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# **Stabilization and Testing of Mercury Containing Wastes: Borden Sludge**

by

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## **Foreword**

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E. Timothy Oppelt, Director  
National Risk Management Research Laboratory

## **Abstract**

This report details the stability assessment of a mercury containing sulfide treatment sludge. Information contained in this report will consist of background data submitted by the generator, landfill data supplied by EPA and characterization and leaching studies conducted by UC and contract laboratories.

Borden Chemicals and Plastics (BCP) provided background data for the time period June 1997 through November 1998. Included in the data summary are total mercury, reactive sulfide, Toxicity Characterization Leaching Procedure (TCLP) and pH information relating to their sulfide treated sludge.

BCP's sulfide sludge is currently being disposed in a subtitle C landfill located in Carlyss, Louisiana. Data on the leachate from the landfill was provided by EPA - OSW.

Samples obtained by UC and EPA personnel at the BCP plant on November 19, 1998 were characterized by UC and two contract laboratories for thermogravimetric analysis, total mercury content, pH, acidity and cation exchange capacity, etc. Leaching tests and analytical work performed by UC and their contract laboratories included the toxicity characteristic leaching procedure (TCLP), solid stability in water, leaching at constant pH values, and acidity.

Preliminary point estimates of measured mercury concentrations in the generated leachates indicate that the mercuric sulfide complex is very strong in low pH environments; however, higher pH conditions may result in mercury mobilization to the aqueous phase.

This report was submitted by the University of Cincinnati (UC) in fulfillment of Contract No. 68-C7-0057 under the sponsorship of the United States Environmental Protection Agency (EPA). This report covers a period from October 1998 through March 1999; laboratory work was completed as of March 1999.

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- Available from Paul Randall, Task Order Manager, U.S. EPA, at [randall.paul@epa.gov](mailto:randall.paul@epa.gov) or by calling 513 569-7673.

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## 1.0 Background

The Borden Chemicals and Plastics plant (BCP) is located in Geismar, Louisiana. The company produces, among other chemicals, vinyl chloride. The vinyl chloride synthesis employs a mercuric chloride catalyst in the process. At intervals, the catalyst is changed resulting in some spillage. A diked concrete pad under the process area catches these spills along with any process leakage etc. The pad is washed with water. The water collected, along with any rain water that falls over the process area, is diverted into two 10,000 gallon tanks. The tank contents are adjusted to a pH between 3.5 and 5, treated with sodium sulfide, and dewatered with diatomaceous earth, added as a filtering aid. The resulting filter cake, which is the subject of this study, is loaded into thirty-cubic-yard steel roll-off boxes. When full, the contents are transported to the subtitle C landfill located in Carlyss, Louisiana.

### 1.1 Waste Characterization

The background BCP (Table 1.1) data provide a range of TCLP values from 0.0120 mg/L to 0.6540 mg/L, with two samples below the detection limit. Of eight TCLP values provided, five are below the TCLP regulatory limit of 0.2 mg/L mercury. Three pH values are provided. The values reported are 9.43, 1.31 and 5.32. These values indicate a highly variable and not well controlled treatment process. (Complete data are provided in Appendix A, available from Paul Randall, see Table of Contents.)

According to the treatment procedure supplied by BCP, the optimum pH range for this process before addition of sodium sulfide, is 3.5 to 5.0. The sulfide used in this process should act as a base. Thus, it is unknown why the pH of the waste after sulfide treatment could be as low as 1.3. On the only other two sampling days for which pH values were supplied, the pH (5.32 and 9.43) was higher than the maximum allowable pH (5.0).

The analytical data provided by BCP indicate that there is a significant amount of reactive sulfide remaining in the samples after treatment. The samples with higher reactive sulfide concentrations produced the lowest TCLP mercury concentrations. The two samples with high reactive sulfide concentrations had TCLP values that were acceptable, while the sample with the lowest reactive sulfide concentration failed the TCLP test. Unfortunately, no pH or reactive sulfide concentrations were provided with the other TCLP results, so direct correlations can not be made. It is surprising, though, that one waste containing 40.0 mg/kg reactive sulfide did not bind up the mercury enough to prevent leaching in the TCLP test.

Based on these results, it appears that it is possible for the Borden company to produce waste forms that will pass the TCLP test. The characteristics of the treated sludge are highly variable and indicate the need for additional process quality control.



### 1.1.1 Data Quality Discussion

The background data presented came from several sources and are considered secondary data by EPA Order 5360.1 CHG 1, July 1998. Some QA information is available for the Gulf Coast Analytical Laboratories data (see Appendix A, Table of Contents) and a summary of this information is presented in Section 4.5. No QA information was available for the SAIC data.

**Table 1.1: Borden Background Data Summary**

Sample Date	Test Date	Type of Analysis	Results	Sample Designation
10/27/97	10/31/97	Total Hg	2.27 mg/kg	9710290009 <sup>1</sup>
10/27/97	10/31/97	TCLP Hg	<0.0002 mg/L	9710290009 <sup>1</sup>
10/27/97	10/31/97	Total Hg	21.4 mg/kg	9710290010 <sup>1</sup>
10/27/97	10/31/97	TCLP Hg	<0.0002 mg/L	9710290010 <sup>1</sup>
02/13/98	02/16/98	pH Extract	9.43	9802130104 <sup>1</sup>
02/13/98	02/17/98	Reactivity Sulfide	165 mg/kg	9802130104 <sup>1</sup>
02/13/98	02/20/98	TCLP Hg	0.0160 mg/L	9802130104 <sup>1</sup>
05/15/98	05/19/98	pH Extract	1.31	9805180094 <sup>1</sup>
05/15/98	05/19/98	Reactivity Sulfide	120 mg/kg	9805180094 <sup>1</sup>
05/15/98	05/26/98	TCLP Hg	0.0120 mg/L	9805180094 <sup>1</sup>
11/11/98	11/13/98	pH Extract	5.32	9811110124 <sup>1</sup>
11/11/98	11/13/98	Reactivity Sulfide	40.0 mg/kg	9811110124 <sup>1</sup>
11/11/98	11/14/98	TCLP Hg	0.3520 mg/L	9811110124 <sup>1</sup>
11/20/98	11/23/98	TCLP Hg	0.0422 mg/L	9811200032 <sup>1</sup>
06/04/97	-----	Total Hg	21,100 mg/kg	BGO6 <sup>2</sup>
06/04/97	-----	TCLP Hg	0.2600 mg/L	BGO6 <sup>2</sup>
06/04/97	06/14/97	Total Hg	17,700 mg/kg	BGO6 <sup>3</sup>
06/04/97	06/11/97	TCLP Hg	0.6540mg/L	BGO6 <sup>3</sup>

(1) Provided by BCP—analysis by Gulf Coast Analytical Laboratories Inc., 7979 GSRI Ave., Baton Rouge, LA.

(2) Provided by EPA—analysis by SAIC

(3) Provided by EPA—analysis by Gulf Coast Analytical Laboratories INC.

## 1.2 Landfill Data

Data supplied by EPA-OSW on the landfill leachate from cells containing the BCP sludge are listed in Table 1.2.

**Table 1.2 Landfill Leaching Data**

Cell <sup>1</sup>	Mercury (µg/L)	pH <sup>3</sup>
5	ND <sup>2</sup>	--
6	0.94	9.51 (average)
14	0.57	--

(1)Cell - the isolated location within the landfill of the stored waste

(2)ND - No data on detection limit value was supplied

(3) Supplied by EPA-OSW

The data in Table 1.2 indicate that the mercury concentration in landfill leachate generated in the vicinity of the Borden waste is highly variable, ranging from 0.94 µg/L to non-detectable. These are actual leachate concentrations before dilution with groundwater, and the values can not be compared directly to TCLP values. TCLP leachate concentrations are based on a leachate/waste ratio of 20:1 (w/w) and TCLP leachate concentrations for this landfill material may be much lower than those actually observed for *in situ* leachate. Typically, voids occupied by leachant in a TCLP test are an order of magnitude greater than that recorded for *in situ* samples, meaning that there may be much more leachant in the TCLP test than in the field, per unit volume of waste. Therefore, the TCLP concentration could be lower. Consequently, these landfill samples may pass the TCLP test, even though their field leachate concentrations may be higher than the TCLP limit.

### 1.2.1 Data Quality Discussion

The data presented in Table 1.2 supplied by EPA-OSW, were defined as secondary data by EPA Order 5360.1 CHG 1, July 1998. No QC information is available. No detection limit value is available. No information is available on the generation of leachate. Only a single pH value was provided and was labeled as an average. Insufficient detail is available to assess the secondary data.

## 2.0 Characterization of BCP Sulfide Sludge

On November 19, 1998, 12 two-liter samples of dewatered sludge were collected from BCP at the Geismar, Louisiana plant by UC and EPA personnel. The samples were obtained by random collection from a full thirty-cubic-yard transport container labeled 4279-30 LCHCWM. Before mixing 6 of the 2 L bottles were sampled for TCLP to assess variability of the waste. To obtain a representative sample, 6 of the partially full 2L bottles were mixed in a five-gallon container for 24 hours prior to sampling. Only one sample was analyzed for total Hg from the homogenized mixture, consequently no statement can be made concerning the effectiveness of the homogenization process. The following characterization data (Tables 2.1 and 2.2) were generated for this waste:

**Table 2.1 Chemical Characterization of BCP Sludge\***

Chemical Parameter	Concentration	Method of Analysis
Total Mercury	8,100 mg/kg	SW-846-7470A <sup>1 4</sup>
Calcium	300 mg/kg	Extraction with Ammonium acetate <sup>2</sup>
Magnesium	30 mg/kg	Extraction with Ammonium acetate <sup>2</sup>
Sodium	660 mg/kg	Extraction with Ammonium acetate <sup>2</sup>
Potassium	29 mg/kg	Extraction with Ammonium acetate <sup>2</sup>
Hydrogen	89 mg/kg	Measuring pH in Adams Evans Buffer Soln. <sup>2</sup>
pH	3.1	pH electrode <sup>2</sup>
pH	3.8	pH electrode <sup>3</sup>
Redox Potential @ 22 C	+393	Redox electrode with Ag/AgCl <sub>2</sub> used as reference <sup>2</sup>
Redox Potential @ 22 C	+420	Redox electrode with Ag/AgCl <sub>2</sub> used as reference <sup>3</sup>
Acidity	7.07 mg CaCO <sub>3</sub> per g of sample	Standard Methods <sup>3</sup>
Cation Exchange Capacity	13.6 meq/100g	Summation of Cations (SSSA) <sup>2</sup>

\*All values are point estimates.

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

(2) Analysis performed by Agvise Laboratories, Northwood, North Dakota - No QA/QC data available

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

(4) See section 4.5.3 for data quality analysis

**Table 2.2 Physical Characterization of BCP Sludge \***

<b>Physical Parameter</b>	<b>Weight Percent</b>	<b>Method of Analysis</b>
0.5 - 2mm	14.5	Pipette Method
0.002 - 0.5mm	74.8	Pipette Method
0.0002-0.002mm	10.7	Pipette Method
Moisture at 1/3 bar	50.7	Gravimetric loss upon drying
Organic Matter	43	Furnace Method
Bulk Density (disturbed)	0.35 gm/cc	Weight Ratios

\* All values are point estimates

## **2.1 Thermogravimetric Analysis (TGA)**

### *2.1.1 Background*

Thermogravimetry measures the weight change in a specimen as a function of temperature and time. The mode of Thermogravimetry used for this study is known as dynamic thermogravimetry, in which different specimen types are heated in an environment whose temperature is changing in a pre-determined manner at a linear rate. The resulting mass-change versus temperature curve provides information concerning the thermal stability and composition of the specimen.

### *2.1.2 Method*

Thermogravimetric analysis was run on two 100 mg samples of BCP sulfide treated sludge. Samples were warmed with dry nitrogen gas to 50°C for about 10 minutes. A small amount of the sample was lost (probably moisture) during this initial warming in an inert medium. Following this, the heating program was initiated at a constant heating rate of 10°C/min until a temperature of 1000°C was reached. The thermal curves and derivative thermal curves were recorded for each sample by the data acquisition unit of the instrument. (These curves are provided in Appendix B, see Table of Contents.)

### *2.1.3 Results*

The TGA data, generated in duplicate, show four basic inflection points at 167°C, 252°C, 331°C, and 425°C. The initial weight loss between room temperature and 167°C is largely due to loss of moisture. These data indicate a thermally stable waste form. Heat generated in processing or long term storage is unlikely to affect long term stability of the waste.

Between 167°C and 425°C, organic constituents are decomposing rapidly, affecting changes in the waste form. The inflection point at 252°C is most likely the loss of sulfur from the system. The cause of the 331°C inflection point is unknown at this time. Above 450°C little change occurs.

#### *2.1.4 Data Quality Discussion*

Plans for conducting thermogravimetric analyses were not included in the EPA approved Quality Assurance Project Plan.

The thermogravimetric analyzer was calibrated according to the procedures outlined in the Perkin-Elmer manual. Initial calibration was performed on September 9, 1997. There were three calibration procedures performed, two for temperature and one for weight. The temperature calibration involved a furnace calibration and a two point standard curie temperature calibration. The furnace calibration performs a nine point temperature calibration between lower and upper temperature (100°C to 1350°C) limits. The thermocouple temperature is matched to the furnace temperature when the calibration is complete. The two point standard curie temperature calibration was performed using Nickel (magnetic transition temperature 354°C) and Hisat-50 (magnetic transition temperature 1000°C) magnetic standards to perform the curie point temperature calibration.

The weight calibration was performed using a 100 milligram class M calibration standard provided by Perkin-Elmer. Once these calibrations were completed, the results were permanently stored in the computer and incorporated into all runs. Recalibration is necessary only if the equipment is moved, computer software is reinstalled or a new gas supply is used.

### 3.0 Leachability of Sulfide Stabilized Sludge

#### 3.1 Solid Stability in Water

##### 3.1.1 Introduction

This test varies the liquid/solid mass ratio during leaching 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 waste form and the leachate and impede its diffusion from the waste.

##### 3.1.2 Procedure

Samples collected on November 19, 1998 from BCP were dried at room temperature for 24 hours in an exhaust hood.<sup>(1)</sup> 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 corresponding to 5, 10, 25 and 50 g of waste per liter, as reported in Table 3.1. The bottles were capped and tumbled for 18 hours and then each leachate sample was filtered through a 0.45µm filter and placed in a sample container. Each leachate sample was acidified to a pH of less than 2 with HNO<sub>3</sub> 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, mercury present in the leachate did not increase with greater volumes of leachant. Mercury released from Sample 1 was less than the reported detection limit of 0.001 mg/L. In terms of total mercury leached from the waste, the other three samples released similar amounts of mercury. Consequently, it is likely that mercury concentration gradients between the waste form and the leachant do not control leaching rates.

**Table 3.1 Solid Stability in Water Results<sup>1</sup>**

	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>	<b>Sample 4</b>
Liquid/Solid Mass Ratio	200:1	100:1	40:1	20:1
Waste (g/L)/Mercury (mg)	5/40.5	10/81.0	25/203	50/405
Mercury in Leachate(mg/L)	< 0.00100	0.00100	0.00116	0.00304
Total Mercury Leached (%)	—	0.00120	0.00054	0.00074

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

(1) Samples were dried in an exhaust hood rather than by oven drying as required by the QAPP. The modification was made to avoid heating of the wastes to the point where mobility of contaminants could be increased

#### 3.1.4 Data Quality Discussion

The solid stability-in-water test provides only single point indicators 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 solid and solution phases. Section 4.5.5 provides the data quality analysis for Solid Stability in Water Results.

### 3.2 Acidity

#### 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-in-water tests to assess the acid-generating capacity of the waste. 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 thus 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 acidity end point was obtained. The amount of sodium hydroxide required to neutralize the acidity of the sample is expressed as equivalent milligrams (mg) of CaCO<sub>3</sub> relative to a liter (L) of leachate and normalized to a gram (g) of the waste. An Orion electrode was used to measure the pH.

#### 3.2.3 Results

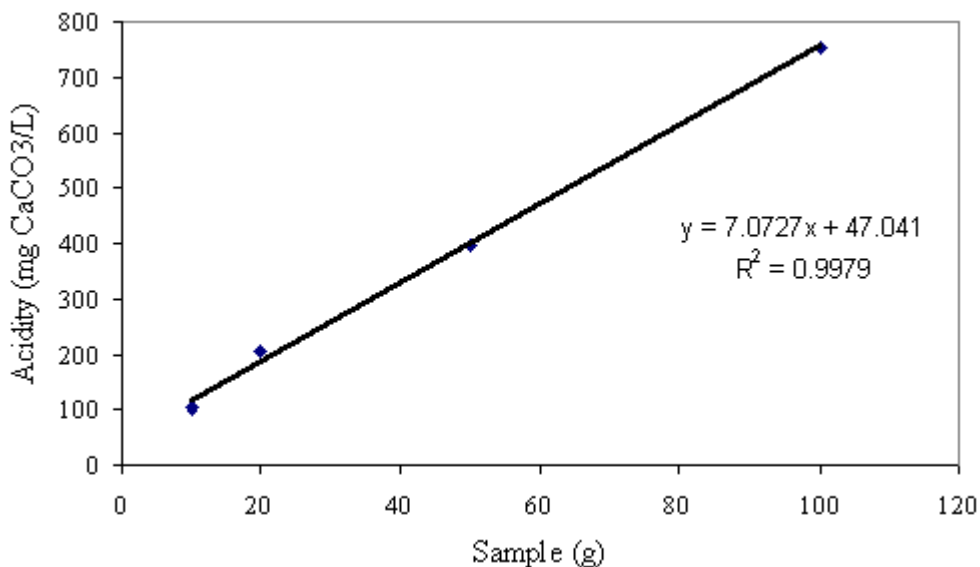
The titration curves are shown in Appendix C (see Table of Contents). The resulting acidity for each sample is shown in Table 3.2, and Figure 3.1 shows measured acidity in the leachate versus mass of the waste.

**Table 3.2 Acidity Results<sup>1</sup>**

Liquid/Solid Ratio (w/w)	20:1	40:1	100:1	200:1
Acidity (as mg CaCO <sub>3</sub> /L)	753.8	397.5	206.3	103.8
Normalized (mg CaCO <sub>3</sub> /g)	15.08	15.90	20.63	20.76

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

**Figure 3.1 Acidity vs. Sample Solid**



The values were normalized to sample weight in order to compare them on a per gram of sample basis. Results suggest that the sample has some buffering capacity in low pH ranges, dropping off above pH 6. The low buffer capacity of the waste may explain the wide variation in pH values reported both for the waste and for the landfill leachate.

#### *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 attempts 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 BCP waste was 3.8, which 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 waste 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 HNO<sub>3</sub> 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 of the material obtained from BCP on November 19, 1998 prior to mixing. TCLP results fall in a range of values from 0.00247 mg/L to 0.06555 mg/L, all well below the regulatory limit (0.2 mg/L). The sample pH was within the acceptable range for waste treatment. It appears that the mercury in this sample was well stabilized.

**Table 3.3 TCLP Results<sup>1</sup>**

Sample	TCLP Limit	1	2	3	4	5	6
TCLP (mg/L)	0.2	0.00247	0.00879	0.04100	0.06555	0.00498	0.04167 <sup>2</sup>
Total Mercury (mg/kg)		8,870	8,020	4,830	3,890	4,290	3,330

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

(2) The datum represents an undiluted result that exceeds the highest calibration standard (0.04000 mg/L).

### 3.3.4 Data Quality Discussion

Section 4.5.7 provides the data quality analysis for TCLP data.

## 3.4 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

Constant leaching tests were run at pH values of 2, 4, 6, 8, and 10, using 500 ml of deionized water and 25 grams of dried solid to produced 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. Each sample was filtered through a 0.7 µm glassfiber filter, acidified to a pH of less than 2 with HNO<sub>3</sub> and stored at 4°C until analyzed within the 28 day holding-time requirement. Mercury concentrations were measured by CVAAS.

### 3.4.3 Results

Table 3.4 summarizes the reported mercury concentrations for each distinct pH test carried out. As can be seen, leachate mercury concentrations were well below regulatory limits in all samples when the leachant pH was 6.0 or lower. With higher pH leachants, the leachate mercury concentrations dramatically increased. At pH 10, the highest amount of mercury was leached. 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 15 percent of each other. At pH 4 and 6, mercury concentrations fluctuated between the 10 and 24 hour leaching times, but remained within the same order of magnitude. 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. All test blanks except those for a pH of 8 are below the reported detection limit of 0.00100 mg/L. Even for the blanks at pH 8, there is no significant bias, given the comparatively high mercury concentrations reported for the leachate samples.

**Table 3.4 Constant pH Leaching Test Results<sup>1</sup>**

	Leachate Mercury, mg/L					
	pH 2	pH 4	pH 6	pH 8 (1)	pH 8 (2) <sup>2</sup>	pH 10
2 hr	0.01090	0.00634	0.00218	< 0.00100	missing	0.17400
10 hr	0.01480	0.00616	0.00286	0.02060	0.01350	0.37200
24 hr	0.01310	0.00274	0.00582	0.11600	0.40600	1.63000
Blank	< 0.00100	< 0.00100	< 0.00100	0.00274	0.00106	< 0.00100

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

(2) Test duplicate.

### 3.4.4 Data Quality Discussion

Section 4.5.8 provides the data quality analysis for Constant pH Leaching Test results.

## 4.0 Conclusions

### 4.1 Background Data

Background data supplied by BCP and EPA indicate that it is possible for BCP to produce waste forms that will pass TCLP; however, process quality control needs improvement (data quality analysis, Section 4.5.1).

### 4.2 Landfill Data

BCP waste landfill samples were highly variable, with leachate mercury concentrations ranging from 0.94 µg/L to non-detectable (data quality analysis, Section 4.5.2).

### 4.3 Characterization

A thorough physical and chemical characterization of the BCP waste sample proved useful throughout the testing process. Compositional data was used for background information (data quality analysis, Section 4.5.3).

### 4.4 Leaching Tests

The preliminary tests generated single point estimates. Therefore, the following discussion is intended to provide preliminary observations only. Preliminary observations should be qualified based on the QA/QC data quality discussions provided in 4.5.5 (Solid Stability in Water), 4.5.6 (Acidity), 4.5.7 (TCLP) and 4.5.8 (Constant pH Leaching).

Based on solid-stability-in-water tests, it is likely that mercury concentration gradients between the waste form and the leachant do not control leaching rates. A total of six TCLP tests were performed. Mercury concentrations ranged from 0.00247 mg/L to 0.06555 mg/L, all well below the regulatory limit (0.2 mg/L). Acidity testing indicates a small amount of buffering capacity in low pH regions and very little above pH 6. Constant pH leaching revealed mercury concentrations below 0.025 mg/L in all samples where the pH of the sample was 6.0 or lower. With higher pH leachants, soluble mercury concentrations dramatically increased.

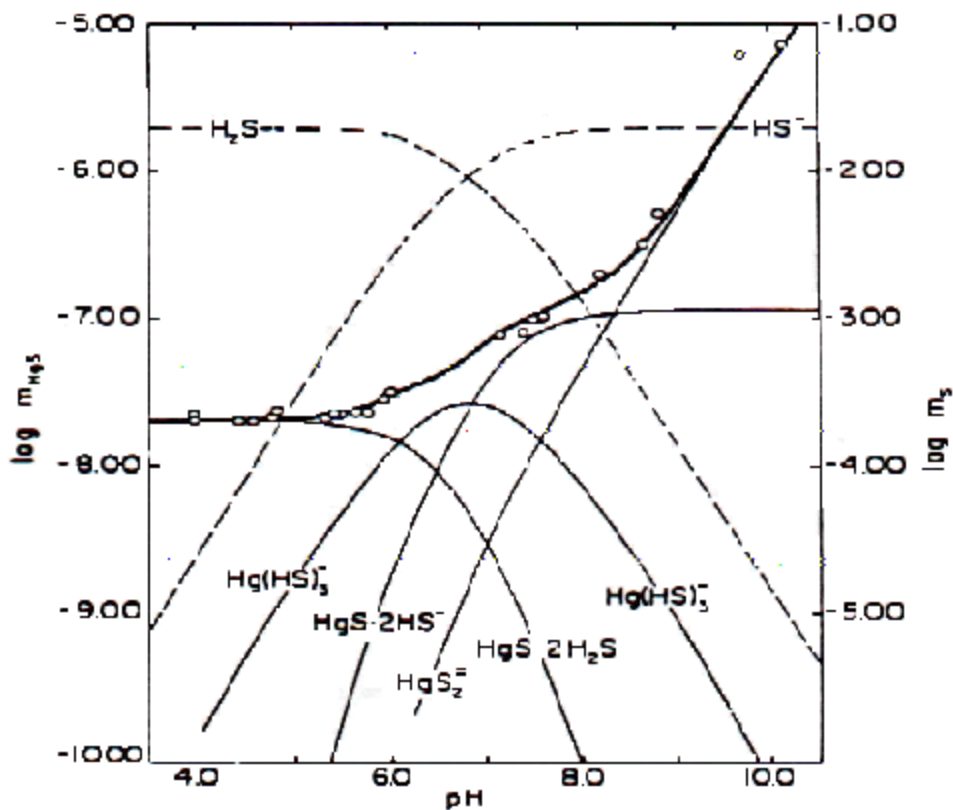
These results may be explained using thermodynamic data for mercuric sulfide. Mercuric sulfide (HgS) is very insoluble in water, with a solubility product,  $K_{sp}$ , of  $10^{-52}$  (Bard, 1966)<sup>1</sup>. However, the solubility of HgS in water can be increased measurably by association with various hydrogen sulfide species to form a number of mercuric-hydrogen-sulfide ions that enhance the solubility of HgS in water (Clever *et al.*, 1985)<sup>2</sup>. These associations can lead to the formation of  $\text{HgS}\cdot 2\text{H}_2\text{S}^0$ ,  $\text{Hg}(\text{HS})_3^-$ ,  $\text{HgS}\cdot 2\text{HS}^-$ ,

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<sup>1</sup> Bard, A.J., Chemical Equilibrium, Harper and Row, Publishers, New York, 1966.

and  $\text{HgS}_2^{2-}$ .  $\text{HgS}\cdot 2\text{H}_2\text{S}^0$  is the dominant water soluble form at pH values less than 6.2, while  $\text{Hg}(\text{HS})_3^-$  is the most soluble form between the pH values of 6.2 and 7.  $\text{HgS}\cdot 2\text{HS}^-$  is the most soluble mercuric sulfide association between the pH of 7 and 8.3, and  $\text{HgS}_2^{2-}$  is the most soluble form of mercuric sulfide above a pH of 8.3. In fact, the solubility of  $\text{HgS}_2^{2-}$  increases linearly with the hydroxyl ion concentration for pH values over 8.3. Figure 4.1 presents a detailed distribution of the various bisulfide species as a function of pH (Clever *et al.*, 1985).

Figure 4.1<sup>2</sup>



<sup>2</sup> Clever, 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.

The above discussion and Figure 4.1 serve to illustrate the effect of pH on the solubility of Hg(II) in water. Furthermore, the figure illustrates the importance of maintaining a pH less than 6 for precipitation of HgS in order to minimize the mobilization of mercury into the aqueous phase.

#### 4.5 Data Quality Discussion

Unprocessed analytical data generated by EEI are provided in Appendix D, see Table of Contents.

##### 4.5.1 Background Data

The background data presented are considered secondary data by EPA Order 5360.1 CHG 1, July 1998. Some QA information is available for the Gulf Coast Analytical Laboratories data (Table 4.1). However, no QA information was available for the SAIC data.

The limited QC data for Gulf Coast Analytical Laboratory Inc. (GCALI) show results for the laboratory control standard (LCS) and an occasional spike sample (Table 4.1). There is no information on initial calibration/blank and continuing calibration/blank or laboratory duplicates. All LCS samples meet the QC criterion of  $\pm 15$  percent of the true value, with the exception of the 10/27/87 TCLP sample.

**Table 4.1 Laboratory QC Data for GCALI Total Mercury and TCLP Result**

Sample ID	True $\mu\text{g/L}$	Found $\mu\text{g/L}$	Percent Recovery	RPD %	Dilution Factor	Reported Result $\mu\text{g/L}$
<b>TCLP Results</b>						
LCS 10/27/97	5.00	4.20	84.0	nr	nr	nr
Spike 10/27/97	5.00	4.50	90.0	nr	nr	nr
LCS 02/13/98	5.00	4.95	99.0	nr	nr	nr
LCS 05/15/98	5.00	4.90	98.0	nr	nr	nr
LCS 11/14/98	5.00	4.57	91.4	nr	nr	nr
LCS 11/23/98	5.00	4.40	88.0	nr	nr	nr
<b>Total Mercury Results</b>						
LCS 10/27/97	5.00	4.70	94.0	nr	nr	nr
Spike 10/27/97	5.00	4.95	99.0	nr	nr	nr

nr = not reported

#### 4.5.2 Landfill Data

The data presented in Table 1.2, are defined as secondary data by EPA Order 5360.1 CHG 1, July 1998. No QC information is available. No detection limit value is available. No information is available on the generation of leachate. Only a single pH value was provided and labeled as an average. Insufficient detail is available to assess these secondary data.

#### 4.5.3 Characterization Data

Twelve samples of BCP sludge were collected by UC and EPA on November 19, 1998 and composited prior to sending off a sample to Environmental Enterprises Inc. (EEI) for total mercury analysis. Table 4.2 summarizes the laboratory QC data for the single mercury result reported in Table 2.1. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 µg/L, with a corresponding correlation coefficient of 0.9993. Initial and continuing calibration standards and blanks were within the control limits. The mercury recovery on the LCS was below the lower limit of 85 percent, and the RPD for the sample and duplicate exceeds the limit of 25 percent. Data pertaining to a laboratory spike were absent.

**Table 4.2 Laboratory QC Data for EEI Total Mercury Result**

Sample ID	True µg/L	Found µg/L	Percent Recovery	RPD %	Dilution Factor	Reported Result µg/kg
<b>Work Order 99-02-413: Total Mercury Results</b>						
ICV	5.00	4.78	95.6	—	—	—
CCV1	5.00	4.64	92.8	—	—	—
CCV2	5.00	4.58	91.6	—	—	—
CCV3	5.00	4.58	91.6	—	—	—
LCS	3,300	2,764	83.8	—	—	—
ICB	<0.50	<0.50	—	—	—	—
CCB1	<0.50	<0.50	—	—	—	—
CCB2	<0.50	<0.50	—	—	—	—
CCB3	<0.50	<0.50	—	—	—	—
01A	—	9.24	—	28.2	1,000,000	9,240,000
01A-duplicate	—	6.96	—		1,000,000	6,960,000

A sample spike was not performed.

#### *4.5.4 Thermogravimetric Analysis*

Plans for conducting thermogravimetric analyses were not included in the EPA approved Quality Assurance Project Plan. Calibration information is provided in Section 2.1.4.

#### *4.5.5 Solid Stability in Water*

Prior to use, the pH meter was calibrated using a two-point calibration with certified calibration standards, pH 4 and pH 10. The calibration efficiency, defined as the measured value divided by the known value, is 1.0097, which is in the range of 1.05 to 0.95 from the QAPP. The experimental blank was run with other samples, but not sent out for Hg analysis. For Hg analysis, these samples were grouped with samples from the constant pH leaching test. Therefore, QC results of this grouping are presented in Section 4.5.7.

#### *4.5.6 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 has a value of 1.02 and is in the range of 1.05 to 0.95, per the QAPP.

#### *4.5.7 Toxicity Characteristic Leaching Procedure*

TCLP was performed on six separate grab BCP sludge samples. The pH meter calibration efficiency is 0.98, and is in the range of 1.05 to 0.95, per the QAPP. Mercury concentration of the method blank is <0.50 µg/L.

Table 4.3 summarizes the laboratory QC data for the total mercury in the solid and TCLP results reported in Table 3.3. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 µg/L, with a corresponding correlation coefficient of 0.9993 for total mercury results and 0.9997 for TCLP results. Initial and continuing calibration standards and blank-16-s were within the control limits, as was the LCS. The RPD for the TCLP sample and duplicate exceeds the limit of 25 percent. Data pertaining to a laboratory spike were absent.

Table 4.3 Laboratory QC Data for EEI Total Mercury and TCLP Result

Sample ID	True µg/L	Found µg/L	Percent Recovery	RPD %	Dilution Factor	Reported Result µg/kg or µg/L
<b>Work Order 98-11-594: Total Mercury Results, µg/kg</b>						
ICV	5.00	4.82	96.4	—	—	—
CCV1	5.00	4.57	91.4	—	—	—
CCV2	5.00	4.62	92.4	—	—	—
CCV3	5.00	4.80	96.0	—	—	—
CCV4	5.00	5.22	104	—	—	—
LCS	10.00	9.50	95.0	—	—	—
ICB	<0.50	<0.50	—	—	—	—
CCB1	<0.50	<0.50	—	—	—	—
CCB2	<0.50	<0.50	—	—	—	—
CCB3	<0.50	<0.50	—	—	—	—
CCB4	<0.50	<0.50	—	—	—	—
01A	—	9.29	—	9.59	1,000,000	9,290,000
01A-duplicate	—	4.22	—		2,000,000	8,440,000
<b>Work Order 98-12-164: TCLP Results, µg/L</b>						
ICV	5.00	5.00	100	—	—	—
CCV1	5.00	4.93	91.4	—	—	—
CCV2	5.00	4.57	92.4	—	—	—
CCV3	5.00	4.61	96.0	—	—	—
CCV4	5.00	4.93	104	—	—	—
LCS	10.00	9.27	92.7	—	—	—
ICB	<0.50	<0.50	—	—	—	—
CCB1	<0.50	<0.50	—	—	—	—
CCB2	<0.50	<0.50	—	—	—	—
CCB3	<0.50	<0.50	—	—	—	—
CCB4	<0.50	<0.50	—	—	—	—
04A	—	0.55	—	-32.2	100	55.00
04A-duplicate	—	7.61	—		10	76.10

A sample spike was not performed with either set.



#### 4.5.8 Constant pH Based Leaching Test

Prior to titration, the pH meter was calibrated using a two-point calibration with certified calibration standards, pH 4 and pH 10. All calibration efficiencies are in the range of 1.05 to 0.95 from the QAPP.

A test duplicate was run for pH 8. The sample collected at 2 hours for the duplicate run was not analyzed. The RPDs for 10 hours and 24 hours are 42% and 111% respectively, which reflects the variability in homogeneity of the BCP sludge.

Hg concentrations for all experimental blanks are <1.00 µg/L, except for pH 8 runs. The experimental blanks for pH 8 have Hg concentration of 2.74 µg/L and 1.06 µg/L (test duplicates), which indicates very low contamination.

Table 4.4 summarizes the laboratory QC data for the total mercury and TCLP results reported in Tables 3.1 and 3.4. The calibration curve was established using mercury standards of 0.50, 2.00, 5.00, 10.00 and 40.00 µg/L, with a corresponding correlation coefficient of 0.9996 for Work Order 99-03-404 and 0.9997 for the other work orders. Initial and continuing calibration standards and blanks were within the control limits, as was the LCS. There were no RPD or spike results reported for Work Order 99-03-404. The sample and duplicate for the remaining work orders contained mercury below the detection limit of 0.50 µg/L, and no RPD value was calculated. Results for the spike are within control limits.

Table 4.4 Laboratory QC Data for EEI Total Mercury Results

Sample ID	True µg/L	Found µg/L	Percent Recovery	RPD %	Dilution Factor	Reported Result µg/L
<b>Work Order 99-03-404</b>						
ICV	5.00	5.16	103	—	—	—
CCV1	5.00	4.95	99.0	—	—	—
CCV2	5.00	4.78	95.6	—	—	—
CCV3	5.00	4.84	96.8	—	—	—
CCV4	5.00	4.64	92.8	—	—	—
LCS	10.00	9.82	98.2	—	—	—
ICB	<0.50	<0.50	—	—	—	—
CCB1	<0.50	<0.50	—	—	—	—
CCB2	<0.50	<0.50	—	—	—	—
CCB3	<0.50	<0.50	—	—	—	—
CCB4	<0.50	<0.50	—	—	—	—
<b>Work Orders 99-03 494 &amp; 99-03-556</b>						
ICV	5.00	4.92	98.4	—	—	—
CCV1	5.00	4.84	96.8	—	—	—
CCV2	5.00	4.89	97.8	—	—	—
CCV3	5.00	4.82	96.4	—	—	—
CCV4	5.00	4.55	91.0	—	—	—
LCS	10.00	9.15	91.5	—	—	—
ICB	<0.50	<0.50	—	—	—	—
CCB1	<0.50	<0.50	—	—	—	—
CCB2	<0.50	<0.50	—	—	—	—
CCB3	<0.50	<0.50	—	—	—	—
CCB4	<0.50	<0.50	—	—	—	—
03A	—	<0.50	—	NC	2	<1.00
03A-duplicate	—	<0.50	—	NC	2	<1.00
03A-spike	5.00	5.10	102	—	—	—

A sample duplicate and spike are not available for samples associated with Work Order 99-03-404.

NC - not calculated because sample and duplicate are below the detection limit.