

Evaluation of Chemically Bonded Phosphate Ceramics for Mercury Stabilization of a Mixed Synthetic Waste

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Lee A. Mulkey, Acting Director
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Abstract

This experimental study was conducted to evaluate the stabilization and encapsulation technique developed by Argonne National Laboratory, called the Chemically Bonded Phosphate Ceramics technology for Hg- and HgCl₂-contaminated synthetic waste materials. Leachability tests were carried out by the constant-pH leaching test, the Toxicity Characteristic Leaching Procedure (TCLP), and the TCLP "Cage" modification. X-ray diffraction and spectroscopic techniques, using scanning electron microscope, energy-dispersive spectrophotometer, and wave-dispersive spectrophotometer, were used to identify the solid-state mineral phases.

Data obtained from this study showed that stabilization of wastes reduced the leachability of Hg considerably. TCLP results showed that leachability of Hg decreased by a minimum of two orders of magnitude and a maximum of five orders of magnitude. The variation in the decrease in leachability was dependent on the amount and state of Hg in the waste. Maximum reduction in leachability of stabilized wastes was observed with wastes containing elemental Hg at 50 wt% loading, followed by wastes containing HgCl₂ at 50 wt% loading, HgCl₂ at 70 wt% loading, and elemental Hg at 70 wt% loading, respectively. The three test methods produced similar amounts of leached mercury, but the constant-pH leaching procedure samples released slightly higher levels (at pH=2) compared to the TCLP methods. On comparing the results obtained with the standard TCLP and the TCLP "Cage" modification, it was observed that leachates from stabilized wastes containing 50 wt% loading of elemental Hg and HgCl₂ were within the Land Disposal Restrictions (LDR) requirement. Moreover, leachability indices measured with the TCLP "Cage" modification procedure showed high leachability indices, which indicates that Hg was retained well within the solid matrices. However, wastes containing 70 wt% loading of Hg and HgCl₂ had leachate concentrations exceeding the 0.2 mg/L treatment standard and therefore did not meet RCRA disposal requirements.

Comparing typical cost data, as available in the literature, for several competing treatment technologies for mercury-contaminated hazardous wastes, the cost estimate ranges from \$2.88/kg for sulfur polymer cement stabilization/solidification (SPSS) to \$16.37 per kg for conventional Portland cement stabilization (both including disposal). The total cost, including both raw materials, labor, and disposal for the CBPC process at \$15.45 per kg was found to be on the high end of the treatment cost scale.

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Acronyms and Abbreviations

ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
BDAT	best demonstrated available technology
BEI	back-scattered electron imaging
BET	Brunnauer, Emmet, and Teller
CBPC	Chemically Bonded Phosphate Ceramics
CFL	cumulative fraction leached
CFR	Code of Federal Regulations
CVAA	cold vapor atomic absorption
DET	determination of equivalent treatment
EDS	energy-dispersive spectrophotometer
FR	Federal Register
HDPE	high-density polyethylene
ICDD	International Centre for Diffraction Data
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
INEEL	Idaho National Engineering and Environmental Laboratory
ISO	International Standards Organization
LDR	Land Disposal Restriction
MDI	Materials Data, Inc.
MKP	magnesium potassium phosphate hydrate
MLLW	mixed low level waste
MTRU	mixed transuranic waste
MWIR	mixed waste inventory report
NA	not applicable
NRMRL	National Risk Management Research Laboratory

O&M	operation and maintenance
ORP	oxidation-reduction potential
OSW	Office of Solid Waste
PE&I	purchased equipment and installation
RCRA	Resource Conservation and Recovery Act
rpm	rotations per minute
rcf	relative centrifugal force
SAIC	Science Applications International Corporation
SEI	secondary electron imaging
SEM	scanning electron microscope
SPSS	sulfur polymer cement stabilization/solidification
S/S	solidification/stabilization
TCLP	Toxicity Characteristic Leaching Procedure
UC	University of Cincinnati
UHP	ultrahigh purity
U.S. DOE	United States Department of Energy
U.S. DOT	United States Department of Transportation
U.S. EPA	United States Environmental Protection Agency
UTS	Universal Treatment Standard
WDS	wave-dispersive spectroscopy
WPI	Waste Policy Institute
XAFS	x-ray absorption fine structure
XRD	x-ray diffractometer

1.0 Introduction

1.1 Background

The development of effective treatment options for mercury-contaminated solid wastes is a significant technical and practical challenge due to several factors, including the limited economic benefit derived from mercury recovery/recycling; the high toxicity, volatility, and environmental mobility of mercury; and the varied nature and composition of industrial waste products. As an inorganic element, mercury cannot be destroyed, but it can be converted into less soluble or leachable forms to inhibit migration into the environment after disposal. The management and ultimate disposal of mercury-contaminated hazardous waste are controlled by United States Environmental Protection Agency (U.S. EPA) regulations known as the Land Disposal Restrictions (LDRs) (40 Code of Federal Regulations [CFR] Part 268). Under the current LDR program, the U.S. EPA has established thermal recovery (e.g., roasting/retorting) as the best demonstrated available technology (BDAT) for treatment of wastes containing greater than 260 mg/kg of mercury. For treatment of wastes with less than 260 mg/kg of mercury, other extraction technologies (e.g., acid leaching) or immobilization technologies (e.g., solidification/stabilization [S/S]) may be considered (U.S. EPA, 1999a). Also, because mercury contained in radioactive or mixed waste is not suitable for thermal recovery and recycling, the U.S. EPA recognizes that S/S may be an appropriate treatment option for heavily contaminated mercury mixed wastes or debris (Waste Policy Institute [WPI], 1999).

Stabilization involves a chemical immobilization of hazardous constituent, through chemical bonds to an immobile matrix, or chemical conversion to an immobile species, thereby reducing vaporization or leaching to the environment (Science Applications International Corporation [SAIC], 1998). A potential advantage of using a stabilization technology is that it produces a more stable and less leachable contaminant of concern. However, stabilization processes do not reduce total mercury concentrations; rather, they reduce the leachability of the mercury, yielding

a product that still may require disposal in a landfill. There may also be a resulting increase in the volume of contaminated materials (Stepan et al., 1993).

According to the Resource Conservation and Recovery Act (RCRA) LDR rules, mercury hazardous waste is defined as any waste that has a Toxicity Characteristic Leaching Procedure (TCLP) value greater than 0.2 mg/L. Mercury-contaminated wastes that exceed this value must be treated to meet the Universal Treatment Standard (UTS) of 0.025 mg/L or less prior to disposal in a landfill.

The U.S. EPA's Office of Solid Waste (OSW) is proposing revisions to the LDRs for mercury. The revisions may allow wastes containing greater than 260 mg/kg of mercury to be stabilized as a means of treating the wastes, just like wastes with less than 260 mg/kg of mercury. As part of these revisions, the U.S. EPA is evaluating technologies that may stabilize mercury in contaminated wastes. The work included in this study was conducted to evaluate the capability of effectively stabilizing mercury-containing test materials using Argonne National Laboratory's (ANL's) patented mercury S/S technology known as Chemically Bonded Phosphate Ceramics (CBPC) technology (Ceramicrete™ [Wagh et al., 1997]). This technique was developed at ANL to stabilize various U.S. Department of Energy (U.S. DOE) waste streams.

U.S. DOE facilities have accumulated large volumes of elemental mercury; one location has an estimated 730 metric tons (Fuhrmann et al., 2002). Thirty-six U.S. DOE sites are storing about 167,600 m³ of mixed low level waste (MLLW) and mixed transuranic waste (MTRU) that are not being treated (Klassy, 2002). More than 1,400 waste streams comprise this inventory, which is heterogeneous both physically and chemically. Of this amount, approximately 28% (or 46,900 m³) has been labeled as mercury-contaminated. The majority of waste is in the form of debris, soils, sludges, and wastewaters. U.S. DOE projects that an additional 45,000 m³ of MTRU and 170,000 m³ of MLLW will be generated over the next ten years, primarily from environmental restoration and decontamination and decommissioning activities (U.S. DOE, 2000). U.S. DOE assumes that the wastes generated in the future will possess physical and chemical characteristics similar to those in the present inventory.

S/S processes are effective in treating a variety of “difficult-to-manage” waste materials for disposal or reuse. It is one of the most commonly used techniques because of its relatively simple and inexpensive nature, compatibility with a variety of waste disposal environments, and ability to meet stringent processing and performance requirements. The hydration reaction results in several chemical and physical mechanisms that combine, capture, and/or immobilize contaminants. The chemical mechanisms involve chemical change through transformation (soluble salt of hazardous metals to a relative insoluble silicate, hydroxide, or carbonate form). The physical mechanisms involve the capture (encapsulation) of hazardous constituents within the resulting physical structure of the solidified waste matrix. However, some fundamental aspects, such as the chemical mechanisms of hydration, the bonding between the waste materials with cement, and detailed microstructural and microchemical studies of stabilization, are still poorly understood and lack quantification.

Among the different available S/S technologies, the CBPC technology is based on fabrication of dense, strong, and insoluble ceramics at low temperatures by acid-base reactions. The rationale for using thermodynamically stable phosphate materials for hazardous materials is that the resulting phosphates of the contaminants are extremely insoluble compounds. Also, because this treatment occurs at low temperatures, it presents no contaminant volatilization problems such as those faced in high-temperature stabilization technologies.

In support of OSW’s effort to revise the LDR, U.S. EPA’s National Risk Management Research Laboratory (NRMRL) is interested in investigating the CBPC technology in order to evaluate its efficacy in permanently and cost-effectively managing mercury waste streams. Battelle was tasked with the responsibility of conducting a study to evaluate the CBPC technology in reducing the leachability of mercury from a sample. This document reports the results of a bench-scale study evaluating the use of ANL’s Ceramicrete™ stabilization process to effectively stabilize mercury-containing test materials using University of Cincinnati (UC) Constant pH Leaching Procedure and TCLP. Characterization of release rates and leaching potentials from waste materials often is used to predict the impact of contaminant release on the surrounding environment or to evaluate the efficacy of treatment processes such as S/S.

The physical and chemical properties of mercury are summarized in Table 1.

Table 1. Physical and chemical properties of mercury

Physical Properties	
Atomic number	80
Atomic weight	200.59
Atomic radius	1.5 Å
Atomic volume	14.81 cm ³ /g-atom
Boiling point	357.73°C (675°F)
Boiling point/rise in pressure	0.0746 °C/torr
Melting point	-38.87°C (-37.97°F)
Conductivity (heat)	0.022 cal/s/cm ³ · °C
Resistivity (heat)	95.8 × 10 ⁻⁶ ohm/cm at 20°C (68°F)
Contact angle	132 degrees
Surface tension (in air)	436 dyn/cm at 20°C (68°F)
Viscosity	1.554 cp at 20°C (68°F)
Density	13.546 g/cm ³ at 20°C (0.489 lb/in ³ at 68°F)
Diffusivity (in air)	0.112 cm ² /s
Electron configuration	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
Heat capacity	0.0332 cal/g at 20°C (0.060 Btu/lb at 68°F)
Henry's law constant	0.0114 atm · m ³ /mol
Interfacial tension (Hg/H ₂ O)	375 dyn/cm at 20°C (68°F)
Ionization potential	10.4375 ev (first) 18.751 ev (second)
Saturation vapor pressure	0.16 N/m ² (pascal) at 20°C (68°F)
Vaporization rate (still air)	0.007 mg/cm ² · hr for 10.5 cm ² droplet at 20°C (68°F)
Chemical Properties	
E ⁰ for Hg ²⁺ + 2e ⁻ = Hg(l)	0.854 V
E ⁰ for Hg ₂ ²⁺ + 2e ⁻ = 2Hg(l)	0.788 V
E ⁰ for 2Hg ²⁺ + 2e ⁻ = 2Hg ₂ ²⁺	0.920 V
Electronegativity	1.92 (Pauling scale)
Solubility (in water)	60 – 80 µg/L at 20°C (68°F)

1.2 Chemically Bonded Phosphate Ceramics

1.2.1 Process

CBPCs are prepared by acid-base reactions between an inorganic oxide and phosphoric acid solution (Wagh et al., 2001). This process has the advantage that it can be used to treat both acidic and alkaline wastes within a wide range of pH values. Moreover, both solid and liquid wastes can be treated, as the process employs solid powder and phosphate solution for the reaction. The solid waste material is crushed to aid in the mixing step and mixed with a solidifying powder (binder), and then reacted with the liquid. The preferable particle size range of solid waste materials is 4 to 75 µm (Singh et al., 1998). The liquid waste can be mixed with the phosphoric acid and then reacted with the inorganic oxide powder. After the solution and the

powder are mixed, the slurry can be transferred into molds for setting. The mixing step ensures that the waste particles are completely encapsulated or coated with binder. A schematic diagram of the Ceramicrete™ process is shown in Figure 1.

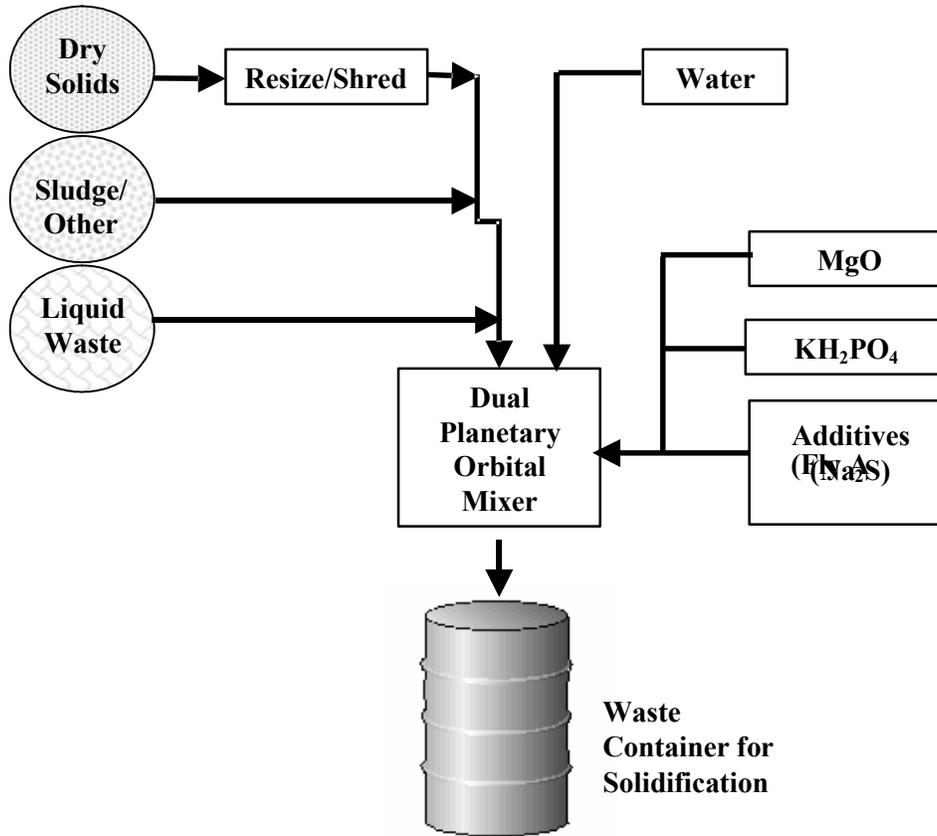


Figure 1. Ceramicrete™ process diagram

1.2.2 Chemistry of Chemically Bonded Phosphate Ceramics and Mercury

Phosphate ceramics are formed by reaction between magnesium oxide (MgO) and mono-potassium phosphate (KH₂PO₄) in solution. The reaction is governed by the reaction:



Magnesium potassium phosphate hydrate (MKP), MgKPO₄ · 6H₂O, is a hard, dense ceramic, and acts as a crystalline host matrix for the waste. The bulk ceramic then encapsulates the Hg contaminants in the dense crystalline matrix of MKP.

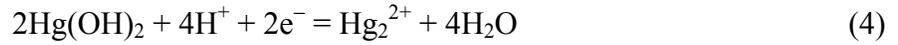
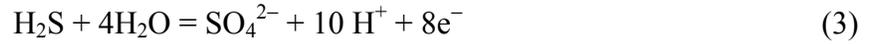
The suitability of phosphates for containing hazardous wastes has been elaborated by Wagh et al. (2001). Phosphates are extremely insoluble in groundwater, which ensures that the phosphate-based final waste forms will protect groundwater from contamination by the contained waste. Phosphates can be easily applied and handled, as phosphates can be used in solid form at room temperatures. Phosphate-bonded ceramics are nonflammable inorganic materials and hence are safe during transportation and storage. As the final waste form is synthesized at a low temperature, volatilization is not a risk. Furthermore, because there is no thermal treatment of the waste streams, the fabrication steps and processing equipment needs are simple. A short setting time is particularly advantageous because it minimizes worker exposure to contaminants. Finally, the raw materials required for fabricating the waste forms are readily available at comparatively low cost.

CBPC waste stabilization is conducted by slowly stirring a mixture of the waste, a small amount of sodium sulfide (Na_2S) (0.5 wt%), MgO , and KH_2PO_4 in water. The Na_2S was added to act as a binder (Wagh et al., 2001). Dissolution of KH_2PO_4 yields potassium phosphates and hydrogen ions. The increase in acidity increases the solubilities of MgO , Hg-compounds, and leads to the release of Mg^{2+} (magnesium) and Hg^{2+} (mercury) ions. The released Hg^{2+} is then converted to cinnabar (HgS) by hydrogen sulfide (H_2S), or common alkali sulfides (Na_2S , K_2S). The expected reaction between sulfide and Hg-compounds such as HgO and H_2S is given by



The solubility product and solubility of HgS are 2×10^{-49} and 4.5×10^{-25} mol/L, which indicates that it is a very insoluble compound. Also, considering the Gibbs free energy (ΔG) values of HgO , H_2S , HgS , and H_2O , which are -58.5 kJ/mole, -33.4 kJ/mole, -50.6 kJ/mole, and -237.1 kJ/mole, respectively (Wagh et al., 2001), the net change in free energy for reaction (2) is -195.8 kJ/mole, which indicates that the reaction will occur spontaneously.

Proper care should be taken to maintain appropriate amounts of Na₂S as excess sulfide leaches Hg. In the presence of excess sulfides, the reduction reaction initiates, and that may reduce Hg²⁺ to Hg₂SO₄ (Conner, 1990; Pourbaix, 1966).



Hg₂SO₄ has a solubility product (K_{sp}) value of 7.99×10^{-7} , which indicates that it is considerably more soluble than HgS.

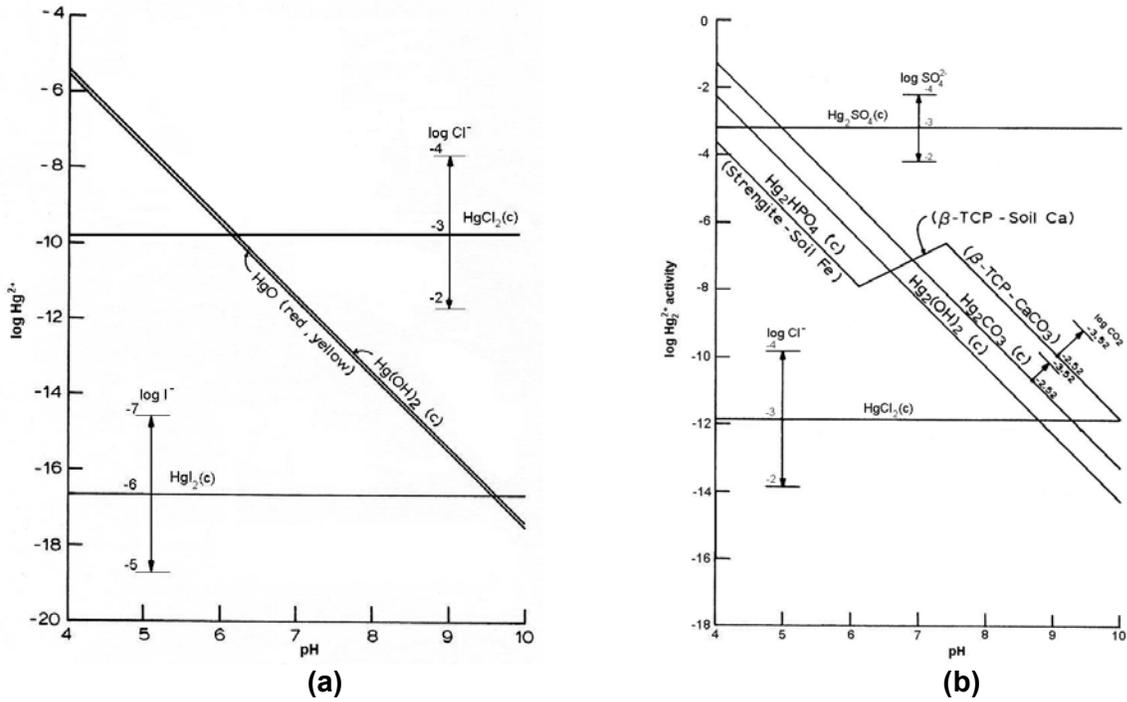


Figure 2. The solubilities of (a) Hg(II), and (b) Hg(I) minerals.

Mercury is generally classified as a chalcophilic element; that is, one that tends to concentrate in sulfide minerals. It exists primarily in three oxidation states: 0, +1, and +2. The solubilities of Hg(II) and Hg(I) as a function of pH are shown in Figure 2.

The halide minerals ($\text{HgCl}_{2(c)}$) are generally more soluble than oxides and hydroxides (Figure 2a). The solubility of $\text{HgSO}_{4(c)}$ is too high to appear in Figure 2a. The decreasing order of solubilities of the oxides of Hg(II) in water are: $\text{Hg}(\text{OH})_{2(c)} > \text{HgO}$ (red, hexagonal) $> \text{HgO}$ (yellow, orthorhombic) $> \text{HgO}$ (red, orthorhombic). The solubilities of Hg(I) minerals are plotted in Figure 2b. The order of decreasing solubilities of Hg(I) compounds are: $\text{Hg}_2\text{SO}_{4(c)} > \text{Hg}_2\text{CO}_{3(c)} > \text{Hg}_2(\text{OH})_{2(c)} > \text{Hg}_2\text{HPO}_{4(c)}$. The solubility of $\text{Hg}_2\text{HPO}_{4(c)}$ shifts with changes in phosphate activity. Decreasing phosphate solubility below that of beta-tricalcium phosphate (β -TCP) allows $\text{Hg}_2\text{HPO}_{4(c)}$ to become more soluble, and less likely to precipitate. The four halides, Hg_2X_2 , all occur, with the chloride, bromide, and iodide all being insoluble in water. Hg_2F_2 is rapidly hydrolyzed to HF, $\text{Hg}(\ell)$, and HgO. $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ are very soluble in water to give stable solutions from which the insoluble halides can be easily precipitated.

The addition of H_2S or alkali metals sulfides to aqueous Hg^{2+} precipitates the highly insoluble, black mercuric sulfide (HgS).



When this black solid is heated or treated in other ways, it is changed into a red form that is identical as the mineral cinnabar. In this red form, HgS has a distorted NaCl structure in which the $(\text{Hg} - \text{S})_{\infty}$ chain can be recognized (Cotton et al., 1999).

Knowledge of the complexes formed between the mercury and different ligands is very important in understanding mobilization or immobilization of mercury. Mercury is a “soft” cation, showing a strong preference for Cl, Br, I, P, Se, and certain N-type ligands. It displays coordination numbers of 2 through 6, with a preference for the lower ones. Mercury has a great affinity for ligands with sulfur and the other chalcogenides (Cotton et al., 1999). In presence of water, hydroxide, chloride, and sulfide are considered to control speciation of mercury (Schuster, 1991).

Leermakers et al. (1995) estimated that more than 90% of mercury was found as HgCl_2 at a salinity greater than 25%. In anoxic environments containing dissolved sulfide, mercury is expected to combine with sulfide to form mercuric sulfide species, such as $\text{HgS}_{\text{solid}}$ and $\text{Hg}(\text{SH})_{2(\text{aq})}$ (Dyrssen and Wedborg, 1991; Ravichandran, 1999). Some important stability constants (k) of complexes between mercury and various ligands are summarized in Table 2.

Table 2. Stability constants (k) of complexes between mercury and various ligands (Martell et al., 1998; Ravichandran, 1999)

Ligand (L)	Formula	HgL		HgL ₂	
		Log k	T (°C), I(M)	Log k	T (°C), I(M)
Chloride	Cl^-	7.3	25, 0	14	25, 0
Carbonate	CO_3^{2-}	11.0	25, 0.5	—	—
Hydroxide	OH^-	10.6	25, 0	21.8	25, 0
Sulfate	SO_4^{2-}	1.3	25, 0.5	—	—
Sulfide	S^{2-}	—	—	37.7	20, 1.0
Phosphate	PO_4^{3-}	9.5	25, 3.0	—	—

Note: I = ionic strength.

2.0 Materials and Methods

2.1 Ceramicrete™ Composition and Preparation

CBPC technology, as developed at ANL with funding from U.S. DOE's Mixed Waste Focus Area, was tested at Battelle using surrogate wastes that simulated a secondary waste resulting from low temperature destruction of organics by a process called "DETOX," invented by Delphi Corporation. This waste stream represents either actual waste streams generated at U.S. DOE facilities, or secondary waste streams that may be generated during destruction of organics (Rogers and Goldblatt, 2000; Mayberry et al., 1992). The waste stream generally contains a mixture of ferric oxide and ferric chloride, or ferric phosphate, as major components. This surrogate waste material has been used in a full-scale low-level mixed waste treatment demonstration at the U.S. DOE's Savannah River Site (Rogers and Goldblatt, 2000). Although DETOX waste material may not be similar in chemical or physical composition to the other U.S. DOE radioactive, Hg-containing waste streams, this waste material has been used as a synthetic surrogate.

The experiments were conducted with two types of wastes, in which the mercury was present as either HgCl_2 or elemental Hg. Each of these wastes was prepared by mixing approximately 1,132 g of Fe_2O_3 and 60 g of FeCl_3 in a 1-L flat-bottomed high-density polyethylene (HDPE) container. About 8 g of HgCl_2 , which was crushed with a spatula in a polyethylene beaker, was added to one of the above $\text{Fe}_2\text{O}_3/\text{FeCl}_3$ mixtures to make the HgCl_2 unstabilized waste. The elemental Hg unstabilized waste stream was prepared by adding approximately 6 g of elemental Hg to the second $\text{Fe}_2\text{O}_3/\text{FeCl}_3$ mixture. Five alumina balls were placed in each of the above mixtures to homogenize the solids, and both the containers were placed on rollers overnight. Approximately 500 g of each of the homogenized wastes were set aside into two different containers to be used in subsequent experiments as the "unstabilized waste" samples. The

remaining 700 g of each of the two wastes were further divided into two groups, defined as 50 wt% and 70 wt% loading wastes, and stabilized with the Ceramcrete™ binder.

Approximately 300 g of each of the unstabilized wastes, containing either HgCl₂ or elemental Hg, was mixed with 2 g of Na₂S and 160 g of deionized water to prepare slurries (Table 3). These waste samples were defined as “50 wt% loading wastes.” The wt% loadings were reported based on dry weight basis. The slurry in each container was mixed with a spatula for about 10 minutes. Three alumina balls were added to each container, which were placed on the roller for about two hours. The remaining 400 g of each of the unstabilized wastes were mixed with 2.67 g of Na₂S and 120 g of deionized water (Table 3). These waste samples were defined as “70 wt% loading wastes.” The same procedure used to prepare the 50 wt% loading wastes was followed to prepare the 70 wt% loading wastes. The slurries were mixed for about 10 minutes, and three to five alumina balls were added to each container before placing them on the roller for about two hours.

Table 3. Sample compositions of stabilized wastes

Waste Loading (wt%)	Waste Form Composition (g)	Waste Form Density (kg/m ³)
50	HgCl ₂ waste	300
	Na ₂ S·9H ₂ O	2
	MKP binder	300
70	HgCl ₂ waste	400
	Na ₂ S·9H ₂ O	2.67
	MKP binder	172
50	Hg waste	300
	Na ₂ S·9H ₂ O	2
	MKP binder	300
70	Hg waste	400
	Na ₂ S·9H ₂ O	2.67
	MKP binder	172

Note: MKP binder is a 1 M:1 M mix of MgO and KH₂PO₄.

After mixing was complete, approximately 300 g of MKP binder was added to the 50 wt% loading wastes containing either HgCl₂ or elemental Hg, and mixed for approximately 15 minutes. MKP is the ceramic binding phase, and was obtained by reacting calcined magnesium oxide (Martin Marietta, Baltimore, MD) with a solution of monopotassium phosphate (Monsanto

Chemical Company, St. Louis, MO) as described by Singh et al. (1998). Also, about 172 g of MKP binder was added to the 70 wt% loading wastes, containing either HgCl₂ or elemental Hg, and mixed for approximately 5 minutes. The samples were then transferred into 2-inch (diameter) × 4-inch (length) plastic vertical cylindrical molds and allowed to sit until solidified. The molds then were cured by air-drying for about three weeks. All samples prepared in the above manner were used for the subsequent leaching and characterization experiments.

2.2 Experiments Conducted

The particle sizes of the test samples described in Section 2.1 were reduced to less than 9.5 mm in diameter by grinding and sieving techniques. The particles of the unstabilized wastes were already much less than 9.5 mm size and therefore did not require further grinding. Kosson et al. (2002) reported that a particle size of 9 mm would require 40.5 days to achieve a condition equivalent to 2 mm size for 48 hrs of equilibration time. They also reported that a minimum sample size of 80 g for particle size <5 mm is needed to get a representative sample.

2.2.1 Characterization of Waste Samples

Different physical and chemical tests of the treated and untreated samples were performed to characterize the waste materials. Surface area analysis, bulk density tests, visual observation (surface spalling, crack development, color, surface pore size and condition), and electron microscopic analyses were conducted, as the size, surface heterogeneity of particles in the waste often indicates the potential for water movement through the material and compressibility.

Single-point determinations of specific surface area of the powdered samples were performed using N₂ adsorption by continuous flow method (ASTM D4567) with a Micromeritics Flowsorb II 2300 instrument. The instrument uses Brunnauer, Emmet, and Teller (BET) gas adsorption (helium/nitrogen mixture) technique for measuring specific surface area of powdered or granular samples. The surface area was measured by determining the quantity of a gas that adsorbs as a single layer of molecules, a so-called monomolecular layer, on a sample. The area of the sample is thus calculated directly from the number of gas-adsorbed molecules, which is derived from the gas quantity at the prescribed conditions, and the area occupied by each. Bulk

density is a measure of the weight of the soil per unit volume (g/cm^3). All samples were analyzed in duplicate.

All samples were studied by optical light microscopy prior to investigation by x-ray diffractometer (XRD), scanning electron microscope (SEM), and energy-dispersive spectrophotometer (EDS). An optical microscope (manufacturer: ZEISS) was used to examine the microstructure of the samples. Solid samples were turned to finely divided powder by gentle grinding that was not sufficient to destroy the structure. Sizes and shapes of the solid waste material were uniform between the samples. A fully automated Rigaku wide-angle goniometer D-Max-B diffractometer was used to conduct the x-ray diffraction analysis of the powdered random-oriented unstabilized and stabilized samples. Jade Plus software was used to enhance the diffraction pattern by reducing noise, baseline correction, and alignment with internal standards. An automated search-match routine assisted in identifying diffraction peaks based on cataloged d-spacings and relative intensity data from databases for inorganic compounds and minerals.

Scanning electron microscopic study was conducted by placing a portion of the sample on carbon planchettes (using adhesive tape), which were then carbon-coated for electrical conductivity. A JEOL 840A SEM was used to collect images. The resolution of the instrument is approximately 6 nm, and magnifications ranging from 10 to 300,000X. A variety of imaging modes were used for examination of samples, including secondary electron imaging (SEI) and back-scattered electron imaging (BEI). The SEM is equipped with an Oxford Inca 300 EDS for semi-quantitative analyses.

Polished thin sections were carbon-coated for electrical conductivity prior to electron microprobe analysis. A JEOL 733 Superprobe was used to collect images and elemental maps using EDS capabilities, and wave-dispersive spectroscopy (WDS). This microscope was operated through a PC based controlling system manufactured by Advanced Microbeam, Inc. Photomicrographs of selected areas were obtained using SEI and BEI imaging modes with a secondary electron image resolution of 7 nm.

2.2.2 Leaching Tests

Leaching tests have been recognized as the primary and the most widely used indicator for evaluating the retention capacity of the solidified matrix. In leaching tests, the waste is exposed to a leachant and the amount of contaminant in the leachate (or extract) is measured and compared to a previously established standard (such as a regulatory standard of baseline leaching data).

Three extraction tests were conducted in this study: (1) UC's Constant pH Leaching Procedure; (2) TCLP; and (3) TCLP "Cage" Modification. Figure 3 is a schematic representation of the experimental design for the different leaching tests used for this study.

UC's Constant pH leaching Procedure and standard TCLP require sample size reduction and involve the agitation of ground and pulverized waste in a leachant using a leachant/waste ratio of 20:1. However, shortcomings of selecting a size reduction approach are: (a) contamination of the sample, (b) partitioning of contaminants into a specific size fraction, and (c) loss of contaminants, particularly volatile mercury. Efforts were taken to avoid contamination of samples by using clean and washed separate hammer, anvil, mortar, pestle, and nylon (nonmetal) screens for individual samples. No effort was taken to measure volatile Hg generated, if any.

Currently, assessment of treatment technologies, which includes both conformance with BDAT and establishing performance for a determination of equivalent treatment (DET), is performed using TCLP. However, TCLP has been extensively criticized (U.S. EPA, 1991, 1999b) as it was designed to simulate leaching during waste co-disposal with municipal solid waste in a landfill. TCLP test only concentrates to one pH range, and Kalb (2001) reported that it is not representative of long-term landfill conditions. UC's Constant pH leaching procedure was used as it covers pH range 2 to 12. Typically, S/S materials are formed into monoliths that may be disposed in regulated landfills. To compensate effect of artificial particle size requirements, TCLP "cage" modification tests were conducted.

The final leachate was analyzed for heavy metals to determine the degree of elution of the components from the solidified matrix into the leachant. The Leachability Index derived from the above procedures was used to compare the leaching resistance of S/S-treated waste and also to indicate the contaminant release rate.

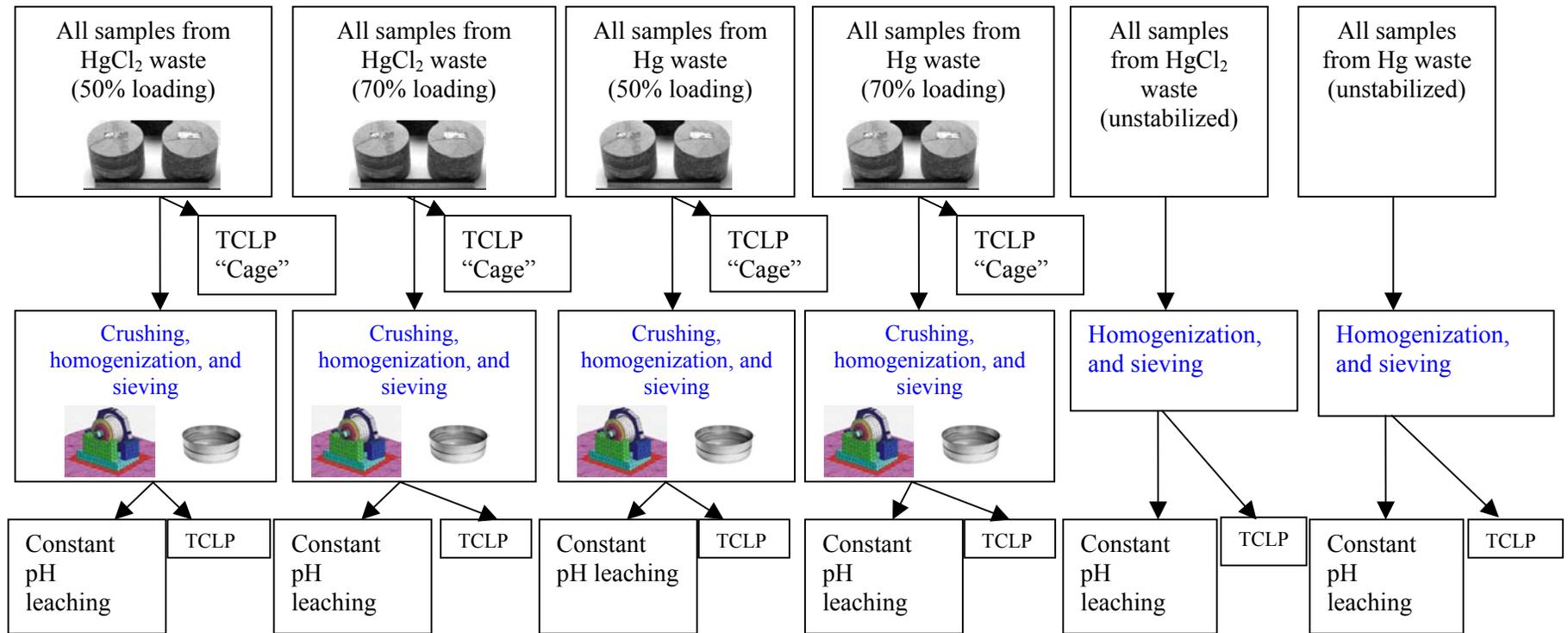


Figure 3. Schematic diagram of the experimental test matrix

2.2.2.1 UC Constant pH Leaching Procedure

The UC Leaching Procedure (UC, 1999; Rieser et al., 2001) was performed on both the stabilized (solid) and unstabilized wastes and is as follows. Leachant at pH values 2, 4, 6, 8, 10, and 12 were prepared for each pH test by adjusting the pH of deionized water with stock solutions of 0.1 N nitric acid (HNO₃) or 0.1 N sodium hydroxide (NaOH), which were prepared using reagent grade chemicals. Duplicates were conducted at three alternate pH values (i.e., at pH values 2, 6, and 10). For each leach test, 25 g of the test samples, prepared as described in Section 2.1, were placed in separate acid-washed and labeled 1-L polyethylene bottles. 500 mL of the appropriate leachant then was added to each of these bottles. Initial pH readings were taken for each bottle to represent the initial time (t=0) value. Adjustments were made using 0.1 N HNO₃ or 0.1 N NaOH to reach the target pH value. Appropriate leachant with no solid material was used as laboratory control blanks. Each bottle then was placed on a tumbler, as shown in Figure 4, and tumbled at 30 ± 2 rotations per minute (rpm) in a rotary agitation apparatus at room temperature (25 ± 2 °C) for 24 hours. The pH of the suspension was monitored frequently and adjusted as needed over the 24-hour period. Concentrations of Hg in leachates from the two unstabilized wastes were compared with those from the different stabilized wastes.

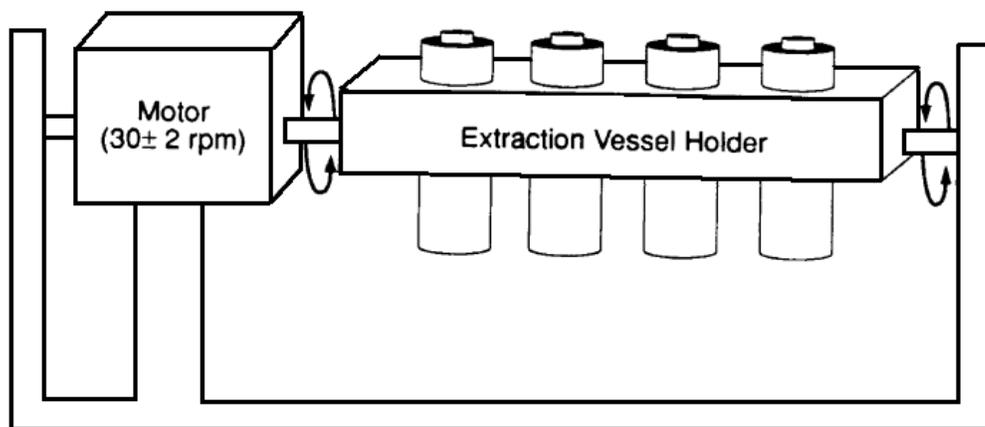


Figure 4. Rotary agitation apparatus

After 24 hours, the tumbling was stopped for all samples and blanks, at which time both pH and oxidation-reduction potential (ORP) readings were taken for all samples before filtration using a Corning pH/ion meter (Model 450). pH is a measure of the degree of acidity or alkalinity of a

matrix. U.S. EPA SW-846 Method 9045 was followed for measuring and reporting pH. The ORP was measured as per ASTM D1498 and Standard Methods for the Examination of Water and Wastewater Part 2580. The ORP values were converted and reported as Eh.

The suspension of the test samples was filtered through 0.7- μm (nominal) binder-free borosilicate glass fiber TCLP filters using a pressure filtration unit, pressurized with ultrahigh purity (UHP) nitrogen. The acid-treated, low-metal, binder-free borosilicate glass fibers (Whatman) are designed to meet ore size requirements for use in U.S. EPA SW-846 Method 1311 (TCLP). The filtrate was collected in a 500-mL polyethylene bottle, and then acidified with 0.1 N HNO_3 to obtain a pH less than 2, and finally stored at $4 \pm 2^\circ\text{C}$. Approximately 20 mL of the filtered, unpreserved sample was analyzed for turbidity using the HACH 2100N turbidimeter. The filtrate was analyzed for mercury concentration using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The leachable fraction, which is the amount of a particular heavy metal extracted relative to the amount in the untreated waste material, was derived from the leaching test results.

2.2.2.2 TCLP Procedure

TCLP (U.S. EPA SW-846, Method 1311) was performed on both the stabilized (solid) and unstabilized wastes. The determination of appropriate extraction fluid was conducted as per Section 7.1.4 of Method 1311. The TCLP extraction fluid #1 (Section 5.7.1 of Method 1311) was prepared by adding 5.07 mL of glacial acetic acid (CH_3COOH) to 500 mL of deionized water. Thereafter, 64.5 mL of 1 N NaOH was added to the acetic acid solution before making up a volume of 1 L. The pH of this leachant was 4.93 ± 0.05 . The polyethylene bottles, filter holders, and filters were all used as described in the UC method. Twenty-five grams of each dry solid sample (manually crushed to <9.5 mm) was weighed and transferred into 1-L polypropylene bottles. Five hundred milliliters of the TCLP leachant was added to each of the bottles. The pH was recorded to the nearest 0.1 pH unit and the initial value was recorded. Blank samples consisted of 500 mL of the TCLP leachant without solid. Duplicate TCLP tests were conducted for all stabilized and unstabilized samples. The TCLP bottles were tumbled at 30 ± 2 rpm in a rotary agitation apparatus (see Figure 4) at room temperature ($25 \pm 2^\circ\text{C}$) for 18 hours (Li et al., 2001). After 18 hours, the tumbling was stopped for all samples and blanks,

at which time both pH and oxidation-reduction potential (ORP) readings were taken for all samples before filtration. At the end of the extraction, the leachate was filtered, analyzed for turbidity, preserved, and analyzed for mercury concentration, following the methods described in Section 2.2.2.1.

2.2.2.3 TCLP “Cage” Modification Procedure

The third and final leaching test was performed using only solid stabilized wastes, which were not grounded, containing either elemental Hg or HgCl₂ at both the 50 and 70 wt% loadings. The standard TCLP (U.S. EPS SW-846, Method 1311) requires that all samples be passed through a 9.5-mm screen before leaching. However, this requirement may not be appropriate for S/S-treated wastes that have been solidified (per 53 Federal Register [FR] 18792) to withstand both chemical and physical environmental stresses encountered after disposal (Means et al., 1995). Studies in 1988 (53 Federal Register [FR] 18792) modified the standard TCLP so that the S/S-treated waste can be tumbled in a cage suitable to maintain the well-stabilized wastes more or less intact, while the poorly stabilized wastes significantly degrade. This protocol requires no preliminary size reduction of samples (Means et al., 1995).

Cylindrical solidified matrix (monolithic materials), obtained from cured plastic mold containing stabilized samples, was cut to specimens with height/diameter ratio of 0.5. These specimens were suspended in a TCLP solution, which was prepared as previously described in this section. The samples each were placed in 1-L polyethylene bottles with 500 mL of TCLP solution. Cotton thread was acid-washed to remove any contaminants, and then washed thoroughly with deionized distilled water. This thread was used to crosstie the cylindrical specimen (create a cage) and keep the sample suspended in the polyethylene bottle. A blank containing only 500 mL of TCLP solution also was prepared. Each bottle was then placed on a tumbler (Figure 4). Rapid and continuous tumbling (30 ± 2 rpm) was maintained throughout the experiment at room temperature (25 ± 2 °C). The dimensions of the solid material were recorded at 0.5, 3, 6, 24, 48, and 72 hours after starting the experiments, resulting in six leachates with leaching intervals of 0.5, 2.5, 3, 18, 24, and 24 hours. The leachant was refreshed with an equal volume of TCLP solution using a liquid to surface area ratio of 10 ± 0.2 mL/cm². The blank sample remained on the tumbler throughout the experiment. After 72 hours, the tumbling was stopped for all samples, including

the blank. Both pH and ORP readings were taken for all samples before filtration. At the end of the extraction, all samples were analyzed for turbidity and preserved following the methods described in Section 2.2.2.1. The mercury content in the filtrate was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin Elmer Elan 6000 spectrometer (U.S. EPA Method 200.8: EPA/600/4-79/020). The mercury present in the solid samples was analyzed by cold vapor atomic absorption (CVAA) using a Perkin Elmer 5100 AA spectrometer (U.S. EPA SW-846 Methods 7470A and 7471A) attached with Flow Injection Automated System, in which the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passed through a quartz cell positioned in the light path of an atomic absorption spectrophotometer. The detection limit for this method is 0.2 µg/L.

All experimental treatments in this study were conducted using MilliQ water. All experiments used acid-washed (50% HNO₃) HDPE plastic bottles, unless mentioned otherwise. The mercury standard was purchased from Fisher. All other chemicals were of analytical quality and obtained from Alfa Aesar.

The calibration curve was established for leachate samples using mercury standards of 2.5, 5.0, 10.0, 25.0, 50.0, 100.0, and 250.0 µg/L, with a correlation coefficient of 0.9998. Initial and continuing calibration standards and the laboratory control samples were within the laboratory control limit of 85 to 115%. After every 10 samples, and after the final sample, a continuing calibration verification standard was analyzed. Results for the laboratory duplicates and spike were within the stated QAPP control limits of ±20% (duplicate) and 75 to 125% (spike recovery).

3.0 Results and Discussion

3.1 Characterization of Waste Samples

The physical and chemical characterization of the waste samples was conducted by measuring the bulk density and the surface areas of the samples, along with conducting optical light microscopy, electron microscopy, and x-ray diffractometry measurements. Physical characterization involved inspection of the samples to determine its physical form, and chemical waste characterization involved determination of the chemical components and properties of the waste.

Bulk densities and surface areas of the CBPC waste samples, as measured, are presented in Table 4.

Table 4. Bulk density and surface area of Hg-contaminated samples

Sample Description	Bulk Density (g/cm ³)	Surface Area (m ² /g) ^(a)
Unstabilized sample containing elemental Hg	—	6.2 ± 0.14
Unstabilized sample containing HgCl ₂	—	6.35 ± 0.21
Stabilized sample containing elemental Hg at 50 wt% loading	2.197	1.85 ± 0.21
Stabilized sample containing elemental HgCl ₂ at 50 wt% loading	2.198	1.9 ± 0.14
Stabilized sample containing elemental Hg at 70 wt% loading	2.271	4.4 ± 0.14
Stabilized sample containing elemental HgCl ₂ at 70 wt% loading	1.978	7.0 ± 0.14

(a) Mean and standard deviation values are indicated.

Bulk densities of the unstabilized samples were not measured. Data obtained showed that bulk densities of the stabilized samples were similar.

3.1.1 Optical Light Microscopy

Optical micrographs (at 100X magnification) of stabilized waste material containing HgCl_2 at 50 wt% and 70 wt% loadings are shown in Figure 5. The micrographs show heterogeneity of the samples with respect to both particle sizes and type (as seen from the difference in the shading). This heterogeneity is applicable to most stabilization processes, and not just the CBPC process, because wastes are composed of discrete particles and aggregates of particles with differing sizes, densities, and strengths.

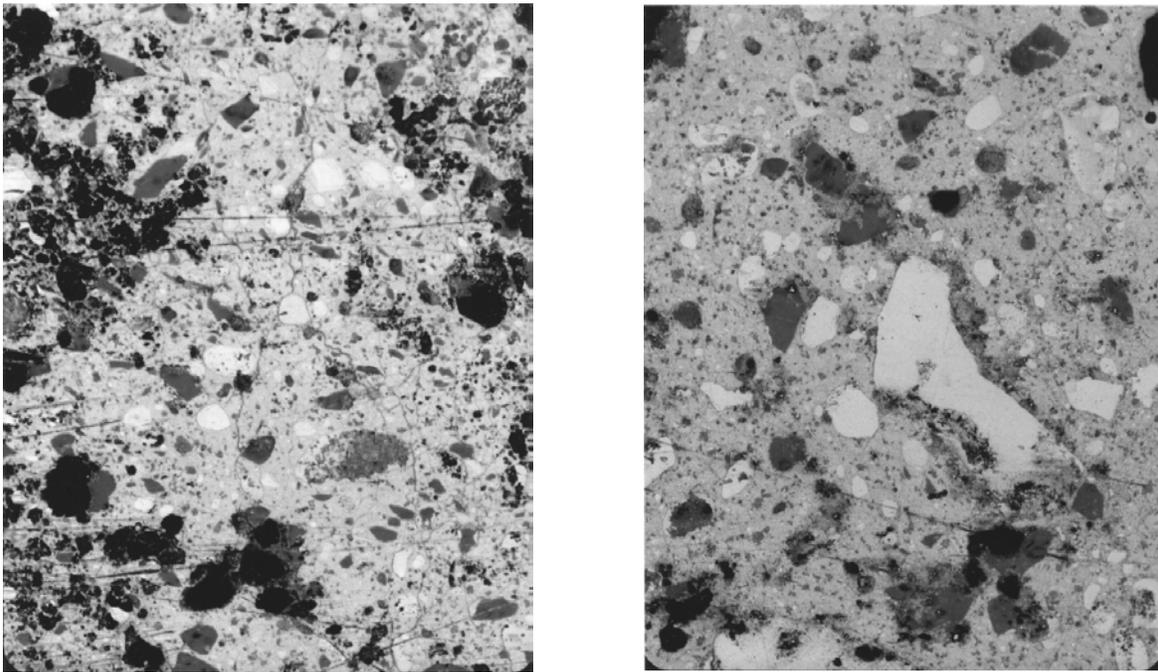


Figure 5. Optical micrographs at 100X of stabilized waste material containing HgCl_2 at 50 wt% (right) and 70 wt% (left) loadings.

3.1.2 X-Ray Diffractometry

Diffractograms of both unstabilized and stabilized (70 wt%) waste samples containing HgCl_2 are shown in Figures 6 and 7, respectively. Peaks in the diffractograms were identified by comparing the data obtained with organic and inorganic databases from the International Centre for Diffraction Data (ICDD) Powder Diffraction Database, and Materials Data, Inc. (MDI) Jade software for pattern treatment and search-match. Both unstabilized and stabilized samples showed strong

peaks of hematite. Stabilized samples showed the presence of cinnabar (HgS), MKP, sylvite, and periclase (Figures 7 and 8).

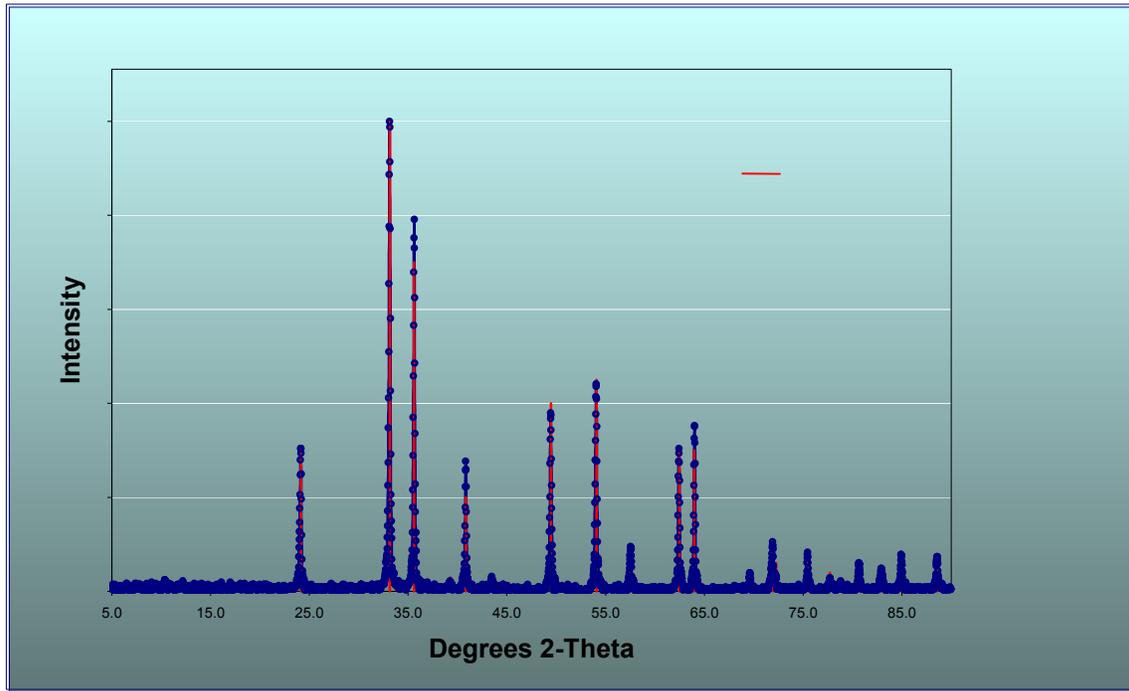


Figure 6. X-ray diffractogram of powdered unstabilized waste containing 70 wt% HgCl_2

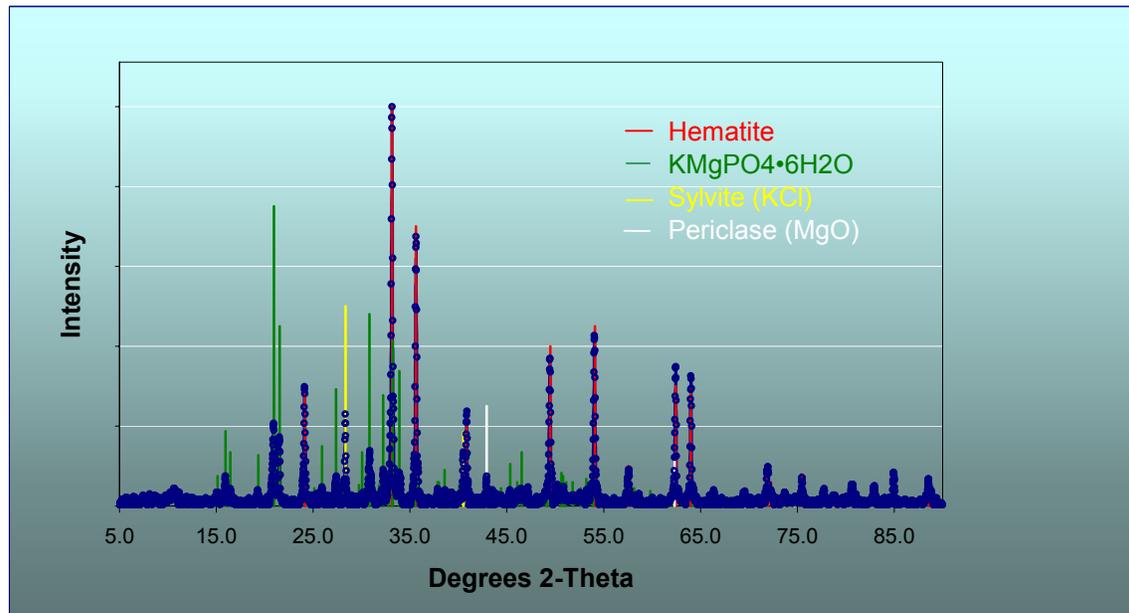


Figure 7. X-ray diffractogram of stabilized solid waste containing 70 wt% HgCl_2 – overall view

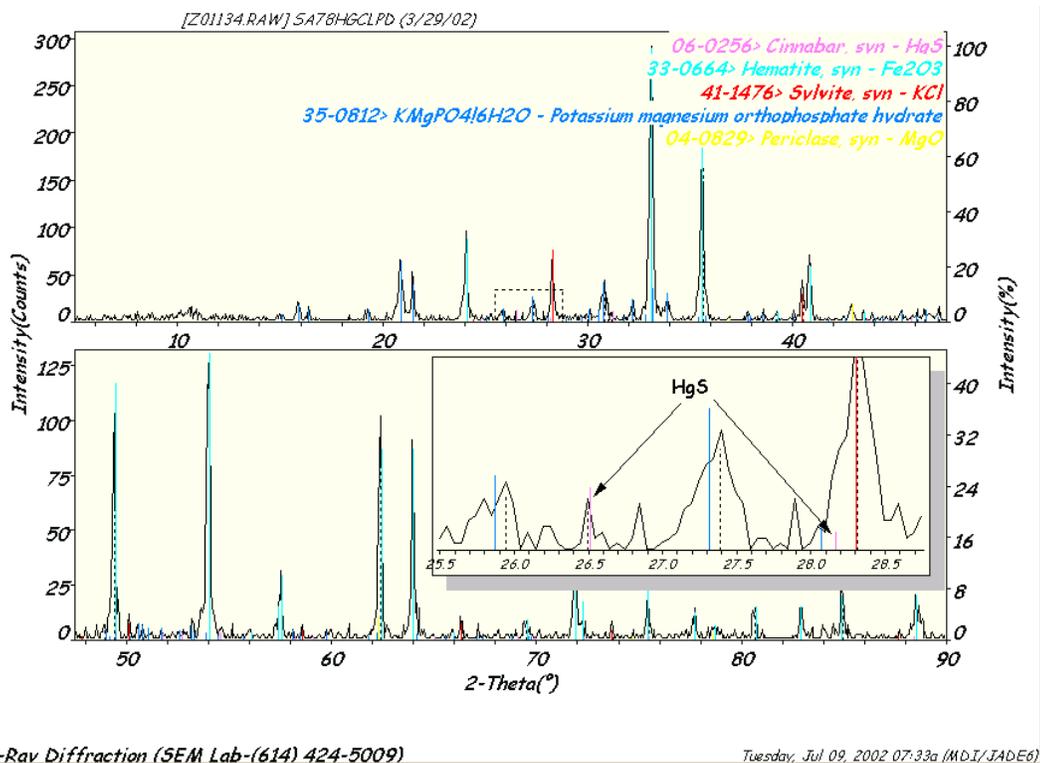


Figure 8. X-ray diffractogram of stabilized waste containing 70 wt% HgCl_2 – detailed view

In particular, Figure 8 shows the presence of peaks due to cinnabar at 26.5° and 28.2° 2θ . These data suggest that stabilization of wastes have led to the formation of cinnabar. Similar features were also observed for the samples containing Hg.

3.1.3 SEM-EDS

The ground and unprocessed solid samples also were analyzed with SEM and EDS to confirm and characterize the presence of inorganic Hg phases in the sediments. Scanning electron micrographs of cured and stabilized wastes containing HgCl_2 were obtained at 2500X magnification and shown in Figure 9. The presence of small crystals can be seen in the micrograph. Singh et al. (2000) also identified dense, crystalline structures with a small amount of pores. Pores allow water to penetrate the waste form and leach to the environment.

The areas on the solid samples selected for EDS analysis are shown in Figure 10a. These two areas are selected due to their marked difference in appearance. Figures 10b and 10c show the peak intensities for each element detected for areas (a) and (b).

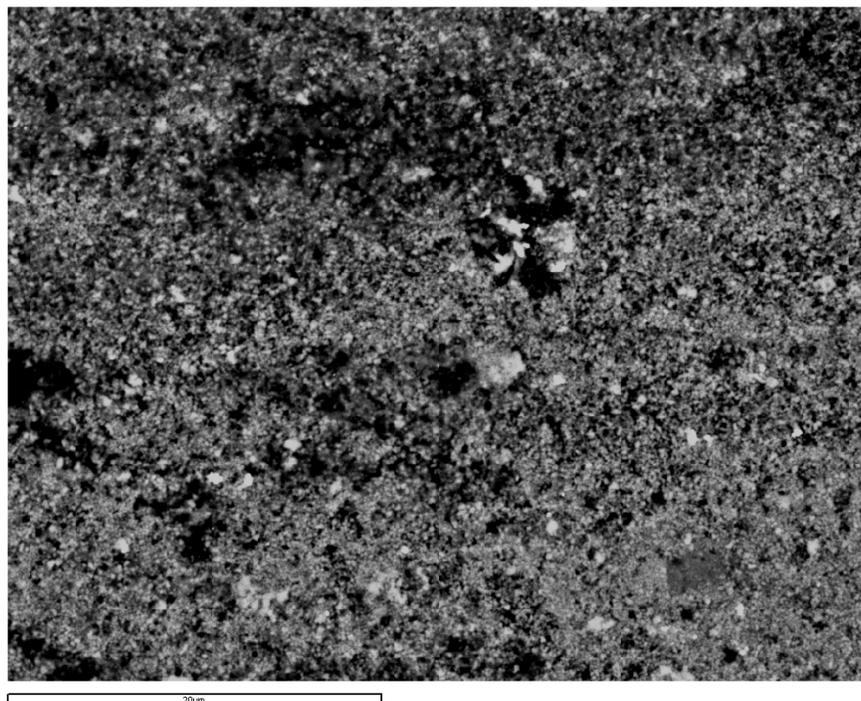


Figure 9. Scanning electron micrographs of mounted sample of stabilized and cured waste containing 70 wt% HgCl_2 (magnification 2500X)

Quantification of the peak intensities are shown in Figure 10d, where all elements detected are expressed as weight percents. As expected the most prevalent elements are Fe and O, as the waste samples were prepared with considerable amounts of Fe_2O_3 . The most important difference between the two selected areas is that mercury is present only in area (a), but not in area (b). The presence of Hg and S in equivalent amounts are shown in Figures 10b; therefore, it can be inferred that HgS has formed. Among the different elements found in area (a), seven elements were selected for detailed analysis, as shown in Figure 11. Line scans for Hg, S, K, P, O, Mg, and Cl were obtained and shown in Figures 11b and 11c. Similar features also were observed for the waste containing Hg. Figure 11 shows a typical distribution of elements in a particular area. Particles with mercury sulfide (HgS) phase were identified using SEM-EDS, EDS line scans of the selected elements, and WDS image maps (Figure 12). However, the two

most common HgS polymorphs, cinnabar and metacinnabar, cannot be distinguished using EDS. The EDS and WDS images on Figures 11 and 12 show that mercury is adsorbed on the surface on particular sites where high sulfur concentrations exist. Karatza et al. (2000) also reported similar observations in their SEM results.

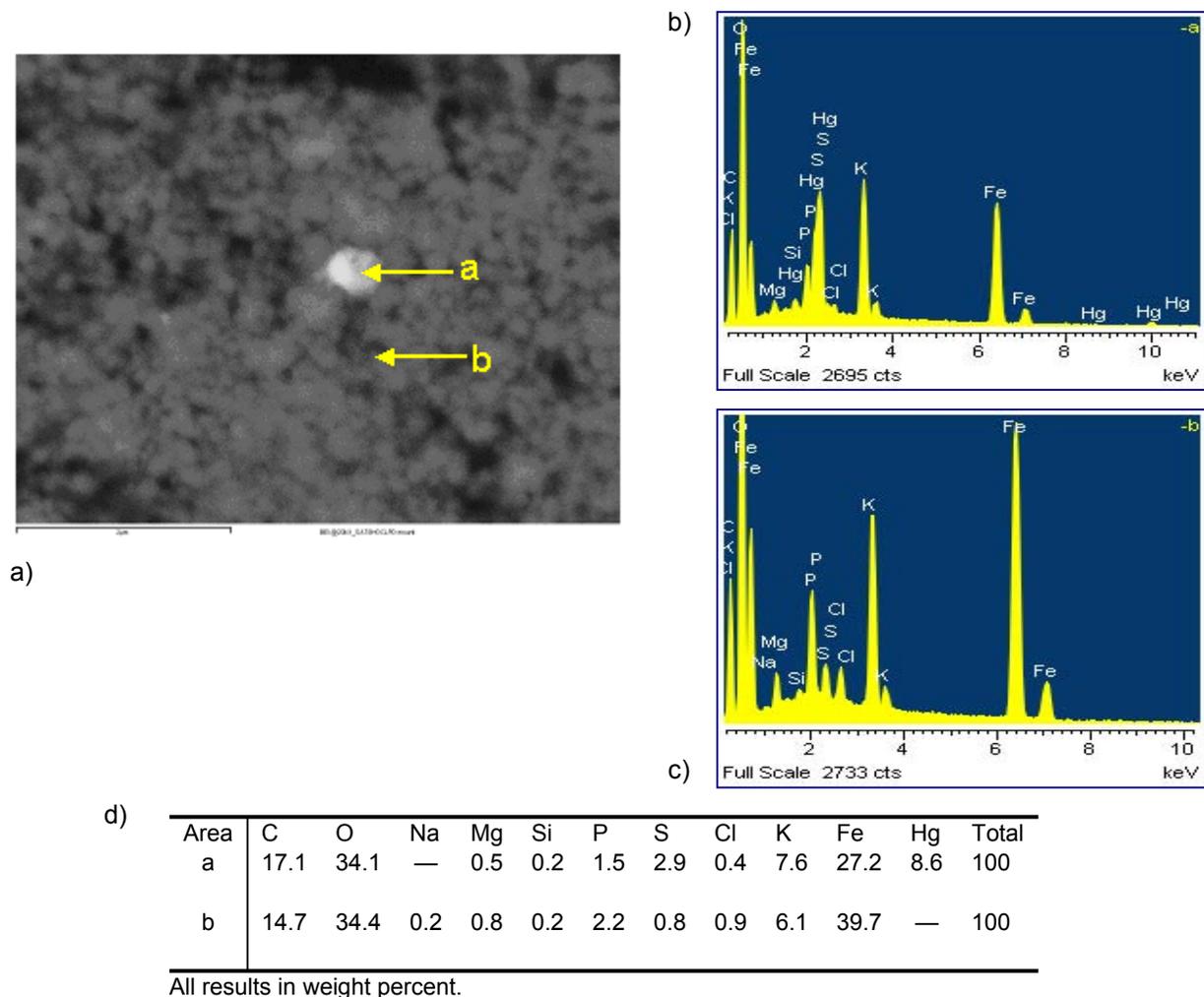


Figure 10. EDS a) image, b) and c) spectral patterns, and d) spot chemical analysis of cured, stabilized sample containing 50 wt% loading HgCl₂

Huggins et al. (1999) used X-ray Absorption Fine Spectra (XAFS) spectroscopy to examine mercury sorption on activated carbon, and determined that sulfur (S), the activating element, formed a sorption complex with mercury on the surface of the sulfur-activated carbon.

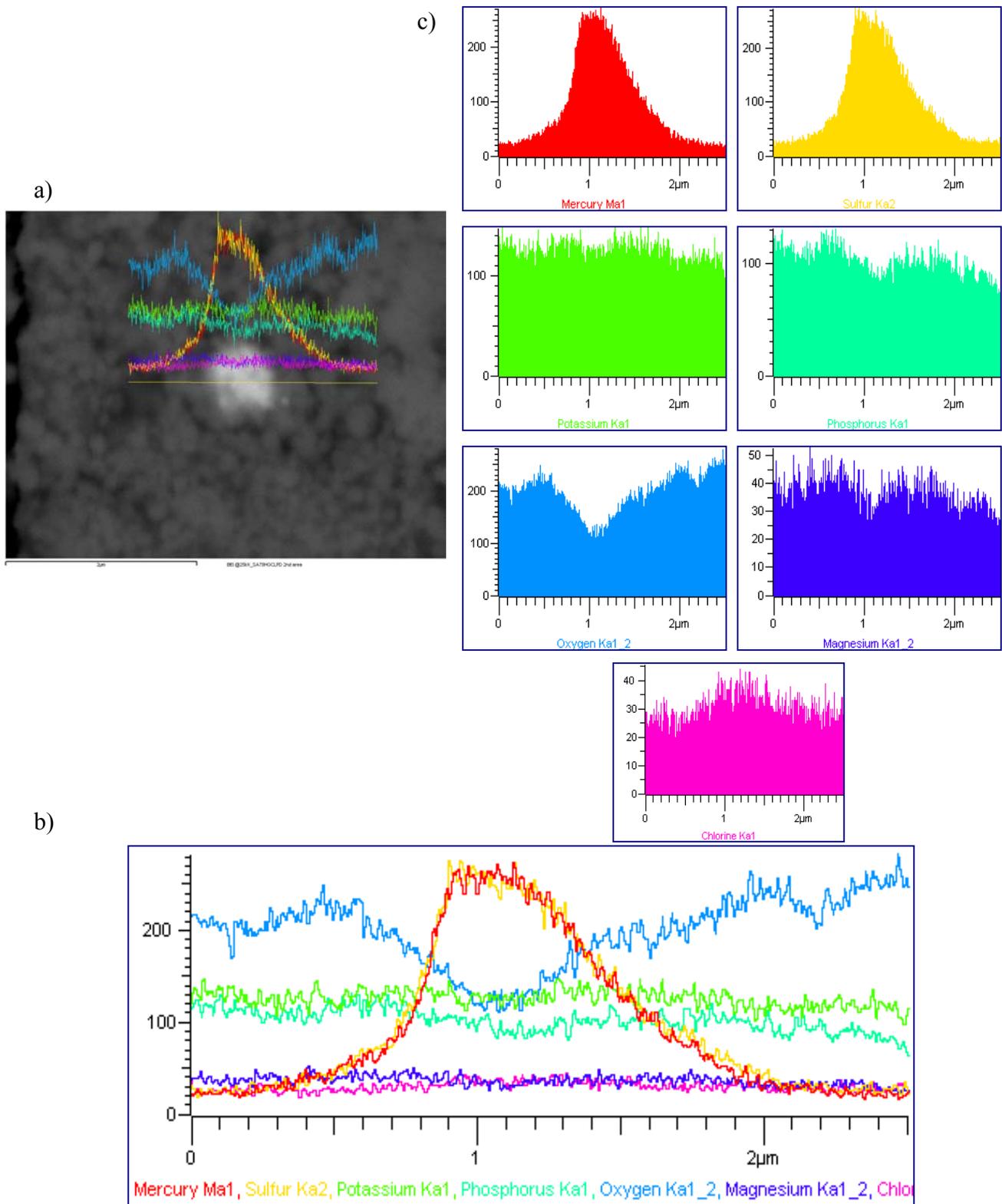


Figure 11. Energy-dispersive spectrophotometer a) image and superimposed line scans, b) elemental line scans, and c) elemental distributions for area A of Figure 10a

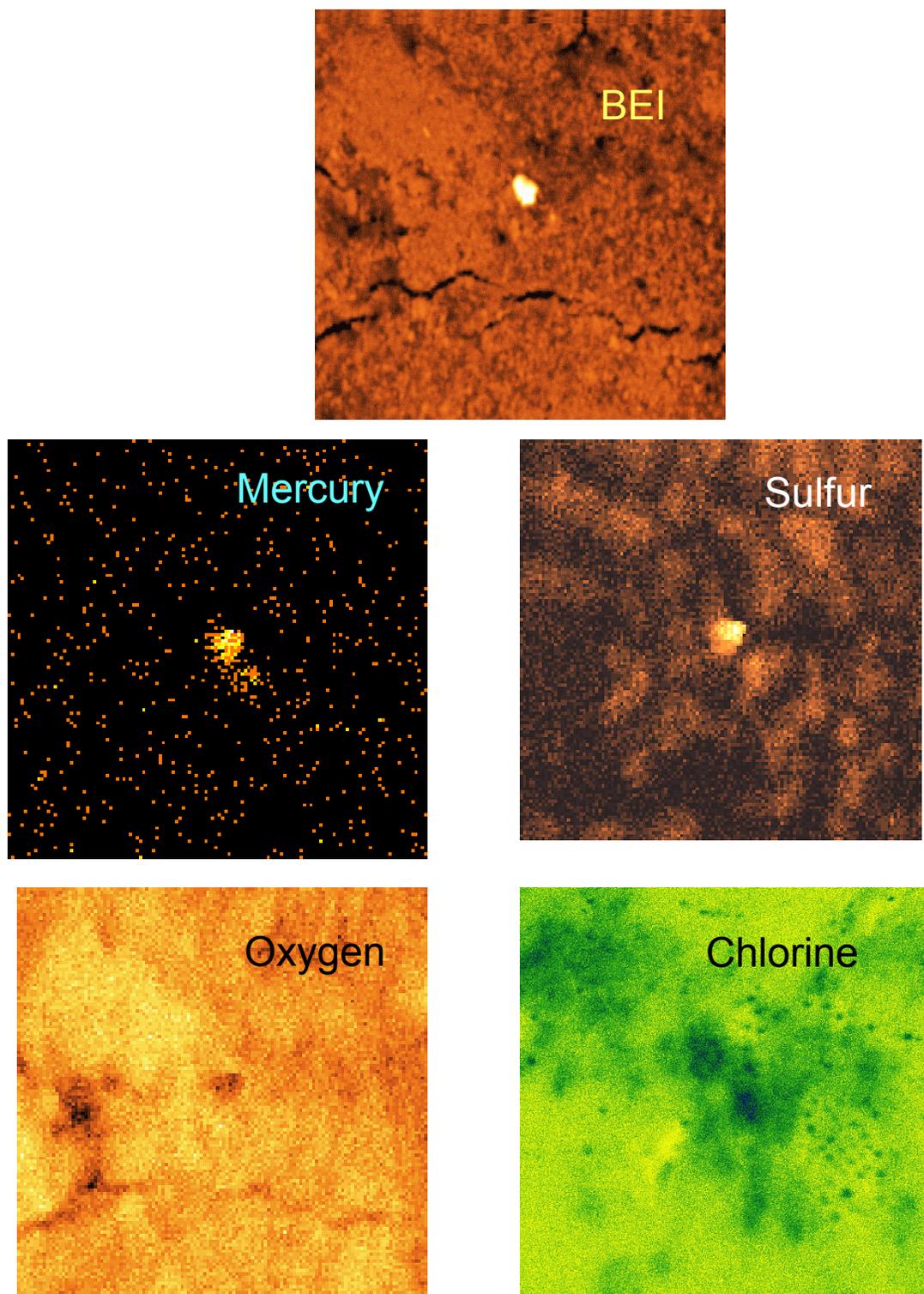


Figure 12. Wave-dispersive spectroscopy images maps at 3600X

3.2 Leaching Tests

Leaching tests measure the potential of a stabilized waste to release contaminants to the environment. The waste is exposed to a leachant and then the amount of contaminant in the leachate (or extract) is measured. Potential effects of the reduction in contaminant concentration per unit mass of waste due to binder addition was taken into consideration to evaluate the performance of S/S treatment by leaching tests.

The leaching behavior of all types of materials is related to several critical factors, including specific element solubility and availability or release potential. Solubility can be influenced by pH, complexation by involved species, and oxidizing/reducing properties. Several leaching methods to remove soluble components from a solid matrix are regulatory methods, mandated to characterize materials (promulgated and approved by a regulatory agency to generate specific information for submission in a legal context); others are approved by organizations (ASTM, ISO) for establishing compliance to particular specifications. Many leaching methods were developed for application to municipal solid waste or industrial wastes prior to disposal. Some are intended to simulate natural conditions, whereas the intent of others is to obtain information about the nature of the extractable material in a particular solid.

3.2.1 University of Cincinnati Constant pH Leaching Procedure

Leaching of mercury for different unstabilized and stabilized wastes were monitored as a function of pH. The pH values ranged between 2 and 12. Additionally, pH, Eh, and turbidity of the leachate were measured. Tables 5a, 5b, and 5c show the results obtained with wastes containing elemental Hg, while Tables 6a, 6b, and 6c show the results obtained with wastes containing HgCl₂.

Concentrations of Hg in the leachates showed a dramatic decrease as a result of stabilization of wastes. This is shown in Figures 13 and 14, as well as in Tables 5 and 6. The decrease in Hg leachability was of the extent of approximately two orders of magnitude. Maximum decrease in leachability was observed with 50 wt% loading, and there is an increase in leachability when the

Hg loading increased from 50 wt% to 70 wt%. The only exception was for the waste containing HgCl_2 at pH 2. This indicates that there is an upper limit to the ability of the CBPC technique.

In general, leachability was higher at low pH, indicating the adverse effect of acidic environment on the stabilization wastes. Also, comparing the amount of Hg in the leachate, it was observed that an increase in pH of the leachant led to a decrease in leachability, until it reached highly alkaline conditions ($\text{pH} > 10$). The decrease was marginally higher in the case of waste materials containing elemental Hg (Figure 13) than those containing HgCl_2 (Figure 14).

Measured values of pH of the leachates were similar to the respective targeted pH (Tables 5 and 6). The two most important factors controlling the solubility and mobility of an element are oxidation potential (Eh) and hydrogen ion activity (pH) (Thornber, 1992). The Eh of a solution is a measure of the oxidizing (lose electron) or reducing (gain electrons) tendency of the solution. Protons and electrons are transferred in most reactions. These reactions are represented with lines that have slope equal to the ratio of the number of protons transferred to the number of electrons transferred (Fairbridge, 1972). On comparing the Eh values as a function of final pH values, it was noted that the unstabilized wastes are more sensitive (steeper slope) to the changes in pH conditions than the Eh-pH curves for the stabilized wastes (Figure 15). This lower sensitivity to pH changes of the stabilized wastes compared to the unstabilized wastes indicates that there will be a lesser chance of Hg leaching out of the stabilized wastes and contaminating the water.

The turbidities of the filtered samples were generally less than 3 NTU, with the exception of the following cases: (1) stabilized wastes containing elemental Hg at 50 wt% loading at $\text{pH} = 10$; (2) stabilized wastes containing elemental Hg at 70 wt% loading at $\text{pH} = 12$; (3) unstabilized wastes containing HgCl_2 at $\text{pH} = 2, 4, 6$; (4) stabilized wastes containing HgCl_2 at 50 wt% loading at $\text{pH} = 10, 12$; and (5) stabilized wastes containing HgCl_2 at 70 wt% loading at $\text{pH} = 10$.

Table 5a. Leaching of mercury as a function of pH with unstabilized wastes containing elemental Hg

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Unstabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	263,470	5,269.40	2.2	0.76	2.14
pH = 2 Dup	224,080	4,481.60	2.1	0.76	2.90
pH = 4	15,389	307.78	4.1	0.43	0.44
pH = 6	1,035	20.70	5.9	0.36	1.04
pH = 6 Dup	24,991	499.82	6.2	0.61	0.44
pH = 8	7,670	153.40	8.2	0.60	0.29
pH = 10	15,808	316.16	9.8	0.37	2.20
pH = 10 Dup	17,724	354.48	10.2	0.40	0.61
pH = 12	35,352	707.04	11.9	0.37	1.38

Table 5b. Leaching of mercury as a function of pH with stabilized wastes containing elemental Hg at 50 wt% loading

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Stabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	3,348	66.96	2.3	0.47	1.03
pH = 2 Dup	3,462	69.24	2.4	0.48	0.97
pH = 4	618	12.35	3.9	0.46	0.20
pH = 6	11.8	0.24	6.4	0.41	0.26
pH = 6 Dup	12.7	0.25	6.0	0.41	0.32
pH = 8	3.5	0.07	8.2	0.39	0.13
pH = 10	14.7	0.29	10.1	0.29	11.60
pH = 10 Dup	7.2	0.14	10.3	0.29	14.00
pH = 12	8.6	0.17	11.7	0.24	4.39

Table 5c. Leaching of mercury as a function of pH with stabilized wastes containing elemental Hg at 70 wt% loading

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Stabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	5,947	118.94	2.5	0.45	0.31
pH = 2 Dup	6,439	128.78	2.4	0.47	0.26
pH = 4	1,162	23.24	3.8	0.44	0.08
pH = 6	1,558	31.15	6.2	0.43	0.10
pH = 6 Dup	2,118	42.37	6.2	0.40	0.09
pH = 8	759	15.18	8.3	0.36	0.14
pH = 10	1,431	28.61	9.9	0.30	1.01
pH = 10 Dup	1,289	25.77	10.0	0.31	1.61
pH = 12	1,355	27.09	11.8	0.28	24.70

Table 6a. Leaching of mercury as a function of pH with unstabilized wastes containing HgCl₂

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Unstabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	345,230	6,904.60	2.1	0.79	5.74
pH = 2 Dup	318,530	6,370.60	2.0	0.79	12.80
pH = 4	268,120	5,362.40	4.0	0.51	6.03
pH = 6	213,430	4,268.60	6.3	0.56	20.60
pH = 6 Dup	208,740	4,174.80	6.4	0.51	21.90
pH = 8	87,476	1,749.52	8.3	0.48	0.24
pH = 10	64,580	1,291.60	9.7	0.51	0.87
pH = 10 Dup	49,700	994.00	10.1	0.39	1.07
pH = 12	106,740	2,134.80	12.0	0.32	0.86

Table 6b. Leaching of mercury as a function of pH with stabilized wastes containing HgCl₂ at 50 wt% loading

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Stabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	2,789	55.78	2.3	0.52	0.25
pH = 2 Dup	3,090	61.80	2.3	0.51	0.51
pH = 4	877	17.54	3.8	0.41	0.10
pH = 6	68.1	1.36	6.2	0.35	0.11
pH = 6 Dup	66.2	1.32	6.3	0.33	0.16
pH = 8	95	1.90	8.4	0.29	0.21
pH = 10	167	3.33	9.8	0.28	3.75
pH = 10 Dup	196	3.91	9.7	0.30	4.08
pH = 12	7.2	0.14	11.7	0.22	52.80

Table 6c. Leaching of mercury as a function of pH with stabilized wastes containing HgCl₂ at 70 wt% loading

Sample Description (Targeted pH)	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Stabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
pH = 2	2,008	40.15	2.4	0.48	0.25
pH = 2 Dup	1,931	38.62	2.4	0.47	0.27
pH = 4	1,635	32.70	4.2	0.43	0.11
pH = 6	1,382	27.63	6.3	0.41	0.11
pH = 6 Dup	1,499	29.97	6.2	0.40	0.20
pH = 8	351	7.02	8.2	0.33	0.16
pH = 10	933	18.66	10.2	0.27	6.57
pH = 10 Dup	743	14.86	10.4	0.27	2.44
pH = 12	4,456	89.11	11.5	0.22	0.57

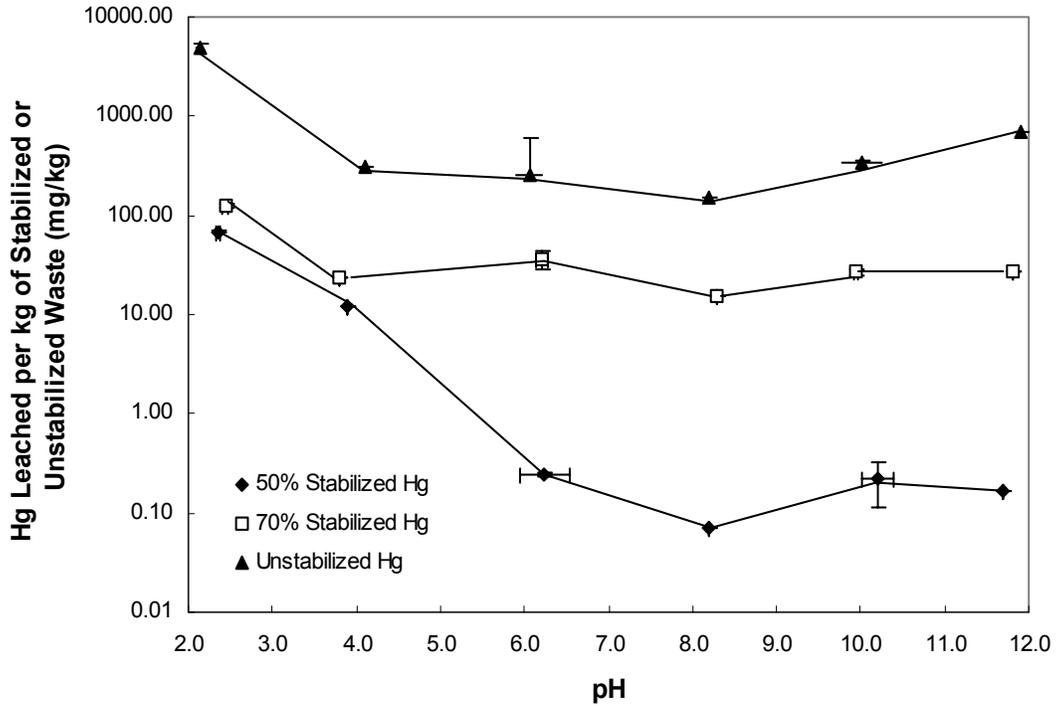


Figure 13. Hg leached per kg of stabilized or unstabilized waste containing elemental Hg at different pH conditions. Standard deviations are indicated by the error bars.

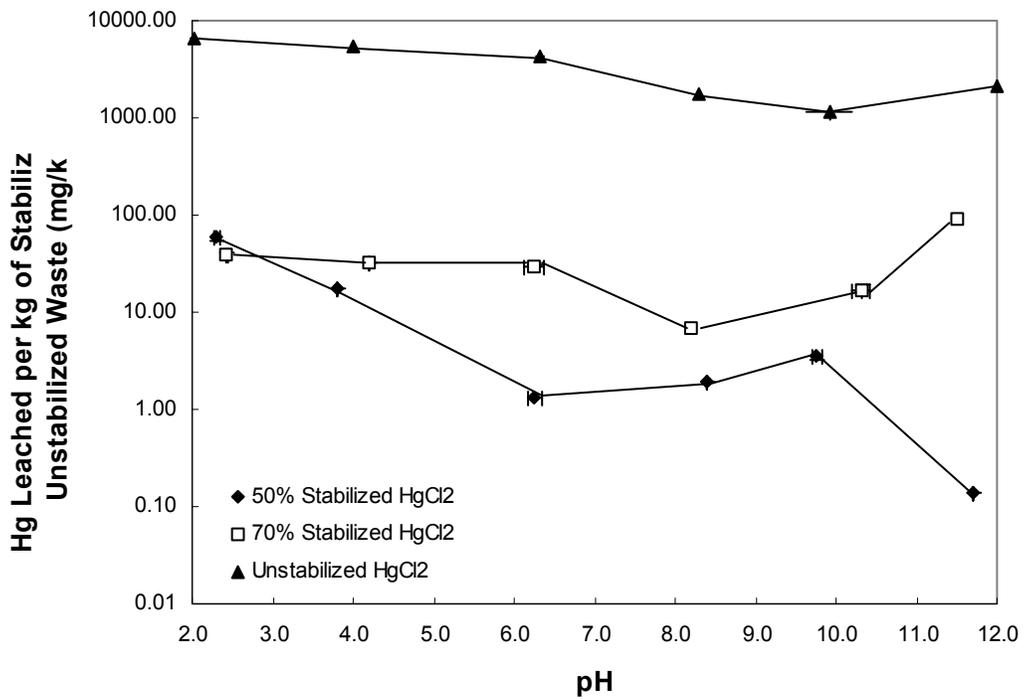


Figure 14. Hg leached per kg of stabilized or unstabilized waste containing HgCl₂ at different pH conditions. Standard deviations are indicated by the error bars.

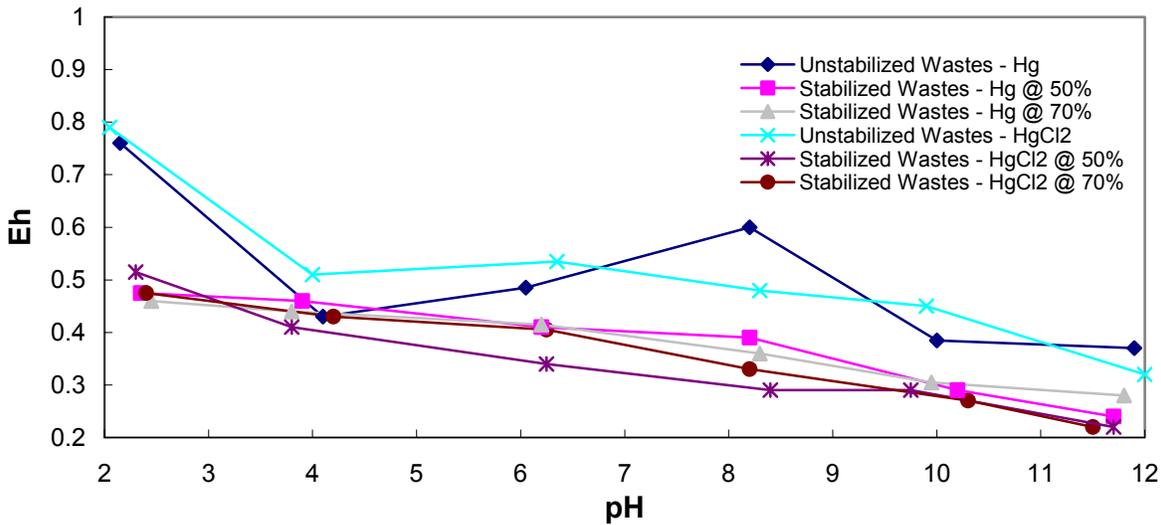


Figure 15. Eh-pH diagram of leachates obtained with the constant pH leaching tests

Zhang and Bishop (2002) used MITEQA2 to simulate the solubility of HgS, and reported that the solubility of HgS is sensitive to pH. The lowest solubility was reported over the pH range of 4 to 6. The solubility increases at both low and high pH conditions. Stumm (1992) reported dependence of dissolution rate of different metal compounds on pH. The dissolution rate is related to the surface charge imparted to the surface by H⁺ and/or OH⁻; the rate increases both with increasing positive surface charge with decreasing pH values of the solution, and with increasing negative surface charge with increasing pH values. The U-shape may not be prominent in all these waste samples due to the effect of hydration, which reflects the pH-independent portion of dissolution rate (Stumm, 1992).

3.2.2 TCLP Procedure

Leaching of mercury for different unstabilized and stabilized wastes were tested using the standard TCLP. Unlike that of the previous constant pH leaching tests, the pH of the leachant is not kept constant. The final pH, Eh, and turbidity of the leachate were measured along with the mercury concentrations in the leachate. Table 7a shows the results obtained with unstabilized wastes containing either elemental Hg or HgCl₂, and Table 7b shows the results obtained with stabilized wastes.

As seen in the case of UC Constant pH leaching procedure, Figures 16 and 17 show that the concentrations of Hg in the leachates decreased as a result of stabilization of wastes. This is also shown in Tables 7a and 7b. The decrease in Hg concentration in the leachate decreased by two orders of magnitude for stabilized wastes containing elemental Hg at 70 wt% loading, whereas in all the other cases decrease in leachability was of three orders of magnitude, with stabilized wastes containing elemental Hg at 50 wt% loading showing four orders of magnitude decrease. The Hg concentrations in the leachate of stabilized TCLP samples were very similar to the concentrations in the leachate from pH 8 stabilized samples from UC's constant pH procedure.

Measured values of pH of the leachates showed that leaching of unstabilized wastes slightly lowered the pH of the leachant, but there is some significant increase in the pH of the leachate from the stabilized wastes (final pH 7.4 to 8.1). It is also noted that the turbidities of the filtered leachate from the unstabilized wastes were considerably higher than that of the stabilized wastes. The turbidities of the filtered leachate from the stabilized waste were all less than 1 NTU.

High Hg wastes are required to be treated such that the treated wastes should meet a numerical treatment standard of 0.20 mg/L prior to land disposal, as measured by the TCLP (Morris et al., 2002). On comparing this limit to the results obtained from TCLP, it was seen that only wastes containing 50 wt% loading of elemental Hg met this requirement.

Table 7a. Leaching of Hg with unstabilized wastes containing either Hg or HgCl₂ (TCLP Method)

Sample Description	Concentration of Hg in Leachate ^(a) (µg/L)	Hg Leached per kg of Unstabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate ^(b) (NTU)
Hg unstable	223,290	4,465.80	4.2	0.48	3.09
Hg unstable Dup	176,960	3,539.20	4.2	0.48	13.80 ^(c)
HgCl ₂ unstable	224,840	4,496.80	4.0	0.48	13.70 ^(c)
HgCl ₂ unstable Dup	282,350	5,647.00	4.1	0.49	53.30

(a) Concentration of Hg measured after centrifugation of the turbid leachate (shown in column "Turbidity of Leachate") at 15,400 relative centrifugal force (rcf) for 30 min in Eppendorf microcentrifuge, model 5415C. The measured turbidities of the leachate, after centrifugation, were ≤0.1 NTU. Centrifugation of the leachate passed through 0.7-µm glass filter was conducted to avoid interference of Hg associated to colloidal particles.

(b) Turbidity of the leachate after passing through 0.7-µm glass filter only.

(c) Concentration of Hg was measured for two turbid samples only (one Hg unstable Dup and HgCl₂ unstable), and their concentrations were 276,820 µg/L and 283,650 µg/L, respectively.

Table 7b. Leaching of Hg with stabilized wastes containing either Hg or HgCl₂ (TCLP Method)

Sample Description	Concentration of Hg in Leachate (µg/L)	Hg Leached per kg of Stabilized Waste (mg/kg)	Final pH	Final Eh (V)	Turbidity of Leachate (NTU)
Hg stable 50 wt%	21.2	0.42	8.0	0.30	0.17
Hg stable 50 wt% Dup	6.6	0.13	8.1	0.35	0.11
Hg stable 70 wt%	2,107	42.14	7.4	0.41	0.16
Hg stable 70 wt% Dup	2,245 ^(a)	44.90	7.4	0.41	0.31 ^(b)
HgCl ₂ stable 50 wt%	105	2.11	8.1	0.37	0.16
HgCl ₂ stable 50 wt% Dup	101	2.01	8.1	0.38	0.16
HgCl ₂ stable 70 wt%	379	7.58	7.8	0.39	0.09
HgCl ₂ stable 70 wt% Dup	450	8.99	7.8	0.39	0.12

(a) After centrifugation at 15,400 relative centrifugal force (rcf) for 30 min.

(b) Concentration of Hg in the leachate after passing through 0.7-µm glass filter (without centrifugation) was not measured.

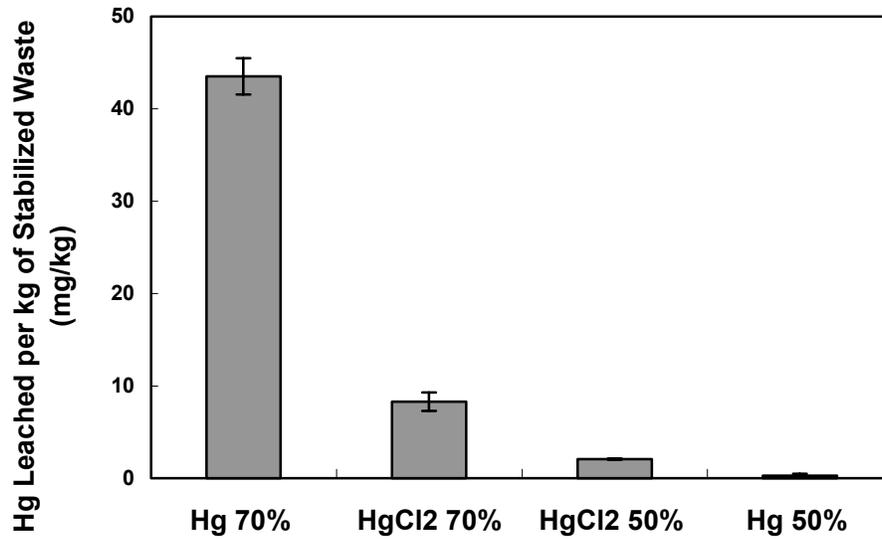


Figure 16. Mercury leached per kg of stabilized waste containing Hg and HgCl₂ by TCLP Method. Standard deviations are indicated by the error bars.

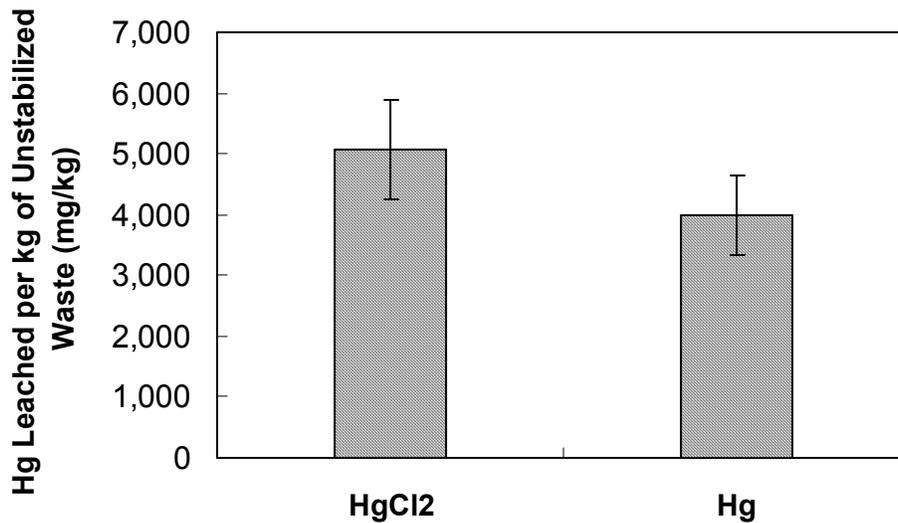


Figure 17. Mercury leached per kg of unstabilized waste containing Hg and HgCl₂ by TCLP Method. Standard deviations are indicated by the error bars.

3.2.3 TCLP “Cage” Modification Procedure

The standard TCLP requires that all samples be passed through a 9.5-mm screen before leaching. However, because this requirement may not be appropriate for S/S-treated wastes that have been solidified to withstand the environmental stresses encountered after disposal, an experiment was

designed to determine the leaching potential of unprocessed CBPC material. This protocol required no preliminary size reduction of samples (Means et al., 1995). These types of monolithic leaching methods are used to evaluate the release of elements from a material that normally exists as a massive solid. Because of the nature of this experiment, unstabilized material was not used for this method. The release of an element is a function of the exposed surface area as opposed to the mass. Flow-around systems relate solubility to the surface area of a particular volume, whereas the flow-through systems also consider the internal pore surface.

The leaching rate, (ℓ) (cm/day), of mercury from the monolithic materials was calculated as (Kim et al., 1992; Chan et al., 2000):

$$\ell = \frac{a_n V}{A_0 S t_n} \quad (7)$$

where V/S is the specimen volume/surface area ratio (cm), a_n is the amount of Hg leached during interval n (mg), A_0 is the amount of Hg initially present in the specimen (mg), and t_n is leaching time since the beginning of the first leaching interval (hour).

The cumulative fraction leached (CFL) relative to the total mass of the waste sample was calculated using the following relation:

$$CFL = \frac{\sum a_n V}{A_0 S} \quad (8)$$

The effective diffusion coefficient or effective diffusivity (D) is a measure of the diffusivity of the mercury in the monolith specimen of solidified waste for each leaching interval, and is

$$D = \pi \left[\frac{a_n / A_0}{\Delta t_n} \right]^2 \left(\frac{V}{S} \right)^2 T \quad (9)$$

where $\Delta t_n = t_n - t_{n-1}$, duration of the n leaching intervals, and T is the leaching time representing the cumulative time in the middle of the interval n (hour).

$$T = \left[\frac{1}{2} (\sqrt{t_n} + \sqrt{t_{n-1}}) \right]^2 \quad (10)$$

Leachability index, L (dimensionless), gives an indication of the effectiveness of the S/S technique for control of leaching, and can be calculated as

$$L_i = \frac{1}{n} \sum \left[\log \left(\frac{\beta}{D} \right) \right]_n \quad (11)$$

where β is a defined constant ($1.0 \text{ cm}^2/\text{s}$) (Chan et al., 2000).

The bulk densities of the cylindrical solidified materials and their leachability indices are tabulated in Table 8. Photographs of the monoliths, before and after they were tumbled in a cage during TCLP type extraction, are shown in Figures 18 and 19.

Table 8. Bulk densities, sizes, and leachability indices of waste materials

Sample Description	Bulk Density (g/cc)	Dimension of Solid (height cm × diameter cm)		L □
		Initial	Final	
50 wt% stabilized Hg	2.197	2.5 × 5.0	2.4 × 4.8	14.94
70 wt% stabilized Hg	2.271	2.5 × 5.0	2.2 × 2.5	11.13
50 wt% stabilized HgCl ₂	2.198	2.45 × 5.0	2.2 × 4.8	12.33
70 wt% stabilized HgCl ₂	1.978	2.5 × 5.0	2.1 × 2.9	10.52

The leachability indices for different loadings of stabilized waste materials were calculated by using Equation (11). A large value of L (>6) implies smaller values for contaminant diffusion (Morgan and Bostick, 1992) and a correspondingly lower contaminant release from the solidified matrix. The obtained leachability indices of 14.9, 11.1, 12.3, and 10.5 for 50 wt% Hg, 70 wt% Hg, 50 wt% HgCl₂, and 70 wt% HgCl₂, respectively, exceeded the guidance value of 6, which indicates that Hg is retained well within the solid matrices.

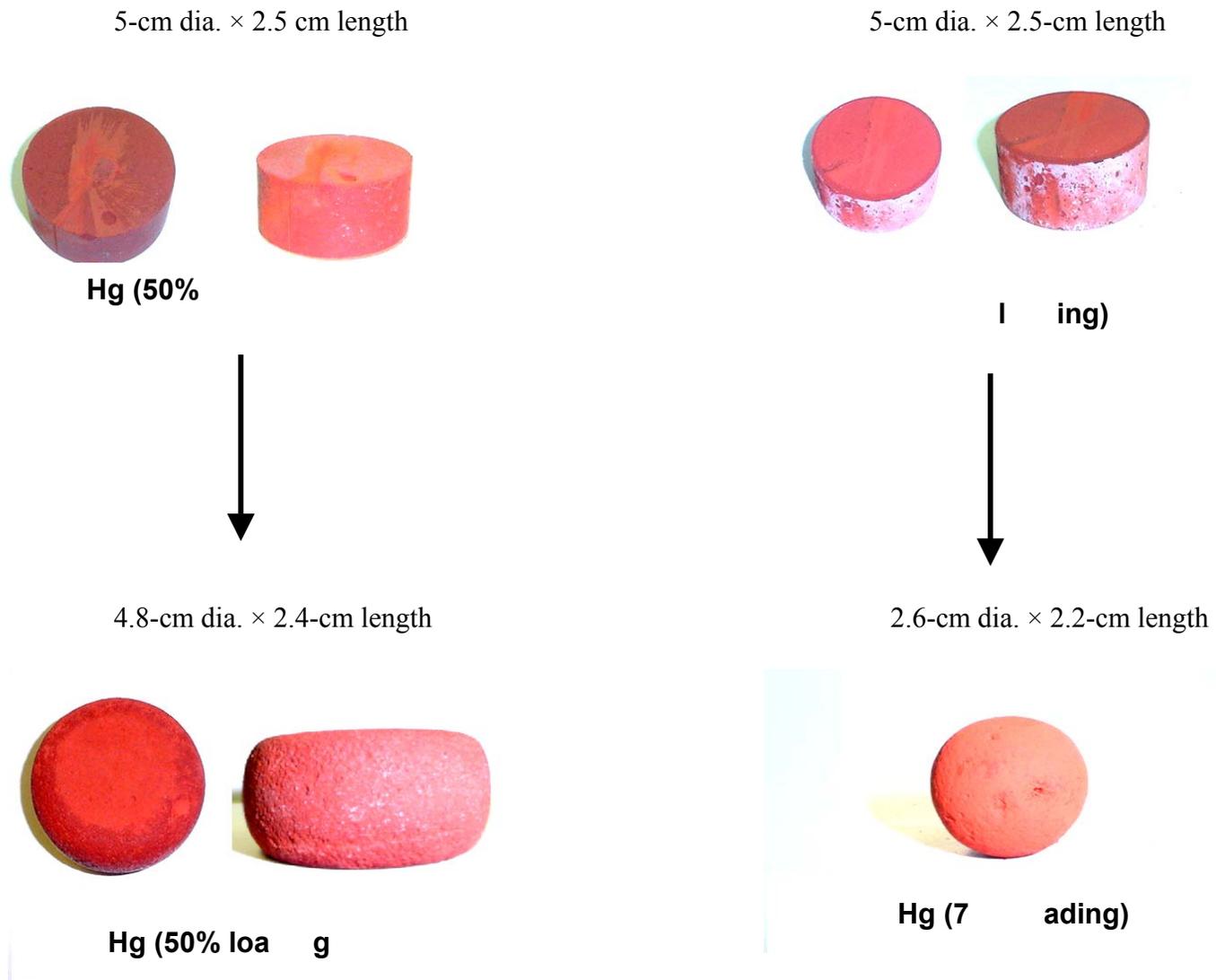


Figure 18. Photographs of TCLP “Cage” modification study with Hg-loaded samples

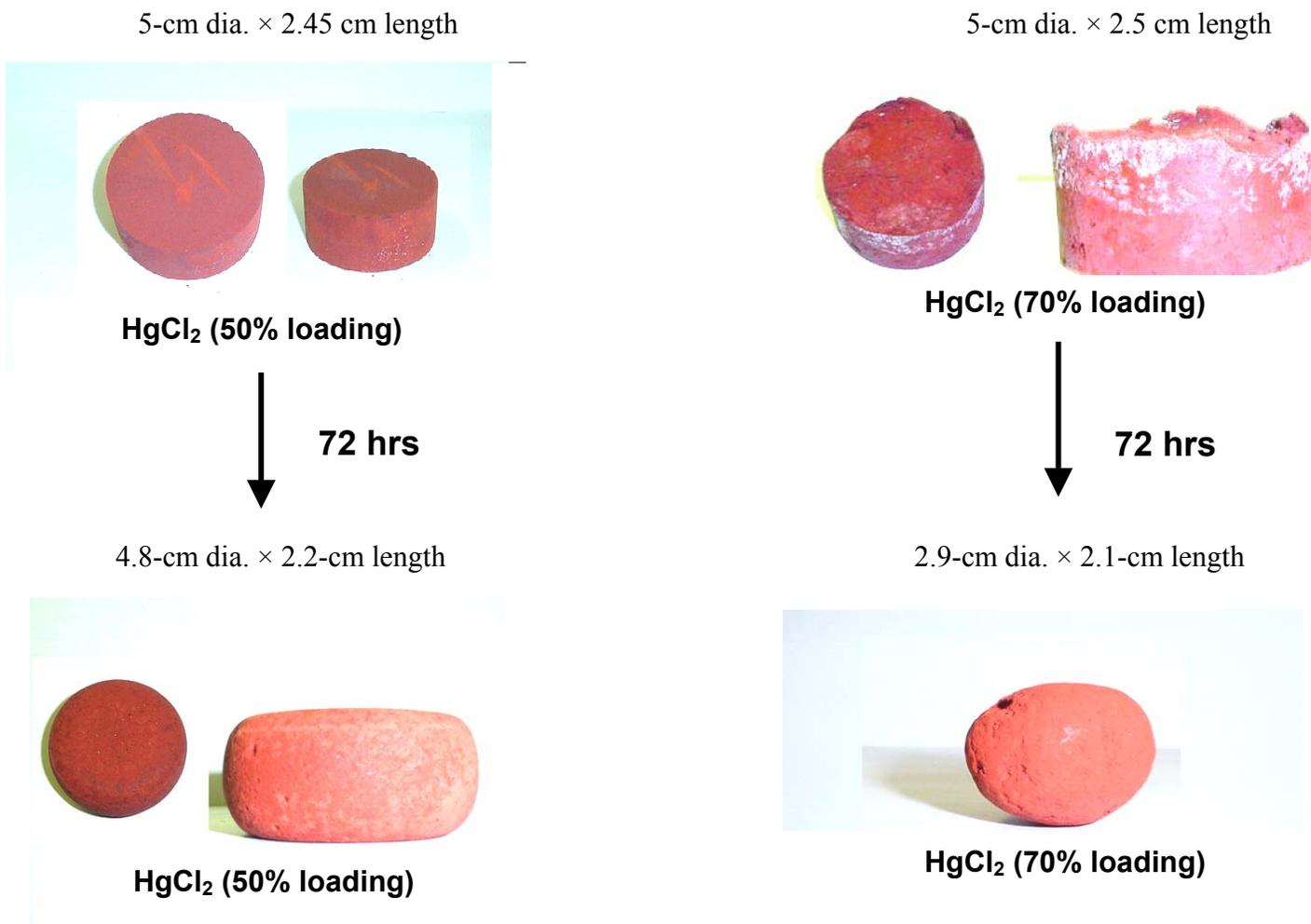


Figure 19. Photographs of TCLP “Cage” modification study with samples loaded with HgCl₂

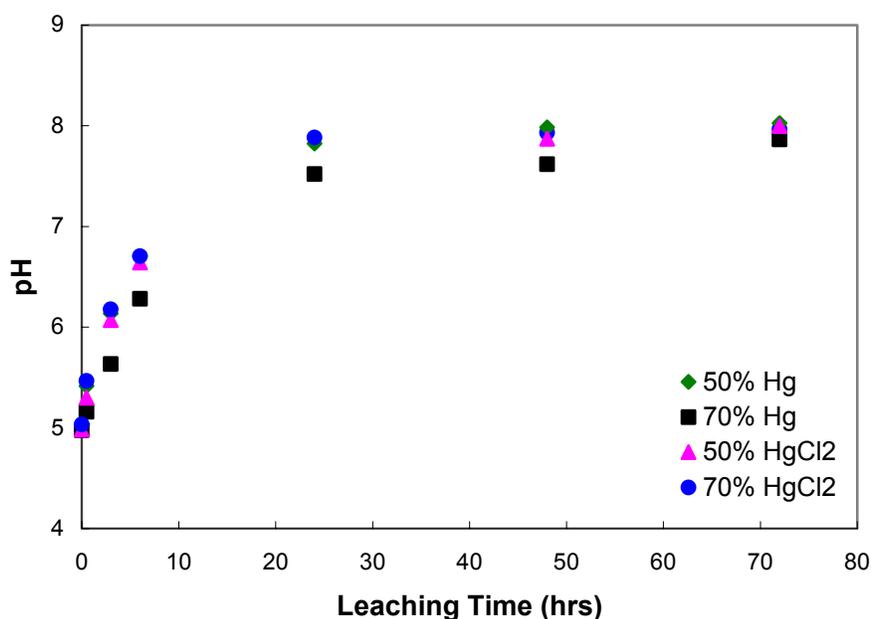


Figure 20. Change in pH with leaching time for stabilized wastes

The change in pH during the leaching time is shown in Figure 20. Within the first 24 hours, the solution pH increased starting from about 5.0, and stabilized at 8.0. The pH values reached a plateau after 24 hours of leaching.

The leaching rates of Hg from waste materials at different loadings decreased from a higher initial leaching rate, and a subsequent decrease in the rate (Figure 21). The 50 wt% waste loadings showed lower leaching rates than the 70 wt% waste loadings. During the first interval, the leaching rates were 4.7×10^{-7} cm/hour, and 1.3×10^{-4} cm/hour at 50 wt% and 70 wt% Hg loadings, and 1.2×10^{-4} cm/hour, and 4.4×10^{-4} cm/hour at 50 wt% and 70 wt% HgCl₂ loadings, respectively. The overall leaching rates of waste materials containing HgCl₂ were higher than that containing elemental Hg. Leaching rates for 70 wt% loadings for both Hg and HgCl₂ were higher than the 50 wt% loading. This is because over the course of the experiment (72 hours) 50 wt% Hg solid was least affected by dissolution and hence had the highest leachability index of 14.94 (Table 8). Therefore, based on the results from the TCLP “cage” modification procedure, 50 wt% Hg was the most stable of the four wastes.

The CFL was calculated according to Equation (8) and plotted against the square root of leaching time (Figure 22).

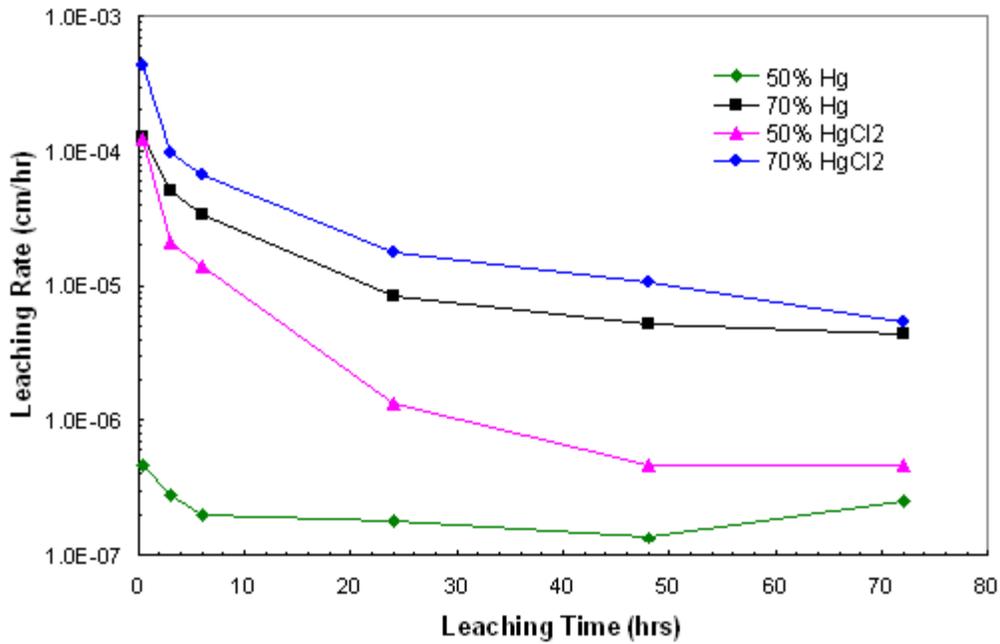


Figure 21. Leaching rate of Hg from stabilized matrix at different waste loadings

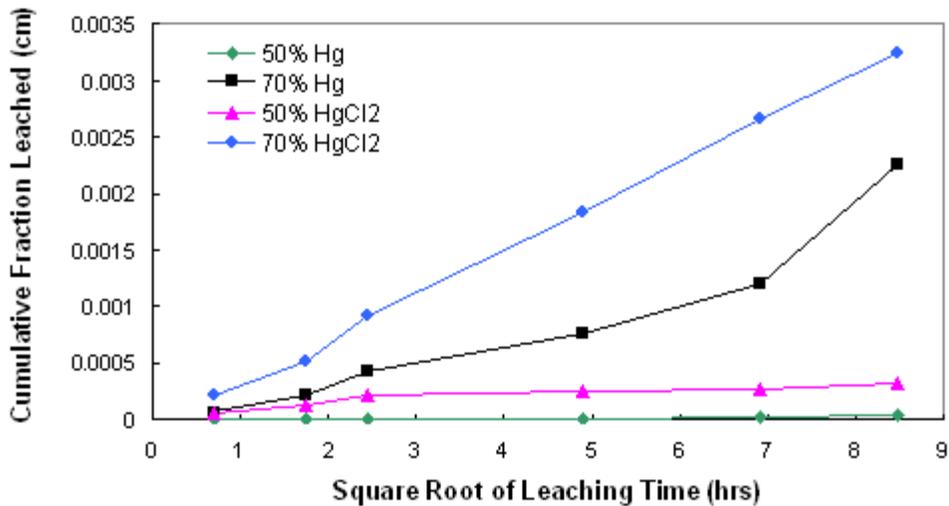


Figure 22. CFL from stabilized matrix at different waste loadings

A linear relationship between the CFL and square root of leaching time indicates that diffusion is the dominant transport mechanism. However, when the cumulative amounts of mercury leached at different time intervals were plotted in Figure 23, the results show that nearly all of the leach-

ing occurred during the first 5 hours. As the test samples shrunk significantly, it appears that the controlling process was surface dissolution of Hg from the stabilized matrix. The 50 wt% waste loadings also showed lower CFL than 70 wt% waste loadings. The overall CFLs for a three-day period for the different waste loadings are as follows: 3.2×10^{-5} cm for stabilized waste containing elemental Hg at 50 wt% loading, 2.3×10^{-3} cm for stabilized waste containing elemental Hg at 70 wt% loading, 3.2×10^{-4} cm for stabilized waste containing HgCl₂ at 50 wt% loading, and 3.2×10^{-3} cm for stabilized waste containing HgCl₂ at 70 wt% loading. Cumulative amounts of Hg leached during different time intervals are shown in Figure 23.

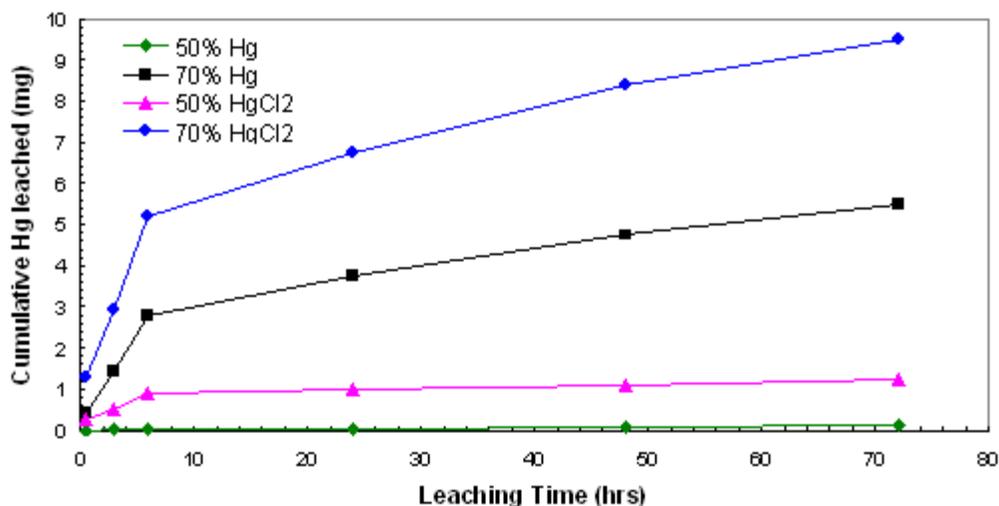


Figure 23. Cumulative amount of Hg leached during different time intervals

3.3 Comparison of Leaching Tests

This section compares the results of the three separate experimental methods (UC Constant Leaching procedure, TCLP, and TCLP “Cage” modification) performed on the mercury waste material. The total mercury content in the waste materials and mercury concentrations in the leachate from the unstabilized and stabilized waste materials are shown in Figure 24.

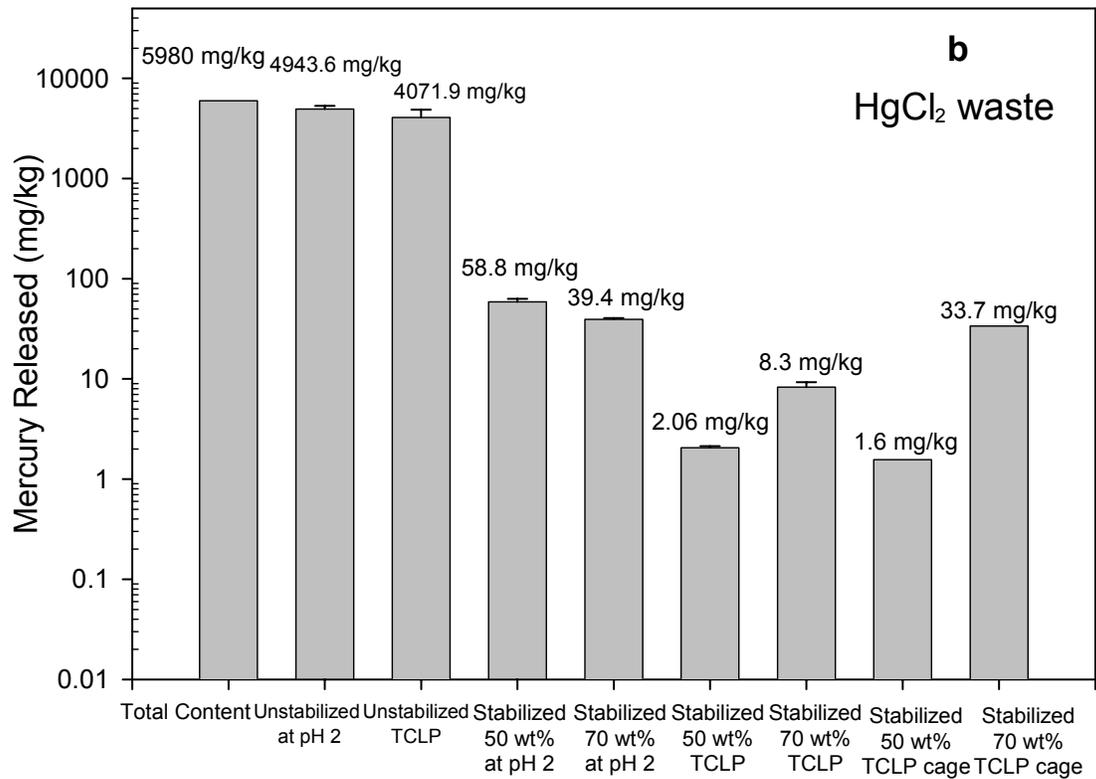
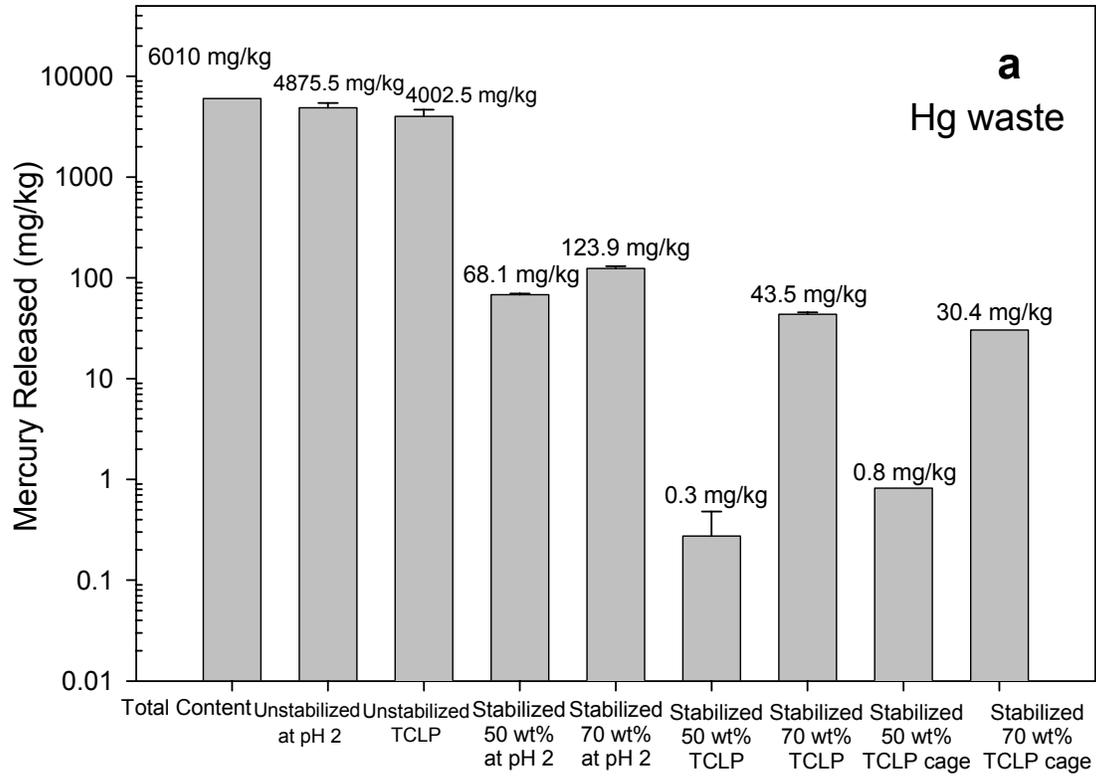


Figure 24. Mercury released in the leachate from a) Hg waste, and b) HgCl₂ waste

Results from the UC Constant Leaching Procedure are shown in Figure 24 for the pH 2 samples only. This pH released the highest amount of mercury into the leachate and therefore represents the worst case scenario. TCLP “Cage” results are shown for the cumulative amount of mercury released into solution over the 72-hr period. The total concentrations for the mercury samples were 6,010 mg/kg for Hg wastes and 5,980 mg/kg for HgCl₂ wastes. Although HgCl₂ samples released more total mercury, the percent released was approximately the same for HgCl₂ and Hg samples. The unstabilized material at pH 2 released approximately 80% of the mercury into the leachate. The amount released from the unstabilized material for the TCLP method was approximately 65% of the total mercury. The slightly lower release percentage for the TCLP method compared to the UC procedure is probably due to the more alkaline conditions of the TCLP method. Results for the UC procedure showed that leaching of mercury was lowest at pH 8, which corresponds to the approximate final pH of the TCLP samples (Section 3.2.1).

The percent of total mercury released dropped significantly for the stabilized waste material compared to unstabilized waste material. This is because the mercury within the stabilized wastes has become immobile (through the CBPC process), thereby reducing leaching. In addition, the three test methods produced similar amounts of leached mercury, with the TCLP releasing slightly lower amounts compared to the UC procedure. As previously mentioned above, the slightly lower release percentage for the TCLP method compared to the UC procedure is probably due to the more alkaline conditions of the TCLP method.

Both TCLP methods (standard and “cage”) produced similar results for all four waste types. In both methods the amounts of mercury released was lower for the 50 wt% samples than for the 70 wt% samples. This indicates a limitation of the process studied. It appears that the CBPC technique is suitable for decreasing the leachable Hg from a solid waste, but when there is very high amounts of Hg, it can not stabilize the Hg waste completely.

4.0 Cost Evaluation

One objective of this project was to provide an estimate for capital and operational costs and to summarize the key assumptions used in a preliminary economic analysis of the CBPC encapsulation process for mercury-contaminated Delphi DETOX™ wastes.

The U.S. DOE ANL has six patents covering the use of CBPCs for the encapsulation of hazardous wastes. This encapsulation method is also referred to as the Ceramicrete™ process. In collaboration with ANL and the U.S. EPA, Battelle evaluated the ability of the Ceramicrete™ process to stabilize and encapsulate a synthetic waste stream comparable to the secondary waste generated during the Delphi DETOX™ wet oxidation process. This synthetic waste stream consisted of 94.3 weight percent (wt%) hematite (Fe_2O_3), 5 wt% ferrous chloride (FeCl_2), and 0.67 wt% mercuric chloride (HgCl_2) on a dry weight basis. The synthetic waste stream first was stabilized with sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) to reduce the leachability of mercury and then encapsulated with the CBPC binder at two different waste loadings (50 wt% and 70 wt% as shown in Table 3).

As a brief summary of the process, first enough water is added to the waste in the disposal drum to reach a stoichiometric water content. Next, sodium sulfide is added to stabilize the mercury and then calcined magnesium oxide and monopotassium phosphate binders are blended in a one-to-one molar ratio and added to the mix. The water, binders, additional ingredients, and waste typically are mixed for about 30 minutes. After mixing is stopped, the waste form typically will set in about two hours, and cure in about three weeks. A volume expansion can be expected to occur after the slurry, containing waste materials, binder, and water, has been fully cured in the drum. The magnitude of the expansion was assumed to be 35% as stated in the U.S. DOE report (U.S. DOE, 1999a). It is assumed that only 65% of the usable space of the drum could be filled with the slurry. The full-scale system will consist of a planetary-type mixer, two hoppers for

chemical addition, a rolloff box for waste storage, and a pump to transfer the waste materials into a 55-gallon drum. After the stabilization agent and CBPC binders are thoroughly mixed into the waste in the 55-gallon drum, the waste form is cured, sealed, and shipped off-site for disposal. Off-site disposal costs are not estimated.

The following assumptions were made to complete this preliminary economic analysis, which is based on the purchased equipment costs, estimated material costs, and estimated labor input:

- Major purchased equipment will include a 55-gallon planetary type mixer, two 100-ft³ hoppers for chemical addition, one 20-yd³ closed-top, rolloff box for waste storage, and a sludge pump for waste transfer to the waste form drums.
- Direct and indirect capital costs are a fixed percentage of purchased equipment and installation costs, as summarized in Table 9. The costs of electrical wiring, instrumentation, controls, site preparation, professional labor, and other fees were estimated using the percentage ranges described in the U.S. Army Corps of Engineers Guidance Document *Engineering and Design - Precipitation/Coagulation/Flocculation* (2001). These percentage factors were taken to be representative of costs for the installation of small-scale, on-site treatment systems.

Table 9. Summary of capital costs for Ceramicrete™ process

	Unit Cost	Units	Total
Purchased Equipment and Installation (PE&I):			
Including 55-gallon planetary mixer, two hoppers, rolloff box, and waste transfer pump.	NA	NA	\$41,667
Direct Costs:			
Electrical, Instrumentation, and Controls	23%	(% of PE&I)	\$9,583
Piping and Other Materials	21%	(% of PE&I)	\$8,750
Site Preparation	7%	(% of PE&I)	\$2,917
			\$21,250
Indirect Costs:			
Engineering and Supervision	29%	(% of PE&I)	\$12,084
Construction Expenses	32%	(% of PE&I)	\$13,334
Contractor's Fees	7%	(% of PE&I)	\$2,917
Contingency	27%	(% of PE&I)	\$11,250
			\$39,584
Total Capital Cost			\$102,502

NA = not applicable.

Other assumptions are:

- Materials include 55-gallon United States Department of Transportation (U.S. DOT) 7A drums, sodium sulfide, and Ceramicrete™ binders.
- The processing rate is estimated at nine drums per day for a small-scale batch system (U.S. DOE, 1999a).
- This yields a treatment capacity of 512,206 kg or 565 tons per year of the Delphi DETOX™ wastes at a 50 wt% loading or 838,387 kg or 924 tons per year at a 70 wt% loading.
- Waste composition, waste loading, and waste form composition are as summarized in Table 3.
- Ceramicrete™ binder formulation is 1M:1M MgO to KH₂PO₄.
- Total usable space per drum is 7.35 ft³ (Peters and Timmerhaus, 1991).
- Volume expansion of 35% occurs after the waste form has cured.
- Work crew includes two technicians for operational labor of process equipment and one supervisor for management, health and safety, and other compliance work as needed.
- Labor rates are based on Level C worker protection.

Tables 9, 10, and 11 summarize the preliminary (e.g., order of magnitude) cost estimate for the Ceramicrete™ process. As summarized in Table 9, the capital costs are estimated at approximately \$102,000. As summarized in Table 10, at a 50 wt% loading, the treatment cost is estimated at \$4.62 per kg or \$4,191 per ton. As summarized in Table 11, at a 70 wt% loading, the treatment cost is estimated at \$2.49 per kg or \$2,254 per ton. Only the 50 wt% loading CBPC

waste form passed TCLP requirements. This represents a large increase in the overall volume of the treated wastes and would contribute to substantially higher disposal costs for this waste

Table 10. Operation and maintenance costs and total treatment cost at 50 wt% loading

Operation and Maintenance (O&M) Costs	Unit Cost	Units	Quantity	Total
Operating labor	\$48.22	per man-hour	17,520	\$844,783
Supervisory labor	\$2,489	per week	52	\$129,788
55-gallon drum (U.S. DOT 7A)	\$100.00	each	3,285	\$328,500
Sodium sulfide (Na ₂ S)	\$0.21	per lb	7,528	\$1,543
CBPC binders (MgO and KH ₂ PO ₄)	\$0.85	per lb	1,129,202	\$959,822
			Total O&M per year:	\$2,264,436
Total treatment cost (per unit weight of waste)			\$4.62	\$/kg
			\$4,191	\$/ton

Table 11. Operation and maintenance costs and total treatment cost at 70 wt% loading

Operation and Maintenance (O&M) Costs	Unit Cost	Units	Quantity	Total
Operating labor	\$48.22	per man-hour	17,520	\$844,783
Supervisory labor	\$2,489	per week	52	\$129,788
55-gallon drum (U.S. DOT 7A)	\$100.00	each	3,285	\$328,500
Sodium sulfide (Na ₂ S)	\$0.21	per lb	12,337	\$2,529
CBPC binders (MgO and KH ₂ PO ₄)	\$0.85	per lb	794,768	\$675,552
			Total O&M per year	\$1,868,256
Total treatment cost (per unit weight of waste)			\$2.49	\$/kg
			\$2,254	\$/ton

material. However, an estimate of the disposal costs is beyond the scope of this report and will vary widely depending on the final waste classification (e.g., low-level waste, RCRA hazardous, etc.) and the transportation costs to the specific disposal site.

Several treatment options are available for mercury-contaminated wastes. Thermal recovery may be considered, but it is generally unsuitable for radioactive wastes and/or those wastes with low mercury concentrations (e.g., <260 mg/kg). Acid leaching or soil washing can be used to recover mercury from low concentration wastes, but this approach results in a secondary wastewater stream that must be further treated. In general, the preferred treatment alternatives include some variation of encapsulation, stabilization, and/or amalgamation. CBPC is both a stabilization and encapsulation process. Other materials reported in the literature for the stabilization

and/or encapsulation of mercury-contaminated wastes include sulfur polymer cement, asphalt, polyester resins, synthetic elastomers, polysiloxane, sol-gels, Dolocrete™, and carbon/cement mixtures. Polyethylene also is employed for hazardous waste encapsulation. However, the high process temperatures involved increase the potential for volatile losses of mercury and therefore limit the effectiveness of this approach. Vitrification is another encapsulation technology, but it too is not suited for mercury-contaminated wastes due to elevated process temperatures. Examples of commercially available amalgamation technologies include the proprietary DeHg® amalgamation process and the Permafix® sulfide process.

Table 12 includes a summary of typical cost data, along with vendor information, for several competing treatment technologies for mercury-contaminated hazardous wastes. The CBPC cost data in Table 12 include both the cost estimate developed in this study (which does not account for disposal costs) and the cost estimate developed by U.S. DOE ANL investigators (which accounts for disposal costs). Most of the cost data presented is from extensive U.S. DOE studies for the treatment of mixed waste streams containing high levels of mercury (e.g., >260 mg/kg). The reader is referred to these documents for an in-depth review of the performance of these competing mercury treatment technologies (U.S. EPA, 1999a-d). The additional expense involved in dealing with mixed wastes is reflected in the relatively elevated cost estimates, which range from \$2.88/kg for sulfur polymer cement stabilization/solidification (SPSS) to \$16.37 per kg for conventional Portland cement stabilization (both including disposal). The CBPC process is generally on the high end of the treatment cost scale at \$15.45 per kg (including disposal). In general, cost comparisons are difficult to make based on literature values alone due to the variation in production scales, waste types, waste loading, waste chemical and physical properties, and the levels of contaminants in each study.

Table 12. Summary of cost and vendor information for encapsulation and other treatment technologies

Technology	Developer/Vendor	Estimated Full-Scale Costs	Reference
CBPC	Argonne National Laboratory, IL	\$2.49 to \$4.62 per kg (not including disposal) \$15.45 per kg (including disposal)	Section 4.0, Table 10 U.S. DOE (1999a)
SPSS	Brookhaven National Laboratory, NY	\$2.88 per kg	Morris et al. (2002)
Polyethylene (on-site pour)	Envirocare, UT	\$95 per ft ³	U.S. DOE (1998)
Arrow-Pak (HDPE)	Boh Environmental, New Orleans, LA	880 drums for \$1,100,000	Hanford (2002)
Ultra-Macroencapsulation System	Ultra-Tech, International, FL	\$480 to \$700 (30" dia, 40" height) \$20,000 (6' x 6' x 20')	Ultra-Tech (2002)
Polyester Resin	SGN Eurisys Services Co., Richland, WA	\$11.52 per kg	U.S. DOE (1999b)
Synthetic Elastomer	No vendor information available	\$0.03/kg of used tire rubber, 4 wt% in treated soil	Meng et al. (1998)
Polysiloxane	Orbit Technologies, Carlsbad, CA	\$1,900 per ft ³	U.S. DOE (1999c)
Sol-Gels	Pacific Northwest National Laboratory, Richland, WA	NA	U.S. DOE (1999d)
Other Technologies			
Cement-Based Stabilization/Solidification	Various	\$16.37 per kg	U.S. DOE (1999a) U.S. DOE (1999c)
DeHg [®]	Nuclear Fuel Services, TN	\$8.48 per kg	Morris et al. (2002)
Acid Extraction	Environmental Technologies International, Wyomissing, PA	\$0.11 to \$0.28 per kg	Mulligan et al. (2001)
Thermal Recovery	Mercury Recovery Services, New Brighton, PA	\$0.72 to \$1.10 per kg	Mulligan et al. (2001)
X-Trax [™] Thermal Desorption	Remediation Technologies, Tuscon, AZ	\$0.11 to \$0.66 per kg	Mulligan et al. (2001)
Vitrification	Westinghouse Science and Technology Center, Pittsburgh, PA	\$0.44 to \$0.96 per kg	Mulligan et al. (2001)

Note: The cost data presented above are meant to provide an order-of-magnitude cost range for each technology. True technology costs will be specific to the waste type, waste chemical and physical properties, and the levels of contaminants in the waste.

5.0 Conclusions

This document reports the results of a bench-scale study evaluating the use of ANL's Cerami-crete™ stabilization process to effectively stabilize mercury-containing test materials. As part of the efforts by U.S. EPA's Office of Solid Waste on revising the LDR, the U.S. EPA is considering the feasibility of requiring an encapsulation step prior to land disposal of treated (i.e., stabilized chemically-fixed) Hg wastes. Encapsulation refers to a family of processes wherein hazardous solids are mixed with an organic polymeric substance or another material to encapsulate the waste stream; the mixture is allowed to cure into a solid mass prior to disposal. These processes are applicable to a wide variety of wastes, but are used primarily for wastes containing hazardous metals.

Data obtained from this study showed that stabilization of wastes reduced the leachability of Hg considerably. TCLP results showed that leachability of Hg decreased by a minimum of two orders of magnitude and a maximum of five orders of magnitude. The variation in the decrease in leachability was dependent on the amount and state of Hg in the waste. Maximum reduction in leachability was observed with stabilized wastes containing elemental Hg at 50 wt% loading, followed by stabilized wastes containing HgCl₂ at 50 wt% loading, HgCl₂ at 70 wt% loading, and elemental Hg at 70 wt% loading, respectively. The three test methods produced similar amounts of leached mercury, but the UC Constant pH Leaching Procedure samples released slightly higher levels (at pH=2) compared to the TCLP methods. Both TCLP methods produced similar results for all four waste types. In both cases the amounts released were lower for the 50 wt% samples than for the 70 wt% samples, and this indicates that the CBPC technique is not fully capable of stabilizing solid wastes with high mercury levels.

According to the Federal Register (Volume 64, Number 103) May 28, 1999, all wastes containing Hg can be grouped under two categories: low Hg subcategory with a total Hg concentration

less than 260 mg per kg of wastes, and high Hg subcategory with a total Hg concentration equal to or more than 260 mg per kg of wastes. High Hg wastes are required to be treated such that the treated wastes should meet a numerical treatment standard of 0.20 mg/L prior to land disposal, as measured by the TCLP (Morris et al., 2002 state that this requirement is for <260 mg/kg wastes, has that changed). On comparing this limit to the results obtained with the standard TCLP and the TCLP “Cage” modification, it was seen that leachates from stabilized wastes containing 50 wt% loading of elemental Hg and HgCl₂ were approximately close to this requirement. Additionally, leachability indices measured with the TCLP “Cage” modification procedure showed high leachability indices ($L > 6$), which indicates that Hg is retained well within the solid matrices. Wastes containing 70 wt% loading of Hg and HgCl₂ had leachate concentrations exceeding the 0.2 mg/L treatment standard and therefore would not meet RCRA disposal requirements.

6.0 Future Needs

The U.S. EPA is preparing an Environmental Impact Statement (EIS), which will decide how to manage or dispose of mercury-contaminated material over the long term using a chemical stabilization or encapsulation process. The regulatory requirements affecting waste treatment facilities will continue to change. U.S. EPA is considering replacing TCLP with a suite of tests (that may or may not include TCLP) for hazardous waste characterization and compliance with LDR treatment standards. The U.S. EPA has stated two difficulties with the TCLP: 1) it does not take into account all of the parameters affecting leaching; and 2) it has been applied in situations where it may not be appropriate (U.S. EPA, 1999b).

Several portions of the TCLP have been recommended for review and changes including the time-frame of 18 hours, the starting pH, the solid/liquid ratio, particle size reduction, etc. The TCLP “Cage” modification experiments performed in this study addressed the particle size reduction changes. For this study the TCLP “Cage” modification was run for 72 hours compared to 18 hours for the standard TCLP. For future experiments it would be beneficial to run comparison experiments of the standard TCLP and TCLP “Cage” modification for 90 days or more to better determine the long-term effects of leaching. Tests also could be designed to compare several stabilization or encapsulation technologies using the same waste and leaching procedure. Experiments designed to simulate actual field or land disposal conditions also would be beneficial in predicting a more realistic leaching potentials.

In regards to cost-effectiveness, it may be beneficial to perform experiments with waste loading between 50 wt% and 70 wt% to determine if there is a waste loading that will both meet the disposal requirements and also provide a costs savings over the 50 wt% waste loading.

Revision of the waste testing requirements could have a large impact on the volumes and types of waste categorized as mixed wastes. Such revisions also could impact requirements for mixed waste treatment and disposal and associated costs of mixed waste management system. It also is known that environmental restoration activities will generate additional quantities of MLLW or TRU. An uncertainty with evaluation of stabilization technology also resides in the specific MLLW/TRU waste generated. Waste streams that may be different from those in the current inventory have the potential to have different dissolution chemistry.

The leachability assessment of this study has been limited to evaluation of leaching or release of Hg from synthetic waste and was conducted using only short term experiments. Zhang and Bishop (2002) reported that the adsorption equilibrium of mercury and powder reactivated carbon was reached within 24 h. However, the leachability increases with time. Treated mercury waste materials aged over longer time span have shown increases in Hg leachability (Kosson et al., 2002). Inclusion of release of mercury as a function of aging will be helpful to estimate efficacy of the treatment process in the long-term scenario. Other long-term disposal issues to study include degradation of the stabilized or encapsulated material, diffusion of contaminants from the treated waste, and the overall strength of the waste material. U.S. DOE (1999a) lists as a future need the ability to quantify and qualify any biological degradation in processes using phosphate-bonded ceramics. The reliance on waste characterization as a basis for decision-making calls for the need for improved knowledge of the long-term leaching behavior. Moreover, the materials in field sites do not remain fully saturated over the assessment interval due to cyclic patterns. Evaluation based on a continuously saturated matrix cannot adequately simulate real scenarios.

This study used DETOX waste material to provide a general understanding of the CBPC technology. However, a study using additional waste materials, especially non-synthetic material and a comparison of several leaching procedures, will be helpful to U.S DOE in evaluating the overall effectiveness of CBPC technology and will aid U.S. EPA in developing the future regulatory framework for Hg-contaminated waste.

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