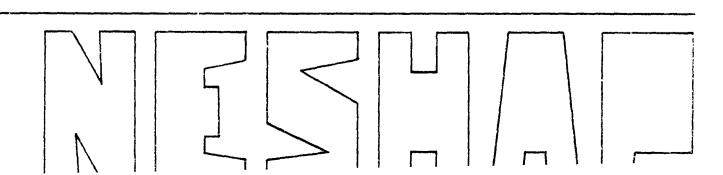
United States Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park NC 27711 ÉPA-450/3-84-014 December 1984

Air

## SEPA

# Review of National Emission Standards for Mercury





## Review of National Emission Standards for Mercury

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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#### ENVIRONMENTAL PROTECTION AGENCY

Background Information for Review of the National Emission Standards for Mercury

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- 1. The Federal Register notice summarizes information gathered during the review, proposes the addition of monitoring and reporting requirements to the standard for mercury-cell chlor-alkali plants, and proposes to allow the owner or operator of any affected facility 15 days to verify the validity of source test data prior to reporting the results to the Administrator.
- 2. Copies of this document have been sent to the following Federal Departments: Labor, Health and Human Services, Defense, Transportation, Agriculture, Commerce, Interior, and Energy; the National Science Foundation; the Council on Environmental Quality; State and Territorial Air Pollution Program Administrators; EPA Regional Administrators; Local Air Pollution Control Officials; Office of Management and Budget; and other interested parties.
- 3. The comment period for review of this document is 75 days from date of proposal in the Federal Register. Mr. Gilbert H. Wood may be contacted at (919) 541-5578 regarding the date of the comment period.
- 4. For additional information, contact:

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5. Copies of this document may be obtained from:

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#### EXECUTIVE SUMMARY

The national emission standard for mercury was promulgated by the U.S. Environmental Protection Agency (EPA) on April 6, 1973. The standard regulates those sources that have the potential to emit mercury in a manner that could cause the daily mercury ambient concentration averaged over 30 days to exceed 1.0  $\mu g/m^3$  (4.37 x10-7 gr/ft³), a guideline value for adverse health effects. Initially the standard regulated mercury air emissions from mercury-cell chlor-alkali plants and mercury ore processing facilities. The standard was amended on October 14, 1975, to also regulate mercury air emissions from sludge incineration and drying plants. Testing procedures were amended in 1978 and 1982.

This study was made to assess the need to revise the standard for mercury. Sources subject to the standard were identified, and information was obtained on compliance and enforcement experience. Part of the study was devoted to determining the need to include sources not covered by the standard. Information was gathered from EPA files, literature reviews, plant visits, telephone contacts with EPA region and State personnel, and through information requests to industry personnel. The following paragraphs summarize the findings of this study.

#### 1.1 SUMMARY--REVIEW OF SOURCE CATEGORIES REGULATED BY STANDARD

#### 1.1.1 Compliance Status

There are 24 mercury-cell chlor-alkali plants, 1 mercury ore processing facility, and approximately 172 sludge incineration plants and 5 sludge drying plants subject to the national emission standard for mercury. All affected facilities are currently in compliance with the mercury emission limits set by the standard. The mercury ore processing facility and sludge incineration and drying plants meet the standard without

specific controls for mercury, with emissions ranging from 0 to 1,234 g/d total mercury (0 to 2.7 lb/d). Mercury-cell chlor-alkali plants reduce mercury air emissions using the following control techniques: cooling, mist elimination, chemical absorption, activated carbon adsorption, and molecular sieve adsorption. All mercury-cell chlor-alkali plants have elected to demonstrate compliance with approved EPA design, maintenance, and housekeeping practices for cell rooms in lieu of testing cell room emissions. Compliance tests conducted since 1973 show that for several facilities the combined mercury emissions from the hydrogen and end-box ventilation systems approach the emission limit set for these gas streams.

#### 1.1.2 Enforcement Aspects

State and EPA regional personnel responsible for enforcing the mercury standard have not encountered any significant enforcement problems. Presently there are no monitoring or reporting requirements for chloralkali companies in the standard. Because of the importance of cell-room housekeeping and maintenance practices to controlling emissions from mercury-cell chloralkali plants and because some plants are approaching the limit set for the combined hydrogen gas and end-box ventilation streams, there is a need for monitoring requirements for housekeeping and maintenance practices and for control equipment performance. This is consistent with comments made by EPA regional and State enforcement personnel.

#### 1.2 SUMMARY--INVESTIGATION OF OTHER SOURCE CATEGORIES

Mercury is emitted to the atmosphere from a number of sources in addition to those regulated by the national emission standard. Sources include power plants, nonferrous smelters, solid waste incinerators, by-product mercury from gold mining, battery manufacturing, mercury vapor lamp manufacturing, instrument manufacturing, paint manufacturing, manufacture of mercury compounds, laboratory use of mercury, use of dental amalgams, and secondary mercury recovery. Only battery manufacturin and secondary mercury recovery were selected for investigation as candidate for regulation based on the probable magnitude of their air emissions.

#### 1.2.1 Mercury Emissions Potential From Battery Manufacturing

Mercury in the form of zinc amalgam, mercuric oxide, mercuric chloride, or mercurous chloride is a component of most primary batteries and some storage batteries. Information on facilities manufacturing mercuric oxide-zinc, mercuric oxide-cadmium, alkaline-manganese, and Leclanche carbon-zinc batteries was obtained in this study. This information indicates that one large integrated mercuric oxide battery manufacturi facility (battery manufacture, oxide manufacture, and secondary recovery at one site) and several large alkaline-manganese battery manufacturing facilities have the potential for significant mercury emissions.

Ambient mercury levels greater than  $1 \mu g/m^3$  (4.37 x10-7 gr/ft³) have been measured over a 6- to 9-hour period at points on the plant perimeter of an integrated mercuric oxide battery manufacturing facility. Atmospheric dispersion modeling, however, showed that the maximum 30-day average ambient mercury concentrations would not approach the health effects guideline. Mercury vapor emissions at this facility are largely uncontrolled, while particulate mercury emissions are generally well controlled by baghouses and other particulate filters.

A large alkaline-manganese battery manufacturing facility may use up to 910 kg/d (2,000 lb/d) of mercury. Mercury vapor emissions are uncontrolled at these plants. Particulate mercury emissions can be controlled by baghouses. Industry estimates suggest that mercury air emissions may reach 800 g/d (1.8 lb/d) from some of these plants. Atmospheric dispersion modeling indicated that the health effects guideline would not be exceeded at these facilities.

### 1.2.2 Mercury Emissions Potential From Secondary Mercury Recovery

Large secondary mercury recovery retorting operations have the potential for significant uncontrolled mercury vapor emissions because of the amount of mercury recovered. Information on three mercury recovery facilities was obtained in this study. Emissions are controlled by a water spray at the first facility, a water scrubber and charcoal filter in series on an experimental basis at the second facility, and a condenser at the third facility. Estimated emissions are not large enough to cause the ambient concentration guideline to be exceeded.

at the third facility. Estimated emissions are not large enough to cause the ambient concentration guideline to be exceeded.

#### 2. CURRENT STANDARDS

#### 2.1 NATIONAL EMISSION STANDARD

#### 2.1.1 Affected Facilities

The national emission standard for mercury was developed to regulate sources that have the potential to emit mercury in a manner that could cause the inhalation health effects limit of 1.0  $\mu g/m^3$  (4.37 x10-7 gr/ft³) of mercury (daily concentration averaged over 30 days) to be exceeded. Based on this criterion, the national emission standard for mercury has been applied to stationary sources that process mercury ore to recover mercury, use mercury chlor-alkali cells to produce chlorine gas and alkali metal hydroxide, and incinerate or dry wastewater treatment plant sludge.

#### 2.1.2 Controlled Pollutant and Emission Levels

Allowable emission limits for the affected facilities were derived from the ambient concentration guideline by using atmospheric dispersion models. The national emission standard limits mercury emissions to the atmosphere as follows:

- 1. Mercury ore processing facility--2,300 g (5 lb) per 24-hour period
- 2. Mercury cell chlor-alkali plant--2,300 g (5 lb) per 24-hour period and
- 3. Sludge incineration plants, sludge drying plants, or combination of these that process wastewater treatment plant sludges--3,200 g (7 lb) of mercury per 24-hour period.

"Mercury" means the element mercury, excluding any associated elements, and includes mercury in particulates, vapors, aerosols, and compounds.

#### 2.1.3 Testing Requirements

Performance tests to verify compliance with the mercury standard must be conducted within 90 days of the effective date of the standard for existing sources and of the initial startup date for new sources. The following EPA reference methods are used to determine compliance:

- 1. Method 101--Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants--Air Streams:
- 2. Method 101A--Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators;
- 3. Method 102--Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants--Hydrogen Streams; and
- 4. Method 105--Method for Determination of Mercury in Wastewater Treatment Plant Sewage Sludges.

Owners or operators of mercury chlor-alkali cells may test cell room emissions by passing all air in forced gas streams through stacks suitable for testing. Alternatively, ventilation emissions of 1,300 g/d (2.8 lb/d) of mercury may be assumed if compliance with approved design, maintenance, and housekeeping practices is demonstrated. This alternative effectively results in an emission limit of 1,000 g/d (2.2 lb/d) of mercury for the hydrogen and end-box ventilation streams. Stack sampling requirements for mercury recovery retorts at chlor-alkali plants are not specified in the standard.

Owners or operators of sludge incineration and drying plants may elect to conduct stack tests using Method 101A. Alternatively, they may demonstrate compliance by determining the mercury concentration of the sludge using Method 105. Mercury emissions are estimated using the equation:  $E_{\text{H}\alpha} = 1 \times 10^{-3} \text{ cQ}$ 

where  $E_{Hq} = mercury emissions, g/d;$ 

c = mercury concentration in sludge on a dry solids basis,  $\mu g/g$ ; and Q = sludge charging rate, kg/d.

#### 2.1.4 Monitoring Requirements

No monitoring requirements for mercury ore processing facilities or mercury cell chlor-alkali plants are included in the national emission standard. A monitoring requirement is included for sludge incineration and drying plants. Sources that exceed 1,600 g/d (3.5 lb/d) of mercury

emissions must monitor and report emissions at intervals of at least once per year.

#### 2.2 STATE REGULATIONS

State air regulations listed in the <u>Environment Reporter</u> were compared with the national emission standard for mercury to identify differences. Of the 50 States, District of Columbia, and Puerto Rico, 28 do not have specific mercury regulations. Twenty States and Puerto Rico have adopted the mercury national emission standard by reference or have regulations identical to the national standard. Two States, Colorado and Oregon, apply the 2,300 g/d (5 lb/d) limit to all sources using mercury. The State of Wisconsin has an ambient air standard for mercury of 1  $\mu$ g/m³ (4.37 x10-7 gr/ft³) on a 30-day average for all mercury emission sources in addition to an emission limit of 2,300 g/d (5 lb/d) for chlor-alkali plants and ore processing facilities.

#### 2.3 REFERENCE FOR CHAPTER 2

 Memorandum, M. Sauer, MRI, to N. Georgieff, EPA. March 25, 1983. State mercury air emission regulations. Docket No. A-82-41, Document No. (II-B-7).

#### 3. MERCURY-CELL CHLOR-ALKALI PROCESS

#### 3.1 INTRODUCTION

Three types of electrolytic cells are used in the U.S. to produce chlorine and caustic: the mercury cell, the diaphragm cell, and the membrane cell. Mercury is emitted to the atmosphere only from the mercury-cell process.

There are 32 chlorine producing companies, with 60 chlor-alkali plants, in the U.S. Mercury-cell technology is used at 24 plants, diaphragm-cell technology is used at 34 plants, and membrane-cell technology is used at two plants. Mercury-cell chlor-alkali plants in the U.S. are listed in Table 3-1 along with the year built and type of cells used at each plant.

Average chlorine production by all processes increased only slightly from 25,855 Mg/d (28,500 tons/d) in 1973 to 26,243 Mg/d (28,928 tons/d) in 1981.<sup>2</sup> Total installed chlorine capacity increased from 26,892 Mg/d (29,643 tons/d) in 1973 to 35,835 Mg/d (39,502 tons/d) in 1981.<sup>2</sup> The percent of total installed chlorine capacity using mercury cells decreased from 25 percent in 1973 to 19 percent in 1982.<sup>3</sup> The chlor-alkali industry used 6,516 flasks (225 Mg [248 tons]) of mercury in 1982.

It is probable that no new mercury-cell chlor-alkali plants will be built in the U.S. in the future. A No new plants have been built since the national emission standard was promulgated in 1973. There has been some new construction in the chlor-alkali industry but not in the mercury-cell segment. In the future, membrane-cell technology may take precedence over both the mercury-cell and diaphragm-cell technologies.

TABLE 3-1. MERCURY-CELL CHLOR-ALKALI PLANTS IN THE UNITED STATES<sup>5</sup>

Company/location	Year built	Cell type
Convent Chemical Company <sup>a</sup>	1966	De Nora 24H5
(Subsidary of B. F. Goodrich)		
Calvert City, Ky.		
Diamond Shamrock Corp.,		
Deer Park, Tex. a	1938	De Nora 18 SGL;
0.7 av. 5.3 b		(also diaphragm cell)
Delaware City, Del. <sup>b</sup> Mobile, Ala.	1965	De Nora 18x4
Modile, Ala.	1964	De Nora 18x4
Muscle Shoals, Ala.b	1952	De Nora 24x2M
deorgia Pacific Company	1965	De Nora 18x4
Bellingham, Wash.		
Linden Chemicals & Plastics, Inc.	1062	Column V-200
Acme, N.C.	1963 1963	Solvay V-200
Ashtabula, Ohio <sup>d</sup> Brupswick Ga	1957	Olin EllF
Brunswick, Ga. <sup>a</sup> Linden, N.J. <sup>a</sup>	1956	Solvay V-100
Emden, m.o.	1550	BASF-Krebs (1969); Krebs (1963)
Moundsville, W. Ya. <sup>a</sup>	1953	Solvay S60
Orrington, Maige	1967	De Nora 24H5
Syracuse, N.Y.	1927	Solvay S60 (1953);
	all of the ?	(also diaphragm cell)
Monsanto Company <sup>b</sup>	1922	De Nora 18x6
Sauget, III.		
Occidental Chemical d	1971	Uhde 20 sq. m
Corporation/IMC Corporation		•
(Hooker-Sobin Joint Venture)		
Niagara Falls, N.Y.		
Olin Corporation		
Augusta, Ga. a	1965	Olin EllF
Charleston, Tenn. <sup>a</sup>	1962	Olin E11F, E812
McIntosh, Ala.	1952	01in E8
Niagara Falls, N.Y. <sup>a</sup>	1897	Olin E11F (1960)
PPG Industries, Inc.	1047	Do Novo 4005 (1000).
Lake Charles, La.ª	1947	De Nora 48H5 (1969);
New Martinsville, W. Va. <sup>a</sup>	1943	(also diaphragm cell)
new ratetilisvitte, w. va.	1343	Uhde 20 sq. m (1958); (also diaphragm cell)
Stauffer Chemical Company		(a.130 arapin agiii cerr)
LeMoyne, Ala.	1965	De Nora 22x5
St. Gabriel, La. a	1970	Uhde 30 sq. m
Vulcan Materials Company,		arrange and and
Chemicals Division		
Port Edwards, Wis.	1967	De Nora 24H5

<sup>&</sup>lt;sup>a</sup>Electrolytic plant producing caustic soda, chlorine, and hydrogen from brine

brine.

Electrolytic plant producing caustic soda, caustic potash, chlorine, and chydrogen from brine.

chydrogen from brine.
CPulp mill.
Electrolytic plant producing caustic potash, chlorine, and hydrogen from brine.

#### 3.2 PROCESS DESCRIPTION

#### 3.2.1 Mercury-Cell Process

A flow diagram for the production of chlorine and caustic using mercury cells is given in Figure 3-1. Purified brine is fed from the main brine treatment section through the inlet end box to the electrolyzer, where it flows between a stationary graphite or metal anode and a flowing mercury cathode. The spent brine is recycled from the electrolyzer to the main brine treatment section through a dechlorination step. Chlorine gas is formed at the anode of the electrolyzer and is collected for further treatment. The gas is cooled, dried by scrubbing with concentrated sulfuric acid, and compressed. The dry chlorine gas may be used directly or may be liquified.<sup>6</sup>

The sodium is collected at the cathode of the electrolyzer, forming an amalgam. The sodium amalgam flows from the electrolyzer through the outlet end box to the decomposer, where it is the anode to a short-circuite graphite or metal cathode in an electrolyte of sodium hydroxide solution. Water is fed to the decomposer and reacts with the sodium amalgam to produce elemental mercury, sodium hydroxide solution, and by-product hydrogen gas.

The stripped mercury is returned to the cell. The caustic soda solution generally leaves the decomposer at a concentration of 50 percent sodium hydroxide by weight. This solution is usually filtered to remove impurities. The filtered caustic solution may be further concentrated by evaporation. The by-product hydrogen gas from the decomposer may be vented to the atmosphere, burned as a fuel, or used as a feed material in other processes. <sup>6</sup>

The inlet end box is a receptacle that is placed on the inlet end of the electroylzer to provide a convenient connection for the stripped mercury as it returns from the decomposer to the electrolyzer. Also, it keeps the incoming mercury covered with an aqueous layer. The outlet end box is a receptacle that is placed on the outlet of the electrolyzer to provide a convenient means for keeping the sodium amalgam covered with an aqueous layer and for the removal of thick mercury "butter" that is formed by impurities. 6,7

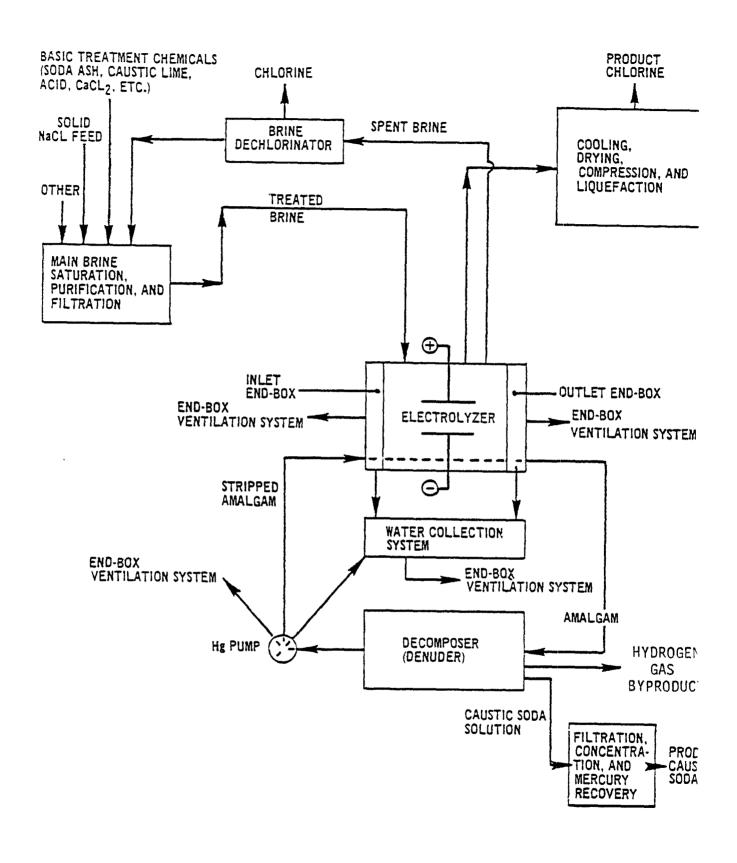


Figure 3-1. Basic flow diagram for mercury-cell chlor-alkali operation.8

The end-box ventilation system applies suction to the end boxes, the sumps for the mercury pumps, and the water collection system to reduce mercury vapor emissions to the cell room. A large quantity of ventilation air is used to keep the mercury vapor concentration of the cell room at allowable levels. Typical volumes for cell room ventilation air range from 94 to 425 standard m<sup>3</sup>/s (200,000 to 900,000 scfm). 9

Several chlor-alkali companies recover mercury from sludges by using retorts on-site. Sludges are loaded into the retort and indirectly heated to high temperature to vaporize the mercury. The mercury vapor is cooled in a water-cooled condenser outside the retort and is recovered. Mercury recovery retorts are typically operated on an intermittent basis, one to several times per month. 10,11 Secondary recovery of mercury is discussed further in Chapter 6.

#### 3.2.2 Mercury Emission Sources

The major sources of mercury emissions to the atmosphere are:

- (1) the hydrogen by-product stream, (2) end-box ventilation system, and
- (3) cell room ventilation air. The hydrogen by-product stream leaving the decomposer is saturated with mercury vapor and may carry mercury in the form of fine droplets. The amount of mercury emitted by the end-box ventilation system depends on the degree of mercury saturation and the volumetric flow rate.

Mercury enters the cell room air from a number of sources, which include: (1) end-box sampling, (2) removal of mercury butter from end boxes, (2) cell maintenance and rebuilding operations, (4) other maintenance work that exposes internal surfaces of pipes and equipment, (5) accidental mercury spills, (6) leaks from cells and mercury pumps, and (7) cell failure and other unusual circumstances. 12

#### 3.3 CONTROL TECHNOLOGY

Control techniques used to reduce mercury emissions from the hydrogen stream and end-box ventilation stream are: (1) cooling, (2) mist elimination, (3) chemical absorption, (4) activated carbon adsorption, and (5) molecular sieve adsorption. These are described briefly in this section. For more detailed descriptions, see References 13 and 14. Also discussed in this section are housekeeping practices for the cell room and the use of nonmercury cell technology.

No new control technology has been developed in the chlor-alkali industry since the national emission standard was promulgated in 1973.9 3.3.1 Cooling

Cooling may be used as the primary control technique for the hydrogen stream or the end-box stream, or it may precede other control techniques. Hydrogen leaves the decomposer at 93° to 127°C (200° to 260°F) and passes into a primary cooler. Water at ambient temperature is typically used in a shell-and-tube heat exchanger to cool the stream to 32° to 43°C (90° to 110°F). A mercury knockout drum following the cooler separates the condensed mercury from the hydrogen stream. An additional direct or indirect cooler using chilled water or brine may further cool the hydrogen stream to 3° to 13°C (37° to 55°F). Direct-contact coolers using chilled water or brine require water treatment systems.

The end-box ventilation air can be cooled similarly to the hydrogen stream. Direct-contact coolers are used more than indirect coolers due to the presence of mercuric chloride particulate matter in the gas stream.

#### 3.3.2 Mist Elimination

The cooled gas stream is typically passed through a mist eliminator. Two basic types of mist eliminators remove mercury mist from gas streams. One consists of a fiber pad enclosed in screens, and the other uses a converging-diverging nozzle. Trapped particles are removed from the mist eliminators by spray washing.

#### 3.3.3 Chemical Absorption

Scrubbers using depleted brine or a sodium hypochlorite (NaOCl) solution have been used for mercury removal from hydrogen and end-box ventilation gas streams. In the depleted brine scrubbing system, the spent brine discharged from the cell is used as the scrubbing medium in a sieve plate tower or a packed-bed scrubber. Mercury vapor and mist form soluble mercury complexes upon contact with the scrubbing solution. The scrubbing solution is returned to the mercury chlor-alkali cell where the mercury is recovered by electrolysis.

#### 3.3.4 Activated Carbon Adsorption

Sulfur- and iodine-impregnated carbon adsorption have been used by several companies to reduce the mercury concentration in the hydrogen

gas stream. Prior to carbon adsorption, primary and secondary cooling followed by mist elimination have usually removed about 90 percent of the mercury content of the hydrogen stream. 15 The mercury vapor remaining in the stream is adsorbed by the carbon and chemically reacts with the sulfur or iodine to form mercury compounds. Several adsorber beds may be placed in series. A vendor has reported typical outlet concentrations below 50 parts per billion by volume (ppbv) that may approach 1 ppbv. 16 3.3.5 Molecular Sieve Adsorption

Mercury vapor can be removed from the hydrogen gas stream or end-box ventilation stream by adsorption on a proprietary molecular sieve adsorbent. 9 The PuraSiv-Hq<sup>®</sup> system developed by Union Carbide Corporation is used by five chlor-alkali companies in the U.S.9 Following cooling and mist elimination, the hydrogen gas stream passes through one of two adsorption beds. Eighty to ninety percent of the treated hydrogen gas passes out of the system to disposal or usage. The remainder is heated to 316°C (600°F) and used as a recycle-regeneration stream for removing entrapped mercury from the second adsorber bed. After passing through the second adsorption bed, this gas stream is cooled and is combined with the incoming mercury-laden hydrogen stream from the primary cooling section. At any time, one bed is undergoing adsorption, and the other is undergoing regeneration. The concentration of mercury in the effluent has been guaranteed to be lower than 60 ppbv on average. 17 Some operational problems have been reported with molecular sieves currently in operation. The most common difficulties involved excessive moisture buildup; however, to date all problems have been corrected. 9

Union Carbide no longer supplies the PuraSiv-Hg<sup>®</sup> process to control mercury emissions from chlor-alkali plants. However, Union Carbide could provide a license to its patents and technology. 18

#### 3.3.6 Housekeeping Practices

The mercury national emission standard allows chlor-alkali companies the option of either modifying the cell room so stack sampling can be used or complying with approved maintenance and housekeeping practices that will minimize mercury emissions from the cell room. All chlor-alkali companies have opted to follow the EPA recommended housekeeping practices in lieu of stack testing. An emission limit of 1,300 g/d (2.8 lb/d) of

total mercury is assigned to the cell room when the housekeeping practices are followed. The housekeeping practices recommended by the EPA are listed in Appendix A of this document.  $^{19}$ 

#### 3.3.7 Nonmercury-Cell Technology

Mercury emissions from chlor-alkali operations can be eliminated by switching to a nonmercury technology, either the diaphragm- or membrane-cel technology. In the diaphragm cell, the electrolytic reaction products are separated by an asbestos diaphragm. Chlorine is generated at the anode on one side of the diaphragm, and caustic soda and hydrogen gas are produced at the cathode on the other side. Several disadvantages of the diaphragm-cell process preclude it from being a universal substitute for the mercury-cell process. A lower grade caustic (i.e., greater sodium chloride content) is produced by the diaphragm-cell process, and the caustic at about 11 percent by weight must be evaporated to obtain a 50 percent solution.<sup>20</sup> A second disadvantage is that diaphragm-cell plants may discharge asbestos in their wastewater streams.

The membrane cell process is free from both mercury and asbestos contaminants. In the membrane cell, a synthetic cation exchange membrane separates the electrolytic reaction products. As in the standard diaphragm cell, chlorine gas is generated at the anode on one side of the membrane, and caustic soda and hydrogen gas are produced at the cathode on the other side. The membrane allows passage of only sodium ions from the anode to cathode compartment. This results in production of caustic that is purer and more concentrated than that from standard diaphragm cells. The caustic solution produced by membrane cells can be up to 25 to 30 percent caustic by weight. This caustic solution must also be evaporated to obtain a 50 percent solution.

Japan is presently committed to convert all mercury-cell chlor-alkali operations to membrane-cell operations. In 1979, Japanese government committees judged that membrane-cell technology had reached a technical level suitable for commercial application.  $^{23}$ ,  $^{24}$  There are presently two commercial and two pilot chlor-alkali plants employing membrane cells operating in the U.S. $^{25}$ ,  $^{26}$ 

Most chlor-alkali companies employing mercury-cell technology have considered using the membrane-cell technology. However, the current

economic conditions of the chlor-alkali industry and the cost of switching to membrane cells are a major impediment to replacement at this time.<sup>27</sup>

#### 3.4 WASTE DISPOSAL

Because of its vaporization properties, mercury can be emitted to the atmosphere from mercury contaminated waste products. Techniques used to remove mercury from wastewater and solid waste products are discussed below.

#### 3.4.1 Wastewater

Potential sources of mercury-laden wastewater discharges at a mercury-cell chlor-alkali plant include: (1) cell room floor washing, (2) caustic filter backwash, (3) cell end-box washing, (4) brine purges and filter washing, (5) mercury pump seal water, and (6) direct-contact cooling of the hydrogen stream. 9

Wastewater is typically treated at a central treatment plant located on-site. A commonly used treatment method is precipitation with sodium sulfide or sodium hydrosulfide followed by filtration.

Mercury-cell chlor-alkali plants are subject to effluent limitations guidelines and new source performance standards for the mercury content of wastewater effluents.  $^{27}$ 

#### 3.4.2 Solid Waste

Potential sources of mercury-contaminated solid waste at a chlor-alkal plant include: (1) wastewater treatment solids, (2) mercury-contaminated equipment, (3) brine purification solids, (4) caustic filter backwash, (5) spent carbon from carbon bed adsorbers, and (6) retort ash. 9
Mercury may be recovered from certain sludges in retorts as described previously. Sludges and solid wastes generated in the process are typically disposed in a hazardous waste landfill.

#### 3.5 COMPLIANCE TEST RESULTS

All operating chlor-alkali plants are in compliance with the national emission standard for mercury according to the EPA Compliance Data System and EPA regional and State contacts.<sup>28</sup> Following the promulgation of the standard, all plants were required to demonstrate compliance.

Test results for the hydrogen gas stream and the end-box ventilation system are given in Table 3-2. Mercury emissions from the hydrogen gas

stream ranged from 1 to 891 g/d (0.002 to 2.0 lb/d). The lower mercury emission levels were generally measured on hydrogen streams controlled by molecular sieve or carbon adsorption control systems. (Performance problems encountered with these and other control devices are discussed in the next section.) Most mercury emission levels above 400 g/d (0.88 lb/were measured on hydrogen streams controlled by cooling systems alone. For the end-box ventilation stream, mercury emissions generally ranged from 1 to 428 g/d (0.002 to 0.94 lb/d). Test methods used followed EPA Method 101 for the end-box ventilation streams and Method 102 for hydrogen streams. No data are available for cell room emissions because all mercury-cell chlor-alkali companies have opted to follow the EPA cell room housekeeping practices instead of testing cell room emissions.

#### 3.6 COMPLIANCE AND ENFORCEMENT ASPECTS

#### 3.6.1 Compliance Problems

Compliance problems noted by several companies include cell room floor maintenance, training of operation and maintenance personnel, and control system failures. The most common control system failures occur in the hydrogen cooling systems. Duplicate systems are usually installed as backups to correct this problem. These backup systems have become increasingly important in plants where molecular sieves are used. This is due to regeneration problems that arise in the molecular sieves when the primary hydrogen coolers are fouled or fail. No other control problems were reported by industry.

Information on mercury-cell chlor-alkali plants was obtained from States, EPA regions, and information requests to the industry. Each contact was asked to express his or her views on the appropriateness of the current standard. Two companies noted that the standard is reasonable and should not be changed.  $^{29}$ ,  $^{30}$  No chlor-alkali company suggested any changes to the mercury emission level or to the EPA test methods. One company noted that the cell room design, maintenance, and housekeeping practices are achievable, and EPA's figure of 1,300 g/d (2.9 lb/d) of mercury emissions assumed for the cell room when these practices are followed is reasonable.  $^{31}$  The EPA design, maintenance, and housekeeping practices for the cell room are listed in Appendix A. One company had the following comments on the housekeeping practices for the cell room:  $^{32}$ 

TABLE 3-2. COMPLIANCE TEST RESULTS FOR MERCURY EMISSIONS FROM HYDROGEN STREAMS AND END-BOX VENTILATION STREAMS AT MERCURY-CELL CHLOR-ALKALI PLANTS 9

Plant		Cl <sub>2</sub> production		Total Hg <sup>b</sup> emissions					
A 350 HE, KD, CP, SP, HE, ME, HE, CB 1979 6 0.01 16  B 300 CO, CP, CP, CO, CP, 1974 1 0.002 N  CB 120 CO, CP, CP None 1977 0.25 0.001 N 1978 0.41 0.001 N 1980 162 0.36 N 1980 90 0.20 N 1981 6 0.01 N 1982 9 0.02 N 1982 9 0.02 N 1982 9 0.02 N 1983 3 0.01 N 1984 6 0.01 N 1984 6 0.01 N 1985 6 0.01 N 1986 162 0.36 N 1987 7 0.25 0.001 N 1988 6 0.01 N 1988 6 0.01 N 1988 6 0.01 N 1988 6 0.01 N 1988 7 0.02 N 1988 8 0.19 1 1981 88 0.19 1 1981 88 0.19 1 1981 88 0.19 1 1981 88 0.19 1 1981 88 0.19 1 1987 163 0.36 N 1977 163 N 1977 163 0.36 N 1977 163 N 1977 17	Plant	rate,	Control dev			H <sub>2</sub>		En	d-box
SP, HE, ME, HE, CB  8 300 CO, CP, CP, CO, CP, 1974 1 0.002 M CB CH, D  120 CO, CP, CP None 1974 145 0.32 M SP, CH 1977 0.25 0.001 N 1978 0.41 0.001 N 1980 90 0.20 M 1980 90 0.20 M 1981 6 0.01 N 1980 90 0.20 M 1982 9 0.02 M 1982 9 0.02 M  CO, CP, CH None 1979 7 0.002 M KO, CB 1980 3 0.01 M 1980 162 0.36 M 1980 90 0.20 M 1981 80 0.01 M 1980 90 0.20 M 1981 80 0.01 M 1980 162 0.36 M 1981 80 0.01 M 1980 90 0.20 M 1981 80 0.01 M 1980 90 0.20 M 1981 80 0.01 M 1982 9 0.02 M  CO, CP, CH None 1979 7 0.002 M 1980 3 0.01 M 1980 3 0.41 M 1980 30.41 M 1980 3	code	tons/a	H <sub>2</sub>	End-box	test	g/a	10/0	g/d	1b/d
CB CH, D  CC 120 CO, CP, CP None 1974 145 0.32 None 1978 0.41 0.001 None 1978 0.41 0.001 None 1980 162 0.36 None 1980 162 0.01 None 1980 162 0.01 None 1980 162 0.01 None 1980 162 0.02 None 1980 163 0.02 None 1980 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 163 0.036 0.	A	350	SP, HE, ME,	S, D, B				246 160	0.54 0.35
SP, CH 1977 0.25 0.001 N 1980 162 0.36 N 1980 90 0.20 N 1980 90 0.20 N 1981 162 9 0.02 N 1981 162 9 0.02 N 1981 162 162 N 1982 N 1982 162 N 1982 N 1982 N	В	300			1974	1	0.002	NA	NA
KO, CB 1980 3 0.01 M E 235 CO, CO, CO, D CO, CO, D 1981 354 0.78  F 110 CO, ME, CP BS 1977 239 0.52 4 1981 88 0.19 1  G 300 CO, CP, CH, D NA 1973 420 0.93 16 1974 322 0.71 11 1977 163 0.36 2  H 450 CO, CP, MS S, S 1975 7 0.02 1976 94 0.21 < 1976 57 0.13 N  I 225 CO, R S, S 1973 434 0.96 20  J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55  L 135 CO, CO, S, CB CO 1973 NA NA 1  M 125 CO, CO, CP, S, CO 1974 50 0.11 42 CP,	С	120	CO, CP, CP SP, CH	None	1977 1978 1980 1980 1981	0.25 0.41 162 90 6	0.001 0.001 0.36 0.20 0.01	NA NA NA NA NA NA	NA NA NA NA NA
F 110 CO, ME, CP BS 1977 239 0.52 4 1981 88 0.19 1  G 300 CO, CP, CH, D NA 1973 420 0.93 16 1974 322 0.71 11 1977 163 0.36 2  H 450 CO, CP, MS S, S 1975 7 0.02 1976 94 0.21 < 1976 57 0.13 N  I 225 CO, R S, S 1973 434 0.96 20  J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55 CB  L 135 CO, CO, S, CB CO 1973 NA NA NA 1  M 125 CO, CO, CP, CP, CP, CP, CP, CP, CP, CO, CO, CO, CH, D 1982 295 0.65 23  O 366 CO, CP, CO, CO, CO, CH, D 1982 48 0.11 39  P 314 CO, CO, CO, CO 1981 592 1.31 23	D	400		None				NA NA	NA NA
G 300 CO, CP, CH, D NA 1973 420 0.93 16 1974 322 0.71 11 1977 163 0.36 2  H 450 CO, CP, MS S, S 1975 7 0.02 1976 94 0.21 4 1976 57 0.13 N  I 225 CO, R S, S 1973 434 0.96 20  J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55 CB  L 135 CO, CO, S, CB CO 1973 NA NA NA 1  M 125 CO, CO, S, CB CO 1974 50 0.11 42 CP,	Ε	235	CO, CO, CO, D	co, co, D	1981	354	0.78	1	0.003
1974 322 0.71 11 1977 163 0.36 2  H 450 CO, CP, MS S, S 1975 7 0.02 1976 94 0.21 < 1976 57 0.13 N  I 225 CO, R S, S 1973 434 0.96 20  J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55  CB L 135 CO, CO, S, CB CO 1973 NA NA NA 1  M 125 CO, CO, CP, S, CO 1974 50 0.11 42 CP, CP, CP, CP, CP, CP, CP, CP, CO, CO, CO, CH, D 1982 295 0.65 23  O 366 CO, CP, CO, CO, CH, D 1982 48 0.11 39  CH, CB  P 314 CO, CO, CO, CO 1981 592 1.31 23	F	110	CO, ME, CP	85				48 16	0.11 0.04
1976 94 0.21 < 1976 57 0.13 N  I 225 CO, R S, S 1973 434 0.96 20  J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55  CB CB CB CO, CO, S, CB CO 1973 NA NA NA 1  M 125 CO, CO, CP, S, CO 1974 50 0.11 42  CP,	G	300	CO, CP, CH, D	NA	1974	322	0.71	165 114 23	0.36 0.25 0.05
J 220 CO, SP, B, CO, CO, SP, B, 1974 47 0.10 N D, MS 1979 10 0.02 N K 100 SP, CO, CH, DR, S 1980 157 0.35 55 CB CO, CO, S, CB CO 1973 NA NA NA 1 M 125 CO, CO, CP, S, CO 1974 50 0.11 42 CP, CP, CP, CP, CP, CP, CP, CP, CO, CO, CO, CO, CH, D 1982 295 0.65 23 O 366 CO, CP, CO, CO, CO, CH, D 1982 48 0.11 39 CH, CB P 314 CO, CO, CO, CO 1981 592 1.31 23	н	450	CO, CP, MS	s, s	1976	94	0.21	1 <4 NA	0.002 <0.01 NA
D, MS MS 1979 10 0.02 N  K 100 SP, CO, CH, DR, S 1980 157 0.35 55  L 135 CO, CO, S, CB CO 1973 NA NA NA 1  M 125 CO, CO, CP, S, CO 1974 50 0.11 42  CP,	I	225	CO, R	s, s	1973	434	0.96	201	0.44
CB  L 135 CO, CO, S, CB CO 1973 NA NA 1  M 125 CO, CO, CP, S, CO 1974 50 0.11 42  CP,	J	220	CO, SP, B, CO, D, MS	CO, SP, B, MS				NA NA	NA NA
M 125 CO, CO, CP, S, CO 1974 50 0.11 42 CP, CP, CP, CP, CP, CO, CO,  N 311 CH, CH, MS CH, D 1982 295 0.65 23  O 366 CO, CP, CO, CO, CO, CH, D 1982 48 0.11 39  CH, CB  P 314 CO, CO, CO, CO 1981 592 1.31 23	K	100	SP, CO, CH, DR, CB	S	1980	157	0.35	550	1.21
CP, CP, CP, CP, CP, CP, CO, CO, CO, CH, D 1982 295 0.65 23  O 366 CO, CP, CO, CO, CH, D 1982 48 0.11 39 CH, CB  P 314 CO, CO, CO, CO 1981 592 1.31 23	L	135	CO, CO, S, CB	CO	1973	NA	NA	16	0.036
N 311 CH, CH, MS CH, D 1982 295 0.65 23  O 366 CO, CP, CO, CO, CH, D 1982 48 0.11 39  CH, CB  P 314 CO, CO, CO, CO 1981 592 1.31 23	М	125	CP, CP, CP,	S, CO		50	0.11	428	0.94
CH, CB P 314 CO, CO, CO 1981 592 1.31 23	N	311	CH, CH, MS	CH, D		295	0.65	235	0.52
	0	366		CO, CH, D	1982	48	0.11	390	0.86
	Р	314	CO, CO, CO, CC, F, CO, CO	СО	1981	592	1.31	236	0.52
Q 700 CO, D, MS, CO, SP, B 1975 264 0.58 4 CP, CB	Q	700		CO, SP, B	1975	264	0.58	44	0.10
R 208 CO, S, S CO, CO, CO 1973 NA NA 9	R	208	CO, S, S	co, co, co	1973	NA	NA	90	0.20

TABLE 3-2. (continued)

	Cl <sub>2</sub> produc- tion		_		Total Hg <sup>b</sup> emissions			
Plant code <sup>a</sup>	rate, tons/d	Control dev	ices End-box	Date of test	g/d	H₂ 1a/d	En∈ g/d	d-box lb/d
S	225	CO, D, CH, CP	S, CB	1974 1976 1979 1980 1981 1982 1983	548 891 NA 610 864 NA 528	1.2 2.0 NA 1.3 1.9 NA 1.2	5 7 22 32 7 120 NA	0.01 0.02 0.05 0.07 0.02 0.26
T	520	CO, CH, D, CP, SP, MS	B, B, CO	1976 1978	5 4	0.01 0.01	52 63	0.11 0.14
U	220	CO, CP, S, ME	CO, 8, S	1973	61	0.13	2	0.004

<sup>&</sup>lt;sup>a</sup>Plant names are coded because certain companies requested confidential

CCode for control devices: B = Blower

BS = Brine scrubber

CB = Carbon bed

CC = Centrifugal collector
CH = Chillers

CO = Coolers

CP = Compressors

D = Demister

DC = Dust collector

OR = Oriers

F = Filter

HE ≈ Heat exchanger

KO = Knockout drum

ME = Mist eliminator

MS = Molecular Sieve

R = Refrigeration

S = Scrubber

SP = Separator

treatment of data.  $^{\rm b}$ Test data using EPA Method 102 for  ${\rm H_2}$  stream and EPA Method 101 for end-box ventilation stream.  $^{\rm c}$ NA" indicates that no test data were available.

- 1. Item 12 should be modified to allow the reuse of hydrogen seal pot water, compressor seal water, and hydrogen cooler condensate instead of requiring it to be treated. Additionally, this water should not be restricted from open trenches. The quantity of mercury in this water is insignificant and exposure of this water to the atmosphere poses no hazard for emitting mercury into the air.
- 2. Some decomposer pump sumps do not retain an aqueous layer on top of the mercury since the decomposer vent gases are collected and controlled by the end-box ventilation system. Other systems maintain an aqueous layer over the mercury and some systems may have both methods of control. Either method is adequate by itself, therefore, items 8 and 9 should be modified to allow either method to be used instead of both.

#### 3.6.2 Enforcement Aspects

Mercury-cell chlor-alkali plants are located in 16 States. Thirteen of these States have been granted authority to enforce the national emission standards for hazardous air pollutants. Enforcement personnel representing 11 States and 6 EPA regions were contacted to obtain information on enforcement aspects of the mercury standard. No significant enforcement problems have been encountered. However, enforcement personnel did comment on several aspects of the standard. These comments are summarized below.

As discussed in Chapter 2, there are no monitoring or reporting requirements in the standard for chlor-alkali companies. The EPA Region II office requires that chlor-alkali companies submit a semiannual summary of inspection and maintenance records. State personnel in this region noted that the reporting requirement aids in the enforcement of the standard. It provides them with baseline data to evaluate plant performanc and allows them to spot problems as they develop. <sup>31</sup> An EPA Region III representative believes the reporting requirement is more efficient than conducting full plant inspections. <sup>33</sup> One company contacted in this region noted that the requirement does not affect controls and procedures used to comply with the standard but does create additional paperwork. <sup>31</sup>

Enforcement personnel in five States and two regions believed that some type of specific monitoring and reporting requirements should be included in the standard to ensure compliance. $^{31}$ , $^{33-38}$  One State

representative suggested that monitoring and reporting requirements be instituted only for those facilities encountering compliance problems.<sup>39</sup> A State agency contacted did not feel monitoring and reporting requirements were necessary but did believe that sources should be tested every 3 to 5 years to demonstrate compliance.<sup>40</sup> Other States and EPA regional personnel contacted in this study did not comment on the need for monitoring and reporting requirements.

Two enforcement personnel noted that the cell room housekeeping practices portion of the standard is a subjective evaluation method because it is not quantifiable. <sup>36</sup>, <sup>37</sup>, <sup>41</sup> Additionally, one of these individuals recommended that the EPA should test the cell room vent air and develop a specific numerical emission limit. <sup>36</sup>

#### 3.7 SUMMARY AND CONCLUSIONS

Twenty-four mercury-cell chlor-alkali plants are operating in the United States. All plants are in compliance with the national emission standard for mercury. The EPA cell room housekeeping practices are achievable.

No enforcement problems with the standard have been noted; however, a number of State and EPA regional personnel believe that reporting requirements should be added to the standard.

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#### 4. MERCURY ORE PROCESSING

#### 4.1 INTRODUCTION

Currently only one mercury ore processing facility is in operation in the U.S., the McDermitt Mine in McDermitt, Nevada, operated by Placer Amex, Inc. Two gold mines producing mercury as a by-product also were operating in Nevada in 1982. 1,2 The State of Nevada considers these by-product operations to be insignificant sources of mercury emissions.<sup>3</sup> The national emission standard for mercury does not apply to by-product mercury mines. In 1973, the year of promulgation of the national emission standard, 24 mines produced mercury. Fourteen mines produced less than 10 flasks each in 1973 from mined ore dumps, cleanup operations, or as a by-product. Only six mines were classified as consistent producers. 4 Statistics for number of producing mines, mercury content of ore, mercury production, and total mercury consumption are given in Table 4-1 for the period 1970 to 1982. The large increase in mercury production from 1974 to 1976 was due to startup of the new McDermitt Mine capable of producing 20,000 flasks/yr (690 Mg/yr [750 tons/yr]) of mercury.<sup>5</sup> The average mercury content of ore also increased between 1974 and 1976 due to the higher mercury content of the McDermitt Mine ore. Approximately one-half of the total mercury consumed in the U.S. in 1982 was supplied by domestic production. The remainder was supplied by imports, secondary mercury production, and government sales of strategic materials.

The Bureau of Mines has estimated future probable production of 25,000 flasks of mercury per year based almost entirely on output from the Nevada mine. This is expected to continue until the mine reserves are exhausted, which is expected to occur about 1993. Zero production is forecast for the year 2000. However, a representative of the McDermitt

TABLE 4-1. MERCURY STATISTICS FOR UNITED STATES--1970 TO 19821,7-10

V	No. of producing	of	content ore	Production (No. of	Total consumption (No. of
Year	mines <sup>a</sup>	(kg/mg)	(lb/ton)	flasks) <sup>D</sup>	flasks) 
1970	79	2.0	4.8	27,296	61,503
1971	56	2.1	5.0	17,883	52,257
1972	37	2.7	6.5	7,349	52,907
1973	24	2.5	6.1	2,227	54,283
1974	12	1.8	4.4	2,189	59,479
1975	13	2.8	6.8	7,366	50,838
1976	7	3.9	9.5	23,133	64,870
1977	5	4.1	9.9	28,244	61,259
1978	2	3.0	7.2	24,163	59,393
1979	3	3.8	9.2	29,519	62,205
1980	4	2.7	6.5	30,657	58,983
1981	3	3.3	8.1	27,904	59,244
1982 <sup>c</sup>	3	NA <sup>d</sup>	NA	26,137	49,418

aIncludes mines producing mercury from mined ore, dumps, cleanup operations, or as by-product.

bFlask = 34 kg (76 lb) mercury.

cPreliminary.

dNA = Not available.

Mine has stated that ore deposits at the mine have been found to be more extensive than originally believed, thus extending considerably the potential life of this facility. <sup>11</sup> It is unlikely that other mines will be opened or reopened. The McDermitt Mine has a competitive advantage due to the rich ore deposit and efficient processing. <sup>11</sup>

#### 4.2 PROCESS AND CONTROL TECHNOLOGY DESCRIPTIONS

#### 4.2.1 Process and Control Technology<sup>12</sup>

A flow chart showing the processing of mercury ore is shown in Figure 4-1. The ore is fed to a grinding mill where water is added to produce a slurry. The mercury ore particles are separated as a concentrate by flotation. The concentrate is then thickened, stored, and filtered before being fed to a direct-fired multiple-hearth furnace. Temperatures in the furnace vary between 650° and 870°C (1200° and 1600°F). The calcined ore is discharged from the bottom of the furnace. The mercury vapor-laden gas is discharged from the top of the furnace. The gas then enters a dry cyclone where dust is removed. Fans keep the entire furnace system under a negative-pressure gradient to minimize fugitive emissions of mercury vapor.

The direct-fired multiple-hearth furnace is a result of technological developments occurring since the promulgation of the national emission standard. The multiple-hearth furnace used at the McDermitt Mine replaced the Gould rotary furnace that formerly was used in the industry.

After passage through the cyclone, the gas stream is introduced into banks of vertical tube condensers in series. The mercury in the gas stream is condensed and collected under water in containers called launders. The mercury is then cleaned, stored in bulk, filtered, bottled, and shipped.

The gas stream leaving the condenser is passed through a venturi and impinger tower for particulate removal and through a sulfur dioxide  $(SO_2)$  scrubber. The cleaned gas stream is then exhausted to the atmosphere at ambient temperature.

The systems described above have been designed to control  $SO_2$  and particulate emissions. They coincidentally control mercury to the level of saturated vapor at ambient temperature, the approximate temperature of the exhaust gas stream.

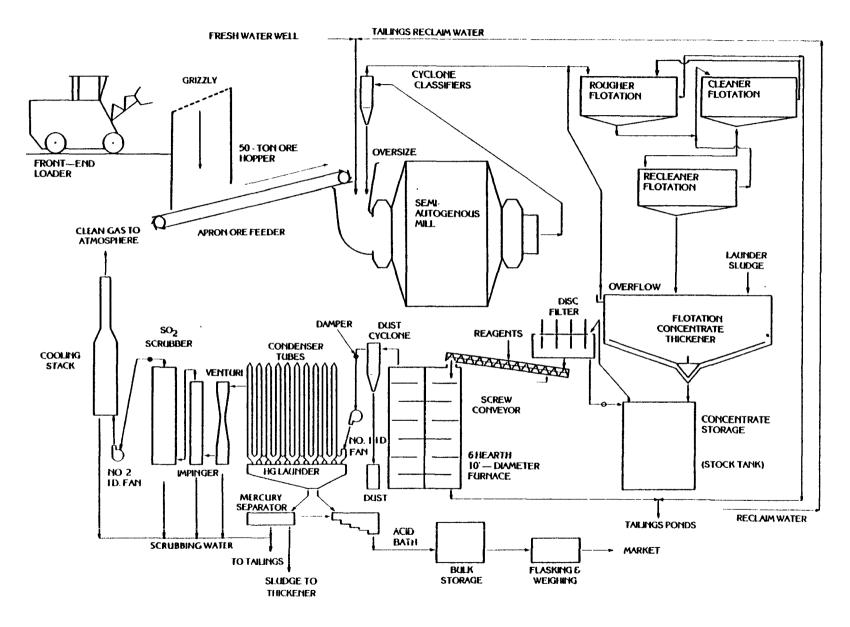


Figure 4-1. Flow chart showing processing of mercury ore. 12

#### 4.2.2 Emission Sources

The major emissions of mercury from a mercury ore processing operation occur from the cooling stack.

#### 4.2.3 Wastes<sup>12</sup>

Tails from the flotation operations, calcines from the furnace, dust captured by the cyclone, and scrubbing water are sent to a series of large, shallow ponds. Treatment consists of natural evaporation over a period of about 9 months.

#### 4.3 COMPLIANCE TEST RESULTS

Mercury emission tests were conducted on the condenser stack of the McDermitt Mine processing facility in 1981. Tests were run in accordance with EPA Method 101. The average emission rate determined in two 2-hour tests was 816 g/d (1.8 lb/d) of mercury.  $^{12}$  The maximum daily emission rate from this source was calculated to be approximately 1,360 g/d (3.0 lb/d) of mercury assuming stream saturation.  $^{13}$  Thus, this facility is in compliance with the national emission standard.

The McDermitt Mine has had no problems in complying with the standard. The control technology for  $SO_2$  and particulate emissions has been reliable.  $^1$ 

#### 4.4 ENFORCEMENT ASPECTS

No problems with enforcement of the standard for mercury ore processing were noted either by EPA regional or State personnel contacted during this study.  $^3$ ,  $^{14}$ 

#### 4.5 SUMMARY AND CONCLUSIONS

U.S. This facility is in compliance with the national emission standard for mercury. No enforcement problems with the standard have been encountered by EPA regional or State personnel.

#### 4.6 REFERENCES FOR CHAPTER 4

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- 13. Memorandum from Atkinson, D., MRI, to Project File 7703-L. August 8, 1983. Calculation of maximum mercury emission rate from the McDermitt Mine. (II-B-15).
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## SLUDGE INCINERATION AND DRYING

## 5.1 INTRODUCTION

Information on sludge incineration and drying was obtained primarily from the EPA Stationary Source Compliance Division and from telephone contacts with EPA regional personnel and State personnel. According to the EPA Compliance Data System report for the mercury national emission standard, there were 172 incineration sites subject to the national emission standard at the end of 1982. The total number of municipal and industrial wastewater sludge incinerators at these sites is estimated to be in the range of 258 to 280. Five sludge drying plants with at least 9 dryers were also listed as subject to the standard.

In 1973 there were an estimated 280 municipal sludge incinerators, 17 sludge dryers, and an undetermined number of industrial sludge incinerators. A 1975 EPA estimate of growth through 1980 placed the number of sewage sludge incinerators in 1980 at 725. The anticipated growth in sludge incineration as a sludge disposal technique did not materialize; the number of sludge incinerators today is essentially the same as in 1973. Future growth potential of sludge incineration was not examined.

Vendor sales information indicates that the typical size of new sludge incineration plants increased during the period from 1973 to 1981. In 1973, EPA estimated the size distribution of sludge burning plants in terms of dry solids burning capacity. A size distribution of new plants constructed between 1974 and 1981 was developed from installation lists obtained from the two major vendors of multiple-hearth and fluidized-bed incinerators. 4,5 The size distributions are compared in Table 5-1. As shown in this table, the majority of new sludge incineration plants are of greater than 45-Mg/d (50-ton/d) capacity.

TABLE 5-1. SIZE DISTRIBUTION OF SLUDGE INCINERATION PLANTS EXISTING IN 1973 AND CONSTRUCTED BETWEEN 1974 AND 19816,7

Plant size (dry solids burning capacity) Mg/d tons/d		Plant existing No. of plants		Plants constructed betwee 1974 and 1981 No. of % of plants tota	
<4.5	<5	17	7	2	5
4.5-45	5-50	173	73	10	26
45-227	50-250	37	16	19	50
>227	>250	6	3	7	19
TOTAL		233	100	38	100

## 5.2 PROCESS AND CONTROL TECHNOLOGY DESCRIPTIONS

## 5.2.1 Sludge Incineration

Incinerators are used for treatment of sludge produced by municipal or industrial wastewater treatment plants. Incineration is a two-step process that involves first drying and then combustion. In all furnaces, the temperature of the dewatered feed sludge is raised to  $100^{\circ}$ C ( $212^{\circ}$ F) to evaporate water from the sludge; then, the temperature of the water vapor, air, and sludge is increased to the ignition point of the sludge volatiles. Two major types of sludge incinerators are used in the U.S.: the multiple-hearth and the fluidized-bed. These are described in the following sections. Other incineration processes in limited use are the electric furnace, single hearth cyclonic furnace, and high-pressure/high-temperature wet air oxidation. Detailed descriptions can be found in the EPA Process Design Manual for Sludge Treatment and Disposal.<sup>8</sup>

- 5.2.1.1 Multiple-Hearth Incineration. 8 The multiple-hearth furnace is the most widely used sludge incinerator in the U.S. A process flow diagram for sludge incineration in a multiple-hearth furnace is shown in Figure 5-1. The multiple-hearth furnace consists of a cylindrically shaped steel shell containing a series of refractory hearths, one above the other. The multiple-hearth furnace can have from 4 to 14 hearths. A central shaft supports rabble arms above each hearth, which rake the sludge across the hearth in a spiral pattern. The sludge is fed in at the top hearth and successively drops down to the next hearth. Combustion air is supplied at the bottom of the furnace. The countercurrent flow of rising hot combustion gases and descending sludge provides contact, which ensures combustion of the sludge. Supplemental fuel may be supplied. Cooling air for the central shaft and rabble arms is supplied at the bottom of the furnace. After cooling the shaft, the air is either discharged to the atmosphere or returned to the bottom hearth as preheated air for combustion. Incineration temperatures range from 760° to 927°C (1400° to 1700°F).
- 5.2.1.2 <u>Fluidized-Bed Incineration</u>.<sup>8</sup> Fluidized-bed furnaces are also used to incinerate wastewater treatment plant sludges. A process flow diagram for sludge incineration in a fluidized-bed furnace is shown in Figure 5-2. The fluidized-bed furnace is a cylindrically shaped

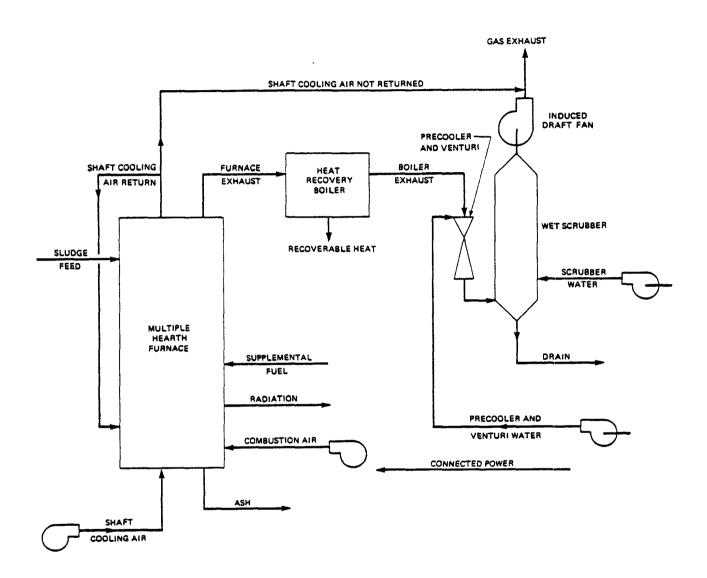


Figure 5-1. Process flow diagram for sludge incineration in a multiple-hearth furnace. 9

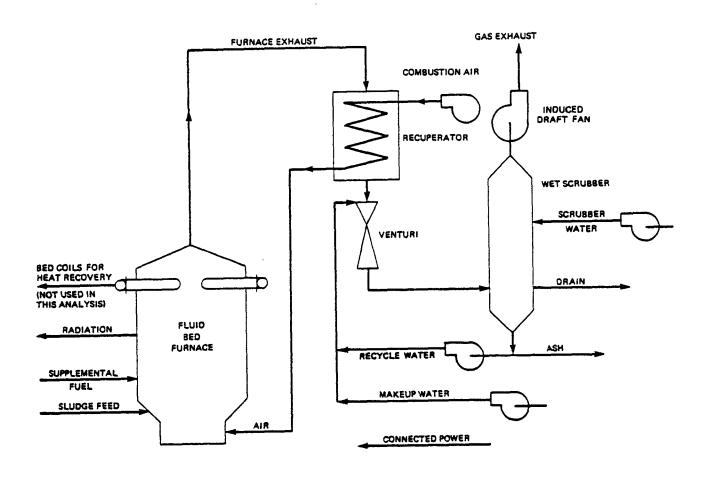


Figure 5-2. Process flow diagram for sludge incineration in a fluidized-bed furnace. 10

steel shell that contains a sand bed and fluidizing air diffusers. Sludge is injected either above or directly into the bed, and air is introduced at the bottom of the bed to fluidize the mixture of sand and sludge. Combustion occurs in the bed at 760° to 816°C (1400° to 1500°F). Supplemental fuel may be supplied. Ash is carried out the top of the furnace with the combustion exhaust.

5.2.1.3 Control Technology for Sludge Incineration. Wet scrubbers are typically used to control particulate emissions to meet the new source performance standard for incinerators that burn municipal wastewater sludge. Some mercury may be incidentally removed by the wet scrubbers. Common scrubber configurations include variable throat venturi scrubbers in series with cyclonic mist eliminators, venturi scrubbers in series with perforated-plate impingement scrubbers, or multiple series of perforated-plate impingement scrubbers. Pressure drops may range from 1,493 to 8,709 Pa (6 to 35 in. WG). 11

# 5.2.2 Sludge Drying<sup>12</sup>

Heat drying is used to evaporate water in the sludge. Conventional heat-drying systems include rotary kiln drying, flash drying, drying in incinerators, and spray drying. Before heat drying, the sludge is usually mechanically dewatered. In the dryer, water that was not mechanica separated is evaporated without decomposing the organic matter in the sludge solids. The solids temperature in the dryer must be kept between 60° and 93°C (140° and 200°F). The dried sludge is either stored in bulk for disposal or sent to a furnace for incineration. The exhaust gas stream may go to a treatment system for removal of particulate matter and odors. Control techniques that can be used to treat emissions from sludge drying include afterburners, cyclones, wet scrubbers, electrostatic precipitators, and baghouses.

### 5.3 COMPLIANCE TEST RESULTS

The compliance status for sludge incineration and sludge drying plants is listed by the EPA's Compliance Data System (CDS). The CDS indicates that all facilities presently comply with the national emission standard for mercury. Test results for a number of sludge incinerators were obtained from EPA and State personnel from regions containing significant sludge incineration operations. The mercury content of

muncipal sewage sludge has been reported to range from 0.1 to 89 ppm, have a mean of 7 ppm, and have a median of 4 ppm. <sup>13</sup> Due to its volatility, most of the mercury contained in the sludge feed is vaporized during incineration and is emitted as mercury vapor.

The mercury emission data obtained in this study for sludge incinerate are given in Table 5-2. Mercury emissions were measured either by stack tests using EPA Method 101A or by sludge analysis using Method 105 and calculation of maximum emissions. All test data are less than 3,200 g/d (7 lb/d). Emissions ranged from 0 to 1,234 g/d total mercury (0 to 2.7 lb/d). The highest emissions were associated with the Cleveland, Ohio, and Detroit, Michigan, treatment plants. These were the only plants for which test data were obtained with sludge charging rates of greater than 227 Mg/d (250 ton/d) of dry solids.

## 5.4 ENFORCEMENT ASPECTS

No problems with enforcement of the standard for sludge incineration and drying were noted during this study. None of the persons contacted was aware of any source that was out of compliance with the standard.

### 5.5 SUMMARY AND CONCLUSIONS

All sludge incinerators and dryers are in compliance with the national emission standard for mercury. No problems with enforcement of the standard have been noted.

TABLE 5-2. MERCURY EMISSION DATA FOR SLUDGE INCINERATORS

Plant/location	No. of incin- erators tested	rate,	charging dry solids (tons/day)	To <u>Hg emi</u> g/day	tal ssions <sup>a</sup> (lb/day)	Date of test	Ref. No.
EPA Region I						<del></del>	
Norwalk Sewage Treatment	1	NAb	(NA)	217	(0.48)	1977	14
Norwalk, Conn.							
Metropolitan District Hartford, Conn.	1	NA	(NA)	129	(0.28)	1979	14
New Haven Sewage Treatment Plant, New Haven, Conn.	1	NA	(NA)	423	(0.93)	1981	14
EPA Region II							
Jersey City Sewerage Jersey City, N.J.	1	NA	(NA)	∙32	(0.07)	NA	15
Northwest Bergen Co. Sewage Authority, Waldwick, N.J.	1	3.9	(4.4)	0.1	(0)	1981	15
Parsippany-Troy Hills	1	25.0°	(27.6)	343 <sup>C</sup>	(0.76)	1978	15
Parsippany-Troy Hills, N.J.	1	21.8 <sup>c</sup>	(24.0)	185	(0.04)	1978	15
Stony Brook Sewage Treatment Plant, Princeton, N.J.	1	1.0	(1.1)	37	(0.08)	NA	15
ACSD-N. Plant, Menands, N.Y.	1	NA	(NA)	51	(0.11)	NA	15
ACSD-S. Plant, Albany, N.Y.	1	NA	(NA)	147	(0.32)	NA	15
Amherst STP, Amherst, N.Y.	1	NA	(NA)	33	(0.07)	NA	15
Bath WTP, Bath, N.Y.	1	NA	(NA)	175 <sub>d</sub>	(0.39)	NA	15
Beacon Sewage Sludge In. Beacon, N.Y.	NA 	NA	(NA)		(0.15)	NA	15
Buffalo Sewer Auth. Buffalo, N.Y.	NA NA	NA NA	(NA) (NA)	64 539	(0.14) (1.19)	1976 1977	15 15
			• •	6 <sup>d</sup>			
Liberty STP Little Falls Plant Little Falls, N.Y.	NA 1	NA NA	(NA) (NA)	8	(0.01) (0.02)	NA NA	15 15
Monroe CoSTP, N.Y.	1	NA	(NA)	32-64	(0.07 <del>-</del> 0.14)	NA	15
Monticello STP,	1	NA	(NA)	0	(0)	NA	15
Monticello, N.Y. New Rochelle STP New Rochelle, N.Y.	NA	NA	(NA)	476 <sup>d</sup>	(1.05)	NA	15
Oneida STP, Utica, N.Y.	NA	NA	(NA)	16 <sup>d</sup>	(0.04)	NA	15
Oswego E.S., Oswego, N.Y.	1	NA	(NA)	443	(0.98)	NA	15
Port Washington WPCD Port Washington, N.Y.	1	NA	(NA)	29	(0.06)	NA	15
Saratoga Co., Halfmoon, N.Y.	1	NA	(NA)	177	(0.39)	NA	15
Schenectady STP Schenectady, N.Y.	ī	NA	(NA)	4	(0.01)	NA	15
Tonawanda STP, Tonawanda, N.Y.	1	NA	(NA)	400	(0.88)	NA	15
Watertown STP, Watertown, N.Y.	ī		(NA)	5ء 61ء	(0)	NA	15
Atlantic Co. Sewerage Authority-Coastal Region	1	NA 57 <sup>C</sup>	(63)	61 <sup>C</sup>	(0.13)	1980	15
Atlantic City, N.J. Bayshore Regional Sewage	NA	33 <sup>C</sup>	(36)	0	(0)	1981	15
Authority, Union Beach, N.J. Prasa, Puerto Nuevo, P.R.	NA	NA	(NA)	3	(0.01)	NA	16
EPA Region III							
Allegheny Co. Sanitation Authority, Pittsburgh, Pa.	1	84	(93)	253	(0.56)	1976	17
Erie STP, Erie, Pa.	1	NA	(NA)	600 <sup>e</sup>	(1.32)	1975	17, 18
	1	NA	(NA)	450	(0.9 <del>9</del> )		
Hazelton STP, West Hazelton, Pa.	1	NA 	(NA)	4	(0.01)	1975	17
City of McKeesport McKeesport, Pa.	1	NA	(NA)	25	(0.06)	1978	17

(continued)

TABLE 5-2. (continued)

Plant/location	No. of incin- erators tested	rate,	charging dry solids (tons/day)	To <u>Hg</u> emi g/day	tal ssions <sup>a</sup> (lb/day)	Date of test	Ref. No.
Morrisville Municipal STP	1	0.1	(0.13)	20	(0.04)	1978	17
Morrisville, Pa. Scranton Sewer Authority Scranton, Pa.	1	30	(33)	84	(0.19)	1977	17
Swatara Township, Hummelston, Pa.	1	NA	(NA)	10	(0.02)	1975	17
Huntington Treatment Plant Huntington, Pa.	1	NA	(NA)	9	(0.02)	1975	17
Appolo Treatment Plant Appolo, Pa.	1	NA	(NA)	17 <sup>e</sup>	(0.04)	NA	18
Tyrone Borough Municipal Authority, Tyrone, Pa.	1	NA	(NA)	17 <sup>e</sup>	(0.04)	1977	19
York City Sewer Authority, York, Pa.	1	NA	(NA)	20 <sup>d</sup>	(0.04)	1981	19
EPA Region V							
Metropolitan Wastewater Treatment Plant	1	66 163	(73) (180)	36 <sup>d</sup> 137 <sup>d</sup>	(0.08) (0.30)	1976 1976	20 20
St. Paul, Minn. Seneca Wastewater Treatment Plant, Minneapolis/	1	32	(35)	21 <sup>d</sup>	(0.05)	1976	20
St. Paul, Minn. Mill Creek Treatment Works Cincinnati, Ohio	NA	16.7	(18.4)	77 <sup>d</sup>	(0.17)	1976	20
Muddy Creek Treatment Works Cincinnati, Ohio	NA	2.7	(3.0)	14 <sup>d</sup>	(0.03)	1976	20
Southerly Wastewater Treatment Center, Cleveland, Ohio	4	305	(336)	1,037- 1,220 <sup>d</sup> (at capacity)	(2.29 <del>-</del> 2.69)	1976	20
Detroit Wastewater Treatment Plant, Detroit, Mich.	NA NA NA NA NA NA	306 293 174 602 540 430 406 256	(337) (323) (192) (664) (595) (474) (447) (282)	516 <sup>d</sup> 495 <sup>d</sup> 366 <sup>d</sup> 1,234 <sup>d</sup> 1,107 <sup>d</sup> 600 <sup>d</sup> 752 <sup>d</sup> 312 <sup>d</sup>	(1.14) (1.09) (0.81) (2.72) (2.44) (1.32) (1.66) (0.69)	1977 1977 1978 1979 1979 1980 1981 1982	20 20 20 20 20 20 20 20 20
EPA Region VI							-
North Texas Municipal Water District Wylie, Tex.	NA	12.5	(13.8)	4 <sup>d</sup>	(0.01)	1977-78	22
Olin Corp., Lake Charles, La.	1	2.6	(2.9)	1.5 <sup>d</sup>	(0)	NA	22

<sup>&</sup>lt;sup>a</sup>Except where indicated, it is not known whether emissions were measured in stack test or by sludge analysis. Where measured by sludge analysis, results are maximum emissions, assuming zero percent breduction of mercury by control equipment.

bNA = not available.

CAverage of several runs was computed and is reported here.

Based on sludge test.

Based on stack test.

### 5.6 REFERENCES FOR CHAPTER 5

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- 19. Letter and attachments from Johnson, R., Pennsylvania Department of Environmental Resources, to Newton, D., MRI. February 4, 1983. Information on mercury emissions. (II-D-21).
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- 21. Letter and attachments from Varner, B., EPA Region V, to Newton, D., MRI. March 7, 1983. Information on mercury emissions. (II-D-32).
- 22. Letter and attachments from Taylor, W., EPA Region VI, to Georgieff, N., EPA:ISB. August 24, 1982. Information on mercury emissions. (II-D-11).

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### 6. SOURCES NOT REGULATED BY THE STANDARD

### 6.1 INTRODUCTION

Mercury is emitted to the atmosphere from a number of sources in addition to those regulated by the national emission standard. Sources were investigated as potential candidates for regulation based on whether the source has the potential to emit mercury in a manner that could cause the inhalation health effects limit of  $1.0~\mu g/m^3~(4.37 \text{x} 10^{-7}~gr/ft^3)$  (daily concentration averaged over 30 days) to be exceeded. For the purpose of the following discussion, sources of mercury air emissions are divided into three general categories: (1) sources that process materials containing mercury, (2) sources that use mercury in the process, and (3) sources that recover mercury.

### 6.2 GENERAL

Sources that process material containing mercury include fossil power plants, nonferrous smelters, municipal solid waste incinerators, peat to methanol conversion plants, and geothermal power plants. Power plants emit mercury to the air because of the mercury content of the fossil fuel. Mercury contained in sulfide concentrates may be emitted to the atmosphere during zinc, copper, and lead smelting operations. The EPA did not regulate power plants and smelters under the original standard because it was found that mercury emissions, even assuming restrictive dispersion conditions and uncontrolled emissions, would not cause the ambient concentration guideline to be exceeded. 1,2 A recent study of mercury emissions from power plants supports this conclusion. 3

Solid waste incinerators emit mercury to the air when batteries, control instruments, mercury-containing lamps, and other mercury-containing scrap are incinerated. Mercury air emissions from a solid waste incinerator

(average load of 9 Mg/h [10 tons/h]) were estimated in 1974 to be about 30 g/h (0.07 lb/h) based on the national average for the mercury content of solid waste. Plants currently in operation average approximately the same load capacity as 1974 plants, with the largest plant operating with a load capacity of approximately 36 Mg/h (40 tons/h). Emission levels from these plants would not cause the ambient concentration guideline to be exceeded; therefore, waste incineration was not investigate further in this study.

No peat-to-methanol conversion plants have been constructed in the United States; however, one is under construction in Creswell, North Carolina. It will have the potential for mercury emissions due to the mercury content of peat. The facility has been granted its air permit. Estimates of its yearly mercury emissions are 0.059 Mg (0.065 tons), or 0.0068 kg/h (0.015 lb/h). Because this emission level is below the 0.09-Mg/yr (0.1-ton/yr) guideline for mercury, which would require that the source be permitted specifically for mercury, ambient mercury concentrations are not expected to endanger public health. 6

Geothermal power plants have the potential for mercury emissions because the hot water and steam can dislodge mercury deposits from within the earth. At present, however, there is no indication that uncontrolled mercury emissions from these facilities could approach a level that would cause the health effects guideline to be exceeded. 7,8 One study indicates that daily mercury emissions from geothermal power plants, 25 to 75 megawatts, would be approximately 36 to 144 g, far below the current standards for the regulated source categories. 7

Sources that use mercury and that may emit mercury to the air include: battery manufacturing, mercury vapor lamp manufacturing, by-product mercury from gold mining, instrument manufacturing, paint manufacturing, manufacture of mercury compounds, laboratory use of mercury, and use of dental amalgams. The amount of mercury used in the U.S. in 1982 by each of these as well as other source categories is listed in Table 6-1.9 Because of the large amount of mercury used in battery manufacturing (about one-half of all mercury consumed in U.S.) and concern expressed by one State over mercury emissions at one facility, it was decided to investigate this source further as a candidate for

TABLE 6-1. UNITED STATES MERCURY CONSUMPTION IN 1982 a,9

	Flasks <sup>b</sup>
Chemicals and allied products:	
Chlorine and caustic soda preparation	6,516
Pigments	Mc
Catalysts	W
Laboratory uses	160
Plastic materials and synthetic (processing resins)	W
Paints	6,794
Agricultural chemicals	36
Installation and expansion of chlorine and caustic	1.1
soda plants	W W
Chemicals and allied products, n.e.c.	W
Electrical and electronic instruments:	
Electrical lighting	W
Wiring devices and switches	1,747
Batteries	24,066
Other electrical and electronic equipment	6
Instruments and related products:	
Measuring and control devices	2,916
Dental equipment and supplies	1,027
Other instruments and related products	W
Other identified end uses:	
Refining lubricating oils	W
Other,	3,147
TOTAL	49,418

apreliminary data for 1982.
bone flask = 34 Mg (76 lb).
cW = Withheld to avoid disclosing company proprietary data; included in
d-"Other."

dData do not add to totals shown; totals include estimates for companies reporting annually.

regulation. Findings are presented in Section 6.3. The other sources listed above are not likely to cause the ambient concentration guideline to be exceeded. This determination was made on information on the amounts of mercury consumed and the types of processes involved. $^9$ , $^{10}$ 

Sources that recover mercury from scrap include retorting and distillation operations. Production of secondary mercury totaled 4,244 flasks in 1981 compared to 27,888 flasks produced in 1981 from mining. It was decided to investigate secondary recovery by retorting as a candidate for regulation because of the quantity of mercury handled and the potential for emissions to the air. Findings of this investigation are presented in Section 6.4. Cleaning of mercury by vacuum distillation is done in some facilties where the purity of mercury is important. Maximum mercury emissions from vacuum distillation have been estimated to be 9 g per 345 kg (0.02 lb per 760 lb) of mercury produced. Pecause of the small amount of mercury emissions, it is unlikely that this source could cause the ambient concentration guideline to be exceeded.

## 6.3 BATTERY MANUFACTURING

Mercury in the form of zinc amalgam, mercuric oxide (HgO), mercuric chloride (HgCl $_2$ ), or mercurous chloride (Hg $_2$ Cl $_2$ ) is a component of most primary batteries and some storage batteries. Information on battery manufacturing plants operated by three companies—Union Carbide Corporation Duracell Inc., and Ray-O-Vac Corporation—was obtained through contacts with State agencies and the industry. These companies were selected because they are believed to represent almost all mercury battery manufacturing in the U.S. Information was obtained for five plants manufacturing mercuric oxide–zinc or mercuric oxide–cadmium batteries, seven plants manufacturing alkaline–manganese batteries, and seven plants manufacturing Leclanche carbon–zinc batteries. One mercuric oxide–zinc and two alkaline–manganese manufacturing facilities were visited. The mercury emission potential of battery manufacturing facilities is discussed below.

# 6.3.1 Mercuric Oxide Battery Manufacturing

6.3.1.1 <u>Process</u>. Mercuric oxide is used in the cathodes of mercuric oxide-zinc and mercuric oxide-cadmium cells, and zinc amalgam is used in

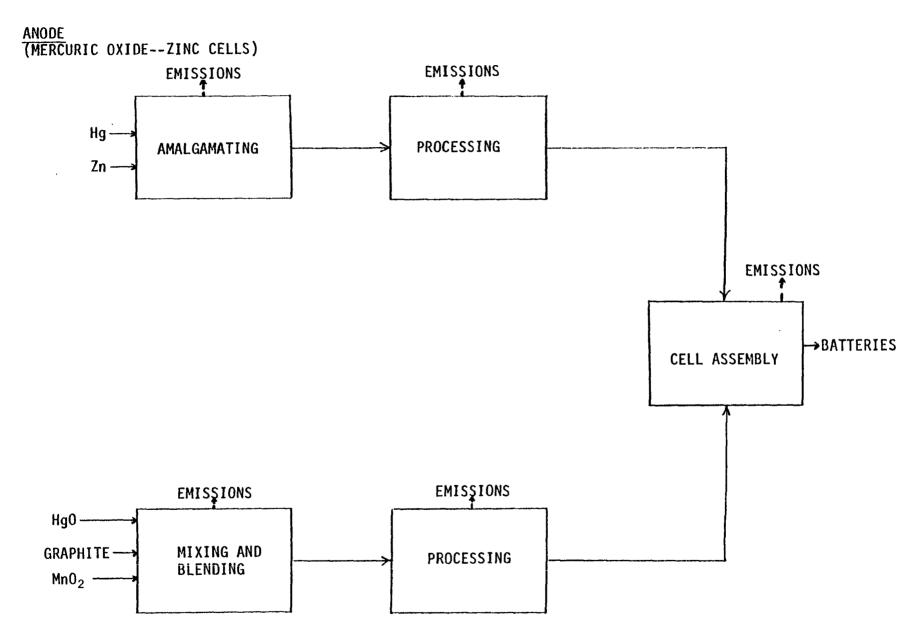
the anodes of mercuric oxide-zinc cells. A general flow diagram for these processes is given in Figure 6-1. The cathode is a mixture of mercuric oxide, graphite, and manganese dioxide. In mercury button cells, this mixture is pre-formed into pellets. The anode is a zinc amalgam. The dried amalgam is pre-formed into pellets for mercury button cells. The anode and cathode are enclosed in a can with appropriate separators, electrolyte, and other components to form a cell. Mercury consumption in each of the five plants manufacturing mercuric oxide batteries ranges from <4.5 to >1,100 kg/d (<10 to >2,500 lb/d) of mercury.

One facility investigated in this study also manufactures mercuric oxide and operates a secondary mercury recovery plant on-site. <sup>14</sup> Mercuric oxide is manufactured in a two-step process at this facility. Figures 6-2 through 6-4 are flow diagrams for this plant. In the first step, mercury and chlorine are combined in a reactor containing a brine solution to form mercuric chloride. Sodium hydroxide is then combined with this product in a second reactor to produce mercuric oxide. The mercuric oxide precipitate is processed and transported to the main plant for cathode manufacture.

The main plant of the integrated battery manufacturing facility (battery manufacture, mercuric oxide manufacture, and secondary recovery at one site) consists of a cathode area, anode room, and cell assembly room. In the cathode area, graphite, manganese dioxide, and mercuric oxide are blended, pelleted, granulated, and consolidated to form the cathode material. In the anode room, anode material is formed by amalgamating zinc and mercury followed by dewatering, traying, drying, sieving, blending, and pelleting steps. Cathode and anode material are combined in the cell assembly area.

Secondary recovery operations at this facility consist of recovery of mercury from batteries and manufacturing scrap in retorts. This process is discussed further in Section 6.4--Secondary Recovery of Mercury in Retorts.

6.3.1.2 <u>Mercury Emissions Potential</u>. This discussion is separated into two sections: the emission potential for an integrated battery manufacturing facility and the emissions potential for other mercuric oxide battery manufacturing facilities.



CATHODE (MERCURIC OXIDE--ZINC AND MERCURIC OXIDE--CADMIUM CELLS)

Figure 6-1. General flow diagram for mercuric oxide battery manufacture.

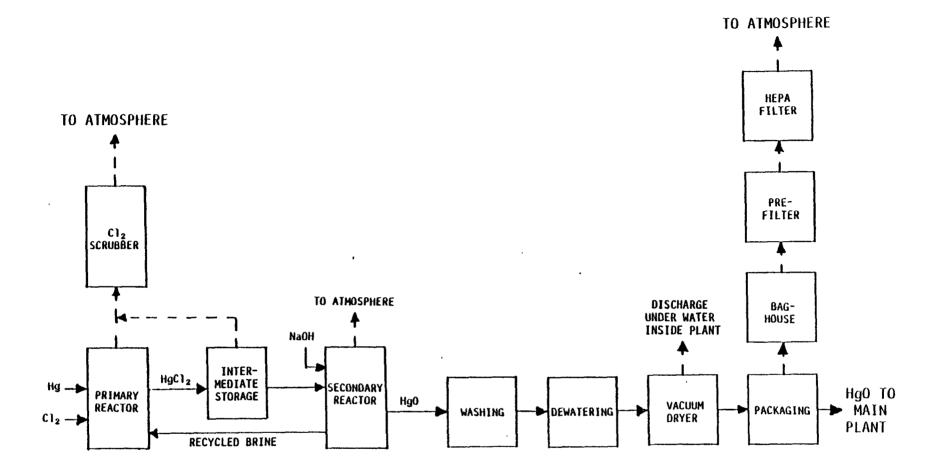


Figure 6-2. Process flow diagram for oxide plant.

Figure 6.3 Drococc flow diagram for main plant

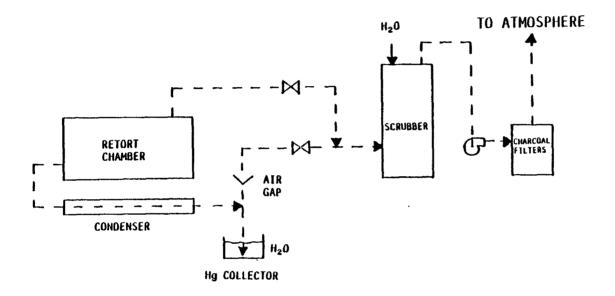


Figure 6-4. Process flow diagram for mercury recovery plant.

6.3.1.2.1 <u>Integrated mercuric oxide battery manufacturing facility</u>. Sources of mercury emissions to the air at the integrated battery facility include sources at the main plant, oxide plant, and recovery plant. Emission sources are listed in Table 6-2 along with control devices and mercury emission estimates and test data if available.

Total mercury emissions from the main plant are estimated to be 97.9 g/d (0.216 lb/d). In the cathode production area of the main plant, particulate mercury emissions originate during the blending, pelleting, handling, compacting, transfer, and consolidating operations. Process and machine enclosure exhaust systems are ducted to baghouses for particulate control. A vacuum system is used for cleanup of spills.

In the anode production area of the main plant, mercury vapor and particulate may be emitted during the multiple-step amalgamation process from the blending of mercury and zinc oxide, and the dewatering, drying, and reblending of the amalgam. These processes are all exhausted uncontrolled to the atmosphere. A vacuum is also used to collect scrap in the anode production area.

In the cell assembly area of the main plant, mercury particulate and vapor emissions can originate from assembly operations because both cathode and anode materials are involved. A baghouse controls particulate emissions from the assembly lines. Ventilation air in the cell assembly area is recirculated through prefilters and charcoal filters.

At the oxide plant, mercury emission sources include: mercury transferring operations open to the atmosphere, reactors, vacuum dryers, packaging, mercury distillation, and roof vents. Emissions from packaging are controlled by a baghouse and particulate filters. Chlorine recovery emissions are controlled by a scrubber, and rear reactor emissions are limited by a condensing duct. Mercury emissions from two sources at the oxide plant—the secondary (rear) reactor and the baghouse on packaging—measured a combined  $118 \, \text{g/d} \, (0.26 \, 1\text{b/d})$  in a  $1981 \, \text{test.}^{15},^{16}$  The company estimated mercury emissions from the room ventilation systems at about  $50 \, \text{to} \, 100 \, \text{g/d} \, (0.11 \, \text{to} \, 0.22 \, 1\text{b/d}).^{17}$ 

At the recovery plant, mercury vapor emission sources include the silver furnace and two mercury retort furnaces. A wet scrubber controls mercury vapor emissions from the mercury retorts. <sup>15</sup> A baghouse controls

TABLE 6-2. EMISSION SOURCE PARAMETERS FOR THE INTEGRATED MERCURY BATTERY MANUFACTURING FACILITY<sup>15-17</sup>

Buildir	ng/source No. description <sup>a</sup>	Emissi g/d	on rate 1b/d	Exit temp. oK	Control device
Main p		<i>J.</i>			
Conti	rol room				
1.	Blending/slugging/compacting/granulating	6.12	0.0135	297	Baghouse
2.	Slugging/granulating	1.22	0.0027	297	Baghouse
3.	Pelleting/consolidating <sup>C</sup>	1.63	0.0036	295	Baghouse
4.	Pelleting/consolidating	0.91 <sup>C</sup>	$0.002^{c}$	295	House vacuum
4a.	Pelleting/consolidating	0.91 <sup>C</sup>	0.002 <sup>c</sup>	295	House vacuum
5.	Pelleting/consolidating	42.46	0.0936	297	Baghouse
5a.	Pelleting/consolidating	6.53	0.0144	297	Baghouse
6.	Blending/compacting/granulating/pelleting/consolidating	1.36 <sup>c</sup>	0.003 <sup>a</sup>	297	Baghouse
Anode	e room				
7.	Amalgam/pelleting	0.91 <sup>C</sup>	0.002 <sup>C</sup>	297	House vacuum
7a.	Amalgam/dewatering	1.82°	0.002 <sub>C</sub>	297	Uncontrolled
7b.	Vacuum dryer	0.46°C	0.001 <sup>c</sup>	297	Uncontrolled
7c.	Blending	0.46 <sup>c</sup> 0.91 <sup>c</sup>	0.002 <sup>c</sup>	297	Uncontrolled
11.	Pelleting/zinc amalgam	4.08 <sup>c</sup>	0.009 <sup>c</sup>	295	Baghouse
<u>Cell</u>	assembly area				
8.	Assembling cells	28.58	0.0630	295	Baghouse
					•

TABLE 6-2. (continued)

	а		ion rate	Exit temp. °K	
Building	/source No. description <sup>a</sup>	g/d	1b/d	•K	Control device
0xide	plant				
9.	HgO transfer/packing	35.92	0.0792	299	Baghouse/HEPA filter
9a.	Cl <sub>2</sub> recovery reactor	- Not te estin	ested or - mated	299	Scrubber
9b.	Rear reactors Room vents	84.10 49.90-99.80 <sup>d</sup>	$0.1854 \\ 0.11-0.22^{d}$	325	Condensing duct Uncontrolled
Recove	ery plant				
10.	Silver furnace	13.61 <sup>c</sup>	0.03 <sup>C</sup>	422	Baghouse
10a & 10b.	Recovery furnaces	122.46	0.270	294	Scrubber
TOTAL		453.79	1.0		

aSource numbers are the same code used by Duracell.
bEmission rates were measured by Duracell except where noted. See Reference 15.
cEstimated emission rate by Duracell.
dEstimated emission rate by Duracell in Reference 17.

silver furnace emissions. Total mercury emission from the recovery plant are estimated by company personnel to be  $136 \text{ g/d} (0.30 \text{ lb/d}).^{15}$ 

Total mercury emissions from all sources at this facility are estimated by company personnel to be a maximum of 454 g/d  $(1.0\ lb/d)$ . The primary emphasis at the plant has been to reduce operator exposure to mercury and to control particulate mercury emissions from the plant. Mercury vapor emissions from the main plant and oxide plant are generally uncontrolled.

In addition to stack testing conducted in 1981 at this facility, ambient monitoring of both mercury particulate and vapor was performed. Particulate mercury measured at three off-site locations ranged from below the detection limit to 0.04  $\mu g/m^3$  (1.75 x10-8  $gr/ft^3$ ).  $^{18}$  Mercury vapor concentrations were measured on- and off-site using a Jerome Model 401 Gold Film Mercury Analyzer. Both instantaneous and time-weighted average measurements (averaged over 6 to 9 hours) using dosimeters were obtained. On-site mercury vapor concentrations ranged from 0 to 14  $\mu g/m^3$  (6.12 x10-6  $gr/ft^3$ ) for instantaneous concentrations and from 0.13 to 8.6  $\mu g/m^3$  (5.68 x10-8 to 3.76 x10-6  $gr/ft^3$ ) for time-weighted concentrations.  $^{19}$  Off-site mercury vapor concentrations ranged from 0 to 2  $\mu g/m^3$  (8.74 x10-7  $gr/ft^3$ ) for instantaneous concentrations and from 0.01 to 5.5  $\mu g/m^3$  (4.37 x10-9 to 2.40 x10-6  $gr/ft^3$ ) for time-weighted concentration with over 80 percent of the time-weighted concentrations being equal to or less than 1  $\mu g/m^3$  (4.3 x10-7  $gr/ft^3$ ).  $^{20}$ 

To investigate the possibility that ambient mercury concentrations at this facility could approach the inhalation health effects guideline, which is a 30-day average concentration, dispersion modeling was performed using emission data supplied by the company. Results indicate a maximum 30-day average concentration of 0.16  $\mu g/m^3$  (6.99 x10-8 gr/ft³) and a minimum of 0.11  $\mu g/m^3$  (4.8 x10-8 gr/ft³). The difference between 30-day average modeling results and the 6- to 9-hour actual measurements is due to such factors as differing meteorological conditions and averaging times.

6.3.1.2.2 Other mercuric oxide battery manufacturing facilities.

Each of the other mercuric oxide battery manufacturing facilities consume one-fourth or less mercury than the integrated battery facility. Estimated

mercury emissions from these facilities range from 2 to <200 g/d (0.003 to <0.4 lb/d). <sup>13</sup> Emission controls used at these facilities include baghouses and charcoal filters. Several of these plants are located in Wisconsin, which has an ambient air standard for all mercury emission sources of  $1 \mu g/m^3$  (4.37 x10-7 gr/ft<sup>3</sup>) on a 30-day average.

# 6.3.2 Alkaline-Manganese Battery Manufacturing

- 6.3.2.1 <u>Process</u>. Zinc amalgam is used in the anode of alkaline manganese cells. The mercury consumption for the amalgamation process at each of the seven plants manufacturing alkaline-manganese batteries ranges from <90 to >910 kg/d (<200 to >2,000 lb/d) of mercury.<sup>13</sup>
- 6.3.2.2 Mercury Emissions Potential. Mercury emissions originate from the amalgamation of zinc and mercury and from cell assembly operations Baghouses may be used to control particulate emissions from cell assembly. There is no indication of control being used for mercury vapor emissions. Mercury emissions estimates ranging from <100 to 800 g/d (<0.2 to 1.8 lb/d) were reported by the industry.  $^{13}$ ,  $^{22}$ ,  $^{23}$  The range of estimates does not correlate with the amount of mercury or controls used at each facility. Different approaches were used by companies to estimate mercury emissions; this may account for the variation in estimates.

Ambient dispersion modeling of the facility with the highest mercury emission level indicates a maximum 30-day average concentration of 0.17  $\mu g/m^3$  (7.43 x10-8 gr/ft<sup>3</sup>) and a minimum of 0.07  $\mu g/m^3$  (3.06 x10-8 gr/ft<sup>3</sup>).<sup>24</sup>

## 6.3.3 Leclanche Carbon-Zinc Batteries

- 6.3.3.1 <u>Process</u>. Purchased mercuric chloride or mercurous chloride is used in a paste that is applied to a paper separator. The paper acts as a separator between the zinc anode can and the cathode. Mercury consumption for each of the seven plants manufacturing Leclanche carbon-zinc batteries ranges from 2 to 19 kg/d (4 to 43 lb/d).<sup>13</sup>
- 6.3.3.2 Mercury Emissions Potential. Mercury emission sources include pastemaking operations, drying ovens, and cell assembly. A baghouse may be used to control particulate emissions, or there may be no control devices.  $^{13}$  Mercury emission estimates ranging from <1 to 170 g/d (<0.002 to 0.4 lb/d) were reported by the industry.  $^{13}$

## 6.4 SECONDARY RECOVERY OF MERCURY IN RETORTS

## 6.4.1 Process

Mercury is recovered from batteries, thermometers, amalgams, switches, and sludges by heating the scrap to about 538°C (1000°F) in retorts to volatilize the mercury, which is condensed outside the retort in water-coordondensers. Two companies in New York and Pennsylvania and one battery manufacturer in North Carolina operate mercury recovery retorts processing between 64,000 and 159,000 kg/yr (140,000 and 350,000 lb/yr) of scrap. 14,25 Several chlor-alkali companies operate small mercury recovery retorts on-si as mentioned in Chapter 3.

# 6.4.2 Mercury Emissions Potential

Mercury vapor emission sources include the condenser exhaust and vapor emitted during unloading operations. The condenser exhaust is controlled to a water spray at the Pennsylvania facility. The mercury emission level from this facility was measured at 840 g/d (1.85 lb/d). Estimated mercur emissions for the New York facility, which uses a condenser, are <1 g/d (<0.002 lb/d).  $^{28}$ ,  $^{29}$ 

The North Carolina battery manufacturing facility has recently installed a water scrubber and charcoal filter to control mercury vapor emissions from the condenser exhaust and unloading operations. This control system is being operated on an experimental basis.  $^{14}$  Personnel at the battery manufacturing facility estimate mercury emissions without the charcoal filter in place to be  $122.5 \text{ g/d} (0.27 \text{ lb/d}).^{15}$  No company estimat of mercury emissions with the charcoal filter operating are available. The recovery operations have not been operated on a normal schedule for several years. It is anticipated that normal operations will resume later this year. An emission test on the exhaust from the scrubber and charcoal filter control system will be conducted by the company at that time.

## 6.5 SUMMARY AND CONCLUSIONS

Mercury emissions to the atmosphere originate from a large number of sources in addition to those regulated by the national emission standard. Of these sources, only battery manufacturing and secondary recovery of mercury were investigated in this study to determine their potential to emit mercury in a manner that could cause the ambient

concentration guideline of  $1.0~\mu g/m^3$  ( $4.37~x10^{-7}~gr/ft^3$ ) to be exceeded. The decision to investigate these two sources was based on information about the amounts of mercury processed, the potential for air emissions, and concern expressed by a State agency about emissions at one mercuric oxide battery manufacturing plant.

Information on battery manufacturing was obtained for several battery types: mercuric oxide-zinc or mercuric oxide-cadmium, alkaline-manganese, and Leclanche carbon-zinc. Of the five mercuric oxide battery plants for which information was obtained in this study, it appears that only one has the potential to cause the ambient concentration guideline to be exceeded. This is an integrated battery manufacturing facility at which mercuric oxide is manufactured, batteries are produced, and mercury is recovered from scrap. Ambient mercury vapor levels (averaged over 6 to 9 hours) greater than 1  $\mu$ g/m³ (4.37 x10-7 gr/ft³) were measured on- and off-site in a 1981 study. However, dispersion modeling at the facility indicated a maximum 30-day average ambient concentration of 0.16  $\mu$ g/m³ (6.99 x10-8 gr/ft³), well below the ambient concentration guideline.

Other mercuric oxide battery manufacturing facilities do not appear to have the potential to cause the ambient concentration guideline to be exceeded. This conclusion is based on information about the amounts of mercury used by these plants and the estimated emission rates provided by the industry.

A large alkaline-manganese battery manufacturing facility may use up to 910 kg/d (2,000 lb/d) of mercury. Mercury emission estimates ranging up to 800 g/d (1.8 lb/d) have been reported by industry. Ambient dispersion modeling of the facility with the highest mercury emission level indicates a maximum 30-day average concentration of 0.17  $\mu$ g/m³ (7.43 x10-8 gr/ft³).

Facilities that manufacture Leclanche carbon-zinc batteries use <23 kg/d (<50 lb/d) of mercury in the form of mercurous chloride or mercuric chloride. Mercury emission estimates ranging to about 170 g/d (0.4 lb/d) have been reported. Due to the small amount of mercury consumed, these sources would probably not cause the ambient concentration guideline to be exceeded.

Large secondary recovery retorting operations have the potential for mercury vapor emissions to the atmosphere because of the amount of mercury recovered. Emissions are being controlled by a water spray tower at one facility, by a condenser at another plant, and by a water scrubber and charcoal filter on an experimental basis at a third facility. Emission test data for one facility and estimates of mercury emissions from the other facilities indicate the health effects guideline will not be exceeded.

### 6.6 REFERENCES FOR CHAPTER 6

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# APPENDIX A. LIST OF EPA DESIGN, MAINTENANCE, AND HOUSEKEEPING PRACTICES FOR CELL ROOMS OF MERCURY-CELL CHLOR-ALKALI PLANTS

- 1. Chlorine cells and end-box covers should be installed, operated, and maintained in a manner to minimize leakage of mercury and mercury-contaminated materials.
- 2. Daily inspection should be made by operating personnel to detect leaks, and immediate steps to stop the leaks should be taken.
- 3. High housekeeping standards should be enforced, and any spills of mercury should be promptly cleaned up, either mechanically or chemically or by other appropriate means. Each cell room facility should have available and should employ a well-defined procedure for handling these situations.
- 4. Floor seams should be smoothed over to minimize depressions and to facilitate washing down of the floors.
- 5. All floors should be maintained in good condition, free of cracking and spalling, and should be regularly inspected, cleaned, and, to the extent practical, chemically decontaminated.
- 6. Gaskets on denuders and hydrogen piping should be maintained in good condition. Daily inspection should be made to detect hydrogen leaks and prompt corrective action taken. Covers on decomposers, end boxes, and mercury pump tanks should be well maintained and kept closed at all times except when operation requires opening.
- 7. Precautions should be taken to avoid all mercury spills when changing graphite grids or balls in horizontal decomposers or graphite packing in vertical decomposers. Mercury-contaminated graphite should be stored in closed containers or under water or chemically treated solutions until it is processed for reuse or disposed.

- 8. Where submerged pumps are used for recycling mercury from the decomposer to the inlet of the chlorine cell, the mercury should be covered with an aqueous layer maintained at a temperature below its boiling point.
- 9. Each submerged pump should have a vapor outlet with a connection to the end-box ventilation system. The connection should be under a slight negative pressure so that all vapors flow into the end-box ventilation system.
- 10. Unless vapor tight covers are provided, end boxes of both inlet and outlet ends of chlorine cells should be maintained under an aqueous layer maintained at a temperature below its boiling point.
- 11. End boxes of cells should either be maintained under a negative pressure by a ventilation system or should be equipped with fixed covers which are leak tight. The ventilation system or end-box covers should be maintained in good condition.
- 12. Any drips from hydrogen seal pots and compressor seals should be collected and confined for processing to remove mercury, and these drips should not be allowed to run on the floor or in open trenches.
- 13. Solids and liquids collected from back-flushing the filter used for alkali metal hydroxide should be collected in an enclosed system.
- 14. Impure amalgam removed from cells and mercury recovered from process systems should be stored in an enclosed system.
- 15. Brine should not be purged to the cell room floor. Headers or trenches should be provided when it is necessary to purge brine from the process. Purged brine should be returned to the system or sent to a treating system to remove its mercury content.
- 16. A portable tank should be used to collect any mercury spills during maintenance procedures.
- 17. Good maintenance practice should be followed when cleaning chlorine cells. All cells when cleaned should have any mercury surface covered continuously with an aqueous medium. When the cells are disassemble for overhaul maintanance, the bed plate should be either decontaminated chemically or thoroughly flushed with water.

18. Brine, alkali metal hydroxide, and water-wash process lines and pumps should be maintained in good condition, and leaks should be minimized. Leaks should be corrected promptly, and in the interim, the leaks should be collected in suitable containers rather than allowed to spill on floor areas.

Reference: U.S. Environmental Protection Agency. Background Information on Development of National Emission Standards for Hazardous Air Pollutants: Asbestos, Beryllium, and Mercury. PB-222802. Research Triangle Park, North Carolina. March 1973. pp. 80-83. Docket No. A-82-41, Document No. (II-A-3).

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## 16. ABSTRACT

This report presents the findings of the 5-year review of the national emission standards for mercury. Industries subject to the existing standard are mercury-cell chlor-alkali plants, sludge drying and incineration plants, and mercury ore processing facilities. Information and estimates are presented concerning processes, mercury emissions, control technology, compliance status, and industry growth. Information is presented about other industry source categories which have mercury air emissions, but are not regulated by the standards.

7. KEY WORDS AND DOCUMENT ANALYSIS						
a. DESCRIPTORS b.IDENTIFIERS/OPEN ENDED TE		c. COSATI Field/Group				
Mercury-cell chlor-alkali Sludge Drying and Incineration Mercury Ore Processing Mercury Battery Manufacturing Air Pollution Pollution Control Emission Standards NESHAP	Air Pollution Control	13b <sub>.</sub>				
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