.1 Solid Stability in Water for Untreated Catalyst

3.1.1 Introduction

This test varies the liquid/solid mass ratio to study the effect of the aqueous contaminant concentration on the diffusion of contaminants from the waste form. If the amount of contaminant released from the waste form

decreases as the liquid-solid ratio decreases, then the contaminant concentration in the leachate may be great enough to reduce the concentration gradient between the leachate and the waste form and impede its diffusion from the waste.

3.1.2 Procedure

Samples of spent mercuric chloride catalyst were dried at room temperature for 24 hours in an exhaust hood.⁽¹⁾ Four tests were run using 10, 20, 50 and 100 grams of waste. Each solid sample was placed in a 2-liter Nalgene HDPE bottle and then filled with 2 liters of deionized water. The bottles were capped and tumbled for 18 hours and then each leachate sample was filtered through a 0.45 μm filter and placed in a sample container. Each leachate sample was acidified to a pH of less than 2 with HNO_3 and stored at 4°C until analyzed within the 28 day holding-time requirement. Mercury concentrations were measured by cold vapor atomic absorption spectroscopy (CVAAS).

3.1.3 Results

As shown in Table 3.1, the aqueous mercury concentration increased and the percent of total mercury leached from the waste decreased as the liquid/solid mass ratio decreased (i.e., the mass of solid increased). In terms of total mercury leached from the waste, Sample 1 released over 4 times more mercury than Sample 4. This observation, along with the higher aqueous concentration seen in Sample 4, suggests that a reduction in the concentration gradient between the leachate and waste may impede the diffusion of mercury from the waste form. Alternatively, the similarity in aqueous concentration for Samples 3 and 4 may indicate a

¹ This represents a change from the QAPP oven drying method. Assuming that moisture could still be present in the catalyst, values obtained could be conservative as compared to the oven dry, dry weight basis. Moisture content analysis, however, showed no moisture present in the catalyst.

solubility limit is controlling the amount of mercury released from the waste.

Table 3.1 Solid Stability in Water for Untreated Spent Catalyst¹

	Sample 1	Sample 2	Sample 3	Sample 4
Liquid / Solid Mass Ratio	200:1	100:1	40:1	20:1
Spent Catalyst (g/L) / Mercury (mg)	5/108	10/216	25/539	50/108
Mercury in Leachate (mg/L)	2.88	4.34	6.30	6.76
Total Mercury Leached (%)	2.7	2.0	1.2	0.6

(1) Mercury Analysis performed by Environmental Enterprises Incorporated, Cincinnati, Ohio

3.1.4 Data Quality Discussion

The solid stability-in-water test provides only single point estimates. As leachates were measured at a single time point (18 hours), there is no information on whether the interval was sufficient to establish mercuric equilibrium between the solid and solution phases. Section 5.2 provides the data quality analysis for Solid Stability in Water Results.

3.2 Acidity of Untreated Catalyst

3.2.1 Introduction

Acidity is related to the capacity of a material to react with a strong base. An acidity titration was run on each leachate produced from the solid stability tests to assess the acidic content of the spent catalyst. Each sample was titrated with a strong base to an end point pH of 9 to obtain a smooth titration curve. Construction of the titration curve identifies the inflection points and determines the buffering capacity of the leachate.

3.2.2 Procedure

A known volume of leachate (40 mL) from the solid-stability-in-water test was placed in a breaker and a 0.1N sodium hydroxide titrant was added to the sample in incremental amounts until the end point was obtained. The amount of sodium hydroxide required to neutralize the acidity of the sample is expressed as equivalent milligrams (mg) of CaCO₃ relative to a liter (L) of leachate and normalized to a gram (g) of the spent catalyst. An Orion electrode was used to measure the pH of the leachate.

3.2.3 Results

The resulting acidity for each sample is shown in Table 3.2, and Figure 3.1 shows measured acidity in the leachate versus mass of spent catalyst. The plot is linear, indicating that acidity is dependent on the amount of spent catalyst available for leaching.

Table 3.2 Acidity Results¹

Liquid/Solid Ratio (w/w)	20:1	40:1	100:1	200:1
Spent Catalyst (g/L)	50	25	10	5
Acidity (as mg CaCO ₃ /L)	51.25	22.50	8.75	7.50
Normalized acidity(mg CaCO ₃ /g)	1.03	0.90	0.88	1.50

(1) Analysis performed by University of Cincinnati, Cincinnati, Ohio

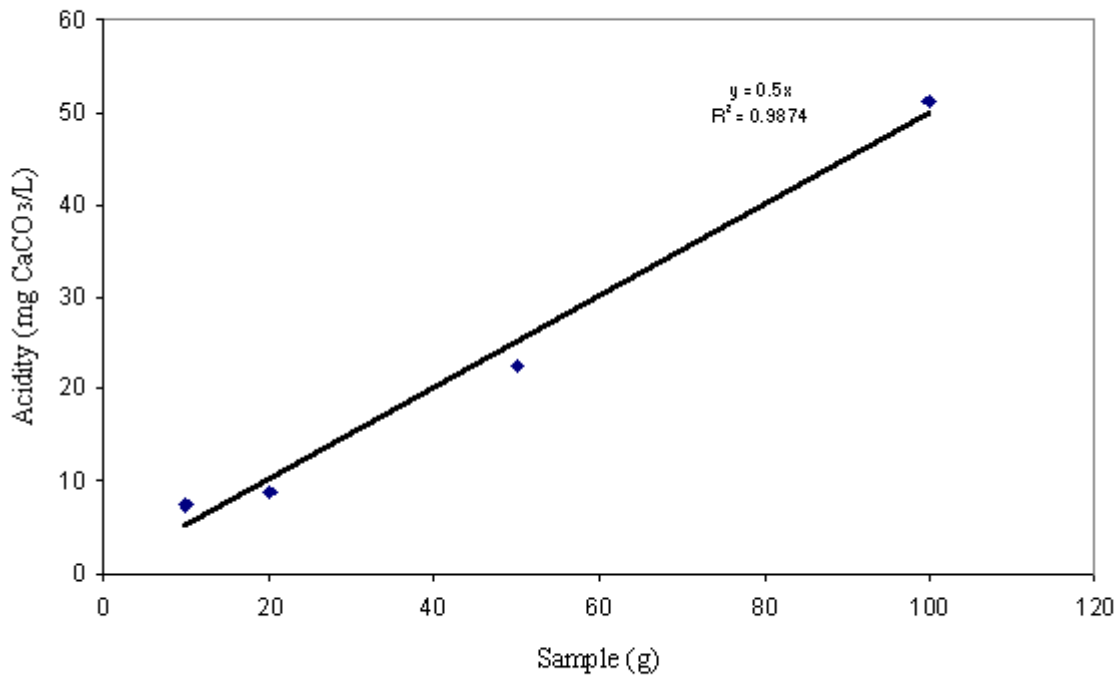


Figure 3.1: Acidity of Untreated Catalyst vs Sample Solid

3.2.4 Data Quality Discussion

Data generated in acidity analyses consist of single point estimates. Section 4.5.6 provides the data quality analysis for the Acidity data.

3.3 Toxicity Characteristic Leaching Procedure (TCLP)

3.3.1 Introduction

This test is used to determine the potential mobility of contaminants in an acetic acid solution that is intended to serve as simulated leachate under landfill conditions.

3.3.2 Procedure

Prior to performing the TCLP analysis, an initial pH measurement of the waste must be made to determine the appropriate pH of the extraction fluid (4.93 or 2.88) that must be used in the test. The pH of the untreated BCP

spent catalyst is 2.10. This pH value is well below pH 5, thus the TCLP method dictates that the extraction fluid corresponding to a pH of 4.93 must be used.

A total of 100 grams of dried spent catalyst were added to a 2-liter container with 2 liters of extraction fluid to yield essentially no head space in the container. The containers were sealed and then rotated end-over-end for 18 hours. Each leachate sample was then filtered through a 0.70 µm filter and placed in a sample container. The leachate samples were acidified to a pH of less than 2 with HNO₃ and stored at 4°C until analyzed within the 28 day holding-time requirement. Mercury concentrations were measured by CVAAS.

3.3.3 Results

Table 3.3 summarizes the analytical results for the TCLP test and indicates that both samples of untreated catalyst had mercury leachate concentrations orders of magnitude above the TCLP limit of 0.2 mg/L.

Table 3.3 TCLP Results for Untreated Catalyst¹

Sample	Limit	1	2
TCLP (mg/L)	0.2	123	120
Total Mercury (mg/kg)		20,800	22,300

(1) Mercury analysis performed by Environmental Enterprises Incorporated, Cincinnati, Ohio

3.3.4 Data Quality Discussion

The relative percent difference for the TCLP duplicate is 2.47%. Laboratory QC data associated with the reported mercury results are presented and discussed in Section 5.1.

3.4 *UC Constant pH Leaching Test*

3.4.1 *Introduction*

Constant pH leaching tests are a means to determine the effect pH has on mobilizing contaminants found in waste samples. The basic premise of this test is to leach samples in a constant pH solution, adjusting the sample pH to the set point as necessary.

3.4.2 *Procedure*

The leaching tests were run at pH values of 2, 4, 6, 8, 10 and 12 using 500 mL of deionized water and 25 grams of dried solid to produce a liquid/solid mass ratio of 20:1. A duplicate test was run at a pH value of 8. The samples were stirred using stirring bars on stir plates throughout the experiment. The pH was maintained at the initial value for a 24 hour period, with samples being extracted for analysis at 2, 10 and 24 hours. The samples were filtered through a 0.7 μm glassfiber filter, acidified to a pH of less than 2 with HNO_3 and stored at 4°C until analyzed within the 28 day holding-time requirement. All samples were analyzed via CVAAS.

3.4.3 *Results*

Table 3.4 summarizes the reported mercury concentrations for each distinct pH test carried out. At a pH of 2, a steady-state condition may have been reached between 10 and 24 hours, as the mercury concentrations for these time intervals are within 10 percent of each other. For other pH values, it is hard to tell if a steady-state condition was reached because mercury concentrations continued to increase through the entire time interval. A longer testing period is recommended for future research. In any event, the mercury concentrations are highest at the low and high pH values, with the minimum values observed at a pH of 8. All sample test blanks are below the method detection limit of 0.0005 mg/L, indicating cross-contamination of the experimental samples is not evident. Laboratory QC data associated with the reported mercury results are presented and discussed in Section 5.2.

Table 3.4 Constant pH Leaching Results for Untreated Catalyst¹

	Mercury (mg/L)						
	pH 2	pH 4	pH 6	pH 8 (1)	pH 8 (2)	pH 10	PH 12
2 hr	13.8	5.74	4.28	2.12	1.78	1.14	8.58
10 hr	19.2	9.82	9.36	7.00	9.72	11.4	13.4
24 hr	17.6	15.0	12.8	10.3	11.3	14.0	26.6
Blank	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005

(1) Mercury analysis performed by Environmental Enterprises Incorporated, Cincinnati, Ohio

3.5 RU-SR002.1 (Solubility and Release as a Function of pH)

3.5.1 Introduction

The pH leaching tests developed at Rutgers University are an alternate means to determine the effect pH has on the stability of a sample. The basic premise of this test is to adjust the initial pH to the desired set point and then allow the pH of the solid and liquid system to reach its natural endpoint.

3.5.2 Procedure

Using the acidity or alkalinity data on the solid samples, an acid or base addition schedule is developed to set the initial pH ranges of 3 to 12. Based on this schedule, the acid or base is added to 75 mL of deionized water and 15 g of dry sample (particle size less than 5 mm) to produce a liquid/solid mass ratio of 5:1. The sample containers are sealed and tumbled in an end-over-end fashion for 14 days and then centrifuged to separate the solid and liquid phases prior to pH measurement. Following pH measurement, the samples are filtered through 0.45 µm polypropylene filters, acidified to a pH of less than 2 with HNO₃ and stored at 4°C until analyzed within the 28 day holding-time requirement. All samples in this study were analyzed via CVAAS.

3.5.3 Results

Table 3.5 summarizes the reported mercury concentrations for each pH test. Leaching of the spent catalyst lowered the pH of all leachate samples, except for the test carried out at a pH of 12. The pH 12 test also produced a significantly higher mercury concentration relative to the other tests. Observation of the mercury concentrations and corresponding pH values indicates that there is no positive or negative trend between the two parameters. These results are somewhat different than those reported in Section 3.4, where a minimum mercury concentration is observed to occur at a pH of 8. Other notable observations on the data in Table 3.5 are the poor replication of results for the pH 10 test and the high mercury concentration measured in the blank. Poor replication of the pH 10 test may indicate heterogeneity in the distribution of mercury in the spent catalyst, which may also account for the scatter of measured concentrations across the tested pH range. The elevated mercury concentration in the experimental blank indicates that some cross-contamination may be present in the reported results, although this is not a significant bias given the high mercury concentrations reported for the leachate samples. Laboratory QC data associated with the reported mercury results are presented and discussed in Section 5.2.

Table 3.5 RU-SR002.1 Leaching Results for Untreated Catalyst¹

Initial pH	12	11	10	9	8	7
Final pH	12.9	8.28	7.87	6.41	4.69	3.95
Mercury (mg/L)	190	15.1	17.6	29.7	23.3	22.8
			27.7 ⁽²⁾			
Initial pH	6	5	4	3	Natural₍₃₎	Blank
Final pH	3.29	3.41	2.17	0.89	2.10	5.47
Mercury (mg/L)	19.4	16.3	14.8	59.1	10.4	0.38
				59.0 ⁽²⁾		

(1) Mercury analysis performed by Environmental Enterprises Incorporated, Cincinnati, Ohio

(2) Indicates test duplicate

(3) As received.

4.0 Stabilization Treatments

4.1 *Stabilization of BCP Spent Catalyst by Sulfide*

4.1.1 *Introduction*

Sulfide is one of the most widely used reactants for stabilizing mercury waste streams because of the low solubility of mercuric sulfide. The mechanism of sulfide-induced treatment is expected to be precipitation. However, due to the complexity of mercury-sulfide chemistry and the compositional variability in mercury waste streams, the process of sulfide-induced stabilization of mercury wastes has not been sufficiently developed. Therefore, further research is needed to optimize process-controlling parameters. In this study, pH and sulfide dosage were varied to test their effects on the stabilization of spent BCP mercuric chloride catalyst.

4.1.2 *Procedure*

The procedure and test matrix for sulfide stabilization of spent BCP mercuric chloride catalyst is briefly described below:

1. Weigh 20 g of catalyst (approximately 431 mg of mercury) and an amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ sufficient to meet the indicated S/Hg molar ratio (Table 4.1). Place the solids into HDPE bottles.
2. Add 200 mL of deionized Ultra-filtered (D.I.U.F) water into the bottles (a liquid/solid mass ratio of approximately 10 is maintained due to the complete dissolution of the sodium sulfide).
3. Adjust the pH of the above mixtures to the initial pH values (2, 4, 6, 8 and 10) using 1N NaOH and/or 2N HNO_3 .
4. Tumble the mixtures for 24 hours and then take a final pH measurement.
5. Filter the mixtures through a 0.45 mm glass fiber filter and collect a 100 mL filtrate sample.
6. Acidify the sample to a pH of less than 2 with HNO_3 and store at 4°C (up to 28 days) until analyzed for total mercury by CVAAS.

7. Dry the filter cakes (i.e., the stabilized spent catalyst) in an oven at 40 °C until the mass is stable to within +/- 0.01 g (overnight is generally sufficient to obtain the required control).
8. Weigh 10 g of the stabilized and dried spent catalyst and submit the samples for TCLP testing and analysis by CVAAS.

Table 4.1 Sample Test Matrix

S/Hg Ratio	pH 2	pH 4	pH 6	pH 8	pH 10
0 (Blank)	X	X	X	X	X
1	X	X	X	X	X
3	X	X	X	X	X
5	X	X	X	X	X
7	X	X	X	X	X

4.1.3 Results

Table 4.2 and Figure 4.1 summarize the results for sulfide-stabilized BCP spent catalyst. Experimental duplicates were run for S/Hg = 3/pH = 6 and S/Hg = 5/pH = 4 (Table 4.2). Results are expressed as measured mercury concentration in the leachate and as the percent of total mercury leached from the untreated and treated spent catalyst [e.g., $((92.8 \text{ mg/L} * 0.2 \text{ L}) / 431 \text{ mg}) * 100 = 4.31 \%$]. Mercury concentrations in the filtered leachate obtained from treated spent catalyst are well below those obtained from the untreated waste, with the exception of the pH 8 and 10 results for a S/Hg molar ratio of 3. The anomalous mercury value of 207 mg/L for these two samples exceeds the highest mercury value reported for leachate obtained from the untreated waste, indicating problems may have occurred with filtration of the samples. Therefore, these data points are rejected. Laboratory QC data and experimental duplicates associated with the reported mercury results are presented and discussed in Section 5.2.

Below a pH of 5, there is no improvement in the stabilization of mercury in the spent catalyst when using an S/Hg molar ratio above 3. Above a pH of 5, analytical results appear to be quite scattered for S/Hg molar ratios of 3, 5 and 7.

There are no clear trends toward increasing or decreasing mercury concentrations over the pH interval of 6 to 10 for the individual S/Hg molar ratios of 3, 5 and 7. However, there is an overall trend toward decreasing mercury concentrations at pH 8 and 10 as sulfide increases, suggesting the mercuric sulfide solubility product is controlling mercury concentrations.

The above observations are also reflected in the calculated values for percent total mercury released to the leachate. In a 24-hour period, 4.0 to 6.5 percent of the mercury is released to leachate that contacts the untreated waste. The addition of sulfide to the spent catalyst suppresses the release of mercury to the leachate for all treated samples, except the two anomalous sample results at S/Hg = 3. Again, this is consistent with the precipitation of mercuric sulfide from the leachate as it contacts the treated waste forms.

Table 4.2 Mercury Results for Sulfide Stabilization

Target	Molar Ratio														
pH	S/Hg = 0			S/Hg = 1			S/Hg = 3			S/Hg = 5			S/Hg = 7		
	pH ⁽¹⁾	Hg mg/L ⁽²⁾	Hg % ⁽³⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	Hg % ⁽³⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	Hg % ⁽³⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	Hg % ⁽³⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	Hg % ⁽³⁾
2	2.01	92.8	4.31	1.96	12.3	0.571	2.02	0.0310	0.001	2.14	0.120	0.006	2.22	0.0314	0.001
4	4.31	140	6.50	3.93	4.40	0.204	3.38	0.0129	0.001	3.58	0.0402	0.002	4.51	0.0970	0.005
6	7.12	101	4.69	5.87	3.87	0.180	3.99	13.6 ⁽⁴⁾	0.635	5.44	0.0260	0.001	5.40	0.266	0.012
8	7.96	86.8	4.03	7.59	3.71	0.173	7.83	207	9.61	8.68	37.3	1.73	8.99	1.58	0.073
10	9.83	88.1	4.09	8.86	5.93	0.276	9.36	207	9.61	9.55	8.03	0.373	9.54	0.0561	0.003

(1) The pH values were taken after a 24 hour treatment period.

(2) Concentration in the leachate after filtering.

(3) Percentage of total mercury released from untreated (S/Hg = 0) and treated spent catalyst.

(4) Test duplicates.

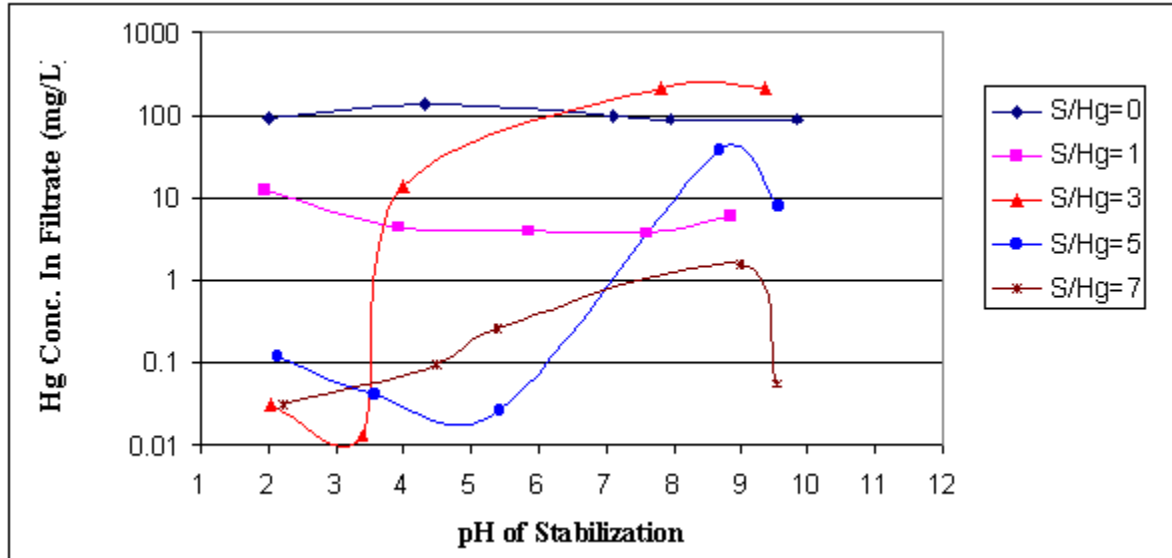


Figure 4.1 Mercury Results for Sulfide Stabilization as a function of stabilization pH

Table 4.3 and Figure 4.2 show the efficiency of the sulfide-stabilization process based on the percentage of total mercury released from the untreated and treated waste. The stabilization efficiency is defined as:

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

The efficiency calculations indicate that treatment of the spent catalyst with sodium sulfide is very effective in lowering mercury concentrations in the leachate. In general, over 90 percent of the mercury released from the untreated waste was retained in the treated waste, with three exceptions noted in Table 4.3. Approximately half of the treated samples retained over 99 percent of the mercury released from the untreated waste.

Table 4.3 Stabilization Efficiency (%)

Target pH	Molar Ratio							
	S/Hg = 1		S/Hg = 3		S/Hg = 5		S/Hg = 7	
	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency
2	1.96	86.75	2.02	99.97	2.14	99.87	2.22	99.97
4	3.93	96.86	3.38	99.99	3.58	99.97	4.51	99.93
6	5.87	96.17	3.99	86.44	5.44	99.97	5.40	99.74
8	7.59	95.73	7.83	(2)	8.68	57.03	8.99	98.18
10	8.86	93.27	9.36	(2)	9.55	90.89	9.54	99.94

(1) The pH values are taken after a 24 hour treatment period.

(2) Efficiency cannot be calculated due to rejected data points.

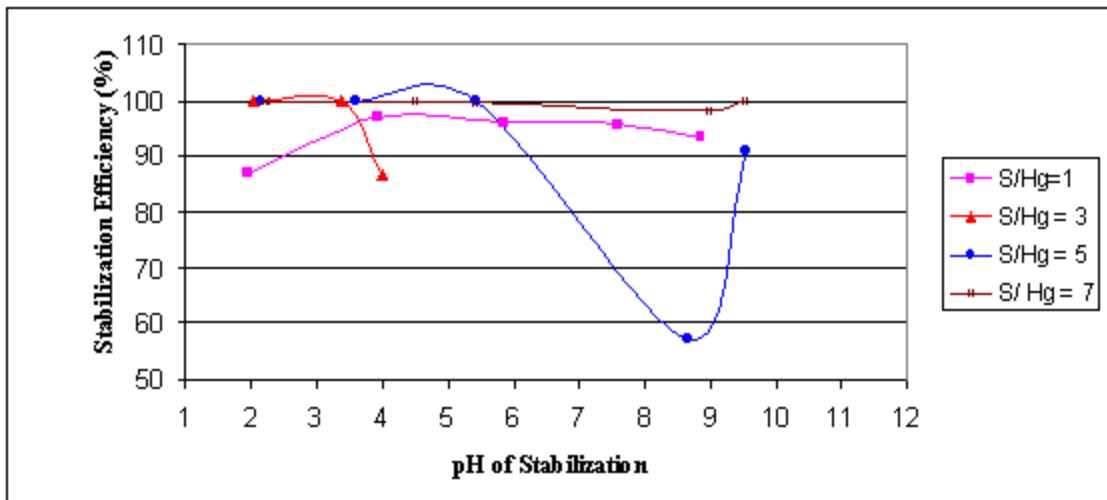


Figure 4.2 Stabilization efficiency(%)

TCLP results for mercury are shown in Table 4.4 and on Figure 4.3. Experimental duplicates were run for S/Hg = 0/pH = 6 and S/Hg = 3/pH = 6 (Table 4.4). At S/Hg molar ratios of 1, 3 and 7, mercury concentrations generally decreased as pH increased, whereas this trend is not evident for results associated with S/Hg = 5. Although the sulfide treatment substantially lowers the mercury concentrations relative to untreated samples, only 5 samples (bold boxes in Table 4.4) passed the TCLP limit of 0.2 mg/L. Results might be improved if the treated solids were dried at 100°C, rather than 40°C, prior to undergoing TCLP testing. A higher drying temperature might promote a higher degree of crystallinity in the mercuric chloride precipitate, with an expected decrease in the amount of mercury leached from the solid. Laboratory QC data

and experimental duplicates associated with the reported mercury results are presented and discussed in Section 5.2.

Table 4.4 TCLP Mercury Results (mg/L) for Sulfide Stabilization

Target	Molar Ratio									
pH	S/Hg = 0		S/Hg = 1		S/Hg = 3		S/Hg = 5		S/Hg = 7	
	pH ⁽¹⁾	TCLP Hg	pH ⁽¹⁾	TCLP Hg	pH ⁽¹⁾	TCLP Hg	pH ⁽¹⁾	TCLP Hg	pH ⁽¹⁾	TCLP Hg
2	2.01	129	1.96	57.5	2.02	13.4	2.14	2.27	2.22	0.476
4	4.31	160	3.93	52.9	3.38	8.34	3.58	0.191	4.51	0.161
6	7.12	130 ⁽²⁾	5.87	39.0	3.99	4.09	5.44	0.343	5.40	0.191
8	7.96	139	7.59	39.7	7.83	7.55	8.68	1.51	8.99	0.0336
10	9.83	128	8.86	37.5	9.36	3.01	9.55	0.531	9.54	0.0185

(1) The pH values are taken after a 24 hour treatment period and represent the pH of the treatment mixture prior to drying the solid and conducting the TCLP test.

(2) Test duplicates.

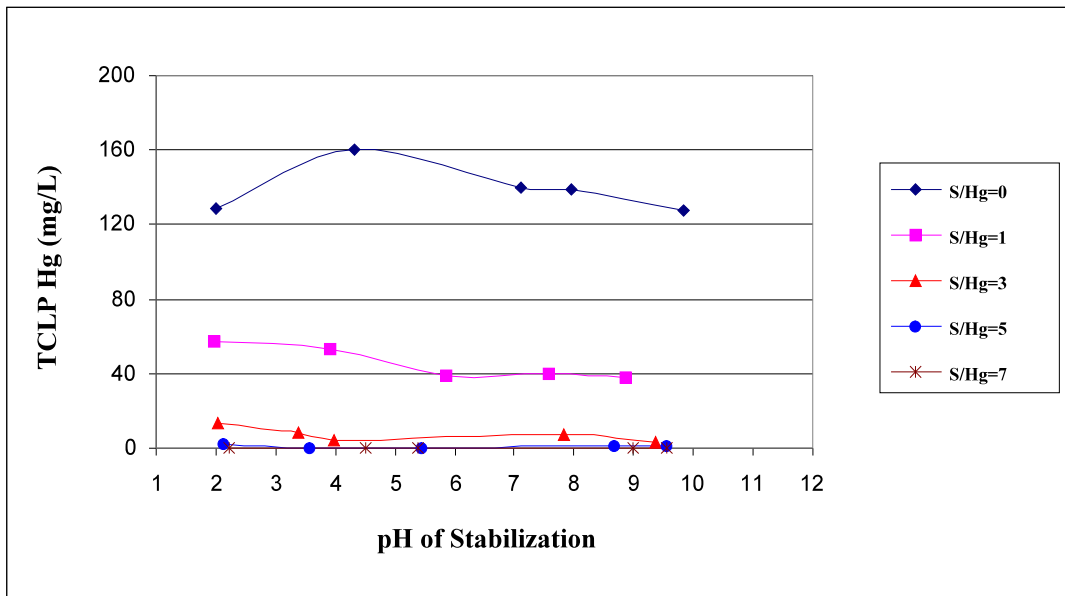


Figure 4.3 TCLP Mercury Results for Sulfide Stabilization

Stabilization efficiencies for the TCLP results are shown in Table 4.5 and in Figure 4.4. The efficiency was calculated as noted above. Except for the stabilization scenarios with S/Hg = 1, the stabilization efficiencies were higher than 90% for all other S/Hg molar ratios. However, the most successful treatment is noted at neutral to high pH for S/Hg = 7, as all these samples passed the TCLP test (Table 4.4).

Table 4.5 Stabilization Efficiency for TCLP Data

Target pH	Molar Ratio							
	S/Hg = 1		S/Hg = 3		S/Hg = 5		S/Hg = 7	
	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency	pH ⁽¹⁾	Efficiency
2	1.96	55.43	2.02	89.61	2.14	98.25	2.22	99.64
4	3.93	66.52	3.38	94.55	3.58	99.88	4.51	99.90
6	5.87	74.34	3.99	97.37	5.44	99.78	5.4	99.88
8	7.59	71.44	7.83	94.57	8.68	98.89	8.99	99.97
10	8.86	72.01	9.36	97.72	9.55	99.59	9.54	99.99

(1) The pH values are taken after a 24 hour treatment period and represent the pH of the treatment mixture prior to drying the solid and conducting the TCLP test.

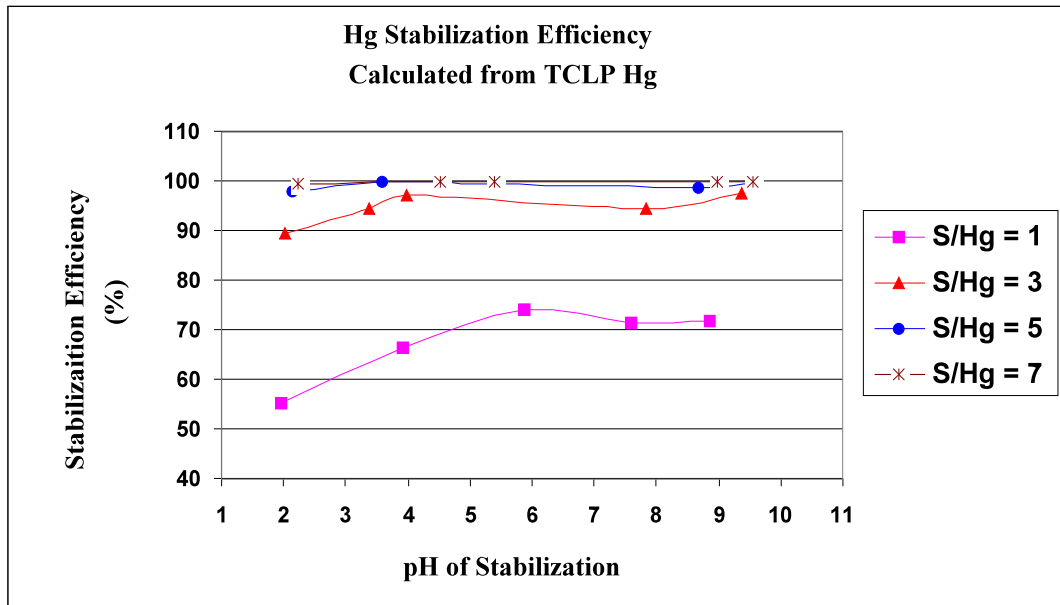


Figure 4.4 Stabilization Efficiency for TCLP Data

4.1.4 Discussion

Mercuric sulfide (HgS) is very insoluble in water, with a solubility product (K_{sp}) of 10^{-52} (Bard, 1966)¹. However, the solubility of HgS in water can be increased by association with various hydrogen sulfide species to form a number of mercuric-hydrogen-sulfide ions that enhance the solubility of HgS in water (Clever *et al.*, 1985)². These associations can lead to the formation of $\text{HgS}\cdot 2\text{H}_2\text{S}^0$, $\text{Hg}(\text{HS})_3^-$, $\text{HgS}\cdot 2\text{HS}^-$, and HgS_2^{2-} (Figure 4.5). $\text{HgS}\cdot 2\text{H}_2\text{S}^0$ is the dominant aqueous specie at pH values less than 6.2, while $\text{Hg}(\text{HS})_3^-$ is the dominant form between the pH values of 6.2 and 7. $\text{HgS}\cdot 2\text{HS}^-$ is the most abundant mercury complex between the pH of 7 and 8.3, and HgS_2^{2-} dominates above a pH of 8.3. In fact, the concentration of HgS_2^{2-} increases linearly with the hydroxyl ion concentration for pH values over 8.3 (Figure 4.5).

According to Figure 4.5, mercury and sulfide reach their highest concentrations above neutral pH by forming complexes with HS^- and S^{2-} . However, the results in Figure 4.5 cannot be reconciled with the experimental results because some of the lowest mercury concentrations were measured at pH 8 and 10 when the S/Hg molar ratio was 7 (1.58 and 0.056 mg/L, Table 4.2). This observation may indicate that the sulfide-stabilization did not reach equilibrium within the 24 hour period. Based on our preliminary research on the formation kinetics of sulfide and mercury surrogates (data not report here), sulfide-stabilization of mercury waste cannot reach equilibrium within 24 hours when high pH and high sulfide dosage are applied. Therefore, a much longer reaction time is recommended for future research.

¹Bard, A.J., Chemical Equilibrium, Harper and Row, Publishers, New York, 1966.

²Clever, H.L., S.A. Johnson, and M.E. Derrick, "The Solubility of Mercury and Some Sparingly Soluble Mercury Salts in Water and Aqueous Electrolyte Solutions," J. Phys. Chem. Ref. Data, Vol. 14, No. 3, 1985.

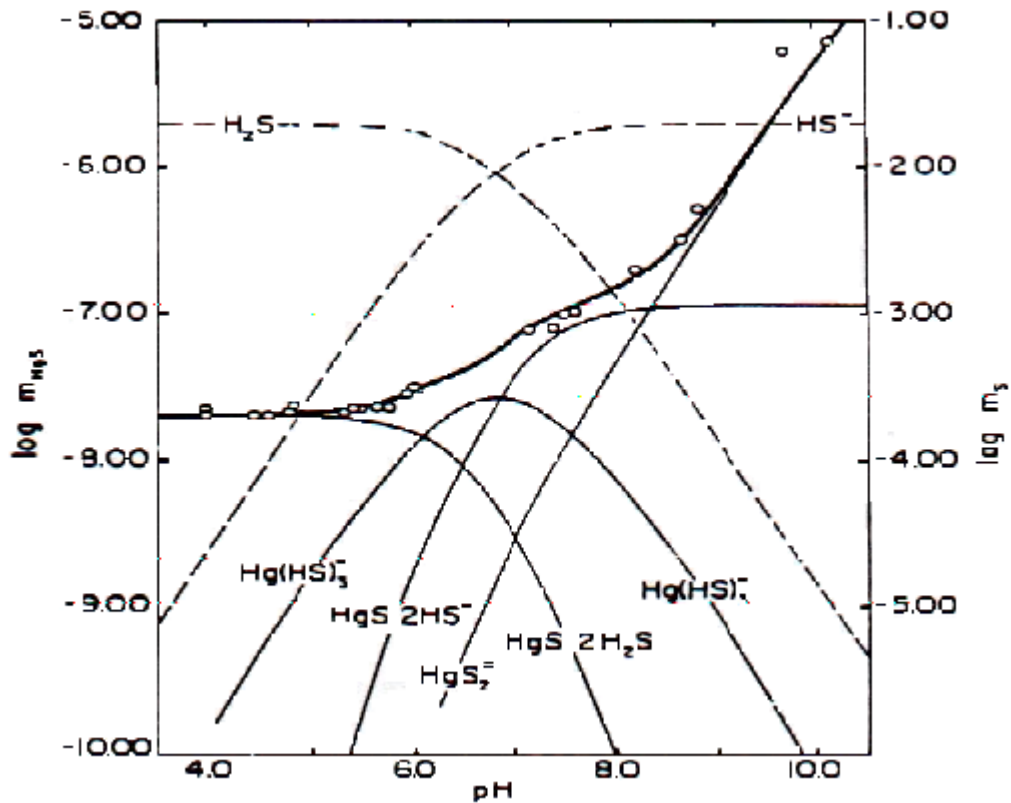


Figure 4.5 Distribution of the various Hg-H-S species as a function of pH

4.2 Stabilization of BCP Spent Catalyst by Phosphate

4.2.1 Introduction

Phosphates have been shown to be effective in stabilizing heavy metals (Cotter-Howells *et.al.*, 1996¹; Eighmy *et.al.*, 1997²; Ma *et.al.*, 1995³; O'Hara *et.al.*, 1988⁴). Mercury phosphates also have very low solubility (Qvarfort-Dahlman, 1975⁵; Clever *et.al.*, 1985⁶). However, there has been little work done on phosphate-stabilization of mercury waste forms. This experiment was designed to investigate the effect of phosphate on mercury stabilization. In this experiment, variables such as pH and phosphate dosage were tested for their effects on phosphate-induced BCP catalyst stabilization.

4.2.2 Procedure

The procedure and test matrix for phosphate stabilization of spent BCP mercuric chloride catalyst is briefly described below:

1. Weigh 20 g of catalyst (approximately 431 mg of mercury) and an amount of Na_2HPO_4 sufficient to meet the indicated P/Hg molar ratio (Table 4.6). Place the solids into HDPE bottles.
2. Add 200 mL of D.I.U.F water into the bottles (a liquid/solid mass ratio of approximately 10 is maintained due to the complete dissolution of the sodium phosphate).
3. Adjust the pH of above mixtures to the initial pH values (3, 6, 8, 10 and 12) using 1N NaOH and/or 2N HNO_3 .
4. Tumble the mixtures for 24 hours and then take a final pH measurement.
5. Filter the mixtures through a 0.45 mm glass fiber filter and collect a 100 mL filtrate sample.
6. Acidify the sample to a pH of less than 2 with HNO_3 and store at 4°C (up to 28 days) until analyzed for total mercury by CVAAS.
7. Dry the filter cakes (i.e., the stabilized spent catalyst) in an oven at 40 °C until the mass is stable to within +/- 0.01 g (overnight is generally sufficient to obtain the required control).
8. Weigh 10 g of the stabilized and dried spent catalyst and submit the samples for TCLP testing and analysis by CVAAS.

4.2.3 Results

Table 4.6 and Figure 4.6 summarize results for the phosphate treatment of spent mercuric chloride catalyst. Experimental duplicates were run for P/Hg = 0.5/pH = 8 and P/Hg = 1/pH = 10 (Table 4.6). The measured mercury concentrations indicate that the addition of phosphate has virtually no effect on stabilizing mercury in the waste form. Over the pH range tested, mercury concentrations in the leachate derived from treated samples were close to those of untreated (P/Hg = 0) samples. Laboratory QC data and experimental duplicates associated with the reported mercury results are presented and discussed in Section 5.3.

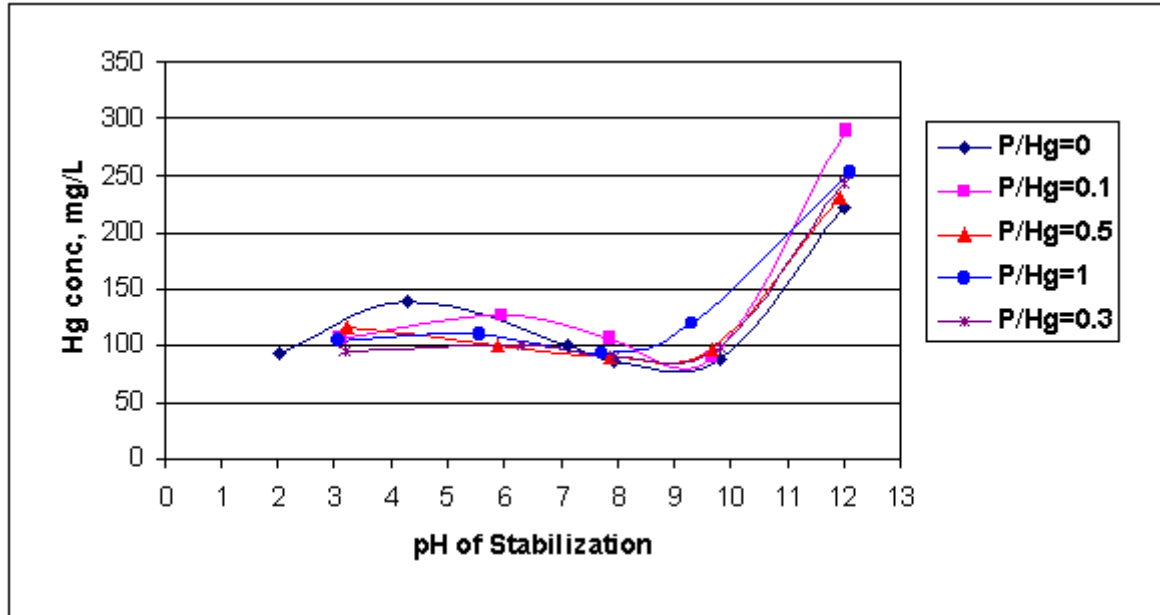


Figure 4.6 Mercury Results (mg/L) for Phosphate Stabilization

Table 4.6 Mercury Results for Phosphate Stabilization

		Molar Ratio									
Target pH	P/Hg=0		P/Hg=0.1		P/Hg=0.3		P/Hg=0.5		P/Hg=1		
	pH ⁽¹⁾	Hg mg/L ⁽²⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	pH ⁽¹⁾	Hg mg/L ⁽²⁾	
2	2.01	92.8									
4/3	4.31	140	3.12	107	3.19	95.4	3.22	115	3.06	104	
6	7.12	101	5.95	127	6.33	100	5.9	100	5.56	110	
8	7.96	86.8	7.89	107	7.93	89.1	7.87	96.2 ⁽³⁾	7.71	92.8	
10	9.83	88.1	9.68	88.9	9.83	99	9.67	79.5	9.32	117	
12	12.00	222	12.01	290	12.00	244	11.93	230	12.11	252	

(1) The pH values are taken after a 24 hour treatment period.

(2) Concentration in the leachate after filtering.

(3) Test duplicates.

Table 4.7 and Figure 4.7 show TCLP results for phosphate-stabilized catalyst. Experimental duplicates were run for P/Hg = 0.5/pH = 8 and P/Hg = 1/pH = 10 (Table 4.7). Obviously, all samples failed the TCLP test. Phosphate-stabilized samples have approximately the same TCLP results as the untreated catalyst. Laboratory QC data and experimental duplicates associated with the reported mercury results are presented and discussed in Section 5.3.

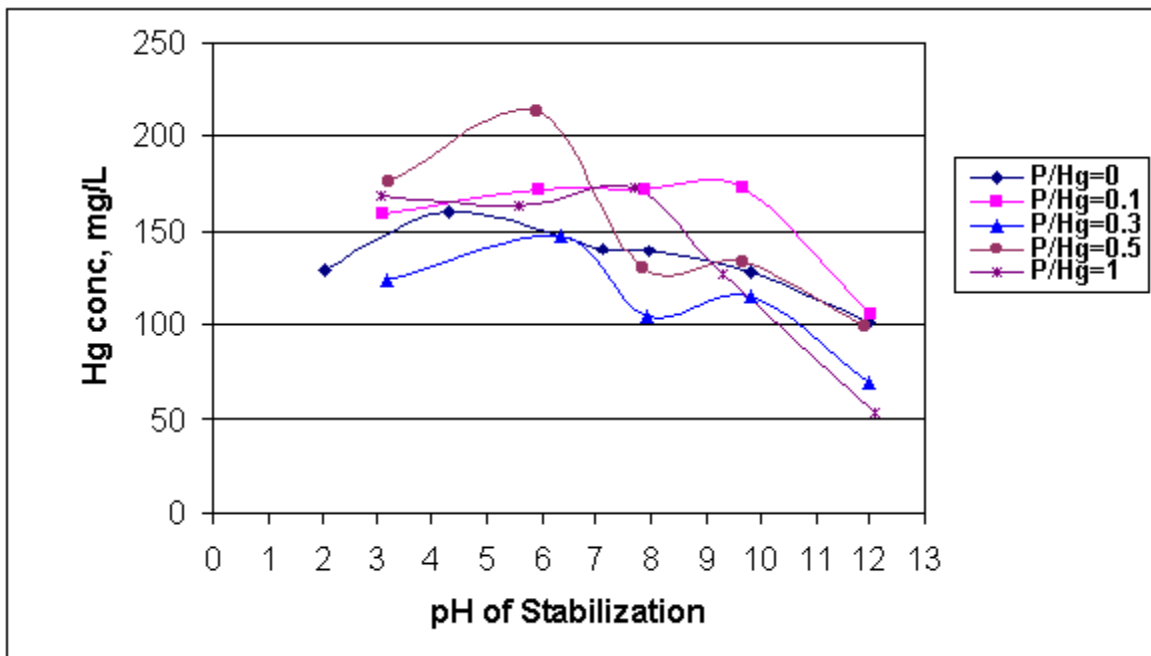


Figure 4.7 TCLP Mercury (mg/L) Results for Phosphate Stabilization

Table 4.7 TCLP Mercury (mg/L) Results for Phosphate Stabilization

pH	Molar Ratio				
	P/Hg=0	P/Hg=0.1	P/Hg=0.3	P/Hg=0.5	P/Hg=1
3	145	159	123	176	169
6	140	172	148	213	163
8	139	172	104	137 ⁽¹⁾	173
				123	
10	128	173	115	133	118 ⁽¹⁾
					135
12	101	105	69.7	99	53.7

(1) Test duplicates

4.2.4 Discussion

The spent mercuric chloride catalyst will release chloride ions during the leaching tests. It has been reported that the presence of chloride ion decreases the formation of mercury phosphate precipitates (Feick *et.al.*, 1972⁷; Wang *et.al.*, 1991⁸), due to the formation of strong aqueous mercury chloride species. This is hypothesized to be the reason why the phosphate treatment was ineffective in this study. Although the same mercury chloride species form in the presence of the sulfide-treated waste, the very low solubility of HgS appears to overcome the association constants of the aqueous mercury chloride species.

5.0 Data Quality

5.1 Background Characterization

Table 5.1 summarizes the laboratory QC data for the total mercury and TCLP results reported in Tables 2.1 and 3.3. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with a corresponding correlation coefficient of 0.9998. Initial and continuing calibration standards and the LCS (Laboratory Control Sample) were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results for the laboratory duplicate and spike are within the stated QAPP control limits of ± 25 percent (duplicate) and 75 to 125 percent (spike recovery).

5.2 Leaching Tests

Table 5.2 summarizes the laboratory QC data for the total mercury results reported in Table 3.1. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with a corresponding correlation coefficient of 0.9996. Initial and continuing calibration standards and the LCS were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results for the laboratory duplicate and spike are within the stated QAPP control limits of ± 25 percent (duplicate) and 75 to 125 percent (spike recovery).

Table 5.3 summarizes the laboratory QC data for the total mercury results reported in Table 3.4. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with a corresponding correlation coefficient of 0.9999. Initial and continuing calibration standards and the LCS were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results

for the laboratory duplicate are within the stated QAPP control limit of ± 25 percent.

A post-digestion spike was not reported for this batch of samples.

**Table 5.1 Laboratory QC Data for EEI Total & TCLP Mercury Results
Background Data**

Sample ID	True mg/L	Found mg/L	Percent Recovery%	RPD	Dilution Factor	Reported Result mg /kg (mg /L)
Work Order 80-04-319: Total Mercury Results						
ICV	5.00	5.18	104	na	na	na
CCV1	5.00	4.89	97.8	na	na	na
CCV2	5.00	4.82	96.4	na	na	na
CCV3	5.00	4.84	96.8	na	na	na
CCV4	5.00	4.87	97.4	na	na	na
LCS	10.00	10.34	103	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
01A	na	6.68	na	282	100,000	668,000
01A-duplicate	na	5.03	na		100,000	503,000
05A-spike	5.00	5.36	107	na	na	na
Work Order 80-04-319: TCLP Mercury Results						
ICV	5.00	5.13	103	na	na	na
CCV1	5.00	5.02	100	na	na	na
CCV2	5.00	5.10	102	na	na	na
CCV3	5.00	5.50	110	na	na	na
CCV4	5.00	4.97	99.4	na	na	na
LCS	10.00	10.80	108	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
22A	na	12.08	na	184	10,000	(121,000)
22A-duplicate	na	11.86	na		10,000	(119,000)
22A-spike	5.00	6.03	121	na	na	na

na = not applicable

Lab reports that a spike was run on diluted sample, post digestion

**Table 5.2 Laboratory QC Data for EEI Total Mercury Result
Solid Stability in Water**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD	Dilution Factor	Reported Result mg /L
Work Order 99-10-276: Total Mercury Results						
ICV	5.00	4.94	98.8	na	na	na
CCV1	5.00	4.62	92.4	na	na	na
CCV2	5.00	4.62	92.4	na	na	na
LCS	10.00	9.91	99.1	na	na	na
ICB	<0.50	0.53	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
05A	na	3.14	na	0.32	2	6.28
05A-duplicate	na	3.15	na		2	6.30
05A-spike	10.00	9.01	90.1	na	na	na

na = not applicable

**Table 5.3 Laboratory QC Data for EEI Total Mercury Result
University of Cincinnati pH Test**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD	Dilution Factor	Reported Result mg /L
Work Order 99-10-211: Total Mercury Results						
ICV	5.00	4.82	96.8	na	na	na
CCV1	5.00	4.81	96.2	na	na	na
CCV2	5.00	4.52	90.4	na	na	na
CCV3	5.00	4.58	91.6	na	na	na
CCV4	5.00	4.45	89.0	na	na	na
CCV5	5.00	4.63	92.6	na	na	na
LCS	10.00	9.72	97.2	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
CCB5	<0.50	<0.50	na	na	na	na
27A	na	0.88	na	2.25	2,000	1,760
27A-duplicate	na	0.90	na		2,000	1,800

na = not applicable

Lab reports that a spike was not run due to reported result exceeding 1,000 mg /L

Table 5.4 summarizes the laboratory QC data for the total mercury results reported in Table 3.5. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with a corresponding

correlation coefficient of 0.9998. Initial and continuing calibration standards and the LCS were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results for the laboratory duplicate and spike are within the stated QAPP control limits of ± 25 percent (duplicate) and 75 to 125 percent (spike recovery).

**Table 5.4 Laboratory QC Data for EEI Total Mercury Result
Rutgers University pH Test**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD	Dilution Factor	Reported Result mg/L
Work Order 99-12-045: Total Mercury Results						
ICV	5.00	4.81	96.2	na	na	na
CCV1	5.00	4.66	93.2	na	na	na
CCV2	5.00	4.75	95.0	na	na	na
CCV3	5.00	4.63	93.0	na	na	na
LCS	10.00	10.40	104	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
01A	na	8.95	na	11.1	20,000	179,000
01A-duplicate	na	10.00	na		20,000	200,000
01A-spike	5.00	4.65	93.0	na	na	na

na = not applicable

Lab reports that a spike was run on diluted sample, post digestion

5.3 Acidity

Prior to the titration, the pH meter was calibrated using a two-point calibration with certified calibration standards, pH 4 and pH 10. The calibration efficiency is defined as the measured value divided by the known value, and the value of 1.02 is in the range of 1.05 to 0.95, per the QAPP.

5.4 Treatment Reagents

Table 5.5 summarizes the laboratory QC data for the total mercury results reported in Tables 4.2 and 4.6. The calibration curves were established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with corresponding

correlation coefficients of 0.999665 and 999693. Initial and continuing calibration standards and the LCS were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results for the laboratory duplicate and spike are within the stated QAPP control limits of ± 25 percent (duplicate) and 75 to 125 percent (spike recovery).

**Table 5.5 Laboratory QC Data for EEI Total Mercury Result
Sulfide and Phosphate Stabilization**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD %	Dilution Factor	Reported Result mg /L
Work Order 80-05-219: Total Mercury Results						
ICV	5.00	4.86	97.2	na	na	na
CCV1	5.00	5.15	103	na	na	na
CCV2	5.00	4.92	98.4	na	na	na
CCV3	5.00	4.63	97.8	na	na	na
CCV4	5.00	4.90	98.0	na	na	na
CCV5	5.00	4.75	95.0	na	na	na
CCV6	5.00	4.65	93.0	na	na	na
LCS	10.00	10.60	106	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
CCB5	<0.50	<0.50	na	na	na	na
CCB6	<0.50	<0.50	na	na	na	na
07A	na	22.24	na	0.495	10,000	222,000
07A-duplicate	na	22.13	na		10,000	221,000
07A-spike	50.0	57.7	115	na	na	na
ICV	5.00	5.15	103	na	na	na
CCV1	5.00	4.62	92.4	na	na	na
CCV2	5.00	5.15	103	na	na	na
CCV3	5.00	4.99	99.8	na	na	na
CCV4	5.00	4.79	95.8	na	na	na
CCV5	5.00	5.19	104	na	na	na
CCV6	5.00	4.97	99.4	na	na	na
CCV7	5.00	4.89	97.8	na	na	na
CCV8	5.00	4.96	99.2	na	na	na
CCV9	5.00	5.07	101	na	na	na
LCS	10.00	9.62	96.2	na	na	na
LCS	10.00	10.06	101	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
CCB5	<0.50	<0.50	na	na	na	na
CCB6	<0.50	<0.50	na	na	na	na
CCB7	<0.50	<0.50	na	na	na	na
CCB8	<0.50	<0.50	na	na	na	na
CCB9	<0.50	<0.50	na	na	na	na
24A	na	7.56	na	11.8	1,000	7,560
24A-duplicate	na	8.51	na		1,000	8,510
24A-spike	5.00	5.37	107	na	na	na

45A	na	11.77	na	0.853	10,000	118,000
45A-duplicate	na	11.67	na		10,000	117,000
45A-spike	5.00	5.78	116	na	na	na

na = not applicable

Lab reports that a spike was run on diluted sample, post digestion

Table 5.6 summarizes the laboratory QC data for the TCLP mercury results reported in Tables 4.4 and 4.7. The calibration curves were established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 mg/L, with corresponding correlation coefficients of 999693 (Work Order 80-050219), 999691 and 999836. Initial and continuing calibration standards and the LCS were within the laboratory control limit of 85 to 115 percent. The initial and continuing blank samples were all below the reporting detection limit of 0.0005 mg/L. Results for the laboratory duplicate and spike are within the stated QAPP control limits of ± 25 percent (duplicate) and 75 to 125 percent (spike recovery).

Table 5.7 summarizes the experimental precision associated with the results for test duplicates (Tables 4.2, 4.4, 4.6 & 4.7). The precision between test duplicates is better than ± 15 percent, which exceeds the precision required for duplicate analytical measurements. Therefore, the experimental reproducibility is considered acceptable.

**Table 5.6 Laboratory QC Data for EEI TCLP Mercury Result
Sulfide and Phosphate Stabilization**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD	Dilution Factor	Reported Result mg /L
Work Order 80-05-219: TCLP Mercury Results						
ICV	5.00	4.86	97.2	na	na	na
CCV1	5.00	5.15	103	na	na	na
CCV2	5.00	4.92	98.4	na	na	na
CCV3	5.00	4.63	97.8	na	na	na
CCV4	5.00	4.90	98.0	na	na	na
CCV5	5.00	4.75	95.0	na	na	na
CCV6	5.00	4.65	93.0	na	na	na
LCS	10.00	9.83	106	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
CCB5	<0.50	<0.50	na	na	na	na
CCB6	<0.50	<0.50	na	na	na	na
42A	na	1.65	na	3.07	100,000	165,000
42A-duplicate	na	1.60	na		100,000	160,000
42A-spike	500	450	90.0	na	na	na
Work Order 80-05-218: TCLP Mercury Results						
ICV	5.00	5.18	104	na	na	na
CCV1	5.00	5.23	105	na	na	na
CCV2	5.00	5.04	101	na	na	na
CCV3	5.00	4.97	99.4	na	na	na
CCV4	5.00	4.98	99.6	na	na	na
LCS	10.00	9.87	98.7	na	na	na
LCS	10.00	9.92	99.2	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
01A	na	1.37	na	12.4	100,000	137,000
01A-duplicate	na	1.21	na		100,000	121,000
01A-spike	5.00	5.38	108	na	na	na
16A	na	4.25	na	1.66	1,000	4,250
16A-duplicate	na	4.18	na		1,000	4,180
16A-spike	5.00	5.13	103	na	na	na
ICV	5.00	5.11	102	na	na	na
CCV1	5.00	5.14	103	na	na	na
CCV2	5.00	5.19	104	na	na	na
CCV3	5.00	5.21	104	na	na	na
CCV4	5.00	5.04	101	na	na	na
CCV5	5.00	5.00	100	na	na	na
CCV6	5.00	4.93	98.6	na	na	na
LCS	10.00	10.06	106	na	na	na
LCS	10.00	10.08	108	na	na	na
ICB	<0.50	<0.50	na	na	na	na
CCB1	<0.50	<0.50	na	na	na	na
CCB2	<0.50	<0.50	na	na	na	na
CCB3	<0.50	<0.50	na	na	na	na
CCB4	<0.50	<0.50	na	na	na	na
CCB5	<0.50	<0.50	na	na	na	na
CCB6	<0.50	<0.50	na	na	na	na

31A	na	1.66	na	5.26	100,000	166,000
31A-duplicate	na	1.75	na		100,000	175,000
31A-spike	5.00	5.13	103	na	na	na
41A	na	1.67	na	1.78	100,000	167,000
41A-duplicate	na	1.70	na		100,000	170,000
41A-spike	5.00	4.94	98.8	na	na	na

na = not applicable

Lab reports that a spike was run on diluted sample, post digestion

**Table 5.7 Experimental QC Data for Test Duplicates
Sulfide and Phosphate Stabilization**

Sample ID	True mg/L	Found mg/L	Percent Recovery	RPD	Dilution Factor	Reported Result mg/L
Work Order 80-05-219: Total Mercury Results for Sulfide Stabilization (Table 4.2)						
15	na	13.57	na	2.33	1,000	13,600
16	na	13.89	na		1,000	13,900
20	na	42.84	na	6.79	1	42.8
21	na	4.02	na		10	40.2
Work Order 80-05-218: TCLP Mercury Results for Sulfide Stabilization (Table 4.4)						
3	na	1.30	na	14.3	100,000	130,000
4	na	1.50	na		100,000	150,000
15	na	4.09	na	3.13	1,000	4,090
16	na	4.22	na		1,000	4,220
Work Order 80-05-219: Total Mercury Results for Phosphate Stabilization (Table 4.6)						
37	na	9.62	na	13.0	10,000	96,200
38	na	8.45	na		10,000	84,500
44	na	12.34	na	5.15	10,000	123,000
45	na	11.72	na		10,000	117,000
Work Order 80-05-218: TCLP Mercury Results for Phosphate Stabilization (Table 4.7)						
44	na	1.18	na	13.4	100,000	118,000
45	na	1.35	na		100,000	135,000
37	na	1.37	na	10.8	100,000	137,000
38	na	1.23	na		100,000	123,000

na = not applicable

6.0 Conclusions

It is concluded from the sulfide-stabilization results that the addition of sodium sulfide to spent BCP mercuric chloride catalyst substantially reduces the amount of mercury released from the waste when it is leached. Mercury stabilization efficiencies exceeded 99 percent and passed the TCLP test at pH values of 4, 6, 8 and 10 at a S/Hg molar ratio of 7. The treatment performance might be increased by allowing more reaction time between the sulfide/waste mixture and by increasing the drying temperature of the treated solid prior to running the TCLP test.

Phosphate failed to effectively stabilize mercury in the BCP spent catalyst. It is hypothesized that the high concentration of chloride ion in the leachate decreases the formation of mercury phosphate precipitates, due to the formation of a strong aqueous mercury chloride complex.

¹ Cotter-Howells, J. and Caporn, S., "Remediation of contaminated land by formation of heavy metal phosphates," *Applied Geochemistry*, 11, 335-342, 1996.

²Eighmy, T.T., Crannell, B.S., Butler, L.G., Cartledge, F.K., Emery, E.F., Oblas, D., Krzanowski, J.E., Eusden, J.D., Jr., Shaw, E.L., and Francis, C.A., "Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate," *Environmental Science and Technology*, 31, 3330-3338, 1997.

³Ma, Q. Y., Logan, T. J. and Traina, S. J., "Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks," *Environmental Science and Technology*, 29, 1118-1126, 1995.

⁴O'Hara, M.J. and Surgi, M.R., "Immobilization of lead and cadmium in solid residues from the combustion of refuse using lime and phosphate," U.S. Patent No. 4,737,356, 1988.

⁵Qvarfort-Dahlman, I., "On some phosphate equilibria," *Chemica Scripta*, 8(3), 112-125, 1975.

⁶Clever, H.L., Johnson, S.A., and Derrick, M.E., "The solubility of mercury and some sparingly soluble mercury salts in water and aqueous electrolyte solutions," *J. Phys. Chem. Ref. Data*, 14(3), 631-680, 1985.

⁷Feick, G., Horne, R.A., and Yeaple, D., "Release of mercury from contaminated freshwater sediments by the runoff of road deicing salt," *Science*, 175, 1142-1143, 1972.

⁸Wang, J.S., Huang, P.M., Liaw, W.K., and Hammer, U.T., "Kinetics of the desorption of mercury from selected freshwater sediments as influenced by chloride," *Water, Air, and Soil Pollution*, 56, 533-542, 1991.