Treatment Technologies For Mercury in Soil, Waste, and Water

Treatment Technologies for Mercury in Soil, Waste, and Water

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Appendix A

Information on Select Mercury Vapor Detection Instruments

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

µg/kg	Micrograms per kilogram
µg/L	Micrograms per liter
µg/m^3	Micrograms per cubic meter
µm	Micron
APC	Air pollution control
APGEN	Applied PhytoGenetics, Inc.
ARAR	Applicable or relevant and appropriate requirement
BDAT	Best demonstrated available technology
BNL	Brookhaven National Laboratory
CAA	Clean Air Act
CBPC	Chemically bonded phosphate ceramics
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
CFM	Chemische Fabrik Marktredwitz
CWA	Clean Water Act
cm	Centimeters
cy	Cubic yards
DM	Deutsche Mark
DoD	Department of Defense
DTC	Dithiocarbamate
EPA	U.S. Environmental Protection Agency
ERT	Emergency Response Team
FATE	Field Analytic Technologies Encyclopedia
FRTR	Federal Remediation Technologies Roundtable
g/cm^3	Grams per cubic centimeter
GFT	Glass furnace technology
g/L	Grams per liter
gpm	Gallons per minute
HEPA	High efficiency particulate air
HTTD	High-temperature thermal desorption
IA	Immunoassay
ISTD	*In situ* thermal desorption
L/min	Liters per minute
LANL	Las Alamos National Laboratory
LDR	Land disposal restrictions
LTTD	Low temperature thermal desorption
MACT	Maximum achievable control technology
MCL	Maximum contaminant level

ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

mg/L	Milligrams per liter
mg/kg	Milligrams per kilogram
mg/m^3	Milligrams per cubic meter
NaDTC	Sodium dithiocarbamate
ND	Non-detect
ng/L	Nanograms/liter
NPL	National Priorities List
NRMRL	National Risk Management Research Laboratory
O&M	Operation and maintenance
OU	Operable unit
P&T	Pump and treat
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PNNL	Pacific Northwest National Laboratory
POTW	Publicly owned treatment works
ppb	Parts per billion
ppm	Parts per million
PRG	Preliminary remediation goal
psi	Pounds per square inch
RCRA	Resource Conservation and Recovery Act
RPM	Remedial project manager
S/S	Solidification/Stabilization
SDWA	Safe Drinking Water Act
SITE	Superfund Innovative Technology Evaluation
SNAP	Superfund NPL Assessment Program
SPC	Sulfur polymer cement
SPSS	Sulfur Polymer Stabilization/Solidification
SVOC	Semivolatile organic compound
TCLP	Toxicity Characteristic Leaching Procedure
Thiol-SAMMS	Thiol Self-Assembled Monolayers on Mesoporous Silica
TLV	Threshold limit value
TOC	Total organic carbon
TWA	Total Waste Analysis
UV	Ultraviolet
VOC	Volatile organic compound
WQC	Water quality criteria
XRF	X-ray fluorescence

FOREWORD

This report provides a synopsis of the availability, performance, and cost of eight technologies for treatment of mercury in soil, waste, and water. The report also describes research under way on innovative methods to treat mercury contamination. The report's intended audience includes hazardous waste site managers; those generating or treating mercury-contaminated waste and wastewater; regulators; and the interested public.

There is a need for cost-effective mercury treatment. Historical use of mercury has resulted in soil and groundwater contamination that may require remediation. Mercury contamination is difficult to treat and may pose a risk to human health and the environment. In addition, some industrial wastes and wastewaters currently being produced require treatment to remove or immobilize mercury.

This report is intended to be used as a screening tool for mercury treatment technologies. It describes the theory, design, and operation of the technologies; provides information on commercial availability and use; and includes data on performance and cost, where available. As a technology overview document, the information can serve as a starting point to identify options for mercury treatment. The feasibility of particular technologies will depend heavily on site-specific factors, and final treatment and remedy decisions will require further analysis, expertise, and possibly, treatability studies.

NOTICE AND DISCLAIMER

Preparation of this report has been funded by the U.S. Environmental Protection Agency (EPA) under Contract Number 68-W-02-034. Information in this report is derived from numerous sources (including personal communications with experts in the field). Not all the source documents have been peer-reviewed. This study has undergone EPA and external review by subject-matter experts. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

A PDF version of Treatment Technologies for Mercury in Soil, Waste, and Water is available for viewing or downloading from the Hazardous Waste Cleanup Information (CLU-IN) system Web site at http://clu-in.org/542R07003. A limited number of printed copies are available free of charge and may be ordered via the Web site, by mail, or by facsimile from:

> U.S. EPA/National Service Center for Environmental Publications (NSCEP)
> P.O. Box 42419
> Cincinnati, OH 45242-2419
> Telephone: (800) 490-9198
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ACKNOWLEDGMENTS

EXECUTIVE SUMMARY

This report contains information on the treatment of soil, waste, and water that contain mercury, a contaminant that is difficult to treat and may cause a variety of adverse health effects in humans. A total of 57 projects were identified, of which 50 provide performance data. Twenty-three of the 57 projects were conducted at pilot scale and 34 at full scale. This information can help managers at sites with mercury-contaminated media and generators of mercury-contaminated waste and wastewater to:

- Identify proven and effective mercury treatment technologies;
- Screen technologies based on application-specific goals, characteristics, and cost; and
- Apply experiences from sites with similar treatment challenges.

This report identifies eight technologies used to treat mercury in soil, waste, and water. These technologies were selected based on the availability of project-specific information for mercury treatment. Other technologies (for example, ion exchange) may be reported as being able to treat mercury contamination but are not covered in this report because project data were not found in the references used. Table ES-1 identifies and briefly describes each of these technologies. Mercury removal and emergency response are also covered briefly in the report, with a link to a guidebook for more detailed information. Treatment of air emissions that contain mercury is not covered in this report; however, technologies used to treat mercury-containing off-gas are mentioned where the information was available. Part II of this report contains more detailed information about each technology, including project-specific data. Case studies for some projects are provided based on the availability of data and the uniqueness of the application. Table ES-2 summarizes the technology applications and performance data identified for each technology and medium. Technologies that are applicable to one type of soil or waste are typically applicable to other types. For example, the media treated in the projects identified for solidification/stabilization include soil, concrete fines, sludge, liquid waste, mine tailings, and elemental mercury. Similarly, technologies that are applicable to one type of water are generally applicable to other types. For example, both groundwater and various types of wastewater are treated in the projects identified for precipitation/coprecipitation.

Mercury occurs naturally in the environment and can be found in elemental (metallic), inorganic, and organic forms. Modern uses for mercury include chemical manufacturing, thermometers, and lighting (mercury vapor and fluorescent lamps). The chemical and allied products industry group is responsible for the largest quantity of mercury used in the United States.

Mercury, particularly the organic methylmercury form, is a potent neurotoxin capable of impairing neurological development in fetuses and young children and of damaging the central nervous system of adults. Mercury regulations span multiple federal and state environmental statutes, as well as multiple agency jurisdictions.

<u>**Soil and Waste Treatment Technologies**</u>

Among the projects identified, solidification/stabilization (S/S) is the most frequently used technology to treat soil and waste contaminated with mercury. The data show that this technology has been used to meet regulatory cleanup levels, is commercially available to treat both soil and waste, and generates a residual that typically does not require further treatment before disposal. However, the data sources used for this report did not contain any information about the long-term stability of mercury-containing soil and waste treated using S/S.

Other technologies for soil and waste, including soil washing, vitrification and thermal treatment, are typically considered for specific applications or soil types, and therefore are not used as often as solidification/stabilization.

Water Treatment Technologies

Among the mercury treatment projects identified, precipitation/coprecipitation is the most commonly used process to treat mercury-contaminated water. The effectiveness of this technology is less likely to be affected by characteristics of the media and contaminants compared with other water treatment technologies.

Alternative mercury treatment technologies include adsorption and membrane filtration; however, these technologies are used less frequently because both are more likely to be affected by characteristics of the media and non-mercury contaminants than is precipitation/coprecipitation. Adsorption tends to be used more often when mercury is the only contaminant to be treated, for relatively smaller systems, and as a polishing technology for effluent from larger systems. Membrane filtration is used less frequently because it tends to produce a larger volume of residuals than do other mercury treatment technologies.

Bioremediation has been used to treat mercury in two pilot-scale studies identified for this report. In one study, mercury ions were converted to elemental mercury by bacteria and then adsorbed onto a carbon unit. In the other study, a series of aerobic and anaerobic biological treatment steps was used to remove mercury from wastewater.

Innovative Approaches for Treatment of Mercury

Innovative approaches for treatment of mercury have been applied at the bench and pilot scale and show potential for deployment at full scale. These technologies include nanotechnology, phytoremediation, air stripping, and *in situ* thermal desorption. In a pilot-scale test of the nanotechnology, thiol-SAMMS (Self-assembled Monolayers on Mesoporous Silica), 97.4 percent of mercury dissolved in an aqueous waste stream was removed after the first treatment round, and 99.4 percent was removed after two additional rounds.

Phytoremediation is also being evaluated for its effectiveness in removal of mercury from sediments and other media. In a bench-scale study of rice genetically engineered for mercury resistance, the concentration of elemental mercury was higher in the genetically-modified germinates than in the wild-type germinates, indicating enhanced mercury-reducing activities of the genetically engineered plants. Eastern cottonwood trees have also been tested in the field for their ability to remediate mercury; however, results from the study were not available when research was conducted for this report.

Air stripping is another technology being evaluated for its ability to remove mercury from water. In a bench-scale study on contaminated groundwater at the Savannah River Site, chemical reduction using stannous chloride followed by collection of the elemental mercury from the water was found to remove low levels of mercury. Stannous chloride at doses greater than 0.011 milligrams per liter (mg/L) resulted in more than 94 percent mercury removal, with the residual total mercury reduced to levels below 10 nanograms per liter (ng/L). However, low doses of stannous chloride showed little removal of mercury.

Mercury Treatment Cost Data

A limited amount of cost data on mercury was found from the sources reviewed. In many cases, only partial cost data were available, such as capital only, or operations and maintenance (O&M) only, or total costs without a breakdown. No mercury-specific cost data were identified for some technologies. A summary of cost data is provided in Table 2.3, with more detailed information presented in Section 3.0 through 10.0. A summary or interpretation of the costs is not provided, however, because mercury treatment is waste- and site-specific and because of the variation in the type and quality of information available.

Table ES-1
Overview of Selected Mercury Treatment Technologies

Technology	Description
Technologies for Soil and Waste Treatment	
Solidification/ Stabilization	Physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms.
Soil Washing/ Acid Extraction	Uses the principle that some contaminants preferentially adsorb onto the fines fraction of soil. The soil is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentrations in the remaining soil. Acid extraction uses an extracting chemical, such as hydrochloric acid or sulfuric acid.
Thermal Desorption/ Retorting	Application of heat and reduced pressure to volatilize mercury from the contaminated medium, followed by conversion of the mercury vapors into liquid elemental mercury by condensation. Off-gases may require further treatment through additional air pollution control devices such as carbon units.
Vitrification	High-temperature treatment that reduces the mobility of metals by incorporating them into a chemically durable, leach-resistant, vitreous mass. The process also may cause contaminants to volatilize, thereby reducing their concentration in the soil and waste.
Technologies for Water Treatment	
Precipitation/ Coprecipitation	Uses chemical additives to: (a) transform dissolved contaminants into an insoluble solid, or (b) form insoluble solids onto which dissolved contaminants are adsorbed. The insoluble solids are then removed from the liquid phase by clarification or filtration.
Adsorption	Concentrates solutes at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column. Contaminants are adsorbed as contaminated water is passed through the column.
Membrane Filtration	Separates contaminants from water by passing the water through a semi-permeable barrier or membrane. The membrane allows some constituents to pass, while it blocks others.
Biological Treatment	Involves the use of microorganisms that act directly on contaminant species or create ambient conditions that cause the contaminant to leach from soil or precipitate/coprecipitate from water.

Table ES-2
Summary of Technology Use and Availability of Technology Performance Data for Mercury Treatment

Technology	Media Treated		Number of Projects Identified [a] (Number with Performance Data)		
	Soil and Waste	Water	Pilot Scale	Full Scale	Total
Solidification/Stabilization	◆	-	6 (6)	12 (6)	18 (12)
Soil Washing	◆	-	6 (6)	2 (2)	8 (8)
Thermal Treatment	◆	-	5 (5)	3 (3)	8 (8)
Vitrification	◆	-	2 (2)	1 (1)	3 (3)
Precipitation	-	◆	0	11 (11)	11 (11)
Adsorption	-	◆	2 (2)	4 (3)	6 (5)
Membrane Filtration	-	◆	0	1 (1)	1 (1)
Bioremediation	-	◆	2 (2)	0	2 (2)
Total	**-**	**-**	**23 (23)**	**34 (27)**	**57 (50)**

[a] Projects were identified through previously compiled sources and information gathered from readily available data. The applications include only those identified during the preparation of this report and are not comprehensive.

- Not applicable

Source: Adapted from data in Sections 3.0 to 10.0.

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PART I

OVERVIEW

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1.0   BACKGROUND

1.1   Introduction and Purpose of Report

This report provides information on the current state of treating mercury in environmental media such as soil, groundwater, and waste. Elemental mercury has a high vapor pressure which causes it to evaporate to the atmosphere easily and potentially become an inhalation hazard. Organic mercury, particularly methylmercury, is a potent neurotoxin capable of impairing neurological development in fetuses and young children and damaging the central nervous system of adults. In addition to the toxicity, mercury behaves in a complex manner depending on its form, oxidation state, and environmental conditions, such as pH. These factors contribute to making the treatment of mercury challenging. Project-specific information on treatment technologies for mercury contamination in environmental media and waste is provided in this report and can be used by remediation site managers, hazardous waste generators, and the public to:

- Identify proven and effective mercury treatment technologies;
- Screen technologies based on application-specific goals and characteristics and cost; and
- Apply experience from sites with similar treatment challenges.

Air emissions are not covered in this report; however, more detailed information on air pollution control (APC) technologies can be found on the U.S. Environmental Protection Agency's (EPA's) mercury Web page at http://www.epa.gov/mercury/control_emissions/technology.htm.

The term "soil" as used in this report includes soil, debris, sludge, sediments, and other solid-phase environmental media. "Waste" includes nonhazardous and hazardous solid waste generated by industry. "Water" includes groundwater, drinking water, nonhazardous and hazardous industrial wastewater, surface water, mine drainage, and leachate. Most sources used for this report contained information about treatment of mercury in soil, sludge, sediments, waste, groundwater, and wastewater. Limited information was identified on treatment of drinking water.

Part I of this report, Overview and Findings, contains an executive summary, an introduction, and a comparison of mercury treatment technologies. The introduction describes the purpose of the report, presents background information, discusses ongoing research in mercury treatment, and summarizes the methodology used to gather and analyze data. The Comparison of Technologies section (Section 2.0) analyzes and compares the technologies used for mercury treatment.

Part II of this report contains eight sections, each summarizing information for a specific type of mercury treatment technology. Each summary includes a brief description of the technology, information about how it is used to treat mercury, its status and scale, and data on cost and performance. Case studies for some projects are provided based on the availability of data and the uniqueness of the application. The technology summaries are organized as follows: the technologies typically used to treat soil and waste appear first, in the order of their number of full-scale applications, followed by those typically used for water, in the same order.

1.2   Sources of Information for the Report

This report is based on previously compiled sources on mercury treatment and information gathered from readily available data sources, including:

- Documents and databases prepared by EPA and other federal agencies;
- Technical literature;
- Information supplied by vendors of treatment technologies;
- Internet sites; and
- Information from technology experts.

1.3   Methodology Used to Compile Technology-Specific Information

This report provides information on the eight technologies listed in Table ES-1 in the executive summary. These technologies have been used at the full or pilot scale to treat mercury in soil, waste, and water. Full-scale projects include technologies used commercially to treat industrial waste and to remediate an entire area of contamination. Pilot-scale projects are usually conducted in the field to test the effectiveness of a technology on a specific soil, waste, and water or to obtain information for scaling a treatment system up to full-scale.

The information gathered for this report includes many projects that used treatment trains. Treatment trains consist of two or more technologies used together, either integrated into a single process or operated as a series of processes in sequence. The technologies in a train may treat the same contaminant. A common treatment train used for mercury in water includes pH adjustment as a pretreatment, followed by precipitation, sedimentation, and filtration.

Some treatment trains are employed when one technology alone is not capable of treating all of the contaminants. For example, an aboveground system consisting of electrochemical precipitation, followed by air stripping and granular activated carbon adsorption was used to treat groundwater contaminated with volatile organic compounds (VOC) and heavy metals, including mercury, at the King of Prussia Technical Corporation Superfund Site in New Jersey (Table 8.1). Electrochemical precipitation involves using electricity to convert contaminants to an insoluble form, which can then be removed. The electrochemical treatment and air stripping steps were used to remove most of the heavy metals and VOCs, while the adsorption treatment was a polishing step for the heavy metals, including mercury.

In many cases, the information did not specify the technologies within the train that were intended to treat mercury. Influent and effluent concentrations often were provided for the entire train and not for the individual components. In such cases, engineering judgment was used to identify the technology that treated mercury. For example, a treatment train consisting of precipitation followed by carbon adsorption and pH adjustment was used at the Olin Corporation Site in Alabama (Table 8.1) to treat groundwater contaminated with VOCs and mercury. The precipitation step was assumed to remove most of the mercury, and the carbon unit was assumed to serve as a polishing step.

When a treatment train included more than one potential mercury treatment technology, all mercury treatment technologies were assumed to contribute to mercury treatment unless information indicated otherwise. Information about these projects is presented in all applicable technology sections.

1.4   Background

Mercury occurs naturally in the environment and can be found in elemental (metallic), inorganic, and organic forms. The most common natural forms of mercury are elemental mercury, mercuric sulfide (cinnabar ore), mercuric chloride, and methylmercury. Historically, mercury and its compounds have been used for industrial, medicinal, and cosmetic purposes. Modern uses for mercury include production of chlor-alkali, in wiring devices and switches, measuring and control devices, lighting, and dental work. In 2004, the largest use of mercury was in wiring devices and switches (63 tons), followed by dental work (35 tons), and chlor-alkali production (14 tons). Based on data provided by the chlor-alkali, lamp, and dental industries, it appears that use of mercury declined by more than 50 percent between 1995 and 2004 (Ref. 1.19)

Mercury, and particularly the organic methylmercury form, is a potent neurotoxin capable of impairing neurological development in fetuses and young children and of damaging the central nervous system of adults (Ref. 1.2, 1.21). High exposures to inorganic mercury may damage the gastrointestinal tract, the nervous system, and the kidneys. Both inorganic and organic mercury compounds are absorbed through the gastrointestinal tract and affect other systems via this route. However, organic mercury compounds are more readily absorbed via ingestion than are inorganic mercury compounds (Ref. 1.4).

People are most likely to be exposed to harmful quantities of mercury through consumption of fish contaminated with methylmercury (Ref. 1.3). Elemental mercury causes adverse health effects when it is breathed as a vapor and absorbed through the lungs. These exposures can occur when elemental mercury is spilled or products that contain elemental mercury break and expose the substance to the air, particularly in warm or poorly ventilated indoor spaces (Ref. 1.4). Exposure to inorganic mercury can also occur from drinking contaminated water and touching contaminated water and soil, though these exposures are generally not thought to be harmful at typical ambient levels (Ref. 1.2).

1.5   Environmental Occurrence

Mercury can be found in air, soil, and water. The most prevalent ore form of mercury is cinnabar (mercury sulfide). In the U.S., large naturally occurring cinnabar deposits exist in California, Nevada, Utah, Oregon, Arkansas, Idaho, and Texas. Inorganic mercury also occurs in small amounts in many rock types (for example, granite and shale) (Ref. 1.5). Atmospheric levels of mercury tend to be higher in the vicinity of active volcanoes and significant anthropogenic sources than in other areas. Coal-burning power plants emit more mercury to the air than other anthropogenic sources in the U.S., accounting for about 45 percent of all domestic mercury emissions (Ref. 1.19). Once in the atmosphere, mercury is widely disseminated and can circulate for years, accounting for its wide-spread distribution. Most natural waters, including groundwater and surface waters, also contain naturally occurring mercury in the low micrograms per liter (μg/L) range (depending on the types of rock the water flows through), with freshwater concentrations reported as high as 70 μg/L (Ref. 1.5). Inorganic mercury in the atmosphere that is deposited in water has the potential to be converted to methylmercury, which tends to bioaccumulate in fish and animals (Ref. 1.1).

Of the estimated 111 tons of mercury emitted annually into the atmosphere by anthropogenic sources in the U.S. as of 2002, approximately 45 percent is from utility coal boilers; 10 percent from electric arc furnaces; 9 percent from industrial/commercial/institutional boilers and process heaters; 6 percent from gold mining; and 5 percent from chlorine production. Total estimated emissions decreased 47 percent between 1990 and 2002. However, the actual reduction in emissions has likely been greater than this estimate because two of the biggest 2002 emissions source categories — electric arc furnaces and gold mining — are not included in the 1990 inventory (Ref. 1.19).

At waste sites, mercury occurs in various media, including soil, groundwater, sediment, sludge, and leachate. Thimerosal, an organic form of mercury ($C_9H_9HgO_2SNa$), has been used as a preservative in a number of medicines and can be found in waste streams from hospitals, clinical laboratories, and pharmaceutical industries. Waste sites fall under several cleanup programs, including Superfund responses, Resource Conservation and Recovery Act (RCRA) corrective actions, and state cleanups. Information is available on the occurrence and treatment of mercury at Superfund National Priorities List (NPL) sites. Based on records of decision and other site data, 290 NPL sites include mercury as a contaminant of concern. A contaminant of concern is any compound that is expected to be present at a site based upon past and current land uses and associated releases. Table 1.1 lists these sites by the medium that contains mercury. Soil and groundwater are the most common media, with mercury-contaminated soil at 173 sites and mercury-contaminated groundwater at144 sites. The table shows four sites with air emissions of mercury; however, this actual number is likely larger than four because fugitive

air emissions of mercury may not be incorporated with the emissions inventory estimations technique used. The number of sites in Table 1.1 exceeds the total number of sites with mercury (290) because more than one type of media contaminated with mercury may be present at some sites. Mercury may also be present at sites not listed on the NPL; however, this information was not captured in Table 1.1.

Table 1.1
Number of Superfund Sites with Mercury as a Contaminant of Concern by Media Type
(Total Number of NPL Sites = 290)

Media Type	Number of Sites[a]
Soil	173
Groundwater	144
Sediment	92
Surface Water	43
Debris	35
Sludge	24
Solid Waste	18
Leachate	16
Other	11
Liquid Waste	4
Air	4
Residuals	1

Source: Ref. 1.7 (data through 2000), 1.8, 1.9

[a] Some sites contain more than one type of media contaminated with mercury.

Table 1.2 lists the number of Superfund sites with mercury as a contaminant of concern by site type. The most common site types are landfills, and chemicals and allied products facilities.

Table 1.2
Number of Superfund Sites with Mercury as a Contaminant of Concern by Site Type

Site Type	Number of Sites
Landfills	102
Chemicals and Allied Products	15
Groundwater Plume	14
Metals Fabrication and Finishing	12
Military	11
Batteries and Scrap Metal	9
Transportation Equipment	9
Primary Metals Processing	7
Ordnance Production	6
Mining	5
Electrical Equipment	5
Chemicals and Chemical Waste	5
Research and Development	5
Other	85[a]

Source: Ref. 1.7 (data through 2000), 1.8, 1.9

[a] Includes site types with fewer than five sites, sites where site types were identified as "other" or "multiple," and unspecified waste management.

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Information for Tables 1.1 and 1.2 was compiled from the Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) database (Ref. 1.6), the Superfund NPL Assessment Program (SNAP) database (Ref. 1.7), and the database supporting the document "*Treatment Technologies for Site Cleanup: Annual Status Report (Eleventh Edition)*" (Ref. 1.8).

1.6 Chemistry and Behavior

Elemental mercury is a silver-white, heavy liquid at room temperature. Because of its high surface tension, it forms small compact spherical droplets when it is released in the environment. Although the droplets themselves are stable, the high vapor pressure of mercury compared with other metals causes it to evaporate. Therefore, released or uncovered mercury can rapidly become an inhalation hazard (Refs. 1.1 and 1.5).

The most prevalent oxidation states for mercury are Hg^{+1} (mercurous) or Hg^{+2} (mercuric). The properties and chemical behavior of mercury strongly depend on its oxidation state. Mercury can form a variety of inorganic salts and is unusual among metals because, unlike the reactive alkali and alkaline earth metals, it can form covalent bonds with organic radicals. Most of the mercury encountered in water, soil, sediments, and biota and other environmental media (except the atmosphere) is in the form of inorganic mercuric salts and organomercurics. Organomercurics are defined by the presence of a covalent C-Hg bond. The presence of a covalent C-Hg bond differentiates organomercurics from inorganic mercury compounds that merely associate with the organic material in the environment but do not have the C-Hg bond.

The following mercury compounds are most frequently found under environmental conditions: mercuric salts HgS, HgCl, Hg(OH) and HgS; the methylmercury ion ($HgCH_3^+$) and its compounds methylmercuric chloride (CH_3HgCl) and methylmercuric hydroxide (CH_3HgOH); and, in small fractions, other organomercurics (for example, dimethylmercury and phenylmercury) (Refs. 1.5 and 1.10). Methylmercury — which can cause nervous system damage, especially in fetuses and infants — is formed when mercury enters soil or sediments and is acted on by anaerobic microorganisms (Ref. 1.4). The solubilities of mercury compounds vary, ranging from negligible (HgCl, HgS) to very soluble ($HgCl_2$) (Ref. 1.5). Table 1.3 provides the physical and chemical properties of elemental mercury and some of its compounds (Ref. 1.14).

Ionic forms of mercury are strongly adsorbed by soils and sediments and are desorbed slowly. Clay minerals optimally adsorb mercury ions at pH 6. Iron oxides also adsorb mercury ions in neutral soils. Most mercury ions are adsorbed by organic matter (mainly fulvic and humic acids) in acidic soils. When organic matter is not present, mercury becomes relatively more mobile in acid soils and can evaporate to the atmosphere or leach to groundwater (Ref. 1.5).

Table 1.3
Physical and Chemical Properties of Some Mercury Compounds

Compound Name	Elemental Mercury	Mercuric Chloride	Mercurous Chloride	Methyl-mercuric Chloride	Dimethyl Mercury
Molecular formula	Hg^0	$HgCl_2$	Hg_2Cl_2	CH_3HgCl	C_2H_6Hg
Molecular weight	200.59	271.52	472.09	251.1	230.66
Solubility	5.6×10^{-5} g/L at 25°C	69 g/L at 20°C	2.0×10^{-3} g/L at 25°C	0.100 g/L at 21°C	1 g/L at 21°C
Density	13.534 g/cm^3 at 25°C	5.4 g/cm^3 at 25°C	7.15 g/cm^3 at 19°C	4.06 g/cm^3 at 20°C	3.1874 g/cm^3 at 20°C
Boiling Point (^{o}C)	357	302	384	Not available	93
Melting Point (^{o}C)	-39	277	302	170	- 43
Oxidation State	0	+2	+1	+2	+2

Source: Ref. 1.20, 1.18
Notes:
g/cm^3 = Grams per cubic centimeter
g/L = Grams per liter

1.7   Regulatory Considerations

An improved understanding of the toxic health effects of mercury and its bioaccumulative properties has led to greater regulatory control. Mercury regulations span multiple federal and state environmental statutes, as well as multiple agency jurisdictions. EPA has developed regulations to control mercury emissions to air through the Clean Air Act (CAA); to water through the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA); and from wastes and products through RCRA (Refs. 1.2 and 1.3). For example, EPA regulates emissions of mercury to the atmosphere from stationary sources under various regulations promulgated under the CAA and RCRA. Likewise, under the SDWA, EPA has established a maximum contaminant level (MCL) for mercury of 2 μg/L in drinking water. Under the CWA, EPA has established ambient water quality criteria (WQC) for mercury and has issued technology-based standards for specific industries to control mercury discharges into rivers, streams, lakes, and wetlands (Ref. 1.2). Under RCRA, EPA has identified certain specific wastes that contain mercury as "listed hazardous wastes" and also has provided criteria to determine whether mercury concentrations in nonlisted wastes may meet the definition of a RCRA hazardous waste based on the "toxicity characteristic". Table 1.4 lists the waste codes and descriptions for the RCRA listed wastes that contain mercury.

Nonlisted wastes are defined as hazardous wastes if the concentration of mercury in the waste extract exceeds 0.2 milligrams per liter (mg/L) using the Toxicity Characteristic Leaching Procedure (TCLP) under the RCRA toxicity criteria. Media cleanup standards for releases of mercury under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) are based on applicable or relevant and appropriate requirements (ARAR) in federal and state laws and regulations (for example, MCLs under the SDWA) or site-specific levels, such as preliminary remediation goals (PRG), established by evaluating potential receptors and exposure pathways.

Table 1.4
RCRA Listed Hazardous Wastes for Mercury

Waste Code	Description
K071	Brine purification muds from the mercury cell process in chlorine production, in which separately pre-purified brine is not used
K106	Wastewater treatment sludge from the mercury cell process in chlorine production
K175	Wastewater treatment sludge from the production of vinyl chloride monomer using mercuric chloride catalyst in an acetylene-based process
P065	Mercury fulminate
P092	Phenylmercury acetate
U151	Mercury

Source: Ref. 1.2

Cleanup goals for excavated soils at mercury-contaminated sites are often based on the RCRA land disposal restrictions (LDR), which prohibit land disposal of hazardous wastes and contaminated soils that contain mercury unless the waste or soil is treated to meet specific standards or stringent criteria associated with the regulatory variances that are associated with the LDRs standards. EPA has established different sets of LDR standards for mercury-containing hazardous wastes versus mercury-contaminated soils. The LDR standards for wastes are based on the physical form of the waste that requires treatment and the total mercury content. The LDRs categorize mercury wastes as low mercury wastes, high mercury wastes, or elemental mercury wastes. Table 1.5 describes the LDRs for each of these wastes.

Table 1.5
Land Disposal Restrictions for Low Mercury Wastes, High Mercury Wastes, and Elemental Mercury

Type of Waste	Land Disposal Restrictions
Low mercury waste (contain less than 260 mg/kg of total mercury)	If retorted, 0.2 mg/L TCLP If other technologies are used – 0.025 mg/L TCLP (solidification/stabilization often used to meet this level)
High mercury waste (contain greater than 260 mg/kg total mercury)	Required to be roasted or retorted until waste becomes a low mercury waste. Residuals then required to meet 0.2 mg/L TCLP
Elemental mercury waste (with radioactive contamination)	Required be treated using amalgamation

Source: Ref. 1.10
Notes:
mg/L = Milligrams per liter
mg/kg = Milligrams per kilogram

EPA also has set a LDR standard of 0.15 mg/L for the treatment of wastewater. The LDRs for mercury contamination in soils require treatment to reduce by 90 percent the original concentration of mercury in the soil; however, treatment would not be required if the 90 percent reduction would result in a concentration less than 10 times the appropriate TCLP concentration shown above in Table 1.5. Instead, treatment would be required only to meet 10 times the appropriate TCLP concentration shown in Table 1.5. The treatment standard for contaminated soil is particularly relevant during remedial responses and cleanup because it is less stringent than other LDR standards. The regulations at 40 Code of Federal

Regulations Part 268.9 discuss additional rules about how to identify applicable LDR treatment standards for characteristic hazardous wastes, including hazardous wastes that are listed and also exhibit one or more RCRA characteristics.

1.8   Mercury Removal and Emergency Response

Various steps need to be taken to safely clean up and contain the contamination when an indoor spill of mercury occurs. U.S. EPA Region 5 recommends that the following six "R's" of a response be followed:

- Referral – notifying the appropriate agencies about the spill, for example, the local health agency;
- Reconnaissance – assessing the extent and level of contamination;
- Relocation – determining the need for relocation, notifying residents, and securing alternate accommodations;
- Removal – conducting decontamination, such as bagging contaminated items, cleaning contaminated surfaces with appropriate chemicals, and ventilating the area;
- Replacement – appraising the removed items and restoring the area after decontamination is complete; and
- Reoccupation – notifying residents when buildings are ready for reoccupation and assisting in the reoccupation process.

These six factors are described in detail in the "Mercury Response Guidebook," developed by EPA's Emergency Response Team (ERT) and EPA Region 5 (Ref. 1.13).

The guidebook is designed to assist emergency and remedial professionals to coordinate and clean up indoor mercury spills. States and other EPA regions also may have specific requirements during an emergency response.

1.9   Detection and Site Characterization

Samples may be analyzed to measure the mercury concentration in a controlled laboratory environment or in the field using site characterization techniques. In a laboratory, soil and water samples can be analyzed using several different methods. The most common analytical methods use cold-vapor atomic absorption spectroscopy. For aqueous samples, these methods include 245.1 (manual) (Ref. 1.15), 245.2 (automated) (Ref. 1.15), and SW-846 Method 7470A (Ref. 1.20). For solid samples, these methods include 245.5 (sediment), 245.6 (tissues), and SW-846 Methods 7471A and 7473 (Refs. 1.15, 1.16).

A number of additional analytical procedures are available in laboratories that have the necessary instrumentation. Organomercurial compounds may be analyzed by high-performance liquid chromatography with an electron capture detector using Method 245.8. Total mercury may be measured by atomic fluorescence spectrometry using Method 245.7 (Ref. 1.15) and SW-846 Method 7474 (Ref. 1.21). Mercury may also be analyzed by inductively coupled plasma/mass spectrometry using SW-846 Method 6020A (Ref. 1.15); by anodic stripping voltammetry using SW-846 Method 7472 (Ref. 1.15); and by thermal decomposition, amalgamation, and atomic absorption spectrophotometry using SW-846 Method 7473 (Ref. 1.15). Some of the SW-846 methods require a digestion step (selected from SW-846 Methods 3005A through 3052) before analysis for nonaqueous samples or for all samples (Refs. 1.15, 1.16).

Detection and site characterization of mercury using field-based analytical methods allows for ease of on-site application and quicker decision-making. The technologies are portable and provide continuous, real-time data. Some methods can be used outdoors with hand-held equipment; other, more rigorous methods require the controlled environments of a mobile laboratory.

Field-based analytical methods, with systematic project planning and dynamic work strategies, form the basis of the Triad, an innovative approach to decision-making for hazardous waste site characterization and remediation. The three-pronged approach of the Triad aims to identify and manage decision uncertainties in site cleanup (http://www.triadcentral.org). Systematic project planning ensures that the goals for the project are clearly identified and involves charting the most resource-effective course to reach the desired outcomes. Dynamic work strategies, often in the form of a decision tree approved by the regulatory agency, guide the Triad project teams in making on-site decisions. Using this strategy, future site activities progress based on previous findings in the field. Real-time measurements generated using field-based analytical techniques, rapid sampling platforms (for example, direct-push technologies), geophysical tools, and on-site data management and display software make real-time decision-making possible. Application of the Triad can condense a project's overall budget and lifetime, while increasing the likelihood that the gathered data will guide better, more transparent decisions (Ref. 1.23).

The most commonly used site characterization techniques for mercury are immunoassay (IA) test kits, field-based X-ray fluorescence (XRF) analyzers, and atomic absorption spectrometry instruments. IAs employ antibodies that bind with a target compound or class of compounds. The process is colorimetric, with the change in color indicating the approximate concentrations of the target compound. The presence of the target compound is identified by comparing the color developed by a sample of unknown concentration with the color formed by a standard that contains the analyte at a known concentration. The concentration of the analyte is determined by the intensity of color in the sample. One type of commercially available immunoassay test kit for inorganic contaminants is the BiMelyze immunoassay for mercury in soil and water, manufactured by BioNebraska. The kit measures inorganic mercuric (+2) ions in soil and water and has a detection limit of 0.5 milligrams per kilogram (mg/kg) for soil and 0.25 µg/L for water (Refs. 1.11, 1.12).

XRF is used to characterize the mercury concentration in solid media such as soil and debris. It operates on the concept of energy dispersive X-ray fluorescence spectrometry and responds to all chemical forms of mercury. Samples are bombarded with X-rays produced by radioisotopes. When the X-rays are absorbed by metals in the sample, the atoms emit X-rays of a specific wavelength. Each metal gives off X-rays of different energy levels. The specific type or energy of the emitted X-ray is unique to a metal and is called a "characteristic" X-ray. It is possible to identify and sometimes quantify the composition of metals in a sample by measuring the different energies of X-rays emitted by a sample exposed to an X-ray source. A qualitative analysis of the samples can be made by observing the characteristic X-rays produced. The quantity or intensity of the energy of the X-rays emitted is proportional to the concentration of the target analytes (Refs. 1.11, 1.12).

Field instruments typically use atomic absorption spectrometry for detecting mercury vapor. Four instruments that are representative of available technologies for mercury vapor detection are shown in Appendix A. One of the technologies described in Appendix A is from the Ohio Lumex Company (http://www.ohiolumex.com). This instrument is based on the principle of the Zeeman effect, which involves splitting the spectrum by an applied magnetic field to achieve very low detection levels.

Further information on field-based analytical methods is available on EPA's Dynamic Field Activities web page at http://www.epa.gov/superfund/programs/dfa/fldmeth.htm, and through EPA's Field Analytic Technologies Encyclopedia (FATE) Web site at http://fate.clu-in.org.

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2.0   COMPARISON OF TREATMENT TECHNOLOGIES FOR MERCURY

The following section describes the types of technologies used to treat mercury and the application of the technologies to treat soil, waste, and water.

2.1   Types of Technologies Used

Eight technologies have been identified to treat mercury-contaminated soil, waste, and water at full or pilot scale. Figure 2.1 lists these technologies and categorizes them into two general groups: soil and waste, and water. The technologies are discussed as follows in the remainder of this report: the technologies typically used to treat soil and waste appear first, in the order of their number of full-scale applications, followed by those typically used for water, in the same order. Only one of the eight technologies, solidification/stabilization, has been used to treat elemental mercury; the remainder have been used to treat mercury compounds.

Figure 2.1
Technologies Applicable to Treatment of Mercury-Contaminated Media

Mercury Treatment Technologies
Soil and Waste Treatment • Solidification/Stabilization • Soil Washing • Thermal Treatment • Vitrification ***Water Treatment*** • Precipitation/Coprecipitation • Adsorption • Membrane Filtration • Bioremediation

Table 2.1 summarizes the applicability of the technologies to mercury-contaminated media. Technologies that are applicable to one type of soil or waste are typically applicable to other types. For example, the media treated in the projects identified for solidification/stabilization include soil, concrete fines, sludge, liquid waste, mine tailings, and elemental mercury. Similarly, technologies applicable to one type of water are generally applicable to other types. For example, both groundwater and various types of wastewater are treated in the projects identified for precipitation/coprecipitation.

Regardless of the technology used and the type of media treated, an industrial hygiene review should be conducted during the design phase for the treatment process and an industrial hygiene inspection should be conducted during the initial startup phases for any mercury treatment project. These reviews are particularly important for technologies that concentrate mercury from environmental media, and are necessary to ensure that the treatment processes are designed and operated so that plant personnel will not be exposed at concentrations in excess of the threshold limit value (TLV) for mercury, both elemental (0.025 micrograms per cubic meter [mg/m^3]) and organic (0.01 mg/m^3) (Ref. 2.1).

2.2   Frequency of Technology Use

Figures 2.2 and 2.3 show the number of mercury treatment projects that could be found in the literature for each technology identified. Figure 2.2 shows the number of projects for soil and waste treatment technologies, and Figure 2.3 shows the number of projects for water treatment technologies. The soil and waste treatment technologies listed in Figure 2.2 are described below.

Figure 2.2
Number of Identified Applications of Mercury Treatment Technologies for Soil and Waste
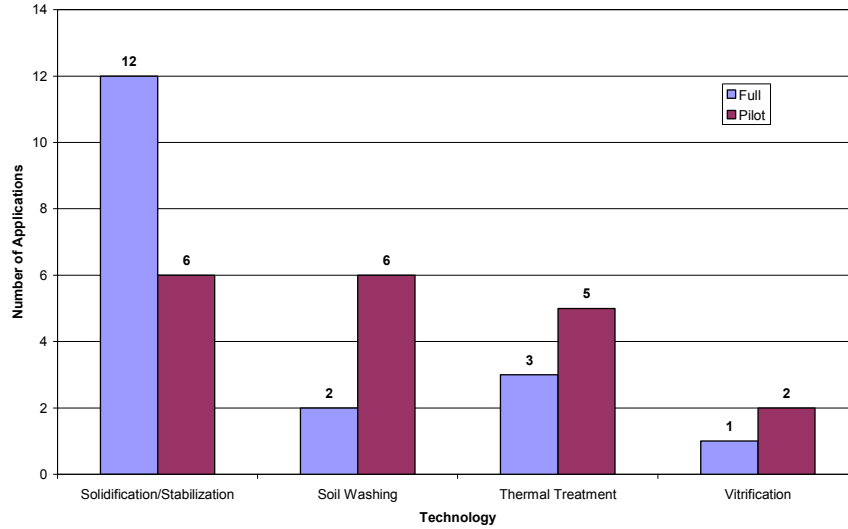
Source: Projects listed in Sections 3.0 to 6.0.

Figure 2.3
Number of Identified Applications of Mercury Treatment Technologies for Water
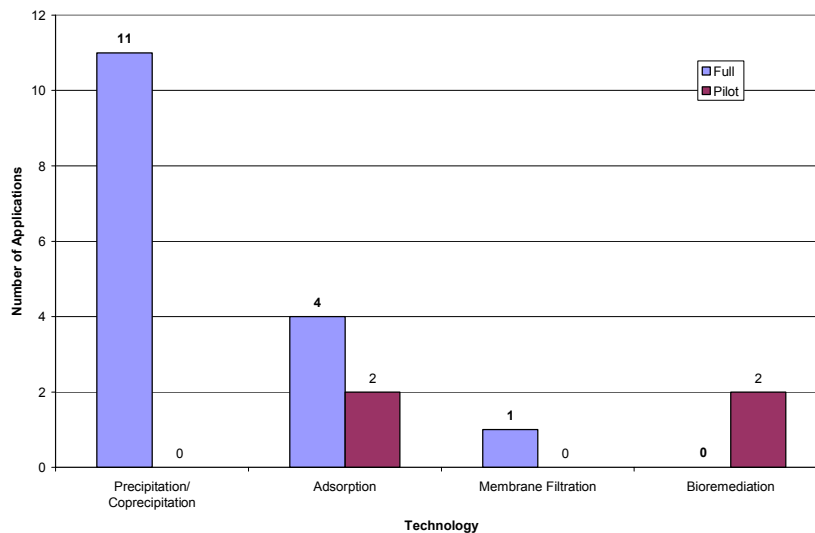
Source: Projects listed in Sections 7.0 to 10.0.

- **Solidification/stabilization** (*in situ* or *ex situ*) is the most frequently used technology for soil and waste contamination in the projects identified. The data show that this technology has been used to meet regulatory cleanup levels, is commercially available to treat both soil and waste, and generates a residual that typically does not require further treatment prior to disposal. Other technologies for soil and waste are typically used for specific soil types.

- **Soil washing/acid extraction** (*ex situ*) is used primarily to treat soils with relatively low clay content because these soils tend to be separable into a highly contaminated fines fraction and a less contaminated sand fraction. It is also less effective for soils with high organic content because organic compounds tend to interfere with contaminant desorption.

- **Thermal treatment** (*ex situ*), such as thermal desorption or retorting, is routinely used to treat industrial and medical wastes that contain mercury, but is also generally not suitable for soils with high clay or organic content and typically requires an APC unit to treat mercury off-gas.

- **Vitrification** (*in situ* or *ex situ*) may be used when a combination of contaminants is present that cannot be treated using only solidification/stabilization. It has also been used for wastes with a high organic content because combustion of the organic content liberates heat, reducing the external energy requirements.

The water treatment technologies listed in Figure 2.3 are described below.

- **Precipitation/Coprecipitation** is the most frequently used technology for water contamination in the projects identified. The effectiveness of this technology is less likely to be reduced by characteristics or contaminants that may affect other technologies, such as hardness or other heavy metals. Systems that use this technology generally require skilled operators; therefore, precipitation/coprecipitation is more cost-effective at a large scale where labor costs can be spread over a larger amount of treated water produced.

- **Adsorption** for mercury treatment is more likely to be affected by media characteristics and contaminants other than mercury when compared with precipitation/coprecipitation. Small-capacity systems using these technologies tend to have lower operating and maintenance costs and require less operator expertise. Adsorption tends to be used more often when mercury is the only contaminant to be treated, for relatively smaller systems, and as a polishing technology for the effluent from larger systems.

- **Membrane filtration** is effective for the treatment of mercury but is used less frequently because its costs tend to be higher and it produces a larger volume of residuals than other mercury treatment technologies. In addition, it is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, colloids, and other contaminants can cause membrane fouling.

- **Bioremediation** (*in situ* or *ex situ*) has been shown to be effective in several pilot-scale studies identified in the research conducted for this report. The mechanisms that enable bioremediation to reduce the concentration of mercury are not fully understood at this time. Mechanisms that have been suggested include converting mercury to species that are retained in the biomass or converting it to species that are more easily removed from water by another technology, such as precipitation or adsorption. Bench-scale and additional pilot-scale studies are being conducted to assess the effectiveness of bioremediation technologies for mercury at full scale.

Table 2.2 is a screening matrix for mercury treatment technologies. It can assist decision-makers in evaluating candidate treatment technologies by providing information on relative availability, cost, and other factors for each technology. The matrix is based on the Federal Remediation Technologies Roundtable (FRTR) Treatment Technologies Screening Matrix (Ref. 2.2). However, it is limited to the technologies addressed in this report, and the technology evaluation criteria have been reassessed to compare the technologies only with those listed in Table 2.2, rather than all treatment technologies. In addition, the table includes information about the factors that affect technology cost and performance. Table 2.2 includes the following information:

- *Development Status* – The scale at which the technology has been applied. All technologies to treat mercury have been applied at full scale, with the exception of bioremediation, which is currently at pilot scale.

- *Treatment Trains* – "Yes" indicates that the technology is typically used in combination with other technologies, such as pretreatment or treatment of residuals (excluding offgas). "No" indicates that the technology is typically used independently.

- *Residuals Produced* – The residuals typically produced that may require additional management. All of the technologies generate a solid residual, with the exception of membrane filtration, which generates only liquid residuals. Vitrification and thermal treatment produce a vapor residual.

- *O&M or Capital Intensive* – This category indicates the main cost-intensive parts of the system. "O&M" indicates that the operation and maintenance costs tend to be high in comparison to other technologies. "Cap" indicates that capital costs tend to be high in comparison to other technologies.

- *Factors that May Affect Performance or Cost* – These include matrix characteristics and operating parameters for each technology that may affect mercury treatment performance or cost. These factors are described in more detail in Sections 3.0 through 10.0.

A limited amount of cost data on mercury treatment was found. Table 2.3 summarizes this information.

Considerations about the Performance and Cost Data Included in this Report

The information in this report is based on previously-compiled sources on mercury treatment and information gathered from readily-available data sources. The data were collected over a period of time (from December 2004 to January 2007), and the level of detail of the performance data varied among projects. Not all the source documents have been peer-reviewed, and most data were not independently verified. The remedial project managers (RPMs) for some Superfund sites were called, however, to verify existing data and obtain additional project information.

Some projects treated numerous contaminants, in addition to mercury. Therefore, mercury may not have been the target contaminant for these projects. In many cases, the cost information was incomplete. For example, some projects included data for O&M costs only, and did not specify the associated capital costs. In other cases, total costs were provided, but a breakdown of these costs was not included. No mercury-specific cost data were identified for some technologies.

The cost data were taken from many types of sources, including EPA, Department of Defense (DoD), other government sources, and information from technology vendors. The quality of these data varied, with some sources providing detailed information about the items included in the costs, while other

sources provided little detail about the basis for costs. In most cases, the specific year for the costs was not provided. The costs in Table 2.3 are reported in the identified references and are not adjusted for inflation. This report does not provide a summary or interpretation of the costs in Table 2.3 because of the variation in the type and quality of information.

In general, Table 2.3 includes only costs specifically for treatment of mercury. General technology cost estimates are unlikely to accurately predict actual treatment costs because mercury treatment is waste- and site-specific.

Other Treatment Technologies for Mercury

This report identifies eight technologies used to treat mercury in soil, waste, and water. These technologies were selected based on the availability of project-specific information for mercury treatment. Other technologies (for example, ion exchange) may be reported as being able to treat mercury contamination but are not covered in this report because project data were not found in the references used.

Table 2.1
Applicability of Mercury Treatment Technologies[a]

Technology	Soil [b]	Waste[c]	Water	
			Groundwater and Surface Water [d]	**Wastewater [e]**
Solidification/Stabilization	◆	◆		
Soil Washing and Acid Extraction	◆	◆		
Thermal Treatment	◆	◆		
Vitrification	◆	◆		
Precipitation/Coprecipitation			◆	◆
Adsorption			◆	◆
Membrane Filtration				◆
Biological Treatment				◆

Source: Sections 3.0 to 10.0 of this report.

Notes:
◆   Indicates treatment has been conducted at full or pilot scale.

[a]   Media indicated here only if project-specific data are available. Some technologies may be applicable to more than one type of media.
[b]   Soil includes soil, debris, sludge, sediments, and other solid-phase environmental media.
[c]   Waste includes nonhazardous and hazardous solid waste generated by industry.
[d]   Groundwater and surface water also includes mine drainage.
[e]   Wastewater includes nonhazardous and hazardous industrial wastewater and leachate.

Table 2.2
Mercury Treatment Technologies Screening Matrix

Technology	Development Status	Treatment Train (excludes off-gas treatment)	Residuals Produced	O&M or Capital Intensive	Factors That May Affect Performance or Cost	
					Matrix Characteristics	Operating Parameters
Soil and Waste						
Solidification/ Stabilization	Full scale	No	Solid	Cap	• pH of media • Presence of organic compounds • Particle size • Moisture content • Oxidation state of mercury	• Type of binder and reagent • Mixing of waste and binder
Soil Washing and Acid Extraction	Full scale	Yes	Solid, Liquid	Cap & O&M	• Soil homogeneity • Presence of organic compounds • Particle size • pH of media • Moisture content	• Temperature
Thermal Treatment	Full scale	No	Solid, Liquid, Vapor	Cap & O&M	• Presence of organic compounds • Particle size • Moisture content	• Residence time • System throughput • Temperature and pressure
Vitrification	Full scale	No	Solid, Vapor	Cap & O&M	• Lack of glass-forming materials • Particle size • Moisture content • Subsurface air pockets • Presence of organic compounds	• Temperature

Table 2.2
Mercury Treatment Technologies Screening Matrix (continued)

Technology	Development Status	Treatment Train (excludes off-gas treatment)	Residuals Produced	O&M or Capital Intensive	Factors That May Affect Performance or Cost	
					Matrix Characteristics	Operating Parameters
Water						
Precipitation/ Coprecipitation	Full scale	Yes	Solid	Cap	• pH of media • Presence of other contaminants	• Chemical dosage
Adsorption	Full scale	Yes	Solid	O&M	• Presence of other contaminants • pH of media	• Fouling of adsorption media • Flow rate
Membrane Filtration	Full scale	Yes	Liquid	Cap & O&M	• Molecular weight of contaminants • Temperature • Presence of other contaminants	• Type of filter • Pressure • Temperature
Biological Treatment	Pilot scale	Yes	Solid, Liquid	Cap	• pH of media • Presence of other contaminants	• Available nutrients • Temperature

Source: Adapted from FRTR Screening Matrix (Ref. 2.1) and Sections 3.0 to 10.0 of this report.

Cap   Capital
O&M   Operation and maintenance

Table 2.3
Available Mercury Treatment Cost Data for Various Technologies

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Solidification/Stabilization								
Bunker Hill Mining and Metallurgical Complex, Idaho	Full	Soil, 30,000 cy, 1997	NA	NA	NA	$230,000	Cost year not specified. Components of total cost not specified.	Section 3.0 Ref. 3.19
Rocky Mountain Arsenal, Colorado	Full	Soil, 26,000 cy	$2.8 million	NA	NA	$2.8 million	The implementation cost is $2.8 million, and there were no direct associated O&M costs. Cost year not specified. Components of total cost not specified.	Section 3.0 Ref. 3.21
DOE Facility, Portsmouth, Ohio	Pilot	Liquid waste (ion exchange resin waste), 99 kg	$30,000	NA	NA	NA	Includes disposal costs. Cost year not specified. Components of total cost not specified.	Section 3.0 Ref. 3.13
Soil Washing								
King of Prussia Superfund Site, New Jersey	Full	Soil, 13,570 cy, October 1993	NA	NA	NA	$7.7 million	Includes all off-site disposal costs for the sludge cake. Cost year not specified. Components of total cost not specified.	Section 4.0 Refs. 4.5, 4.17

Table 2.3
Available Mercury Treatment Cost Data (continued)

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Georgia-Pacific Chlor-alkali Plant, Washington	Full	Sludge, 3,300 lbs/day	$1.25 million	$20,000	NA	NA	Capital cost based on treatment capacity of 2,000 to 3,000 pounds per day. Annual operating costs based on high automation of process and occasional oversight. Cost year not specified.	Section 4.0 Ref. 4.8
Harbauer Facility, State of Bavaria, Germany	Pilot	Soil, 62 tons, November 1994	$30 million	$3.2 million (Total O&M costs)	NA	NA	Costs are estimated and are for a treatment train of soil washing followed by thermal desorption. Costs are based on a 1994 conversion rate of 1.5 DM to $1.	Section 4.0 Ref. 4.13
Thermal Treatment								
Lipari Landfill, OU3, New Jersey	Full	Soil and sediment, 80,000 tons, September 1995	$430,000	$5,019,292 (Total O&M costs)	$68 per ton	$5,449,292	$632,737 of O&M costs were for response to baghouse fire, caustic consumption, and equipment modifications. These costs were not including in the unit cost. Cost year is 1995.	Section 5.0 Ref. 5.8

Table 2.3
Available Mercury Treatment Cost Data (continued)

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Site B (site name and location confidential), Western U.S.	Full	Soil, 26,000 tons, August 1995	$429,561	$2,830,956 (Total O&M costs)	$125 per ton	$3,601,377	$285,000 of O&M costs were for compliance testing and analysis, and $55,860 were for excavation and disposal. These costs were not including in the unit cost. Cost year is 1995.	Section 5.0 Ref. 5.9
Harbauer Facility, State of Bavaria, Germany	Pilot	Soil, 62 tons, November 1994	$30 million	$3.2 million (Total O&M costs)	NA	NA	Costs are estimated and are for a treatment train of soil washing followed by thermal desorption. Costs are based on a 1994 conversion rate of 1.5 DM to $1.	Section 5.0 Ref. 5.5
Vitrification								
Parsons Chemical/ETM Enterprises Superfund Site, Mchigan	Full	Soil and sediment, 3,000 cy, 1994	NA	NA	$267 per cy	$800,000	NA	Section 6.0 Ref. 6.3
Lower Fox River, Wisconsin	Pilot	Sediment, 27,000 lbs, 2001	$12 per ton	NA	NA	NA	Costs are estimated for a full-scale facility treating 600 tons of sediments per day, operating 350 days a year for 15 years. Actual costs for pilot test were not available.	Section 6.0 Ref. 6.4

Table 2.3
Available Mercury Treatment Cost Data (continued)

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Science and Technology Application Research (STAR) Center, Idaho	Pilot	Mixed waste, NA, 1998	$50,000,000 to $86,200,000	$48,000,000 to $62,000,000	NA	$124,000,000 to $184,000,000	Costs are estimated for a full-scale facility treating 23,235 cy of waste over a 5-year period. Actual costs for pilot test were not available.	Section 6.0 Ref. 6.5
Precipitation/Coprecipitation								
Marine Corps Base Camp Lejeune, North Carolina	Full	Groundwater, 41,000 lbs of contaminants removed	$4.66 Million	$1 Million	$49 per lb of contaminant removed	NA	Costs in 2000 dollars. The costs are for the entire treatment, which consists of oxidation, pH adjustment, precipitation, air stripping, and adsorption.	Section 7.0 Ref. 7.8
Squamish Remediation Site, Squamish, Canada	Full	Groundwater, 25 million gallons	NA	NA	$2 per gallon of treated ground-water	NA	The unit cost is for the reagent only. Costs in 2004 dollars.	Section 7.0 Ref. 7.6

Table 2.3
Available Mercury Treatment Cost Data (continued)

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Adsorption								
King of Prussia Superfund Site, New Jersey	Full	Groundwater, 225 gpm, December 1997	$2.03 million	$449,000 (total for performance period is $785,000)	NA	$2.816 million	Costs in 1997 dollars. The costs are for the entire treatment system (chemical precipitation followed by air stripping and granulated activated carbon). The treatment system treated multiple contaminants. Total cost is for the performance period April 1995 through December 1997.	Section 8.0 Ref. 8.1
Civil and Environmental Engineering Department, Villanova University, Pennsylvania	Pilot	Wastewater, 2,000 gallons	$7,700	$6,188	$0.107 capital and annual O&M	$69,580	Costs in 2001 dollars. Costs are projections based on the results of the pilot study. Costs were based on a design life of 10 years. Design volume is 64,980 gallons per year.	Section 8.0 Ref. 8.6
Confidential testing laboratory, Massachusetts	Pilot and Full	Wastewater, 1,800 gallons per day	$60,000	$91,980	NA	NA	Costs in 1992 dollars. Treatment is ongoing thereby affecting the capital cost per gallon. Costs for the pilot study and full-scale operation were combined in the reference.	Section 8.0 Ref. 8.7

Table 2.3
Available Mercury Treatment Cost Data (continued)

Site Name, Location	Scale	Media, Amount Treated, Date	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation/ Comments	Source
Membrane Filtration – No cost data identified								
Bioremediation – No cost data identified								

Notes:

NA   Data not provided
cy   Cubic yards
kg   Kilograms
lb   Pound
DM   Deutsch Mark
O&M Operation and maintenance

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PART II

MERCURY TREATMENT TECHNOLOGY SUMMARIES

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PART IIA

TREATMENT TECHNOLOGIES APPLICABLE TO SOIL AND WASTE

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3.0   SOLIDIFICATION AND STABILIZATION (INCLUDING AMALGAMATION)

Summary

Solidification and stabilization (S/S) is used to treat elemental mercury and mercury-contaminated soil and sludge. This technology has been implemented at full scale and pilot scale. S/S reduces the mobility of contaminants in the media by physically binding them within a stabilized mass or inducing chemical reactions. Amalgamation, the dissolution of mercury in other metals and solidification to form a non-liquid, semi-solid alloy called an amalgam, is often used for elemental mercury.

Technology Description and Principles

S/S is a process that has been used at full scale to treat mercury-contaminated soil and waste. Many pilot- and bench-scale studies also have been conducted to identify binders and reagents that are more effective than conventionally used methods such as cement. S/S involves physically binding or enclosing contaminants within a stabilized mass (solidification) or inducing chemical reactions between the stabilizing agent and the contaminants to reduce their mobility (stabilization) (Ref. 3.1). Figure 3.1 shows a model of an S/S system. Solidification is used to encapsulate or absorb the waste, forming a solid material, when free liquids other than elemental mercury are present in the waste. Waste can be encapsulated in two ways: microencapsulation and macroencapsulation. Microencapsulation is the process of mixing the waste with the encasing material before solidification occurs. Macroencapsulation refers to the process of pouring the encasing material over and around the waste mass, thus enclosing it in a solid block (Ref. 3.2).

Figure 3.1
Model of a Solidification/Stabilization System
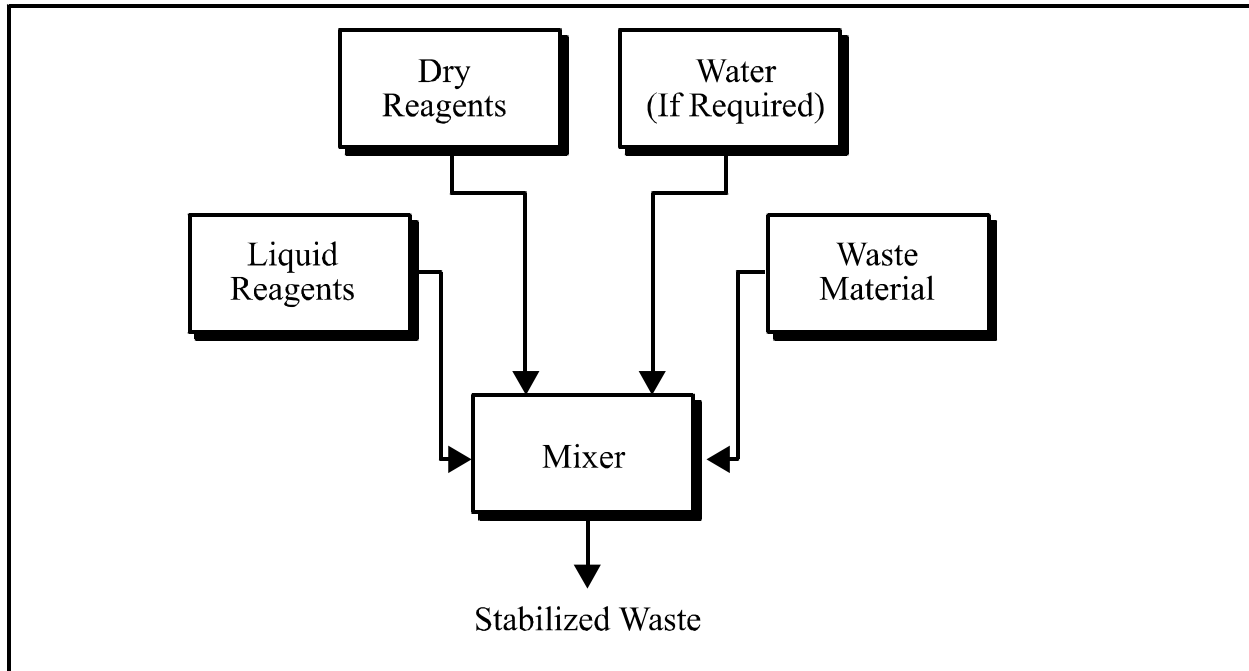
The stabilization process involves mixing soil or waste with binders such as Portland cement, sulfur polymer cement (SPC), sulfide and phosphate binders, cement kiln dust, polyester resins, or polysiloxane compounds to create a slurry, paste, or other semi-liquid state, which is allowed time to cure into a solid form. For *ex situ* S/S processes that involve polyester resins, the resin and the waste are mixed at a low rate for 5 to 10 minutes until a homogeneous mixture is formed. A catalyst is then added to this mixture to initiate a polymerization reaction and mixing continues at a high rate for another 2 to 5 minutes until a rise in temperature signals the inception of curing. This waste-resin mixture is then allowed to cool down to harden (Ref. 3.16).

EPA has identified amalgamation as the best demonstrated available technology (BDAT) for treatment of liquid elemental mercury contaminated with radioactive materials (Ref. 3.3). Amalgamation is the dissolution and solidification of mercury in other metals such as copper, nickel, zinc and tin, resulting in a solid, nonvolatile product. It is a subset of solidification technologies, and it does not involve a chemical reaction. Two generic processes are used for amalgamating mercury in wastes: aqueous and non-aqueous replacement. The aqueous process involves mixing a finely divided base metal such as zinc or copper into a wastewater that contains dissolved mercury salts; the base metal reduces mercuric and mercurous salts to elemental mercury, which dissolves in the metal to form a solid mercury-based metal alloy called amalgam. The non-aqueous process involves mixing finely divided metal powders into waste liquid mercury, forming a solidified amalgam. The aqueous replacement process is applicable to both mercury salts and elemental mercury, while the non-aqueous process is applicable only to elemental mercury (Ref. 3.4). However, mercury in the resultant amalgam is susceptible to volatilization or hydrolysis. Therefore, amalgamation is typically used in combination with an encapsulation technology (Ref. 3.5). The resulting material must be disposed and must meet LDRs.

The S/S process may also include addition of pH adjustment agents, phosphates, or sulfur reagents to reduce the setting or curing time, increase the compressive strength, or reduce the leachability of contaminants (Refs. 3.6, 3.7). Information gathered for this report included 18 projects that treated soil or waste containing mercury using S/S. Twelve projects are full-scale applications, and six are at pilot scale.

Technology Description: S/S reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. It physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms. Amalgamation is typically used to immobilize elemental mercury by dissolving the mercury in another metal to form a semisolid alloy known as an amalgam. The process is a physical immobilization and is often combined with encapsulation to prevent volatization of mercury from the amalgam.

Media Treated:
- Soil
- Sludge
- Other solids
- Liquid wastes
- Industrial waste
- Elemental (liquid) mercury

Technology Description (continued)

Binders and Reagents Used in S/S of Mercury:
- Cement
- Calcium polysulfide
- Chemically bonded phosphate ceramics (CBPC)
- Phosphate
- Platinum
- Polyester resins
- Polymer beads
- Polysiloxane compounds (silicon hydride and silicon hydroxide)
- pH adjustment agents
- Sodium dithiocarbamate
- Sodium metasilicate
- Sodium sulfide
- Sulfur polymer cement (SPC)

Binders and Reagents used in Amalgamation of Mercury:
- Copper
- Tin
- Nickel
- Zinc

Applicability, Advantages, and Limitations

S/S renders mercury more stable and less leachable. However, S/S does not reduce the total mercury content of the waste. Instead, it reduces the leachability of mercury, yielding a product that still may require disposal in a landfill. S/S often increased the volume of contaminated materials (Ref. 3.12).

The applicability of S/S depends on the mobility of mercury, which in turn depends on its oxidation state, the pH of the waste disposal environment, and the specific mercury compound contained in the waste (Ref. 3.6). This mobility is usually measured by testing the leachability of mercury under acidic conditions. Typically, the leachability of mercury increases with a decrease in pH. Therefore, acidic environments may increase the mobility of mercury in stabilized waste. Some studies also suggest that soluble compounds of mercury, such as mercurous sulfate and mercuric sulfate, may form at a higher pH (Ref. 3.2). This complex behavior of mercury in various disposal environments makes it a challenging contaminant to treat. Some S/S processes involve pretreatment of the waste with reagents such as sodium sulfide to convert mercury to a less soluble form (in this case, mercuric sulfide) before stabilization (Refs. 3.6, 3.8, 3.15). Other additives include pH buffers, catalysts such as platinum and sodium sulfide, and other proprietary chemical agents. These processes may render the waste less mobile under a variety of disposal conditions, but also may be more costly by adding more treatment steps.

Factors that Affect S/S Performance and Cost

General factors:
- **pH and redox potential:** The pH and oxidizing or reducing properties of the waste and waste disposal environment may affect the leachability of the treated material because these factors affect the solubility of mercury and its leachability (Refs. 3.2, 3.11).
- **Waste characteristics:** Certain non-mercury compounds in the waste may interact with the chemical reagents used in S/S, thus affecting the performance of the stabilization process. For example, high concentrations of chloride in the waste may render phosphate additive ineffective in stabilizing mercury (Ref. 3.10). Stabilization of dry wastes may be easier and less expensive when compared with S/S of liquid wastes (Ref. 3.13).
- **Particle size distribution:** Fine particulate matter coats the waste particles and weakens the bond between the waste and the binder (Ref. 3.18). Large aggregates in the waste could affect operation of the mixer (Ref. 3.3).
- **Mixing:** Thorough mixing is necessary to ensure that the waste particles are coated with the binder.
- **Type of binder and reagent:** The effectiveness of S/S depends in part on using the right type of binder and reagent. The use of proprietary binders or reagents may be more expensive than non-proprietary binders.
- **Moisture content:** For certain binders to be effective, the waste to be stabilized needs to have a specific moisture content. Therefore, the waste may need to be pretreated to remove the moisture (Ref. 3.2)
- **Equipment scale:** Application of S/S at large scale may reduce the unit costs when compared with a small-scale application.

Factors specific to S/S of mercury-contaminated media:
- **Oxidation state:** The specific mercury compound or oxidation state of mercury may affect the leachability of the treated material because these factors affect the solubility of mercury. In addition, the presence of more than one species of mercury may complicate the treatment process.
- **Amount of mercury in waste:** A higher concentration of mercury in waste may result in a higher concentration of mercury in the leachate.

Type, Number, and Scale of Identified Projects

S/S of soil and waste that contain mercury has been applied at the full scale and tested at the pilot and bench scales. Data sources used for this report included information about 12 full-scale and six pilot-scale applications of S/S to treat mercury. All of the full-scale applications identified at sites in the U.S. are at Superfund sites.

Summary of Performance and Cost Data

Table 3.1 summarizes information for the 12 full-scale and six pilot-scale projects. The performance of S/S treatment is usually measured by leach testing a sample of the stabilized mass. Among the full-scale projects, the media treated include soil and sludge. The amount of media treated ranged between 5,000 and 83,000 cubic yards. Site types include metal mining and smelting; landfills; chemical or radioactive products manufacturing, and wood preserving. Performance data were available for six of the 12 full-scale projects. Of the six projects, three were conducted in the United States (Projects 1, 2, and 6); the other three were conducted in Canada (Projects 3, 4, and 5). The final leachable mercury concentrations

were for 0.05 mg/L for Projects 1, 0.024 mg/L for Project 2, and 0.2 mg/L for Project 6. The final leachable mercury concentrations were 0.01 to 0.04 mg/L for Project 3, 0.05 to 0.105 mg/L for Project 4, and 0.0172 mg/L (first trial) and 0.0728 mg/L (second trial) for Project 6. The regulatory standard in Canada specifies a treatment goal of 0.2 mg/L mercury TCLP before it can be disposed in a nonhazardous landfill. All three projects met the standard.

Performance data were available for all of the pilot-scale projects. The media treated in the projects include soil, sludge, ion exchange resin waste, mine tailings, and elemental mercury. The quantity of media treated ranged from 0.45 kilograms to 330 kilograms. Various types of binders and stabilizing agents were used, including Portland cement, sodium dithiocarbamate, sodium metasilicate, and proprietary stabilizing agents. Performance data show that the final concentration of mercury in the leachate was reduced to below 0.025 mg/L for all six projects. The data sources used for this report did not contain any information about the long-term stability of mercury-containing soil and waste treated using S/S.

Table 3.2 provides cost data for three projects, two full scale and one pilot scale.

Case Study: Allied Technology Group Mercury Stabilization Process

The S/S process was applied at the pilot scale on soils excavated from a Brookhaven National Laboratory (BNL) facility (Ref. 3.9). These soils contained approximately 4,000 mg/kg of mercury. The initial concentration of mercury in the TCLP leachate was 0.282 mg/L. The soil was split into two parts, and each part was treated with a different stabilizing agent in a 7 cubic foot Essick mortar mixer. One portion of the soil was treated with sodium dithiocarbamate (DTC), which reduced the mercury levels in soil to 0.0139 mg/L (TCLP). The other portion of soil was treated with a liquid sulfide formulation, which resulted in a final concentration of 0.002 mg/L of mercury in the TCLP leachate (Project 13, Table 3.1). Both DTC and liquid sulfide additive reduced mercury to below the regulatory limit (less than 0.025 mg/L in TCLP leachate). A total of 200 kilograms of contaminated soil was treated by the end of this project, in November 2000.

Case Study: Brookhaven Chemical Holes

BNL conducted pilot-scale studies to demonstrate treatment of liquid elemental mercury and soils contaminated with mercury using S/S (Ref. 3.3). The treatment process, known as Sulfur Polymer Stabilization/Solidification (SPSS), involved use of SPC as the binding agent. The mercury-contaminated soil was mixed along with the binding and stabilizing agents in a 1 cubic foot pilot-scale vertical cone blender/dryer. SPC was added to the blender first in order to "lubricate" the walls of the mixer, followed by the soil, and another layer of SPC. The soil/SPC mixture was mixed for approximately 3 hours at 40±5 °C. The temperature of the cone blender was then increased to 100 °C to reduce moisture in the soil. After the soil had dried, SPC chips were added to the blender, and the temperature was increased to 135±5 °C to melt the SPC and encapsulate the chemically stabilized mercury waste.

Case Study: Brookhaven Chemical Holes (continued)

There was a slight variation in the treatment process for elemental mercury. First, SPC was added to the blender, followed by liquid mercury in small fractions. This mixture was mixed for approximately 4 hours until the color of the powder changed from bright yellow to dark grey or black, indicating that mercuric sulfide had formed. The vessel temperature was raised to the melting point of SPC (135±5 °C) to encapsulate the mercury. Off-gas generated in this process was passed through an off-gas treatment unit composed of a heat exchanger, a liquid nitrogen cryogenic trap, and an activated carbon filter, before it was vented to the atmosphere. Initial concentrations of leachable mercury in soil ranged from 0.2 to 0.91 mg/L. The concentrations of leachable mercury in the stabilized soil ranged from 0.0005 to 0.016 mg/L (Project 17, Table 3.1). Initial concentrations of leachable mercury were not available for the samples of liquid elementary mercury. Final leachable concentrations for the SPSS-treated elemental mercury ranged from less than 0.0004 to 0.004 mg/L (Project 18, Table 3.1). A total of 330 kilograms of contaminated soil and approximately 62 kilograms of elemental mercury were treated during this project.

Table 3.1
Solidification/Stabilization Treatment Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Final Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Binder or Stabilization Process	Source
1	Metal Mining and Smelting	Soil (*ex situ*); 30,000 cy	Full	Bunker Hill Mining and Metallurgical Complex, Smelterville, Idaho; 1997	0.2 - 65 mg/L [TCLP]	0.05 - 0.1 mg/L [TCLP]	Proprietary stabilizing agents.	3.19
2	Chemical and Allied Products Manufacturing	Soil, 26,000 cy	Full	Rocky Mountain Arsenal, Colorado	965 µg/L [TCLP] 4,300 mg/kg [TWA]	0.024 mg/L [TCLP] 430 - 1,075 mg/kg [TWA]	6% cement slurry	3.21
3	Former Chlor-Alkali Manufacturing Plant	Soil, 7,410 kg (approx. 6.4 cy assuming a soil density of 1.5 g/cm^3) (average of two full-scale trials)	Full	Site name unknown, British Columbia Province, Canada	245 µg/L (average of two full-scale trials)	0.01 - 0.04 mg/L [TCLP] (combined range for two full-scale trials)	Ferric sludge (generated from precipitation process with ferric chloride) - a mixed waste solid consisting of water, humic substances, ferric hydroxides, and small amounts of other metals.	3.22
4	Former Chlor-Alkali Manufacturing Plant	Concrete fines (from demolition of a chlor-alkali plant)	Full	Site name unknown, British Columbia Province, Canada	168 µg/L [TCLP]	0.05 - 0.105 mg/L [TCLP]	Ferric sludge (generated from precipitation process with ferric chloride) - a mixed waste solid consisting of water, humic substances, ferric hydroxides, and small amounts of other metals.	3.22

Table 3.1
Solidification/Stabilization Treatment Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Final Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Binder or Stabilization Process	Source
5	Former Chlor-Alkali Manufacturing Plant	Brine purification sludge, 3,600 kg (approx 3.12 cy assuming a soil density of 1.5 g/cm^3) (first full-scale trial); 1,800 kg (approx. 1.56 cy assuming a soil density of 1.5 g/cm^3) (second full-scale trial)	Full	Site name unknown, British Columbia Province, Canada	188 µg/L [TCLP] (first full-scale trial) 252 µg/L [TCLP] (second full-scale trial)	0.0172 mg/L [TCLP] (first trial, after 7 days of treatment) 0.0728 mg/L [TCLP] (second trial, after 8 days of treatment)	Ferric-lignin derivatives and Portland cement.	3.23
6	Industrial and Municipal Landfills	Soil (*ex situ*)	Full	Cleve Reber, Sorrento, Louisiana; October 1995	N/A	0.2 mg/L [TCLP]	pH control	3.19
7	Industrial Landfill	Soil (*ex situ*), 17,140 cy	Full	Auto Ion Chemicals, Michigan	N/A	N/A	N/A	3.19
8	Industrial Landfill	Sludge, 82,100 cy	Full	Davie Landfill, Florida	N/A	N/A	Cement	3.19
9	Transportation	Soil, 20,000 cy; Sludge, 21,347 cy	Full	Gulf Coast Vacuum Services, Louisiana	N/A	N/A	N/A	3.19
10	Industrial Landfill	Soil	Full	Naval Surface Warfare Center, Dahlgren, Site 9 (1400 Area Landfill), Virginia	N/A	N/A	N/A	3.19
11	Radioactive Products Manufacturing	Soil, 4,667 cy	Full	Savannah River (USDOE), OU 16, South Carolina	N/A	N/A	N/A	3.19
12	Lumber and Wood Products Manufacturing/ Wood Preserving	Soil	Full	Wyckoff/Eagle Harbor, Washington	N/A	N/A	Portland cement (Type II)	3.19

Table 3.1
Solidification/Stabilization Treatment Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Final Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]	Binder or Stabilization Process	Source
13	Research Laboratory	Soil; 200 kg	Pilot	BNL, New York; November 2000	0.282 mg/L [TCLP]	NaDTC: 0.0139 mg/L [TCLP] Sulfide: 0.002 mg/L [TCLP]	Portland cement with NaDTC or liquid sulfide.	3.9
14	DOE Facility	Liquid waste (ion exchange resin waste); 99 kg	Pilot	DOE Facility, Portsmouth, Ohio	1,060 mg/L [TCLP]	0.0012 - 0.0169 mg/L [TCLP]	DTC with polymer beads for absorption.	3.13
15	Research Laboratory	Sludge from LANL; 0.45 kg	Pilot	LANL, New Mexico; September 1998	0.125 mg/L [TCLP]	0.0012 - 0.0169 mg/L [TCLP]	Cement with sodium metasilicate.	3.15
16	Metal Mining (Gold Mine)	Mine tailings; 10.35 kg	Pilot	Newmont Mining Corporation, Yanacocha, Peru	N/A	0.009 - 0.039 mg/L [TCLP]	SPC with sodium sulfide as catalyst.	3.16
17	Research Laboratory	Soil; 330 kg	Pilot	BNL - Chemical Holes, New York	0.20 - 0.91 mg/L [TCLP] 4,190 - 5,570 mg/kg [TWA]	0.0005 - 0.016 mg/L [TCLP]	SPC with proprietary stabilizing agent.	3.5
18	Research Laboratory	Elemental mercury; 62 kg	Pilot	BNL - Chemical Holes, New York	N/A	<0.0004 - 0.004 mg/L [TCLP]	SPC with proprietary stabilizing agent.	3.5

Note:
BNL: Brookhaven National Laboratory
cy: cubic yards
DTC: Dithiocarbamate
kg: Kilograms
LANL: Las Alamos National Laboratory
mg/kg: Milligrams per kilogram
mg/L: Milligrams per liter
µg/L: Micrograms per liter
N/A: Not Available
NaDTC: Sodium dithiocarbamate
SPC: Sulfur polymer cement
TCLP: Toxicity Characteristic Leaching Procedure
TWA: Total Waste Analysis

Table 3.2
Available Mercury Treatment Cost Data**

Site	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation	Source	Project Number in Table 3.1
Bunker Hill Mining and Metallurgical Complex, Idaho	Full	30,000 cy	N/A	N/A	N/A	$230,000	Cost year not specified. Components of total cost not specified.	3.19	1
Rocky Mountain Arsenal, Colorado	Full	26,000 cy	$2.8 million	Not applicable	N/A	$2.8 million	The implementation cost is $2.8 million and there were no direct associated O&M costs. Cost year not specified. Components of total cost not specified.	3.21	2
DOE Facility, Portsmouth, Ohio	Pilot	99 kg	$30,000	N/A	N/A	N/A	Includes disposal costs.	3.13	14

** All costs provided are estimated costs. Cost year is not available for any of the data provided.
Cy: Cubic yards
lb: Pound
kg: Kilogram
N/A: Not available
O&M: Operation and maintenance

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4.0   SOIL WASHING AND ACID EXTRACTION

Summary

Soil washing and acid extraction are used for *ex situ* treatment of mercury-contaminated soil and sediment. These technologies have been implemented at the full scale and pilot scale. In soil washing, the contaminants are preferentially adsorbed onto the fines fraction of the soil or sediment. The separated fines must be further treated to remove or immobilize the contaminant. In acid extraction, the process depends on the solubility of the contaminants in the acidic extraction solution. Spent extraction solution may require further treatment.

Technology Description and Principles

Soil washing is a water-based process that uses a combination of physical particle size separation and aqueous-based chemical separation to reduce contaminant concentrations in soil (Refs. 4.7, 4.12). This process is based on the concept that most contaminants tend to bind to the finer soil particles (clay and silt) rather than the larger particles (sand and gravel). Physical methods can be used to separate the relatively clean larger particles from the finer particles because the finer particles are attached to larger particles through physical processes (compaction and adhesion). This process thus concentrates the contamination bound to the finer particles for further treatment (Ref. 4.7).

Figure 4.1
Model of a Soil Washing System (Ref. 4.7)
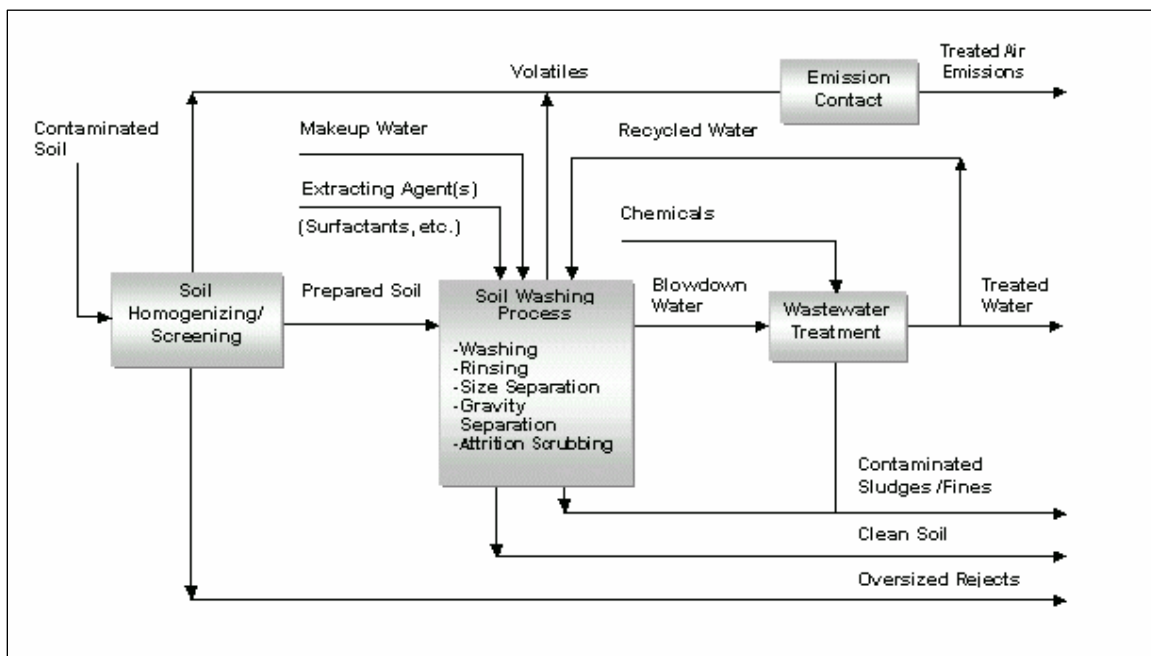
Soil is first screened to remove oversized particles and then homogenized. The soil is then mixed with a wash solution of water or water enhanced with chemical additives such as leaching agents, surfactants, acids, or chelating agents to help remove organic compounds and heavy metals. Particles are separated by size (cyclone or gravity separation, depending on the type of contaminants in the soil and the particle size), concentrating the contaminants with the fines. The resulting concentrated fines or sludge usually require further treatment because the soil washing process removes and concentrates the contaminants but

does not destroy them. The coarser-grained soil is generally relatively "clean," requiring no additional treatment. Wash water from the process is treated and either reused in the process or disposed (Ref. 4.7). Commonly used methods for treating the wastewater include ion exchange and solvent extraction (Ref. 4.14)

Two of the projects in Table 4.1 use the BioGenesis Sediment Decontamination Technology. This technology is designed to decontaminate fine-grained material contaminated with heavy metals, including mercury (Refs. 4.2 and 4.18). The dredged material is first screened to remove oversized debris and then is pre-treated using high-pressure water and proprietary biodegradable surfactants, specialty chemicals, and chelators (Refs. 4.2 and 4.4). In this step, the solid particles physically separate from each other, and naturally occurring organic material breaks up. After pre-treatment, an aeration step introduces air into a chamber of contaminated material, and the resulting floatable organic material and free-phase organic contaminants are then skimmed off the top of the chamber.

A second washing step uses collision impact forces to strip the sorbed contaminants and complex organic coatings from the solid particles (Ref. 4.2). The slurry of solids and stripped organics is then treated in an oxidation and cavitation unit to destroy the organic constituents. Oxidants used include hydrogen peroxide and sodium percarbonate. Then a liquid/solid separation step mechanically removes the decontaminated particles from the liquid phase. The resulting cake, containing cleaned sand, silt, and clay, is mixed with amendments to create beneficial soil products such as topsoil. The contaminated liquid is treated to precipitate metals and remove other contaminants and then is reused in the process (Refs. 4.2, 4.4). This process was used in a pilot application to treat contaminated sediment from the New York/New Jersey harbor. (See case study and Project 3 in Table 4.1.)

Acid extraction is an *ex situ* technology that uses an extracting chemical such as hydrochloric acid or sulfuric acid to extract contaminants from a solid matrix by dissolving them in the acid (Ref. 4.6). It is also known as chemical leaching. Contaminated material is first screened to remove coarse solids. Then acid is introduced into the extraction unit. The characteristics of the treated material, contaminant type, and contaminant concentration determine the residence time in the extraction unit, which usually varies from 10 to 40 minutes (Ref. 4.6). The solid and liquid phases are then separated using hydroclones, and the solids are transferred to a rinse system, where they are rinsed with water to remove entrained acid and contaminants. They are then dewatered and mixed with lime and fertilizer to neutralize any residual acid (Ref. 4.6). The acid extraction fluid and rinse waters are mixed with commercially available precipitants, such as sodium hydroxide, lime, or other proprietary formulations, and a flocculant to remove the heavy metals (Ref. 4.6). The precipitated solids may require additional treatment or may be disposed in a landfill if they meet a TCLP mercury level of less than 0.025 mg/L (Ref. 4.10). Elemental mercury can be recovered from the residual liquid from the precipitation step (Ref. 4.10).

Two of the projects in Table 4.1 employed the REMERC process, a patented acid extraction process that includes a low-temperature extraction technique for recovering mercury and other heavy metals from industrial wastes and contaminated soils (Refs. 4.10, 4.11). This process has been used to treat caustic wastewater sludge that contains mercury from chlor-alkali plants, designated as hazardous waste classification K106 by EPA (Ref. 4.8). The K106 waste consists of mercuric and mercurous chlorides, mercuric sulfide, elemental mercury, and species of mercury absorbed on activated carbon (Ref. 4.10). REMERC can be operated in both batch and continuous modes. This process involves leaching in two stages (at pH 2 and 6), with each leaching step followed by a simultaneous washing and thickening step using a patented thickener (Ref. 4.11). Chlor-alkali plant waste products such as sodium hypochlorite, spent drying sulfuric acid, and depleted waste brine are used as additives to the leaching solution. The mercury-containing solution then flows to a reactor, where triple-distilled quality elemental mercury is recovered using aqueous-phase electrolysis or cementation on iron (Refs. 4.8 and 4.11). This process was used in three projects (Projects 2, 6, and 7) described in Table 4.1.

Technology Description: Soil washing is an *ex situ* technology that takes advantage of the behavior of some contaminants to preferentially adsorb onto the fines fraction. The contaminated soil is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentration in the remaining soil. The contaminated water generated from soil washing is treated with a technology suitable for the contaminants.

Acid extraction is an *ex situ* technology that uses an extracting chemical such as hydrochloric acid or sulfuric acid to extract contaminants from a solid matrix by dissolving them in the acid. The metal contaminants are recovered from the acid leaching solution using techniques such as aqueous-phase electrolysis.

Media Treated:
- Soil (*ex situ*)
- Sediment (*ex situ*)

Agents Used in Soil Washing and Acid Extraction:
- Leaching agents
- Surfactants
- Acids – Hydrochloric acid, sulfuric acid
- Chelating agents
- Sodium chloride

Applicability, Advantages, and Limitations

Soil washing is suitable for use on soils contaminated with semivolatile organic compounds (SVOCs), fuels, pesticides, and some VOCs (Refs. 4.7, 4.12). Soil washing has been used to treat soils contaminated with heavy metals, including mercury. The technology can also be used to recover metals (Ref. 4.7). This technology is best suited to treat contaminated soil composed primarily of larger-grained particles such as sand and gravel, rather than fine-grained particles such as clay and silt (Ref. 4.15). It is also best suited to treat contaminants that preferentially adsorb onto the fines fraction (Ref. 4.14).

An advantage of soil washing is that it can be used to reduce the volume of material that will require further treatment, which potentially lowers the cost of cleanup and disposal of the contaminated material. Soil washing may not be cost-effective for small quantities of contaminated material (Ref. 4.15). Soil washing is usually performed at the site of the contamination, avoiding the risks associated with transporting the contaminated soil off-site to a treatment facility. Chemicals are seldom released from the soil washing process to the air. When the procedure is properly designed and operated, soil washing is relatively safe (Ref. 4.15).

Soil washing is effective on homogenous, relatively simple contaminant mixtures (Ref. 4.14). Its applicability and effectiveness may be limited for complex waste mixtures (such as metals mixed with organic compounds) that make it difficult to formulate the appropriate washing solution. Soils with high humic content may require pre-treatment to prevent interference with contaminant desorption. This process may also have difficulty treating soils with a high (more than 40 percent) silt and clay fraction (Refs. 4.7, 4.12).

Acid extraction is suitable for use on sediments, sludges, soils, and solid wastes contaminated with heavy metals, including mercury (Ref. 4.6). The principal advantage of acid extraction is that hazardous contaminants are separated from soils and sediments, thereby reducing the volume of hazardous waste to be treated (Ref. 4.6).

The effectiveness of acid extraction may be limited in soils with higher clay content, which may reduce the extraction efficiency and require longer contact time (Ref. 4.6). Certain health and safety issues should be considered in using acid extraction, such as emissions from extracting agents (for example, surfactants and concentrated acids) or the corrosivity of strong acids. Exposure to the extracting agents and to the wastewater treatment chemicals may be controlled if the chemicals are added to the system under closed or properly ventilated conditions. Additional respiratory protection (for example, an air-purifying respirator with organic vapor cartridges) may also be used to control inhalation exposures (Ref. 4.6).

Factors Affecting Soil Washing and Acid Extraction Performance and Cost

- **Soil homogeneity:** Soils that vary widely and frequently in characteristics such as soil type, contaminant type and concentration, and where blending for homogeneity is not feasible, may not be suitable for soil washing (Ref. 4.12).
- **Soil type and soil particle size distribution:** A larger amount of treatment residual may require disposal for soils with a high proportion of fines (Ref. 4.14). Soils with high clay content, cation exchange capacity, or humic acid content tend to interfere with contaminant desorption and limit the effectiveness of soil washing and acid extraction (Refs. 4.6, 4.12). Carbonaceous soils tend to neutralize extracting acids and interfere with the acid extraction process (Ref. 4.12).
- **Total Organic Carbon:** Total organic carbon (TOC) affects the desorption of contaminants from the contaminated material and therefore the efficiency of the soil washing process (Ref. 4.20).
- **pH:** pH affects the operation of the soil washing process since the contaminants are extracted from a matrix at specified pH ranges on the basis of the solubility of the contaminant at a particular pH (Ref. 4.20).
- **Multiple contaminants:** Complex, heterogeneous contaminant compositions can make it difficult to formulate a simple washing solution, requiring use of multiple, sequential washing processes to remove contaminants (Ref. 4.12).
- **Moisture content:** The moisture content of the soil may make it more difficult to handle. Moisture content may be controlled by covering the excavation, storage, and treatment areas to reduce the amount of moisture in the soil (Ref. 4.14).
- **Temperature:** Cold temperature can freeze the washing solution and can affect leaching rates (Ref. 4.14).

Type, Number, and Scale of Identified Projects

A total of eight projects were found. Of these eight, five were identified where soil washing was used to treat organic mercury. Of these, one project was conducted at full scale at a Superfund site. Four projects were conducted at pilot scale. Three projects were identified where acid extraction was used to treat inorganic and elemental mercury. Of these, one was conducted at full scale, while two were performed at the pilot scale.

Summary of Performance and Cost Data

Table 4.1 summarizes information for the two full-scale and six pilot-scale projects. The performance of a soil washing or acid extraction treatment is typically measured by leach testing a sample of the treated residue.

The two full-scale projects that used soil washing and acid extraction for treatment of mercury included a waste processing facility and a chlor-alkali plant. The full-scale soil washing project treated 13,570 cubic yards of contaminated soil, with the final concentration of inorganic mercury reduced from 100 mg/kg to 1 mg/kg, a reduction of 99 percent. This project is described in the case study and on Table 4.1 (Project 1). The full-scale project using acid extraction treated up to 3,300 pounds of sludge per day. Performance data indicated a reduction in the concentration of mercury from 60,000 mg/L to 150 mg/L in K106 wastewater sludge, and a TCLP value of less than 0.025 mg/L. This project is described in Table 4.1 (Project 2).

Among the six pilot-scale projects, four used soil washing and two used acid extraction. The first pilot-scale soil washing project treated 700 cubic yards of contaminated sediment from the New York/New Jersey harbor, with the final concentrations of inorganic mercury reduced from 3.1 mg/kg to 0.3 mg/kg (Refs. 4.2 and 4.4). This project is described in the case study and on Table 4.1 (Project 3). The second pilot-scale soil washing project treated 800 liters of homogenized sediment from the Kai Tak Approach Channel in Hong Kong (Table 4.1, Project 4). Performance data indicate a reduction in concentrations of inorganic mercury from 0.73 mg/kg to nearly 0.08 mg/kg (Ref. 4.3). Soil washing was also used at the pilot scale to treat mercury-contaminated soil at a facility in Germany (Table 4.1, Project 5), where inorganic mercury was reduced from 875 mg/kg and a TCLP of 0.082 mg/L to a final concentration of less than 20 mg/kg and a TCLP of 0.006 mg/L. The BioGenesis Sediment Decontamination Technology was used at a pilot scale (See Table 4.1, Project 8) and reduced mercury concentrations from 9.5 mg/kg to 1.49 mg/kg.

The two pilot-scale acid extraction projects were conducted at chlor-alkali plants, and both used the patented REMERC process described previously to treat K106 wastewater sludge. Before treatment, concentration of mercury in the wastewater sludge ranged from 55,000 mg/kg to 110,000 mg/kg. Performance data for both projects indicated nearly 99 percent reduction in the concentration of mercury and a TCLP of less than 0.025 mg/L for the treated material. These projects are described in Table 4.1 (Projects 6 and 7).

Case Study: Soil Washing of Mercury-Contaminated Soil at King of Prussia Superfund Site

The King of Prussia Superfund Site in Winslow Township, New Jersey, is a former waste processing and recycling facility. Soils were contaminated with arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc from improperly disposed wastes (Table 4.1, Project 1). Approximately 13,570 cubic yards of mercury-contaminated soil, sludge, and sediment was treated using soil washing in 1993. This project was EPA's first full-scale application of soil washing to remediate a Superfund site. The system consisted of a series of hydroclones, conditioners, and froth floatation cells. Soil washing additives included a polymer and a surfactant. The treatment reduced concentrations of inorganic mercury from 100 mg/kg to the cleanup goal of 1 mg/kg, a reduction of 99 percent. Residual sludges were disposed off site as nonhazardous waste, and the treated soil was used as backfill at the site.

Case Study: Soil Washing of Sediment from the New York/New Jersey Harbor

Sediments and soils around the New York/New Jersey harbor have been contaminated by various industrial activities from colonial times to the present (Ref. 4.9). Because of the shallow natural depth, the harbor must be periodically dredged to maintain safe passage for vessels, generating millions of cubic yards of contaminated sediment annually that require some form of decontamination for disposal (Ref. 4.1). The harbor sediment is contaminated with polycyclic aromatic hydrocarbons (PAHs), pesticides, dioxins and furans, and heavy metals, including mercury. The sediment in the New York/New Jersey harbor contains 52 percent silt, 42 percent clay, 4 percent sand, and a small fraction of larger grained particles. The total organic content ranges from 3 to 10 percent (Refs. 4.2, 4.9).

The pilot demonstration was conducted from November 1998 to March 1999 and treated 700 cubic yards of a representative sample of dredged material from near a petroleum facility (Table 4.1, Project 3) (Ref. 4.2). The project evaluated the effectiveness of the BioGenesis Sediment Washing Technology, which is designed to decontaminate fine-grained sediment material (Ref. 4.2). Concentrations of inorganic mercury in this sample were found to be about 3.1 mg/kg, which is within the typical range of mercury in New York/New Jersey harbor sediment of 0.2-13.6 mg/kg (Ref. 4.2). This process resulted in a 92 percent removal of mercury, to a final concentration of 0.3 mg/kg. This concentration was below the mercury cleanup criteria of 14 mg/kg (New Jersey Residential Direct Contact Soil Cleanup Criteria) (Refs. 4.2 and 4.4).

Table 4.1
Soil Washing and Acid Extraction Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media (Quantity)	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Final Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Soil Washing or Acid Extraction Process	Source
1	Waste processing facility	Soil (13,570 cy)	Full	King of Prussia Superfund Site, Winslow Township, New Jersey; October 1993	100 mg/kg	1 mg/kg	Soil washing consisting of screening, separation, and froth floatation.	4.5, 4.17
2	Chlor-alkali plant	K106 Waste water sludge (3,300 lbs/day)	Full	Georgia-Pacific Chlor-alkali plant, Bellingham, Washington	60,000 mg/kg	150 mg/kg; <0.025 mg/L [TCLP]	Acid Extraction (REMERC Process) involving leaching with 5 to 27 percent sodium chloride at pH 6, followed by solid/liquid separation and solids washing, followed by a second leaching with 5 to 27 percent sodium chloride at pH 2, followed by a second solid/liquid separation and solids washing and finally mercury recovery on liquid residual using cementation on iron; operated continuously.	4.8, 4.10, 4.11
3	Petroleum facility	Sediment (700 cy)	Pilot	New York/ New Jersey Harbor Sediment Treatment; March 1999	3.1 mg/kg	0.3 mg/kg	Biogenesis Sediment Decontamination Technology. Soil washing consisting of pre-processing, aeration, sediment washing, and cavitation and oxidation.	4.2, 4.4

Table 4.1
Soil Washing and Acid Extraction Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media (Quantity)	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Final Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Soil Washing or Acid Extraction Process	Source
4	N/A	Homogenized sediment (800 liters)	Pilot	Kai Tak Approach Channel, Hong Kong	0.73 mg/kg	0.08 to 0.25 mg/kg	Soil washing consisting of pre-processing, aeration and sediment washing using chelating agents and surfactants.	4.3
5	N/A	Soil (62 tons)	Pilot	Harbauer Facility, State of Bavaria, Germany; November 1994	875 mg/kg; 0.082 mg/L [TCLP]	<20 mg/kg; 0.006 mg/L [TCLP]	Treatment train consisting of soil washing followed by vacuum-distillation process to treat fines.	4.13
6	Chlor-alkali plant	K106 Waste water sludge (volume unknown)	Pilot	BF Goodrich, Calvert City, Kentucky	110,000 mg/kg	220 mg/kg; <0.025 mg/L [TCLP]	Acid Extraction (REMERC Process) involving leaching with 5 to 27 percent sodium chloride at pH 6, followed by solid/liquid separation and solids washing, followed by a second leaching with 5 to 27 percent sodium chloride at pH 2, followed by a second solid/liquid separation and solids washing and finally mercury recovery on liquid residual using mercury recovery aqueous phase electrolysis; operated in batch treatment mode.	4.8, 4.11

Table 4.1
Soil Washing and Acid Extraction Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media (Quantity)	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Final Mercury Concentration (mg/kg) and/or Leachability (mg/L) [Test Method]	Soil Washing or Acid Extraction Process	Source
7	Chlor-alkali plant	K106 Waste water sludge (volume unknown)	Pilot	Pioneer Chlor-Alkali, St. Gabriel, Louisiana	55,000 mg/kg	50 mg/kg; <0.025 mg/L [TCLP]	Acid Extraction (REMERC Process) involving leaching with 5-27 percent sodium chloride at pH 6, followed by solid/liquid separation and solids washing, followed by a second leaching with 5-27 percent sodium chloride at pH 2, followed by a second solid/liquid separation and solids washing and finally mercury recovery on liquid residual using cementation on iron; operated continuously.	4.8, 4.11
8	Chemical Industry contamination of Shipping Canals	Sediment (330 m^3)	Pilot	Venice Port Authority, Venice, Italy,	9.5 mg/kg	1.49 mg/kg	Biogenesis Sediment Decontamination Technology	

Note:
cy: cubic yards
lbs: pounds
mg/L: milligrams per liter
mg/kg: milligrams per kilogram
N/A: Not Available
TCLP: Toxicity Characteristic Leaching Procedure

Table 4.2
Available Mercury Treatment Cost Data for Soil Washing and Acid Extraction

Site	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Total Cost	Cost Explanation	Source	Project Number in Table 4.1
King of Prussia Superfund Site, Winslow Township, New Jersey	Full	13,570 cy	N/A	N/A	$7.7 million	Includes all off-site disposal costs for the sludge cake. Cost year not specified. Components of total cost not specified.	4.5, 4.17	1
Georgia-Pacific Chlor-alkali plant, Bellingham, Washington	Full	3,300 lbs/day	$1.25 million	$20,000	N/A	Capital cost based on treatment capacity of 2,000 to 3,000 lbs/day; Annual operating costs based on high automation of process and occasional oversight. Cost year is not available for any of the data provided.	4.8	2
Harbauer Facility, State of Bavaria, Germany**	Pilot	Soil, 62 tons, Nor 1994	$30 million	$3.2 million	N/A	Costs are estimated and are for a treatment train of soil washing followed by thermal desorption. Costs are based on a 1994 conversion rate of 1.5 DM to $1.	4.13	5

** All costs and amounts treated are estimated.
cy: Cubic yards
lb: Pound
kg: Kilogram
DM: Deutsch Mark
N/A: Not available
O& M: Operation and maintenance

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5.0   THERMAL TREATMENT

Summary

Thermal desorption and retorting are two common *ex situ* methods of thermal treatment for mercury. These technologies have been used to treat mercury-contaminated soil, sediments, and wastes at full scale. Thermal treatment usually involves application of heat and reduced pressure to volatilize mercury from the contaminated medium, followed by conversion of the mercury vapors into liquid elemental mercury by condensation. The liquid elemental mercury collected from the condenser units can be reused or further treated, typically by amalgamation, for disposal. Off-gasses also may require further treatment. Thermal treatment is also used at mercury recycling facilities to treat wastes that contain mercury.

Technology Description and Principles

Thermal treatment has been used at the full scale to treat mercury-contaminated soil and waste. It uses heat to volatilize mercury from the contaminated medium. Thermal treatment processes commonly used to treat mercury-contaminated wastes are thermal desorption and retorting or roasting (Refs. 5.1, 5.2, 5.3).

The main components of a thermal desorption system are a pre-treatment and material handling unit, a desorption unit, and a post-treatment unit for treatment of off-gas and processed medium (soil or waste). Pre-treatment of contaminated media involves removing extraneous matter such as plastic or rubber and dewatering to achieve suitable moisture content (Refs. 5.1, 5.2). The pre-treated waste is then placed in the thermal desorber, where it is heated to volatilize mercury in the waste. Types of thermal desorbers include direct-fired rotary kilns and indirectly heated screw or auger systems. The motion of the rotary drum or auger agitates the waste, promoting mixing and more uniform heating. A typical thermal desorption unit for mercury removal operates at temperatures ranging from 320 to 700 °C (600 to 1,300 °F) (Refs. 5.2, 5.3, 5.5, and 5.10).

The boiling point of elemental mercury at 1 atmosphere pressure is 350°C (662°F), which renders it suitable for removal by thermal processes (Refs. 5.3, 5.4). The high temperatures used in thermal desorption units convert mercury into the gaseous or vapor phase, which is collected and further treated, removing mercury from the contaminated medium.

Off-gas generated by the desorption unit is passed through wet scrubbers or fabric filters to remove particulate matter. The off-gas stream free from particulates is then condensed to collect liquid elemental mercury. The remaining off-gas vapors generated in the process are passed through additional APC devices such as sulfur-impregnated carbon to capture any residual mercury. Mercury reacts with sulfur in the activated carbon to form a more stable compound, mercuric sulfide. Organic contaminants in the off-gas are treated in a secondary combustion chamber or a catalytic oxidizer and then released into the atmosphere (Refs. 5.2, 5.3, and 5.4). Any APC should undergo periodic performance testing to ensure that mercury is not leaking.

A retorting or roasting process is similar to thermal desorption except that it does not involve agitation (Ref. 5.4). The main components of a mercury retort system include a retort oven, condensers, a mercury trap, a sulfonated carbon adsorber, and a vacuum pump. Mercury-contaminated material is placed in pans that are stacked in the retort oven. Retorts can be heated either electrically or with fuel burners. In electric retorts, the heating elements are in direct contact with the contaminated medium, while in fuel-fired retorts the burner heats the air surrounding the retort (Ref. 5.3). The retort chamber typically operates at temperatures of 425 to 540°C (797 to 1004°F) under a vacuum to facilitate volatilization of

mercury. The resulting off-gas is passed through condensers to collect liquid elemental mercury. The off-gas is then passed through sulfur-impregnated carbon to capture any residual mercury (Ref. 5.3). Figure 5.1 presents the flow diagram of a thermal treatment system.

Figure 5.1
Model of a Thermal Desorption or Retort System
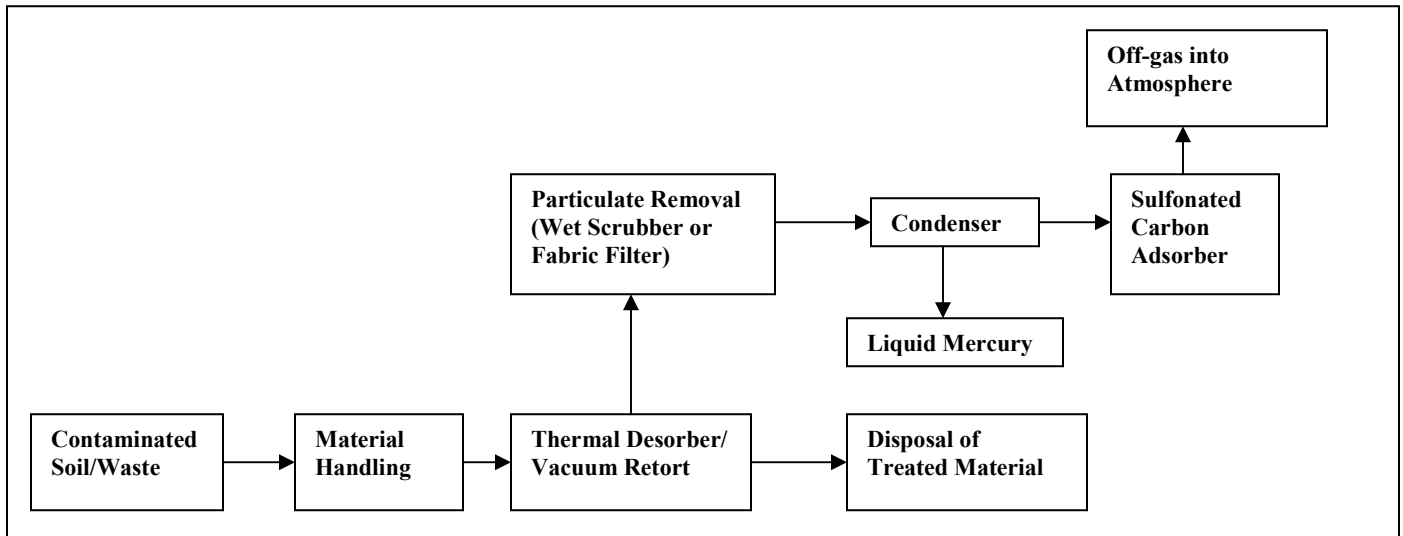
Technology Description: Thermal treatment processes are physical methods to remove mercury from the contaminated medium. Heat is supplied under reduced pressure to the contaminated soil or waste, volatilizing mercury. The off-gas is treated by condensation to generate liquid elemental mercury. The treated medium may be used as fill material or disposed.

Media Treated:
- Soil
- Sludge
- Sediment
- Other solids

Types of Thermal Treatment Systems:
- Rotary kiln – combustion
- Heated screw or auger – hot oil or steam
- Retort – conductive electrical heating or fuel-fired

Applicability, Advantages, and Limitations

Thermal desorption and retorts are used to treat soil and wastes that contain mercury. Thermal desorption treatment systems are more commonly used to treat volatile and semivolatile organic contaminants such as polychlorinated biphenyls (PCBs), PAHs, and pesticides. Because of the high volatility of mercury, they are also applicable in treatment of mercury-contaminated waste (Ref. 5.4). Thermal desorption and retorting are both usually performed at reduced pressures to lower the boiling point of mercury, in turn allowing the unit to be operated at a lower temperature, which reduces energy costs. Operating under a

vacuum also reduces emissions of process gases. In some cases, the treated soil can be used as fill material (Ref. 5.4). In the presence of high concentrations of mercury, the treated wastes may be passed through the system more than once or the residence times may be increased to achieve treatment goals for mercury (Ref. 5.4). APC devices must be used to control emissions of mercury vapors. The vapor density of mercury is seven times higher than of air; therefore, mercury vapors in an air environment tend to settle rather than rise. Because of this property of the metal, the gas outlet and the fugitive emission collection points should be located at the bottom of the thermal desorption or retort chamber. The presence of large quantities of organic materials in a mercury retort system that contain small amounts of oxygen may result in pyrolysis, which can create combustible off-gasses that present an explosion hazard (Ref. 5.3). The presence of larger particles in the contaminated medium may impair heat transfer between the heating elements or the combustion gas and the medium. Conversely, smaller particles may increase the particulate content in the off gas (Ref. 5.6).

Factors Affecting Thermal Treatment Performance and Cost

General factors:
- *Soil type:* Sandy soils are more suitable for thermal treatment than are silty and clay soils. Finer soils and soils with high humic content require longer processing time, which results in increased unit costs (Refs. 5.2, 5.7).
- *Organic content:* The presence of organic materials may present an explosion hazard if the materials pyrolyze (Ref. 5.3). In one project, the presence of elevated levels of sulfur pyrite sparked a fire when it was exposed to high temperatures. This fire destroyed the air emission control equipment (Ref. 5.8).
- *Particle size:* The presence of large particles in the contaminated medium may impair heat transfer between the heating elements or the combustion gas and the medium (Ref. 5.6).
- *Moisture content:* Wastes with moisture content higher than 20 to 25 percent have to undergo pre-treatment (dewatering or mixing with dry materials) before they are loaded into the thermal desorption or retort unit. Pre-treatment can increase the overall processing time and may result in higher treatment costs (Ref. 5.7).
- *Residence time:* A higher concentration of mercury in waste may require a longer residence time to meet treatment goals. This longer residence time can increase the treatment costs (Ref. 5.4).
- *System throughput:* Wastes with moisture content higher than 20 to 25 percent usually must be treated in smaller volumes. This smaller volume may result in reduced throughput and higher treatment costs (Ref. 5.8).

Factors specific to thermal treatment of mercury-contaminated media:
- *Amount of mercury in waste:* A higher concentration of mercury in waste may require the waste to be passed more than once through the treatment system (Ref. 5.4).
- *Operating Temperature and Pressure:* The boiling point of elemental mercury at 1 atmosphere (1,014 kilopascals) is 350 °C. Exposure of mercury-contaminated wastes to higher temperature (380 °C) at a reduced pressure, ranging from 100 to 200 kilopascals, increases the volatility of mercury in the waste (Ref. 5.5). A thermal desorber is exposed to temperatures ranging from 320 to 700 °C (600 to 1,300 °F) to facilitate mercury removal (Refs. 5.2, 5.3, 5.5, and 5.10).

Type, Number, and Scale of Identified Projects

Thermal treatment of soil and waste that contain mercury has been applied at full scale and tested at the pilot scale. Data sources used for this report include information about three full-scale and five pilot-scale applications of thermal technologies to treat mercury. One of the full-scale applications identified is at a Superfund site (Project 1, Table 5.1).

Summary of Performance and Cost Data

Table 5.1 summarizes information for three full-scale and five pilot-scale projects. The performance of thermal treatment is usually measured by leach testing a sample of the treated mass. Among the full-scale projects, the media treated include soil, sludge, and sediment. The amount of media treated during Projects 1 and 2 (Table 5.1) were 80,000 and 26,000 tons. The other full-scale project (Project 8, Table 5.1) involves an ongoing, continuous treatment process that treats approximately 7 tons of mercury-contaminated media per day. Site types include an industrial landfill, a pesticide manufacturing site, and a mercury-recycling site. The initial concentration of mercury at one site was 0.16 mg/kg (Project 2, Table 5.1); the initial concentrations for the other two projects were not available. Final leachable mercury concentrations as measured by the TCLP were less than 0.2 mg/L for Projects 1 and 8 (Table 5.1). The concentration of total mercury was less than 1 mg/kg for Project 1, and it was less than 0.12 mg/kg for Project 2.

Among the pilot-scale projects, the media treated include soil and sludge. The quantity of media treated ranged from 0.5 tons to 62 tons. Performance data show that, for one of the five projects, the final mercury concentration in the leachate was reduced to below 0.025 mg/L (Project 3, Table 5.1). Final concentrations of mercury in the leachate were not available for the other four projects (Projects 4 through 7, Table 5.1). The final concentrations of total mercury for these four projects ranged from 0.01 mg/kg to 18.7 mg/kg.

Table 5.2 provides total actual costs for one pilot-scale and two full-scale projects. Thermal desorption was part of a treatment train, applied after soil washing, for the pilot-scale project. The costs provided for this project (Table 5.2) include soil washing as well. Data sources used for this report did not provide unit costs for any of these projects.

Case Study: Brookhaven Chemical Holes

BNL conducted pilot-scale studies to demonstrate the treatment of mercury-contaminated soil using high-temperature thermal desorption (HTTD) under a high vacuum (Ref. 5.10). The contaminated soil was excavated from the BNL Chemical Holes during a cleanup effort at the research laboratory. The treatment process involved application of heat at temperatures as high as 700 °C (1,300 °F). The mercury-contaminated soil was shredded before it was loaded into the thermal desorption unit. The HTTD unit was then sealed and a vacuum of approximately 25 inches of mercury was applied. Fuel-fired heat was supplied indirectly to the treatment system. As the temperature reached 700 °C (1,300 °F), mercury and other volatile substances in the waste vaporized and were drawn out of the desorber by vacuum. The initial total concentration of mercury in the waste was as high as 5,510 mg/kg, while the leachable concentrations of mercury ranged from 0.2 to 1.4 mg/L (TCLP). The final concentration of total mercury was reduced to less than 10 mg/kg, while the leachable concentrations of mercury ranged from non-detect levels to 0.0084 mg/L (TCLP) (Project 3, Table 5.1). The concentration of mercury in the air emissions ranged from 1 to 29 micrograms per cubic meter ($\mu g/m^3$), which is below the maximum achievable control technology (MACT) standard of 40 $\mu g/m^3$. A total of approximately 3,000 pounds of contaminated soil and sludge were treated during this project (Ref. 5.10).

Table 5.1
Thermal Treatment Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]**	Final Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]**	Process	Source
Thermal Desorption								
1	Industrial Landfill	Soil and Sediment; 80,000 tons	Full	Lipari Landfill, OU3, Pitman, New Jersey; September 1995	N/A	<0.2 mg/L [TCLP] <1 mg/kg	Low temperature thermal desorption (LTTD) system with the following components: a direct-heated rotary kiln; feed metering unit; baghouse; thermal oxidizer; wet quench; acid gas absorber; and control unit that housed the controls, data logger, and analyzers.	5.8
2	Pesticide Manufacturing/ Use	Soil; 26,000 tons	Full	Site B (site name and location confidential), Western U.S.; August 1995	0.16 mg//kg	<0.12 mg/kg	LTTD system with the following main units: feed system, rotary dryer, baghouse, thermal oxidizer, wet quench, and acid gas scrubber. The rotary dryer (desorber) unit consisted of a direct-heated rotary kiln, feed belt, a propane-fired burner, and discharge screw conveyor.	5.9
3	Research Laboratory- Disposal Pit	Waste Sludge; 1.3 tons	Pilot	BNL Chemical Holes, Upton, New York; 2001	8 to 5,510 mg/kg 0.2 to 1.4 mg/L [TCLP]	<10 mg/kg non-detect to 0.008 mg/L [TCLP] <1 to 29 μg/m^3 [air emissions]	High vacuum rotary thermal desorption system with the following components: materials handling unit; indirectly heated, high temperature, high vacuum rotary retort; condensers; high efficiency particulate air (HEPA) filters; and carbon adsorber.	5.10
4	Pesticide and Herbicide Manufacturing/ Use	Soil; 62 tons	Pilot	CFM Site, Bavaria, Germany; November 1994	780 to 1,080 mg/kg[a] 53.5 to 97.3 μg/L [TCLP]	16.2 to 18.7 mg/kg 0.6 to 14.6 μg/L [TCLP]	Treatment train consisting of soil washing and high vacuum thermal desorption. Components of the thermal desorption system include rotary drum dryer; indirectly fired vacuum distillation chamber; condensers; and off-gas treatment unit.	5.5
5	Chlor-alkali Manufacturing	Soil and Sludge; 1 ton	Pilot	Chlor-alkali Plant, Houston, Texas	1 to 350 mg/kg	0.01 to 0.7 mg/kg	High vacuum rotary thermal desorption system with the following components: materials handling unit; indirectly heated, high temperature high vacuum rotary retort; condensers; HEPA filters; and carbon adsorber.	5.11

Table 5.1
Thermal Treatment Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]**	Final Mercury Concentration (mg/kg) or Leachability (mg/L) [Test method]**	Process	Source
6	Metals Recycling	Soil and Sludge; 0.5 tons	Pilot	Metals Recycling Site, Claypool, Arizona	500 to 1,260 mg/kg	0.07 to 5.9 mg/kg	High vacuum rotary thermal desorption system with the following components: materials handling unit; indirectly heated, high temperature high vacuum rotary retort; condensers; HEPA filters; and carbon adsorber.	5.10
7	Aboveground Storage Tank	Soil; 0.5 tons	Pilot	Pipeline Metering Site, Louisiana	5 to 5,770 mg/kg	0.02 to 1 mg/kg	High vacuum rotary thermal desorption system with the following components: materials handling unit; indirectly heated, high temperature high vacuum rotary retort; condensers; HEPA filters; and carbon adsorber.	5.10
Retorting								
8	Metals Recycling	Soil, Sludge, and Debris; 7 tons per day	Full	Mercury Recycling site, Pennsylvania	N/A	<20 µg/L [TCLP]	Advanced programmable high vacuum mercury retorts. Information about system components is not available in the sources used for this report.	5.11, 5.12

Note:
[a] Initial concentration is before soil washing. Information on the concentration of mercury between soil washing and thermal desorption steps in the treatment train was not available in the documents used for this report.
BNL: Brookhaven National Laboratory
CFM: Chemische Fabrik Marktredwitz
lb: Pound
mg/kg: Milligrams per kilogram
mg/L: Milligrams per liter
µg/L: Micrograms per liter
N/A: Not Available
OU: Operable unit
TCLP: Toxicity Characteristic Leaching Procedure
TWA: Total Waste Analysis
**All data for mercury concentration are TWA values unless specified otherwise

Table 5.2
Available Mercury Treatment Cost Data for Thermal Treatment

Site	Scale	Amount Treated	Capital Cost	Total O&M Cost	Total Cost	Unit Costs	Additional Information	Source	Project Number in Table 5.1
Lipari Landfill, OU3, Pitman, New Jersey	Full	80,000 tons	$430,000	$5,019,292	$5,449,292	$68 per ton	Other project costs, including response to baghouse fire, caustic consumption, and equipment modifications, totaled $632,737. However, these costs were not included in calculating the unit cost. Cost year is 1995.	5.8	1
Site B (site name and location confidential), Western U.S.	Full	26,000 tons	$429,561	$2,830,956	$3,601,377	$125 per ton	Other costs include $285,000 for compliance testing and analysis, and $55,860 for excavation and disposal. However, these costs were not included in calculating the unit cost. Cost year is 1995.	5.9	2
Harbauer Facility, State of Bavaria, Germany	Pilot	62 tons	$30,000,000	$3,200,000	N/A	N/A	** Thermal desorption was part of a treatment train, applied after soil washing. Costs are based on a 1994 conversion rate of 1.5 DM to $1.	5.5	4

** Cost data for this project are estimated and include costs for soil washing and thermal desorption.
DM: Deutsch Mark
N/A: Not available
O&M: Operation and maintenance
OU: Operable Unit

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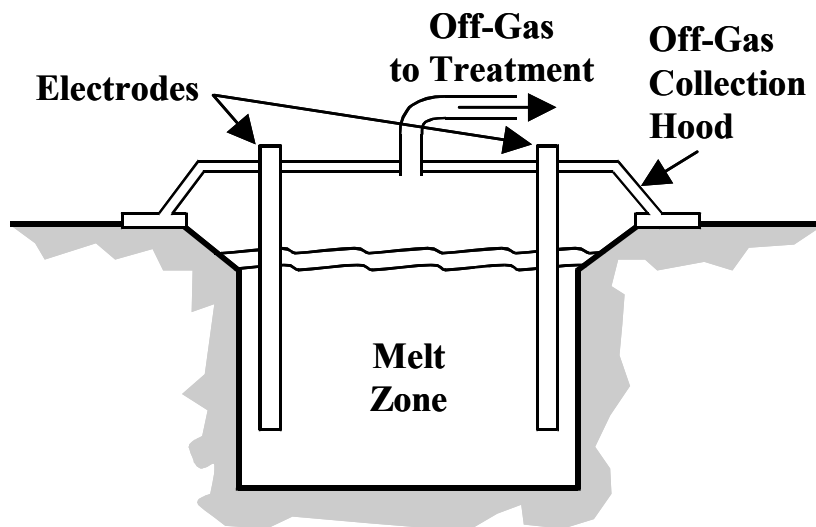
6.0   VITRIFICATION

Summary

Vitrification is used to treat mercury-contaminated soil and sediments *in situ* and *ex situ*. This technology has been implemented at full scale and pilot scale. Vitrification is a high-temperature treatment designed to immobilize contaminants by incorporating them in the vitrified end product, which is chemically durable and leach resistant. This technology typically requires a large amount of energy to achieve vitrification temperatures. Off-gases may require further treatment.

Technology Description and Principles

Vitrification is a high-temperature treatment technology designed to immobilize contaminants by incorporating them into the vitrified end product, which is chemically durable and leach resistant (Ref. 6.1). Figure 6.1 shows a typical vitrification system (Ref. 6.7). Vitrification uses electrical current to heat (melt) and vitrify the treatment material in place. Electric current is passed through soil by an array of electrodes inserted vertically into the surface of the contaminated zone. As soil is non-conductive, a starter pattern of electrically conductive glass frit that contains graphite is placed on the soil in the paths of the electrodes (Ref. 6.1). When power is fed to the electrodes, the graphite and glass frit conduct electricity through the soil, heating the surrounding area and directly melting the adjacent soil. Once molten, the soil becomes conductive. The melt grows outward and downward as power is gradually increased to a full constant operating level. The temperature of the contaminated soil could reach between 1,600 and 2,000 $^{\circ}$C. A single melt can treat a region up to 1,000 tons. Vitrification is used to treat wastes to a depth of 20 feet (Ref. 6.1). Large contaminated areas are treated in multiple blocks that fuse together to form one large treated zone. Specific processes used to treat environmental media and industrial wastes containing mercury are described in Table 6.1.

Figure 6.1
Model of a Vitrification System

Source: Ref. 6.7

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Ex situ vitrification involves heating contaminated material in a melter or furnace. The heat is typically generated by combustion of fossil fuel (coal, natural gas, and oil) or input electrical energy by direct joule heat, arcs, plasma torches, or microwaves (7.1). The melter or furnace is lined with refractory material, which resists chemical and physical abrasion, has a high melting point, and provides a high degree of insulating value to the process. Vitrification systems that have been used to treat mercury-contaminated soil and sediment include the Glass Furnace Technology (GFT) (Ref. 6.4) and the Plasma Hearth Process (Ref. 6.5).

The patented GFT process developed by Minergy Corporation uses a dryer to reduce the moisture content in the waste feed to below 10 percent (Ref. 6.4). The dried feed is mixed with a flux material to control melting temperatures and improve the physical properties of the glass aggregate product. It is then fed to the furnace. Oxygen and natural gas are combusted in the furnace to raise its internal temperature to about 1,600 $^{\circ}$C. PCBs and organic contaminants are destroyed or volatilized at this temperature. The feed melts and metals are encapsulated within a glass matrix. The matrix flows out of the furnace as molten glass. The molten material is then quickly cooled in a water-quench system to form a glass aggregate product. The off-gas from the process enters the air quality control system, which consists of a wet scrubber, a fabric filter, and a carbon filter. The wet scrubber eliminates sulfur dioxide and hydrogen chloride, the fabric filter removes particulate matter (dust), and the carbon filter captures mercury.

The Plasma Hearth Process uses an electric arc to melt non-combustible, inorganic material and volatilize and oxidize organic materials (Ref. 6.5). Inorganic material is collected in the fixed hearth, where it separates by gravity into layers of slag and molten metal. The organic fraction is partially combusted and pyrolyzed, and then is ducted to a secondary combustion chamber where it is subjected to a high temperature in the presence of excess air and a methane flame to complete combustion. After it exits the secondary chamber, the off-gas is quenched to approximately 204°C in an evaporative cooler. The off-gas then enters a baghouse, followed by a carbon filter and a High Efficiency Particulate Air (HEPA) filter bank. The baghouse removes large particulates, the carbon filter removes the volatilized mercury, and the HEPA filter bank removes fine particulates. Figure 6.2 shows a typical *ex situ* vitrification system.

Figure 6.2
Typical *Ex Situ* Vitrification System
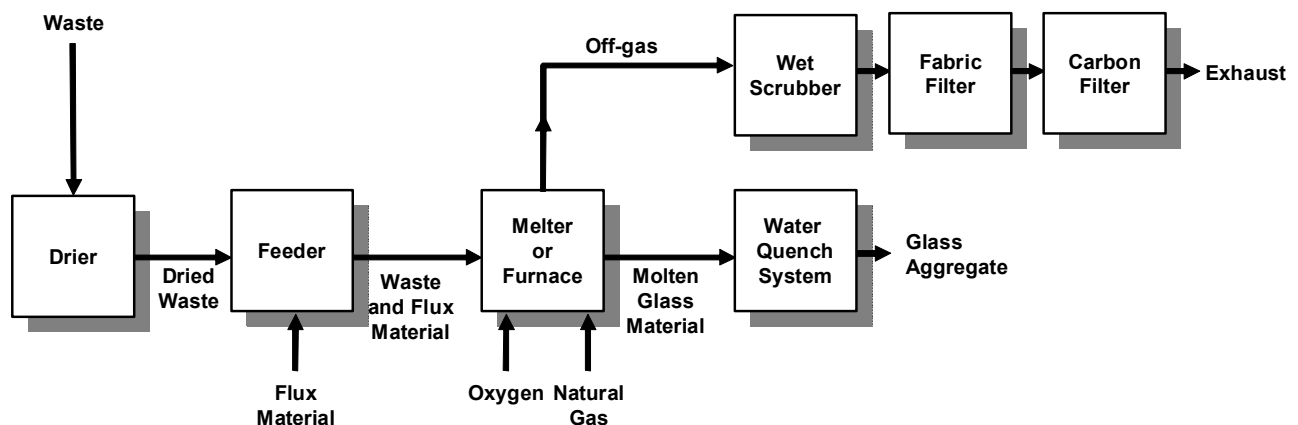
Source: Adapted from Ref. 6.4

Technology Description: Vitrification is a high-temperature treatment designed to immobilize contaminants by incorporating them in the vitrified end product, which is chemically durable and leach resistant. The primary residual generated by this technology is typically glass cullet or aggregate. Secondary residuals generated are air emissions, scrubber liquor, carbon filters, and used hood panels. This process may also cause contaminants to volatilize or undergo thermal destruction, thereby reducing their concentration in the soil or waste.

Media Treated:
- Soil
- Sediments

Energy Sources Used for Vitrification:
- Fossil fuels
- Direct joule heat

Energy Delivery Mechanisms Used for Vitrification:
- Arcs
- Plasma torches
- Microwaves
- Electrodes (*in situ*)

***In Situ* Application Depth:**
- Maximum demonstrated depth is 20 feet
- Very shallow depths or depths greater than 20 feet may require innovative techniques

Applicability, Advantages, and Limitations

The presence of chlorides, fluorides, sulfides, and sulfates may interfere with the process, resulting in higher mobility of mercury in the vitrified product. Feeding additional slag-forming materials such as sand to the process may compensate for the presence of chlorides, fluorides, sulfides, and sulfates (Ref. 6.1). Chlorides in excess of 0.5 weight percent will typically fume off and enter the off-gas. If chlorides are excessively concentrated, salts of alkali, alkaline earth, and heavy metals may accumulate in the solid residues collected by off-gas treatment. Separation of the chloride salts from the residue may be necessary, therefore, if the residue is returned to the process for treatment. Dioxins and furans may also form when excess chlorides are present and enter the off-gas treatment system (Ref. 6.1). The presence of these constituents may also lead to the formation of volatile metal species or corrosive acids in the off-gas (Ref. 6.1).

During vitrification, combustion of the organic content of the waste liberates heat, reducing the external energy requirements. Therefore, this process may be advantageous in the treatment of wastes that contain a combination of mercury and organic contaminants or for the treatment of organo-mercury compounds. However, high concentrations of organic materials and moisture may result in high volumes of off-gas as the organic constituents volatilize and combust and water turns to steam, which may impair the function of the emissions control systems.

Vitrification can also increase the density of treated material, thereby reducing its volume. In some cases, the vitrified product can be reused or sold (Ref. 6.4).

Excavation of soil is not required for *in situ* vitrification. *In situ* vitrification has been used to a depth of 20 feet (Ref. 6.3). Contamination at very shallow depths or depths greater than 20 feet may require innovative application techniques.

Ex situ treatment processes typically are not transportable, and so contaminated materials must be delivered to the facility for treatment. If sediments are treated using this process, the materials must be dewatered before treatment. In cold climates, indoor storage of feed materials may be required to avoid freezing (Ref. 6.4).

High concentrations of mercury in soil or sediment may limit performance of this process. Metals retained in the melt must be dissolved to minimize formation of crystalline phases that can decrease the leach resistance of the vitrified product. Mercury may be difficult to treat because of its high volatility and low solubility in glass (less than 0.1 percent), but may be effectively treated at low concentrations (Ref. 6.1).

Factors Affecting Vitrification Performance and Cost

- **Lack of glass-forming materials:** If insufficient glass-forming materials (SiO_2 at more than 30 percent by weight) and combined alkali (Na + K at more than 1.4 percent by weight) are present in the waste, the vitrified product may be less durable. The addition of frit or flux additives may compensate for the lack of glass-forming and alkali materials (Ref. 6.2).
- **Particle size:** Some vitrification units require that the particle size of the feed be controlled. Size reduction may be required to achieve acceptable throughputs and a homogeneous melt for wastes containing refractory compounds that melt above the unit's nominal processing temperature, such as quartz and alumina. High-temperature processes, such as arcing and plasma processes, may not require size reduction of the feed (Ref. 6.1).
- **Presence of groundwater:** Groundwater control may be required for *in situ* vitrification if contamination is below the water table and hydraulic conductivity of the soil is more than 10^{-4} centimeters per second (cm/sec) (Ref. 6.2).
- **Moisture content:** Wastes that contain more than 25 percent moisture content may require excessive fuel or dewatering before treatment (Ref. 6.1).
- **Subsurface air pockets:** For *in situ* vitrification, subsurface air pockets, such as those that may be associated with buried drums, can cause molten material to bubble and splatter, resulting in a safety hazard (Ref. 6.2).
- **Presence of halogenated organic compounds:** The combustion of halogenated organic compounds may cause incomplete combustion and deposition of chlorides, which can result in higher mobility of mercury in the vitrified product (Ref. 6.1).
- **Metals content:** For *in situ* vitrification, high metals content may result in pooling of molten metals at the bottom of the melt, causing electrical short-circuiting. This technology is not recommended for sites with metals content greater than 25 percent by weight (Ref. 6.6).
- **Organic content:** For *in situ* vitrification, high organic content may cause excessive heating of the melt, damaging the treatment equipment. High concentrations of organic compounds may also create large volumes of off-gas as the organic constituents volatilize and combust and may overwhelm air emissions control systems. This technology is not recommended for sites that contain organic content of more than 7 to 10 percent by weight (Ref. 6.6).
- **Characteristics of treated waste:** Depending on the qualities of the vitrified waste, the treated soil and waste may be able to be reused or sold (Ref. 6.4).

Type, Number, and Scale of Identified Projects

Vitrification of soil and sediments that contain mercury has been applied at the full scale and demonstrated in the field. Data sources used for this report include information about one full-scale and two pilot-scale applications of this technology to treat mercury-contaminated soil and sediments.

Summary of Performance and Cost Data

Table 6.1 summarizes information for one full-scale and two pilot-scale projects. The performance of vitrification treatment is usually measured by leach testing a sample of the final vitrified material.

In the full-scale project, the media treated included soil and sediments. The amount of media treated was 3,000 cubic yards (5,400 tons). The site was an agricultural chemical manufacturing plant. Confirmation coring samples indicated that vitrified materials met cleanup requirements for mercury in soil. Stack gas emissions met off-gas emissions requirements. The cleanup contractor's cost at the site was $1,763,000, of which $800,000 was for vitrification and corresponded to $267 per cubic yard of soil treated (Ref. 6.3).

The pilot-scale project using the GFT was used to treat river sediments contaminated with PCBs and metals. The river sediments were obtained from the Lower Fox River in Green Bay, Wisconsin. Approximately 27,000 pounds of dried sediments were treated using this process. Analytical results for the sediments before treatment indicated that the mercury concentration was about 0.001 micrograms per kilogram (μg/kg) (Ref. 6.4). Confirmation sampling results for the glass aggregate indicated that the mercury concentration was less than 0.0025 μg/kg. The concentration of leachable mercury in the glass aggregate was less than 0.000002 μg/L, as measured by the Synthetic Precipitate Leaching Procedure (SPLP). The cost to treat dewatered sediments was estimated to be $38.74 per ton (see Table 6.1, Project 2).

Performance data for the pilot-scale project using the Plasma Hearth Process were unavailable. Table 6.2 provides cost data for the projects described above.

Case Study: Parsons Chemical Superfund Site

The Parsons Chemical Superfund Site in Grand Ledge, Michigan, was an agricultural chemical mixing, manufacturing, and packaging facility. Full-scale vitrification on site using the Geosafe process was implemented to treat 3,000 cubic yards of soil and sediments contaminated with pesticides and heavy metals, including mercury and dioxin. The technology is capable of treating soil in situ; however, in this case, the contaminant depth was too shallow for the electrodes to be used effectively. Therefore, the technology was adapted by excavating the contaminated soil, placing it in a cell, and treating it in a trench on site. The contaminated area consisted of nine melt cells: eight separate melts were conducted at the site. The duration of each melt was 10 to 19.5 days, and melts required about a year to cool sufficiently to sample. Typical initial concentrations of mercury ranged from 2,220 to 4,760 μg/kg. Results for confirmation coring samples of the final vitrified soil indicated the concentration of mercury to be less than 40 μg/kg. The concentration of leachable mercury in the vitrified soils ranged from less than 0.2 to 0.23 μg/L, as measured by the TCLP. Concentrations of mercury in the off-gas emissions ranged from 12.9 to 17.7 μg/m^3, or 0.0000989 to 0.000125 pounds per hour (see Table 6.1, Project 1).

Table 6.1
Vitrification Treatment Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/kg) or Leachability (µg/L) [Test method]	Vitrified Product and Final Mercury Concentration (µg/kg) or Leachability (µg /L) [Test method]	Vitrification Process	Source
1	Agricultural chemicals manufacturing, formulating, and packaging	Soil and Sediments (*in situ*); 3,000 cy	Full	Parsons Chemical/ETM Enterprises Superfund Site, Grand Ledge, Michigan 1994	2,220 to 4,760 µg/kg (Total) Not analyzed (TCLP)	< 40 µg/kg (Total) 0.2 to 0.23 µg/L (TCLP)	Vitrification (on site)	6.3
2	River sediments	Sediments (*ex situ*), 27,000 lb	Pilot	Lower Fox River, Wisconsin Hazen Research Center, Golden, CO and the Minergy GlassPack Test Center, Winneconne, Wisconsin 2001	< .001 (µg/kg (Total) Not analyzed (SPLP)	glass aggregate; < 0.0025 µg/kg (Total) < 0.000002 µg/L (SPLP)	*Ex situ* Glass Furnace Technology	6.4
3	N/A	Mixed waste	Pilot	Science and Technology Applications Research (STAR) Center, Idaho Falls, Idaho 1998	N/A	N/A	Plasma Hearth Process	6.5

Note:
cy: cubic yards
N/A: Not Available
SPLP: Synthetic Precipitate Leaching Procedure
TCLP: Toxicity Characteristic Leaching Procedure
µg/kg: Micrograms per kilogram
µg/L: Micrograms per liter

Table 6.2
Available Mercury Treatment Cost Data for Vitrification**

Site/ Cost year	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation	Source	Project Number in Table 6.1
Parsons Chemical/ETM Enterprises Superfund Site, Grand Ledge, Michigan	Full	3,000 cy	N/A	N/A	$267 per cubic yard	$800,000	N/A	6.3	1
Lower Fox River, Green Bay, Wisconsin	Pilot	27,000 lbs	$12 per ton	N/A	N/A	N/A	Costs assume that the facility would treat 600 tons of sediments per day and that the facility would operate for 350 days per year for 15 years. Costs are estimated for full-scale remediation. Actual cost for pilot test not available.	6.4	2

Table 6.2
Available Mercury Treatment Cost Data** (continued)

Site/ Cost year	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation	Source	Project Number in Table 6.1
Science and Technology Application research (STAR) Center, Idaho Falls, Idaho	Pilot	N/A	$50,000,000 to $86,200,000	$48,000,000 to $62,000,000	N/A	$124,000,000 to $184,000,000	Cost assumes that the facility would process 23,235 cy of waste over 5 years of operation. Costs are estimated for full-scale remediation. Actual cost for pilot test not available.	6.5	3

** All costs and amounts treated are estimates.
cy: cubic yard
lb: Pound
kg: Kilogram
N/A: Not available
O&M: Operation and maintenance

References

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6.7   U.S EPA Office of Solid Waste and Emergency Response. 2002. Arsenic Treatment Technologies for Soil, Waste, and Water. EPA-542-R-02-004. September. http://www.cluin.org/download/remed/542r02004/arsenic_report.pdf.

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**PART IIB**

TREATMENT TECHNOLOGIES APPLICABLE TO WATER

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7.0   PRECIPITATION/COPRECIPITATION

Summary

Precipitation/coprecipitation is a full-scale technology used to treat mercury-contaminated groundwater and wastewater. Based on the information collected to prepare this report, this technology typically can reduce mercury concentrations to less than 2 µg/L. However, some of the processes used multiple precipitation steps and additional treatment with other technologies such as activated carbon to reach this level.

Figure 7.1
Model of a Precipitation/Coprecipitation System
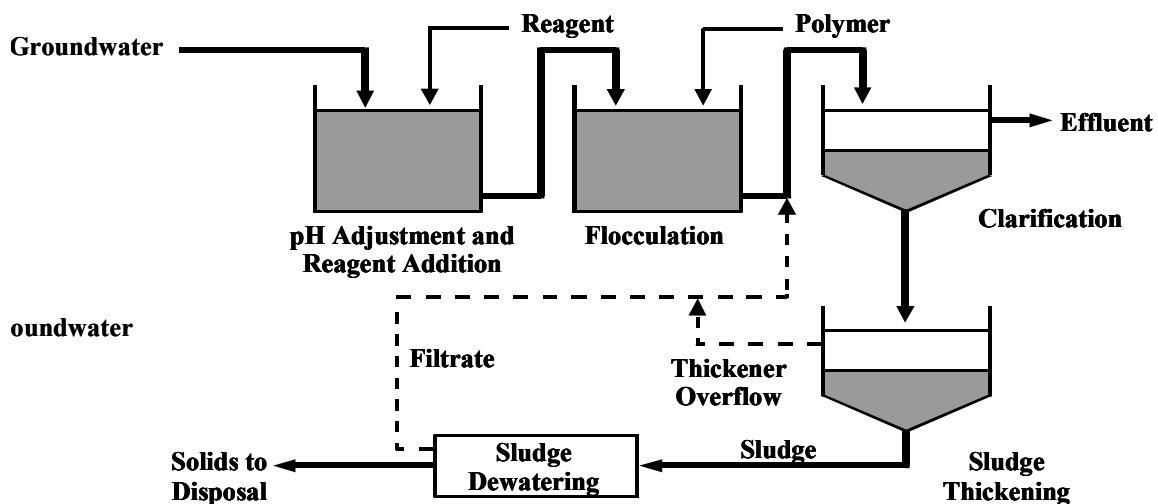
Source: Ref. 7.2

Technology Description and Principles

Technologies were considered precipitation/coprecipitation if they involved the following steps:

- Mixing of treatment chemicals into water;
- Formation of a solid matrix through precipitation, coprecipitation, or a combination of these processes; and
- Separation of the solid matrix from the water.

Precipitation/coprecipitation usually involves pH adjustment and addition of a chemical precipitant or coagulant to transform soluble metals and inorganic contaminants into insoluble metals and inorganic salts (Ref. 7.2). Mercury removal usually includes changing the pH of the water to be treated because removal is maximized at the pH where the precipitated species is least soluble. The optimal pH range for precipitation/coprecipitation depends on the waste treated and the specific treatment process. The precipitated/coprecipitated solid is typically removed by clarification or filtration.

The most common precipitation method used to remove inorganic mercury from wastewater is sulfide precipitation (Ref. 7.1). In this process, the adjusted pH range is between 7 and 9, and a sulfide precipitant (such as sodium sulfide) is added to the wastewater stream. The sulfide precipitant converts dissolved mercury to the relatively insoluble mercury sulfide form.

One coprecipitation process for mercury uses lignin derivatives to form a lignin-mercury colloid. Precipitated solids can then be removed by gravity settling in a clarifier. This process can be enhanced by the addition of a chemical coagulant or settling aid such as ferric chloride, and then flocculation and settling.

Technology Description: Precipitation uses chemicals to transform dissolved contaminants into an insoluble solid (Ref. 7.2). In coprecipitation, the target contaminant may be in a dissolved, colloidal, or suspended form. Dissolved contaminants do not precipitate, but are adsorbed onto another species that is precipitated. Colloidal or suspended contaminants become enmeshed with other precipitated species or are removed through processes such as coagulation and flocculation. Processes to remove mercury from water can include a combination of precipitation and coprecipitation. The precipitated/ coprecipitated solid is then removed from the liquid phase by clarification or filtration. Mercury precipitation/coprecipitation can use combinations of the chemicals and methods listed below.

Media Treated:
- Groundwater
- Wastewater

Chemicals and Methods Used for Mercury Precipitation/Coprecipitation:
- Ferric salts (for example, ferric chloride), ferric sulfate, or ferric hydroxide
- Alum
- pH adjustment
- Lime softening, limestone, and calcium hydroxide
- Sulfide
- Lignin derivatives

Applicability, Advantages, and Limitations

Precipitation/coprecipitation is an active *ex situ* treatment technology designed to function with routine chemical addition and sludge removal. It usually generates a sludge residual, which typically requires treatment such as dewatering and subsequent disposal. Some sludge from the precipitation/ coprecipitation of mercury can be a hazardous waste and require additional treatment such as solidification/stabilization for disposal as a solid waste or could require disposal as a hazardous waste.

Excess use of the chemical sulfide precipitants can form soluble mercury sulfide species. Mercury can resolubilize from sulfide sludges under conditions that exist in landfills (Ref. 7.4), which could lead to mercury contamination of leachate and potential groundwater pollution.

The effluent from mercury precipitation may also require further treatment, such as pH adjustment, before discharge or reuse. Sulfide precipitation of mercury may generate residual sulfide in the effluent. Treatment to remove residual sulfide may be needed before discharge (Ref. 7.1).

Factors Affecting Precipitation/Coprecipitation Performance and Cost

- **pH:** In general, mercury removal will be maximized at the pH where the precipitated species is least soluble. The optimal pH range for precipitation/coprecipitation depends on the waste treated and the specific treatment process. The most effective precipitation of mercury for the sulfide precipitation process occurs within a pH range of 7 to 9 (Ref. 7.1). The most effective precipitation of mercury for the hydroxide precipitation process occurs within a pH range of 7 to 11 (Ref. 7.9).
- **Presence of other compounds:** The presence of other metals or contaminants may affect the effectiveness of precipitation/coprecipitation.
- **Chemical dosage:** The cost generally increases with increased chemical addition. Larger amounts of chemicals added usually results in a larger amount of sludge that requires additional treatment or disposal. Excess use of sulfide precipitant can form soluble mercury sulfide species (Ref. 7.1).
- **Treatment goal:** For some applications, a single precipitation step or using precipitation alone may not achieve the treatment goals. Multiple precipitation steps or the use of additional technologies may be needed to meet stringent cleanup goals, effluent guidelines, or disposal standards.
- **Sludge disposal:** Sludge produced from the precipitation/coprecipitation process could be considered a hazardous waste and require additional treatment before disposal as a solid waste or disposal as hazardous waste (Ref. 7.2).

Type, Number, and Scale of Identified Projects Treating Groundwater and Wastewater Containing Mercury

Precipitation has been applied at full scale to treat groundwater and wastewater contaminated with mercury. Data sources used for this report include information about three full-scale applications for treatment of mercury contaminated groundwater and eight full-scale applications for treating wastewater.

Summary of Performance and Cost Data

Table 7.1 presents the available performance data for full-scale precipitation/coprecipitation treatment of mercury. Table 7.2 provides cost data for two pump-and-treat systems that treated mercury-contaminated groundwater with precipitation/coprecipitation. Three full-scale projects treated contaminated groundwater and eight full-scale projects treated wastewater. The three projects that treated groundwater reduced the mercury concentration to less than 2 µg/L. A total of 41,000 pounds of contaminants were removed from January 1997 to March 1999 at Marine Corps Base Camp Lejeune in North Carolina. The treatment system removed volatile organic compounds and metals, including mercury. The pump and treat (P&T) system included oxidation of ferrous iron to ferric iron, pH adjustment, precipitation, air stripping, and granular activated carbon adsorption. The cost of the P&T system was approximately $49 per pound of contaminant removed. The cost for the precipitation/coprecipitation process alone is not identified or discussed in the references used for this report.

At the Squamish Mercury Remediation Project in British Columbia, Canada (see Table 7.1, Project 2), 25 million gallons of mercury-contaminated groundwater were treated using a coprecipitation process followed by addition of ferric chloride. The treatment reduced the mercury concentration from 15 µg/L to 1 µg/L. The unit cost for the coprecipitating chemical was $2.00 per gallon of water treated. Additional information on the cost is not identified or discussed in the references used for this report.

Precipitation, carbon adsorption, and pH adjustment were used at the Olin Corporation McIntosh Plant Site in Washington County, Alabama, to treat mercury-contaminated groundwater. This treatment reduced the average influent concentration of mercury from 44 µg/L to 0.3 µg/L (Ref. 7.6). No cost data were identified or discussed for this project in the references used for this report.

Of the eight projects that treated mercury-contaminated wastewater, five treated wastewater at chlor-alkali plants. The influent mercury concentration ranged from 362 µg/L to 0.07 µg/L, and the effluent concentration was reduced to less than 2 µg/L in all projects. However, some of the processes used multiple precipitation steps and additional treatment with other technologies such as activated carbon to reach this level. No cost data were identified or discussed for these projects in the references used for this report (Ref. 7.3), except for projects treating wastewater from the centralized waste treatment industry (Projects 10 and 11). Chapter 11 of the reference used for these projects (Ref. 7.10) provides detailed cost data and information on how the costs were derived.

Case Study: Olin Chemical Site

Olin Corporation operated a mercury cell chlor-alkali plant from 1952 to 1982 at the Olin Corporation McIntosh Plant Site in Washington County, Alabama. In 1978, Olin began operating a diaphragm cell caustic soda/chlorine plant, which is still in operation. The plant on site produces chlorine, caustic soda, sodium hypochlorite, and sodium chloride. Releases of mercury and other organic chemicals have contaminated the soil and the shallow groundwater beneath the site.

A P&T remedy is being used for groundwater at this site. The treatment system consists of precipitation, carbon adsorption, and pH adjustment before discharge to the Mobile River. The cleanup level in groundwater is 2 µg/L. The treatment system has reduced the concentration of mercury in the pumped groundwater from 44 µg/L to 0.3 µg/L. The P&T system began operating in 1986 and treats an average of 350 to 400 gallons per minute (gpm) (Ref. 7.6).

Table 7.1
Precipitation/Coprecipitation Treatment Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/L)	Final Mercury Concentration (µg/L)	Precipitating Agent or Process	Source
1	Marine Corps Base	Groundwater	Full	Marine Corps Base Camp Lejeune, North Carolina	N/A	0.025	Oxidation of ferrous iron to ferric iron, pH adjustment, precipitation, air stripping, and granular activated carbon adsorption.	7.7
2	Mercury-Cell Electrolysis process for the production of chlorine and caustic soda	Groundwater	Full	Squamish Remediation Site, Squamish, British Columbia, Canada	15	1	Coprecipitation followed by addition of ferric chloride.	7.5
3	Chlorinated organic pesticides, chlorine, sodium hypochlorite, and caustic soda manufacturing plant	Groundwater	Full	Olin Corp, McIntosh, Alabama	40	0.3	Precipitation, carbon adsorption, and pH adjustment.	7.6
4	Natural gas production	Wastewater	Full	Confidential Site, Gulf of Thailand	9,600	0.035	Thiol-based chelating agent.	7.8
5	Commercial hazardous waste combustor	Wastewater from quench chamber run-	Full	N/A	59.2	21.4	Sodium hydroxide precipitation	7.3
					21.4	2.6	Ferric chloride	

**Table 7.1
Precipitation/Coprecipitation Treatment Performance Data for Mercury (continued)**

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/L)	Final Mercury Concentration (µg/L)	Precipitating Agent or Process	Source
		down and packed tower			2.6	ND *	Sand filtration	
6	Commercial hazardous waste combustor	Wastewater from quench tank, packed tower, and a venturi scrubber	Full	N/A	0.7	0.4	Primary precipitation system: Sulfide precipitation followed by hydroxide precipitation	7.3
					0.4	ND *	Secondary precipitation system: Hydroxide precipitation followed by sedimentation and ultrafiltration	
7	Commercial hazardous waste combustor	Wastewater from quench tank and a wet scrubber	Full	N/A	3.3	ND *	Sulfide precipitation followed by filtration followed by carbon adsorption	7.3
8	Commercial hazardous waste combustor	Wastewater from circulation loop of incinerator	Full	N/A	3.04	0.2	Primary precipitation system: Hydroxide precipitation followed by sedimentation; Secondary precipitation system: ferric chloride precipitation followed by sedimentation	7.3

Table 7.1
Precipitation/Coprecipitation Treatment Performance Data for Mercury (continued)

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/L)	Final Mercury Concentration (µg/L)	Precipitating Agent or Process	Source
9	Commercial hazardous waste combustor	Wastewater from APC system	Full	N/A	219	0.48	Hydroxide precipitation and ferric chloride precipitation followed by sedimentation and sand filtration	7.3
10	Centralized Waste Treatment Facility**	Wastewater from metal bearing liquids and solids	Full	Confidential	115 362	0.20	Selective metals precipitation, liquid solid separation, secondary precipitation, liquid-solid separation, tertiary precipitation, and clarification	7.10
11	Centralized Waste Treatment Facility**	Wastewater from metal bearing liquids	Full	Confidential	102.57	1.67 0.51	Primary precipitation, liquid-solid separation, secondary precipitation and sand filtration	7.10

Note:
* : Detection limits not provided
**: Influent and effluent values provided represent two sets of data collected for the facility
APC: Air pollution control
N/A: Not available
ND: Non-detect
µg/L: Micrograms per liter

Table 7.2
Available Mercury Treatment Cost Data for Precipitation/Coprecipitation

Site/Cost year	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation	Source	Project Number in Table 7.1
Marine Corps Base Camp Lejeune, North Carolina	Full	41,000 pounds of contaminants removed from 1997 to 1999	$ 4.66 Million	$ 1 Million	$49 per pound of contaminant removed	N/A	Costs in 2000 dollars. The costs are for the entire treatment system.	7.7	1
Squamish Remediation Site, Squamish, British Columbia, Canada	Full	25 million gallons	N/A	N/A	$2 per gallon of treated groundwater	N/A	The unit cost is for the reagent only. Costs in 2004 dollars.	7.5	2

N/A: Not available
O&M: Operation and maintenance

References

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        http://www.epa.gov/ORD/NRMRL/pubs/625r97004/625r97004.pdf.

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        http://clu-in.org/download/remed/542r02004/arsenic_report.pdf.

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        Guidelines and Standards for Commercial Hazardous Waste Combustors. EPA-821-R-99-020.
        January. http://epa.gov/waterscience/chwc/final/technical.html.

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        Environmental Protection Agency, to Danielle Wohler, Tetra Tech EM Inc. December 16.

7.7   U.S. Navy and Marine Corps. 2000. Site Specific Report: Marine Corps Base Camp Lejeune,
        Operable Unit 1 and 2. SSR-2539-ENV. January.

7.8   E-mail from Carl Hensman, Frontier Geosciences Inc., to Younus Burhan, Tetra Tech EM Inc.,
        regarding the use of thiol-based chelating agent at a confidential site in Thailand. December 30,
        2004.

7.9   West General Inc. 2005. Mercury solubility – mercury hydroxide curve. January.
        http://www.westgeneral.com/outofthebox/compounds/hgsol.html.

7.10   U.S. EPA. 2000. Office of Water. Development Document for Effluent Limitations Guidelines
        and Standards for the Centralized Waste Treatment Industry – Final.EPA-821-R-00-020. August.
        http://www.epa.gov/waterscience/guide/cwt/final/develop/index.html.

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8.0   ADSORPTION TREATMENT

Summary

Adsorption has been used to remove inorganic mercury from groundwater and wastewater. Based on the information collected for this report, this technology can reduce concentrations of inorganic mercury to less than 2 µg/L. Its effectiveness is sensitive to a variety of contaminants and characteristics of the untreated water. It can be a primary treatment method but is often used as a polishing step (removal of mercury left in the waste stream after a primary treatment process) for other water treatment processes.

Technology Description and Principles

This section describes mercury removal processes that pass water through a fixed bed of media. Some of the processes described in this section rely on a combination of adsorption, precipitation/coprecipitation, pH adjustment, or filtration. Adsorption is used in these processes either as the primary removal mechanism or as a polishing step (Refs. 8.1 and 8.2) to remove residual contamination that was not removed by a primary treatment step. All of the treatment applications identified include adsorption as part of a treatment train rather than as a stand-alone treatment unit. A treatment train is a series of treatments combined in sequence to provide the necessary or required treatment result.

Adsorption of molecules can be represented as a physical reaction:

$$A + B \leftrightarrow A \bullet B$$
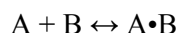
where

"A"	=	The adsorbate (contaminant)
"B"	=	The adsorbent
"A•B"	=	The adsorbed compounds

Adsorbates are held on the surface by various types of chemical forces such as hydrogen bonds, dipole-dipole interactions, and van der Waals forces. If the reaction is reversible, as it is for many compounds adsorbed to activated carbon, molecules continue to accumulate on the surface until the rate of the forward action (adsorption) equals the rate of the reverse action (desorption). When this condition exists, the adsorbent is saturated, and no further accumulation will occur (Ref. 8.7). One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate. Important characteristics that affect adsorbate capacity by an adsorbent are surface area, pore size distribution, and surface chemistry (Ref. 8.7). Water is passed through a bed or adsorbent in adsorption treatment for mercury. Mercury or mercury compounds are adsorbed as the contaminated water passes through the adsorbent, removing them from the water.

The most common adsorbent used for mercury is granular activated carbon (Refs. 8.2, 8.5, and 8.6). One vendor, Selective Adsorption Associates, Inc., also markets sulfur-impregnated activated carbon for mercury adsorption (Ref. 8.8). Another adsorption process, the Lancy Sorption Filter System, uses a patented process to remove mercury from water. This technology is typically used as a polishing step after other treatment processes have been applied. A soluble sulfide is added to the water in a reaction tank in the first stage of the Lancy filtration process, converting most of the heavy metals to sulfides. From the sulfide reaction tank, the solution is passed through the Lancy sorption filter media. Precipitated metal sulfides and other suspended solids are filtered out, and the remaining soluble metals

and sulfides are absorbed by the media. The system generates either a slurry or a solid cake of spent media (Ref. 8.15).

The effectiveness of adsorption is sensitive to a variety of water characteristics. Pretreatment is used in many adsorption systems to alter the characteristics of the untreated water and ensure effective adsorption. For example, adsorption may be preceded by filtration to remove solids that may plug the adsorption bed. Ultraviolet (UV) light treatment may be used to control bacterial growth, which can also plug the adsorption bed and reduce its adsorption capacity. Equalization tanks are often used to ensure a constant flow rate through the bed. This constant flow helps ensure that the residence time is sufficient to remove the contaminants. In addition, high flow rates can cause channelization and erosion of the adsorption bed, which can reduce effectiveness. Adjustment of pH to the range where adsorption is most effective is also a common pretreatment step. After adsorption treatment, the pH may require further adjustment to acceptable criteria of the receiving waters or Publicly Owned Treatment Works (POTW). Once the absorbent bed is saturated, the bed may be regenerated or disposed. The data sources used for this report did not contain information on the management of spent adsorbent used for mercury treatment.

Technology Description: In adsorption, solutes (contaminants) concentrate at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorbent is usually packed into a column. Contaminants are adsorbed as contaminated water is passed through the column. The column must be regenerated or disposed and replaced with new media when adsorption sites become filled.

Media Treated:
- Groundwater
- Drinking water
- Wastewater

Types of Sorbent used to Treat Mercury:
- Granular activated carbon
- Sulfur-impregnated activated carbon
- Lancy filtration

Applicability, Advantages and Limitations

The effectiveness of adsorption is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, and biological growth can cause fouling and plugging. Pretreatment with flocculation, settling, filtration, or oil-water separation may be used to reduce suspended solids and organic compounds. UV light treatment has been used to reduce biological growth before the process is used to adsorb mercury. Spent adsorption media must be regenerated or disposed. Competition for adsorption sites could reduce the effectiveness of adsorption because other constituents may be preferentially adsorbed, resulting in a need for more frequent bed regeneration or replacement.

Regeneration of granular activated carbon usually involves heating to desorb contaminants, which could release volatile mercury compounds. Use of APC equipment may therefore be necessary to remove mercury from the off-gas produced (Ref. 8.11). Further treatment may be necessary before spent adsorption media from mercury treatment systems can be disposed.

Factors Affecting Adsorption Performance and Cost

Contaminant concentration: Competition for adsorption sites can reduce the effectiveness of adsorption if competing contaminants are adsorbed instead of or in addition to mercury, resulting in a need for more frequent bed regeneration or replacement (Ref. 8.12). In addition, the capacity of the adsorption media decreases with increasing contaminant concentration (Refs. 8.13, 8.14). High contaminant concentrations can exhaust the adsorption media quickly, requiring frequent regeneration or replacement.

Fouling: The presence of suspended solids, organic compounds, and solids can cause fouling of adsorption media (Ref. 8.7).

Flow Rate: Increasing the flow rate through the adsorption media can decrease adsorption of contaminants and erode the adsorbent bed (Refs. 8.6 and 8.10).

Wastewater pH: The optimal pH to maximize adsorption of mercury by granular activated carbon is acidic (pH 4-5). Therefore, pH adjustment may be needed both before and after adsorption treatment (Refs. 8.3, 8.4, 8.7 and 8.11).

Spent Media – Spent media that can no longer be regenerated would require treatment or disposal (Ref. 8.9).

Type, Number, and Scale of Identified Projects Treating Water Containing Mercury

Adsorption technologies to treat mercury-contaminated water are commercially available. Data sources used for this report included information about four full- and two pilot-scale applications of adsorption to treat mercury. Two of the projects (Projects 1 and 2) were implemented at Superfund sites.

Summary of Performance and Cost Data

Table 1 summarizes the performance information for the four full- and two pilot-scale applications. The effectiveness of adsorption treatment can be evaluated by comparing influent and effluent contaminant concentrations. Performance data were available for three of the four full-scale processes. Influent concentrations ranged from 3.3 to 60 µg/L in these treatments (Projects 2, 3, and 4). The effluent mercury concentration was below 2 µg/L for all three of these projects. Of the two pilot-scale applications, one (Project 5) reported a mercury influent concentration of 2,500 µg/L and a removal rate of 98 percent. Data on the effluent concentrations were not available for this project. Project 6 reported a mercury influent concentration of 60 µg/L and an effluent concentration below the detection limit. The detection limit was not provided, however.

Table 2 provides the available cost data for mercury adsorption treatment. In one pilot study, the cost of removing thimerosal, a mercury salicylate salt that is used as a bacteriostat/fungistat in many test kits, using granulated activated carbon was $0.107 per gallon of water treated (Ref. 8.5). The capital cost was $0.012 per gallon treated and the O&M cost was $0.095 per gallon treated. Another full-scale treatment system developed for treating thimerosal (Ref. 8.7) reports capital costs of $60,000 and monthly operating costs of $7,665 for a plant designed to treat 1,800 gallons of thimerosal-contaminated wastewater per day.

Reported costs for systems to treat groundwater include $49 per pound of contaminant removed (Ref. 8.2) and $520 per pound of contaminant ($19 per 1,000 gallons of groundwater extracted) removed (Ref. 8.1). However, the costs include removal of other contaminants in addition to mercury. The information sources used for this report did not contain cost data on the granular activated carbon or Lancy filter treatment step alone.

Case Study: Reducing Mercury Discharge at a Testing Laboratory

A testing laboratory in Massachusetts generates wastewater containing thimerosal concentrations averaging 60 µg/L before treatment. In 1992, the laboratory conducted pilot testing of carbon adsorption and constructed a full-scale system. The full-scale system includes a 15-micron bag filter, UV light, an equalization tank with pH adjustment to the 4 to 5 range, granular activated carbon filters, a mixing tank with pH adjustment to 5.5 to 9.5, and a neutralization tank. The micron bag filter was necessary to remove solids that tended to plug the filters. UV light was introduced to control bacterial growth in the carbon adsorption system. Flow equalization was provided to establish constant detention time and avoid channelization of the beds caused by increasing flows experienced when equalization was not included. The pH was adjusted to the range where the adsorptive capacity of the carbon filter is greatest (4 to 5). After the carbon filter, the pH is readjusted to the 5.5 to 10.5 range before the wastewater flows into the neutralization tank. Treated water is finally neutralized to the range accepted by the receiving POTW. This acceptable range was not reported, however. This system reduced the concentration of thimerosal in the wastewater from 60 µg/L to below the goal of 1 µg/L.

Costs for the full-scale treatment system (1,800 gallons per day) include capital costs of $60,000 and monthly operating costs of $7,665.

Table 8.1
Adsorption Treatment Performance Data for Mercury

Project Number	Industry or Site Type	Waste or Media, Quantity	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (μg/L)	Final Mercury Concentration (μg/L)	Adsorption Process or Media[a]	Source
1	Waste disposal and recycling	Groundwater, 225 gpm	Full	King of Prussia Technical Corporation Superfund Site, Winslow Township, New Jersey, December 1997 (Interim Results)	N/A	N/A	Electrochemical precipitation followed by air stripping and granular activated carbon[b]	8.1
2	Chlorinated organic pesticides, chlorine, sodium hypochlorite, and caustic soda manufacturing plant	Groundwater	Full	Olin Corp, McIntosh, Alabama	44 (average)	0.3 (average)	Precipitation, carbon adsorption, and pH adjustment	8.3
3	Hazardous waste combustion	Wastewater stream from flue gas quench and ash/slag quench	Full	N/A	3.3 (first stage Lancy filter) ND[c] (second-stage carbon adsorption)	ND[c] (first Stage Lancy filter) 0.4 (second-stage carbon adsorption)	Lancy filter followed by carbon bed	8.4
4	Testing laboratory	Wastewater discharge from testing laboratory, 1,800 gallons per day	Full	N/A	60 (source of mercury-thimerosol[d])	1	Granulated activated carbon bed	8.7

Table 8.1
Adsorption Treatment Performance Data for Mercury (continued)

Project Number	Industry or Site Type	Waste or Media, Quantity	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/L)	Final Mercury Concentration (µg/L)	Adsorption Process or Media[a]	Source
5	Pharmaceutical industry, hospitals, and clinical laboratories	Pharmaceutical wastewater, 2,000 gallons	Pilot	Civil and Environmental Engineering Department, Villanova University, Villanova, Pennsylvania	2,500 (organic mercury[d]) 1,300 (Hg(II))	99.8 percent mercury removal[e]	Granulated activated carbon bed	8.6
6	Testing laboratory	Wastewater discharge from testing laboratory, 1,800 gallons per day	Pilot	N/A	60 (source of mercury-thimerosol[d])	ND[c]	Granulated activated carbon bed	8.7

[a] Some processes employ a combination of adsorption, precipitation/coprecipitation, pH adjustment and readjustment, and filtration to remove mercury from water.
[b] According to the text, heavy metals were removed by an electrochemical system and granular activated carbon was used to remove organic constituents. The GAC unit will serve as a polishing step for mercury.
[c] Detection limit not provided
[d] Thimerosal: $(C_9H_9HgO_2SNa)$
[e] Final mercury concentration not provided
N/A: Not available
gpm: Gallons per minute
µg/L: Micrograms per liter

Table 8.2
Available Mercury Treatment Cost Data for Adsorption

Site/Cost year	Scale	Amount Treated	Capital Cost	Annual O&M Cost	Unit Cost	Total Cost	Cost Explanation	Source	Project Number in Table 8.1
King of Prussia Technical Corporation Superfund Site, Winslow Township, New Jersey, December 1997 (Interim Results)	Full	225 gpm	$ 2.03 Million	$449,000 (total for performance period is $785,000)	Not available	$2.816 Million	Costs in 1997 dollars. The costs are for the entire treatment system (electrochemical precipitation followed by air stripping and granulated activated carbon). The treatment system treated multiple contaminants. Total cost is for the performance period April 1995 through December 1997.	8.1	1
Civil and Environmental Engineering Department, Villanova University, Villanova, Pennsylvania	Pilot	2,000 gallons (pilot study)	$7,700	$6,188	$0.107 capital and annual O&M	$69,580	Costs in 2001 dollars. Costs are projections based on the results of the pilot study. Costs were based on a design life of 10 years. Design volume is 64, 980 gallons per year.	8.6	5
Confidential testing laboratory in Massachusetts	Pilot and Full	1,800 gallons per day	$60,000	$91,980	Not available	Not available	Costs in 1992 dollars. Treatment is ongoing, thereby affecting the capital cost per gallon. Costs for the pilot study and full-scale operation were combined in the reference.	8.7	4 and 6

gpm   Gallons per minute
O&M   Operation and maintenance

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9.0   MEMBRANE FILTRATION

Summary

Membrane filtration can remove a wide range of contaminants from water. This technology has been used in a limited number of full-scale applications to treat wastewater contaminated with mercury. Before membrane filtration, a pretreatment step may be used to cause mercury to form precipitates or coprecipitates that can be more effectively removed by this technology. Membrane filtration can reduce concentrations of mercury to less than 2 µg/L.

Technology Description and Principles

Membrane filtration passes water through a semi-permeable, microporous membrane to concentrate contaminants into a smaller volume of water. This technology separates the influent into two effluent streams:

1. The permeate, or effluent stream, is the fluid that passes through the membrane. It usually contains reduced levels of contaminants. This stream may or may not contain contaminants at concentrations below the desired levels. If a reduction in concentration is still required, this stream may be sent to additional treatment units. In the case study described later, the permeate is neutralized and sent to an equalization and disposal unit.

2. The concentrate, or reject stream, contains water and contaminants that have not passed through the membrane. The reject may be recycled back through the membrane filtration system to further concentrate the contaminant and reduce the volume of reject. If the concentrate is not recycled, further treatment may include processing in a filter press, as in the case study described later (Ref. 9.5), or dewatering in solar evaporation ponds (Ref. 9.2).

Technology Description: Membrane filtration separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some of the constituents to pass through while blocking others (Ref. 9.4).
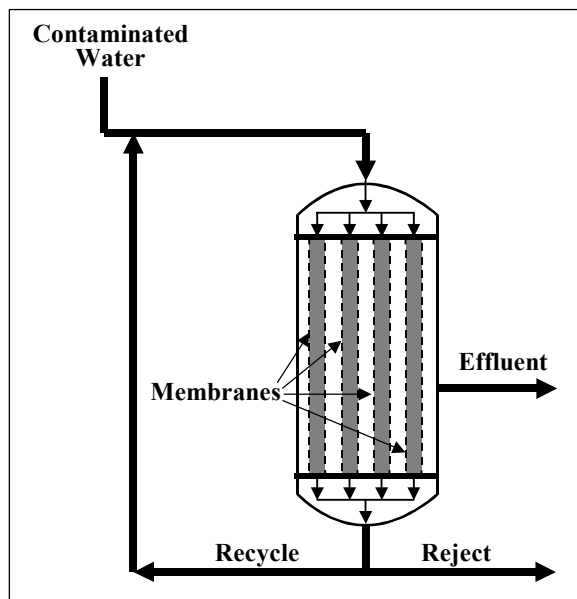
Media Treated:
- Drinking water
- Groundwater
- Surface water
- Industrial wastewater

Types of Membrane Filtration Processes:
- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse osmosis

Figure 9.1
Model of a Membrane Filtration System

Membrane filtration processes vary based on the pore size of the membrane. The pore size is selected based on the molecular weight or size of the target contaminant and the pressure required to move wastewater through the filter (Ref. 9.3). The four types of membrane filtration processes, from largest to smallest filter pore size, are (Ref. 9.1):

1. Microfiltration
2. Ultrafiltration (UF)
3. Nanofiltration
4. Reverse osmosis

UF has been used in a treatment train with precipitation/coprecipitation to treat wastewater that contains mercury. The sources used for this report did not contain information on the use of microfiltration, nanofiltration, or reverse osmosis to remove mercury. Therefore, these technologies are not discussed in this technology summary.

UF units are used to remove oils, suspended particles, and biological solids (Ref. 9.1). UF requires a pressure of 5 to 100 pounds per square inch (psi) to move the fluid through an ultrafiltration filter (Ref. 9.6). UF filters can filter out contaminants with a molecular weight greater than 1000 g/mole (Ref 9.3).

Applicability, Advantages and Limitations

UF is primarily used to remove high-molecular weight contaminants and solids. This technology is usually preceded by precipitation/coprecipitation to cause the mercury species to form or adsorb onto a suspended solid because dissolved mercury species are typically too small to be effectively removed by UF. The energy required to operate membrane filtration units is related to the pressure requirements (Ref. 9.3). This type of treatment may be run in either batch or continuous mode. This technology's effectiveness is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organic compounds, colloids, and other contaminants can cause membrane fouling.

Type, Number and Scale of Identified Projects Treating Water Containing Mercury

The references used for this report included information about one full-scale application of UF to treat mercury-contaminated wastewater.

Case Study: Episode #4671, Hazardous Waste Combustor

Ultrafiltration was included as part of a treatment train used to treat a variety of contaminants in wastewater generated by the APC equipment of a hazardous waste combustor. The wastewater treatment system included a primary and secondary treatment loop. The secondary treatment loop contained a stage for precipitation with sodium hydroxide followed by sedimentation and ultrafiltration. Analysis of samples collected at the influent and effluent of this treatment loop showed that the mercury concentration was reduced from 0.4 µg/L to below the detection limit of 0.2 µg/L (Ref. 9.5).

Summary of Performance Data

UF was used as part of a treatment train consisting of a primary and secondary loop in one application of membrane filtration to mercury-contaminated water. The secondary loop achieved a 54.5 percent reduction in the concentration of mercury. More detailed information about this site is presented in the box labeled "Case Study: Episode #4671". Cost data were not provided for this application.

August 2007

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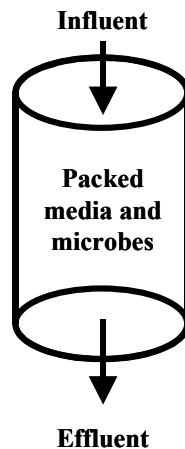
10.0 BIOLOGICAL TREATMENT

Summary

Biological treatment has been tested at pilot scale for *ex situ* treatment of mercury-contaminated wastewater in a limited number of projects. Biological treatment may convert mercury to species that are retained in the biomass or are more easily removed from water by another technology, such as adsorption or precipitation.

Technology Description and Principles

Although biological treatment has usually been applied to degrade organic contaminants, it is also applicable to treat mercury-contaminated wastewater. Figure 11.1 shows a simplified model of a biological treatment system to remove mercury from water (Ref. 11.5).

Figure 10.1
Model of a Biological Treatment System (Ref. 10.5)

Aerobic Biotreatment Process for Mercury

One process that has been applied at a pilot-scale project uses aerobic biological treatment to convert soluble ionic mercury (Hg^{2+}) into elemental or metallic mercury (Hg^0). This reaction is catalyzed by enzymes such as mercuric reductase, which is generated naturally in the cytoplasm of certain bacterial species (Refs. 10.1, 10.2, and 10.3). For example, certain strains of *Pseudomonas* are capable of reducing mercuric ion to elemental mercury. The less soluble elemental mercury collects in the microbial mass as small droplets, which must be subsequently extracted using another technology (Ref. 10.3).

Biological treatment technologies typically require amendments to create optimal growth conditions and provide nutrients to the microbial population. In this process, the treatment system includes pretreatment to adjust the pH to the optimal range of 6.5 to 7.5 using sodium hydroxide and phosphoric acid. An adequate amount of nutrient is required to support microbial growth. Nutrient additives used in this process include sucrose, sodium chloride (NaCl), and yeast extract (Ref. 10.3).

The contaminated water is passed through a packed bed bioreactor. The reactor bed is usually made of materials suitable for microbial growth, such as silica (SiO_2) and alumina (Al_2O_3). Before treatment begins, the microbial inoculum is distributed throughout the bioreactor bed through a series of steps that involves pumping combinations of nutrients, microbes, and wastewater through the bed (Ref. 10.3). After biological treatment, the bioreactor effluent is usually treated by activated carbon to remove residual mercury (Ref. 10.3). The biological treatment process results in solid residuals consisting of dead bacteria and elemental mercury. The sources used for this report do not contain information about the disposal methods for the solid residuals generated by this process.

Aqueous Biocyanide Process

Another process that has been applied at a pilot scale uses a series of aerobic and anaerobic biological treatment steps to remove mercury from wastewater (Refs. 10.1, 10.2). This process is designed primarily to treat cyanide in mining wastewaters, but also removes heavy metals, including mercury. This process uses a fixed-bed reactor with a combination of microbes, including proprietary microbial cultures and microorganisms isolated from the contaminated wastewater. The equipment used in this process includes an aerobic unit and an anaerobic unit, each consisting of a microbial culture tank and a bioreactor vessel. The treatment process involves alternating cycles of treatment and inoculation with periodic flushing between the two cycles. Contaminated wastewater is passed through the aerobic fixed-bed reactor system made of porous ceramic medium. The effluent from the aerobic reactor is then passed through the anaerobic reactor. This biological process converts soluble forms of mercury into less soluble forms, such as sulfides and other mineral phases. However, the references used for this report did not contain more specific information about the mechanism of mercury removal in this process (Refs. 10.1, 10.2).

Technology Description: Biological treatment of mercury-contaminated wastes is catalyzed by microbial enzymes. In one process, the soluble, ionic form of mercury is aerobically converted to insoluble elemental mercury by an enzyme called mercury reductase. The less soluble elemental mercury must be extracted using another technology (Ref. 10.3). In another process, a combination of aerobic and anaerobic treatment methods is used to convert soluble forms of mercury into insoluble mineral phases, such as sulfides (Refs 10.1 and 10.2). The effluent from the biological treatment system is normally subjected to further treatment by an activated carbon bed or precipitation before disposal (Refs. 10.1, 10.2, 10.3, 10.4, and 10.5).

Media Treated:
- Wastewater

Microbes Used:
- Mercury-tolerant strains of *Pseudomonas* spp.
- Proprietary microbial cultures

Amendments Used:
- Sucrose
- Yeast extract
- NaCl
- pH control reagents, such as NaOH and H_3PO_4
- H_2S

Technology Description (continued):

Technology Types Used:
- Fixed-bed aerobic bioreactor
- Fixed-bed bioreactors, with series of aerobic and anaerobic treatment steps

Media for Bed Packing:
- Al_2O_3 and SiO_2
- Porous ceramic medium

Applicability, Advantages, and Limitations

Biological treatment of mercury involves conversion of soluble mercury into a less soluble elemental form or into insoluble mercuric sulfide (Refs. 10.1, 10.3). High concentrations of contaminants such as mercury or chlorine can inhibit microbial activity. Nutrients, pH, and temperature must be maintained at levels that optimize biological activity and growth (Refs 10.1, 10.2, and 10.3). Pretreatment with pH amendment agents such as NaOH or H_3PO_4 is essential to maintain an optimal pH range. Nutrient additives such as sucrose, yeast, and NaCl may be required to support the growth of microbes. The bioreactor effluent typically requires further treatment by methods such as activated carbon adsorption or precipitation to ensure residual mercury is removed before disposal (Refs. 10.3 and 10.4).

Factors Affecting Biological Treatment Performance and Cost

- **pH:** neutral pH of 6.5 to 7.5 is optimal for aerobic biotreatment processes (Ref. 10.3).
- **Contaminant concentration:** High concentrations of mercury may be toxic to microorganisms used in biological treatment (Ref. 10.4).
- **Available nutrients:** The presence of sufficient amount of nutrients, such as sucrose and yeast extract, is crucial to the performance of a biological system because nutrients are essential for the growth of microorganisms (Refs. 10.3 and 10.4).
- **Temperature:** Lower temperatures (35 to 45 °F) decrease biological reaction rates. Heating may be required to maintain biological activity (Ref. 10.4). Temperature higher than 85 °F may be harmful to the microorganisms (Refs. 10.1, 10.3).
- **Chloride concentration:** The presence of chloride at concentrations greater than 0.5 mg/L may inhibit microbial growth (Ref. 10.3).

Type, Number, and Scale of Identified Projects Treating Wastes Containing Mercury

Data sources used for this report included information about two pilot-scale applications of biological treatment to wastewater contaminated with mercury.

Summary of Performance and Cost Data

The information collected to prepare this report contained data on two applications of biological treatment for mercury. Table 10.1 summarizes the performance information for one pilot-scale application for electrolysis wastewater from a chlor-alkali manufacturing plant and one pilot-scale application for metal mining wastewater. Information about the amount of media treated was not available. For Project 1 (Table 10.1), the initial concentration of mercury ranged from 2,000 to 5,000 µg/L. The concentration of mercury in the effluent ranged from 30.7 to 40.7 µg/L. For Project 2, initial concentration of mercury

ranged from 151 to 164 µg/L. The concentration of mercury in the treated effluent ranged from 3 to 11 µg/L. Although significant mercury reductions were achieved, this technology did not reduce the concentration to less than 2 µg/L in either of these applications. However, information on the treatment goals for these applications was not available, and these applications may not have been designed to treat mercury to less than 2 µg/L.

The data sources used for this report did not provide information about the cost of these projects.

Case Study: Echo Bay/McCoy Cove Mine Site, Nevada

An innovative bioremediation process was tested at pilot scale to treat mercury in wastewater from the Echo Bay/McCoy Cove Mine (Table 10.1, Project 2). This project was evaluated by the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program (Ref. 10.1, 10.2). The treatment method used is a proprietary process known as the Aqueous Biocyanide Process. This process consists of aerobic and anaerobic fixed-bed bioreactor units. This application of the Aqueous Biocyanide Process used microorganisms isolated from the mine stream in combination with proprietary microbial cultures. A biofilm of the microbial mass was formed on the reactor bed, which was made of a porous ceramic medium. This biofilm converted the soluble ionic form of mercury (Hg^{2+}) into more stable mineral phases, primarily mercuric sulfide (HgS). The treatment process in this pilot test included aerobic and anaerobic pathways with the following three steps: (1) inoculation of the culture tanks with microbial cultures; (2) treatment of contaminated media fed into the inoculated tanks; and (3) flushing to remove process wastes from the culture tanks. Influent concentrations of mercury ranged from 151 to 177 µg/L. Final concentrations of mercury ranged from 3 to 11 µg/L. The information sources used for this report did not provide data about the total amount of waste treated during this project. The sources also did not provide information about the treatment goals for this project and the disposal methods for the flush water and treated effluent.

Table 10.1
Biological Treatment Performance Data for Mercury

Project Number	Industry and Site Type	Waste or Media	Scale	Site Name, Location, and Project Completion Date	Initial Mercury Concentration (µg/L)	Final Mercury Concentration (µg/L)	Process	Source
1	Chlor-alkali manufacturing	Electrolysis wastewater	Pilot	Chlor-alkali Manufacturing site; Completed	2,000 to 5,600 µg/L	30.7 to 40.7 µg/L	Fixed-bed aerobic bioreactor packed with granular Al_2O_3 and SiO_2 and inoculated with mercury-resistant strains of *Pseudomonas* species. Treatment train consisted of pH amendment by NaOH or H_3PO_4, followed by addition of nutrients including sucrose, yeast extract, and NaCl, treatment in an aerobic bioreactor, and activated carbon adsorption.	10.3
2	Metal ore mining	Mine wastewater	Pilot	Echo Bay/McCoy Cove Mine site, Nevada; Completed; August 1997	151 to 164 µg/L	3 to 11 µg/L	Aerobic and anaerobic fixed-bed bioreactors packed with porous ceramic medium and inoculated with a consortium of site-specific and proprietary microbial cultures.	10.1, 10.2

Note:
µg/L: Micrograms per liter
Al2O3: Alumina
SiO_2: Silica
NaOH: Sodium hydroxide
H_3PO_4: Phosphoric acid

References

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PART III

ONGOING RESEARCH ON MERCURY TREATMENT

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11.0   ONGOING RESEARCH ON MERCURY TREATMENT

Sections 3.0 to 10.0 of this report provide examples of full- and pilot-scale projects of technologies that apply to treatment of mercury. This section summarizes selected bench-scale projects that involve the evaluation of innovative technologies for their ability to treat mercury. The technologies covered include nanotechnology, phytoremediation, and air stripping. Research is under way on reactive capping materials such as bauxite for mercury in sediments (Ref. 11.8). These innovative technologies have the potential to provide more cost-effective and reliable alternatives for mercury treatment. Based on information from the limited number of applications of these technologies that have been identified, they may be used to treat mercury more frequently in the future. However, additional data are needed to obtain a full understanding of their applicability and effectiveness.

11.1   Nanotechnology

An example of research on use of nanotechnology for mercury in an aqueous waste stream is the Thiol Self-Assembled Monolayers on Mesoporous Silica (Thiol-SAMMS). This novel adsorbent was developed by the staff of Pacific Northwest National Laboratory (PNNL). It consists of a nanoporous ceramic substrate with a high surface area made functional by a monolayer of thiol groups. The substrate is typically synthesized through a self-assembly process that uses sol-gel precursors and surfactant molecules. Subsequent calcination to 500°C removes the surfactant templates and leaves nanoporous ceramic substrate with a high surface area, which can be used for self-assembled monolayers of adsorptive functional groups (Ref. 11.1). Thiol functional groups are known to have a high affinity for various heavy metals, including mercury. The thiol groups are embedded in the ceramic substrate on one end and bind with mercury on the other end (Ref. 11.2).

Thiol-SAMMS is capable of selectively binding with mercury and can achieve a mercury loading capacity as high as 635 milligrams per gram. In addition, test data indicate that the mercury adsorption of SAMMS is not significantly affected by the presence of other cations and complexing anions in waste solutions (Ref. 11.2).

A pilot-scale treatability test was conducted to assess the ability of thiol-SAMMS to remove soluble mercury from an aqueous melter condensate waste stream. The treatment was conducted on 160 liters of waste using a module consisting of a batch reactor equipped with a mixer, a filtration unit, a pump, and a holding drum for treated effluent. The waste was filtered into the batch reactor using a 1.0 micron (μm) filtration unit. The initial treatment was conducted by adding 195 grams of thiol-SAMMS (3.5 nanometers pore size). The SAMMS material was stirred into the waste by turning on the mixer. The adsorption reaction was allowed to proceed for 12 hours, when the spent sorbent was separated by pumping the mixture through the filtration unit equipped with a 50-μm filter. An aliquot of treated effluent was removed using a syringe filter and analyzed for residual mercury concentration (Ref. 11.5).

Two more sequential treatment steps were conducted on the treated effluent to achieve higher levels of mercury reduction. In the second step, 248 grams of thiol-SAMMS was added to the effluent from the first treatment. In the third step, approximately 190 grams of thiol-SAMMS material was added to the effluent from the second treatment (Ref. 11.5).

The results showed that the first treatment removed about 97.4 percent of dissolved mercury from the waste with a residual concentration of 0.28 mg/L. The second treatment reduced the residual concentration of mercury to 0.18 mg/L. The final treatment removed 99.4 percent of the dissolved mercury originally present in the untreated waste, resulting in a residual concentration of 0.06 mg/L. These data demonstrate that dissolved mercury in the melter waste stream can be effectively scavenged

using thiol-SAMMS sorbent (Ref. 11.5). The success of these tests, among others, has led PNNL to begin commercializing thiol-SAMMS (Ref. 11.2).

11.2   Phytoremediation

Phytoremediation is another technology that is being evaluated for its effectiveness in removing mercury from sediments and other media. Phytoremediation uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediment, and groundwater. Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants (including the rhizosphere) and that aid in cleanup of the contaminated substances. Plants can be used in site remediation, both through mineralization of toxic organic compounds and through accumulation and concentration of heavy metals and other inorganic compounds from soil into aboveground shoots. Phytoremediation may be applied *in situ* or *ex situ* to soils, sludges, sediments, other solids, or groundwater (Ref. 11.7).

Plants can be genetically engineered to enhance their ability to detoxify mercury. An example of the development of a transgenic plant is the modification of the rice plant (*Oryza sativa*) to remove mercury from aquatic sediments. The plant is injected with a gene (*merA*) that produces an enzyme, mercuric reductase (merA) capable of converting ionic mercury to elemental mercury, which then volatilizes from the sediments (Ref. 11.3). Various studies have been conducted on rice and other plants to evaluate their ability to remediate mercury. Examples of two such studies are provided below. Although both examples show that phytoremediation of mercury is possible, further research and pilot-scale studies will be needed to assess the effectiveness of the technology at full scale. In addition, full-scale implementation will require consideration of issues, such as disposal of contaminated plants and the impacts of volatilized mercury on other ecosystems (Ref. 11.3).

A bench-scale study was conducted to evaluate the ability of transgenic rice to detoxify mercury-polluted aquatic sediments. A culture of rice embryos was injected with *merA,* and the plants were then grown from the embryo culture on different types of media spiked with Hg^{+2} ions. Mercury vapor assays were conducted to study the extent of mercury resistance among the plants and their ability to remove mercury from the substrate. Three 1-week-old germinants of *merA* and the wild type (not genetically engineered) were incubated in 2 millilters of assay medium containing 250 micro molar $HgCl_2$. Incubation was carried out in a specialized reaction tube, and the headspace from the reaction tube was evacuated into a Jerome 431-X mercury vapor analyzer immediately after each seedling was placed in the medium. The headspace was then resampled each minute for 10 minutes. The assays showed that the concentration of elemental mercury was higher in the headspace of the *merA* germinates than in the wild-type germinates, indicating enhanced mercury-reducing activities of the genetically engineered plants. Both sets of plants were able to remove Hg^{+2} ions when grown in a mercury-spiked hydroponics medium. However, the lower concentration of Hg^{+2} in the tissues of the *merA* rice compared with the wild type indicates that more mercury was volatilized from the *merA* plants. These results suggest that genetically engineered rice can remove mercury from its substrate (Ref. 11.3).

In addition to rice plants, cottonwood trees have been evaluated for their ability to remediate mercury. Eastern cottonwood trees (*Populus deltoides*) grow rapidly in a variety of conditions, including riverbanks and floodplains. They have been engineered to express the *merA* gene, convert methylmercury to ionic mercury (*merB* gene), and hyperaccumulate mercury. A field study using these trees was conducted by Applied PhytoGenetics, Inc. (APGEN) in 2003 at a Brownfields site in Danbury, Connecticut, that was formerly used for hat manufacturing. Results of the study, however, were not available when research was conducted for this report (Ref. 11.6).

11.3   Air Stripping

Air stripping is another technology that is being evaluated for its ability to remove mercury from water. Air stripping generally has not been used to remove inorganic compounds such as mercury. However, a bench-scale study was conducted at the Savannah River Site in South Carolina to evaluate whether chemical reduction followed by collection of elemental mercury from the headspace air can remove low levels of mercury from groundwater (Ref. 11.4). The groundwater was obtained from the feed and effluent of an existing groundwater treatment system installed to remediate a chlorinated solvents plume. The technology tested used stannous (Sn^{+2}) chloride to reduce Hg^{+2} to Hg^0, which is volatile (vapor pressure of 0.0027 milligrams per mercury per liter of air), followed by collection of elemental mercury from the headspace air to remove the elemental mercury from water. Mercury concentrations in the extracted groundwater ranged between 120 and 150 nanograms per liter (ng/L), and more than 95 percent of the mercury was Hg^{+2}. Stannous chloride was added to groundwater samples in dosages ranging from 0 to 766 mg/L. After stannous chloride had been added, groundwater samples were sparged with air at an air-water ratio of approximately 30 to 1. Stannous chloride doses greater than 0.011 mg/L resulted in more than 94 percent mercury removal, with the residual total mercury reduced to levels below 10 ng/L. However, low doses of stannous chloride (less than 0.00023 mg/L) showed little removal of mercury.

This study indicates that chemical reduction coupled with air stripping is effective for treating mercury. The technology does not produce any liquid or solid secondary wastes, and off-gas treatment may not be required for the expected air concentrations and mass release. If necessary, however, off-gas treatment could be incorporated using a low-temperature treatment system for gas-phase elemental mercury. As a result, it is a promising, low-cost option for treating mercury and is expected to cost less than conventional metal treatment technologies. Before it is implemented in the field, however, the environmental effects of introducing stannous chloride should be evaluated. Successful development of a chemical-reduction-based treatment system requires additional data on the key scientific questions (for example, stoichiometry and robustness) and engineering evaluation of whether reliable long-term operation can be achieved (Ref. 11.4).

11.4   *In Situ* Thermal Desorption (ISTD)

ISTD is being evaluated for its ability to treat mercury. ISTD is a soil remediation process that applies both heat and a vacuum to the subsurface to extract and degrade contaminants.

Laboratory soil column experiments have been conducted that show that ISTD is capable of treating mercury-contaminated soils. In one such experiment, approximately 15.03 grams of mercury were injected into a column packed with Ottawa sand. Experiments were performed at 244°C and an airflow rate of 76 mL/minute. Analysis of the soil after remediation showed that only 11.1 mg of mercury remained in the soil after the experiment, corresponding to a removal efficiency of 99.9% (Ref. 11.9). This study indicates that ISTD has the potential to remove mercury from contaminated soil. Further research activities are ongoing to determine the effectiveness of the technology in the field.

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Appendix A

Information on Select Mercury Vapor Detection Instruments

	Jerome 431	Jerome J405	Jerome 471	Mercury/ Emp-1	Vm-3000	Lumex RA-915+	Lumex RA-915+/RP-91C	Lumex RA-915+/Pyro 915
Manufacturer	Arizona Instrument, LLC, AZ	Arizona Instrument, LLC, AZ	Arizona Instrument, LLC, AZ	Nippon Instruments Corporation, Japan	Mercury Instruments GmbH, Germany	Lumex, Russia (final assembly- Twinsburg, Ohio)	Lumex, Russia (final assembly- Twinsburg, Ohio)	Lumex, Russia (final assembly- Twinsburg, Ohio)
Distributor	–	–	–	Brandt Instruments Inc., LA	ST2 Service Technologies, Inc. CO	OhioLumex Co., OH	OhioLumex Co., OH	OhioLumex Co., OH
Units	mg/m^3	$\mu g/m^3$	$\mu g/m^3$	mg/m^3	$\mu g/m^3$	ng/m^3	ppb	ppb
Range	.003 to 0.999 mg/m^3	0.5 to 999 $\mu g/m3$	0.030 to 250 $\mu g/m3$	Zero to 0.999 1 to 5.00	Zero to 100 Zero to 1000 Zero to 2000	Zero to 500,000	10ppb to 1000ppm	0.5 ppb-100ppm
Methodology	Change in resistance of gold after mercury absorption	Change in resistance of gold film after mercury absorption	UV Atomic Absorption Spectrometry	Ultraviolet absorption "cold vapor measuring technique"	Ultraviolet absorption "cold vapor measuring technique"	Zeeman atomic absorption spectrometry-high-frequency modulation of light polarization	Zeeman atomic absorption spectrometry-high-frequency modulation of light polarization Direct, (no sample preparation) solid/ water analysis in 2 minutes	Zeeman atomic absorption spectrometry-high-frequency modulation of light polarization Direct, (no sample preparation) solid/ water analysis in 2 minutes
Accuracy, percent	±5% at 100 ug/m^3	±10% at 1 $\mu g/m3$	±10% at 0.5 $\mu g/m3$	5	–	+/-10%	+/-10%	+/-10%

	Jerome 431	Jerome J405	Jerome 471	Mercury/ Emp-1	Vm-3000	Lumex RA-915+	Lumex RA-915+/RP-91C	Lumex RA-915+/Pyro 915
Sensitivity	0.003 mg/m^3	0.013 µg/m^3	0.001 µg/m^3	0.001 (low range) 0.01 (high range)	0.1	0.5 ng/m^3	10 ppb	500 ppt
Response Time	12 seconds – sample mode 4 seconds – survey mode	12 seconds- sample mode 2 seconds- survey mode	40-55 seconds until 1st reading, then 1 reading every second	Instantaneous and 5-minute averages	1 second	1 second	90 seconds	90 seconds
Wavelength	Not applicable	Not applicable	253.6 nm	254 nm	253.7 nm	254 nm	254 nm	254 nm
UV source	Not applicable	Not applicable	Mercury Vapor Lamp	Low-pressure mercury discharge lamp	Electrodeless Hg low pressure lamp	Glow discharge mercury lamp	Glow discharge mercury lamp	Glow discharge mercury lamp
Stabilization	Not applicable	Not applicable	20 minutes	Reference beam	Reference beam and thermal	5 minutes	1 hour	1 hour
Optical cell	Not applicable	Not applicable	Dual-reference and sample cell	—	Fused silica, 25 centimeters long	Multi-path cell, 10 meter	Multi-path cell, 12 cm.	Multi-path cell, 24 cm
Heating of cell	Not applicable	Not applicable	Not applicable	—	70°C	Not required	Heated, 700°C	Heated, 700°C
Pump	0.75 L/min	0.75 L/min	5 L/min	1.5 L/min	Membrane, 2 L/min	10 L/min	4 L/pm	4 L/pm
Filter	Yes	Yes	Yes	Glass wool	PTFE, 1 µ, 47-50 mm diameter	Yes	Yes	Yes

	Jerome 431	Jerome J405	Jerome 471	Mercury/ Emp-1	Vm-3000	Lumex RA-915+	Lumex RA-915+/RP-91C	Lumex RA-915+/Pyro 915
Calibration	Factory	Factory	Factory	Automatic, using an absorber	Factory	Daily by built in test cell/factory calibration once per year	Daily	Daily
Power	115 V or 230 V	100-240V AC	100-240V AC	None	230 V / 50/60 Hertz or 110-120 V / 50/60 Hertz optional	220 V, 50 Hertz or 110 V, 60 Hertz	220 V, 50 Hertz or 110 V, 60 Hertz	220 V, 50 Hertz or 110 V, 60 Hertz
Battery	Internal Ni-Cd batteries, (5 hours capacity)	Internal rechargeable NiMH (24 hours capacity)	Rechargeable NiMH (16 hours capacity)	Integrated rechargeable battery (11 hours capacity)	Integrated 12 V batteries, (6 hours capacity)	Built-in 6 V, rechargeable lead acid	Built-in 6 V, rechargeable lead acid	Built-in 6 V, rechargeable lead acid
Weight	3.18 kg	2.27 kg	8.2 kg	4.2 kg	Approx. 7 kg	7.2 kg (16 Lbs)	11 kg (24 Lbs)	11kg (24 Lbs)
Dimensions (W x H x D)	15.6 x 33.8 x 10.4 cm	16 x 16.5 x 28 cm	15.5 x 20.5 x 48.5 cm	11.3 x 23.8 x 25.6 cm	45 x 15 x 35 cm	46 x 21 x 11 cm (18 x 8 x 4.3 inches)	46 x 21 x 26 cm (18 x 8 x 12 inches)	46 x 21 x 26 cm (18 x 8 x 12 inches)
RS 232 standard (interface)	None	USB (host and slave)	USB slave	None	Yes	Yes - datalogger	Computer	Computer

Sources:

Personal communication between Raj Singhvi, EPA Emergency Response Team (ERT) and Marti Otto, EPA Office of Superfund Remediation and Technology Innovation (OSRTI). March 6, 2006.

E-mail from Joseph Siperstein, Ohio Lumex Co., to Martha Otto, EPA, regarding the Lumex RA-915+, Lumex RA-915+/RP-91C, and Lumex RA-915+/Pyro 915 instruments. March 26, 2007.

cm	Centimeter
—	Information not available
kg	Kilogram
L/min	Liters per minute
$\mu g/m^3$	Micrograms per cubic meter
mg/m^3	Milligrams per cubic meter
ng/m^3	Nanograms per cubic meter
nm	Nanometer
ppb	Parts per billion
ppm	Parts per million
V	Volts

Treatment Technologies For
Mercury in Soil, Waste, and Water

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Washington D.C. 20460