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FINAL REPORT

MERCURY CONTROL TECHNOLOGY ASSESSMENT STUDY

International Minerals and Chemicals Corporation
Chemicals Group
Orrington, Maine

Indepth Survey Report
for the Site Visit of
March 25-26, 1982

Contract No. 210-81-7107

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Submitted to:

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FOREWORD

A Control Technology Assessment (CTA) team consisting of members of Dynamac Corporation, Enviro Control Division, met with representatives of the International Minerals and Chemicals Corporation (IMC) Chemicals Group, Chlor-Alkali Plant, in Orrington, Maine, on March 25 and 26, 1982, to conduct an indepth survey on the techniques used to control worker exposure to mercury. Participants in the survey were:

Dynamac Corporation

David C. D'Orlando, Environmental Engineer
Robert Reisdorf, Industrial Hygienist

International Minerals and Chemicals Corporation

Peter DeAngelis, Plant Manager
Victor Perreault, Technical Supervisor

The indepth CTA survey was completed in 2 days. The survey included personal and area air monitoring and detailed inspections of mercury controls.

CONTENTS

INTRODUCTION

CONTRACT BACKGROUND

The Mercury Control Technology Assessment Study has been initiated to assess the current technology used to protect workers from exposure to mercury. The objective is to identify the methods employed by industries in controlling worker exposure to elemental mercury and mercury compounds. A result of the study will be the publication of a comprehensive document describing the most effective means to control emissions and exposures. This report will be available to companies that handle mercury in order to transfer technology within the major mercury-using industries. The study will also identify areas where additional research is necessary.

JUSTIFICATION FOR SURVEY

The IMC Chemicals Group, Chlor-Alkali Plant, was selected for a survey because of its use of mercury in the electrolytic process of chlorine and caustic production. The plant was recommended as having an effective mercury control program. Control strategies at the IMC plant include natural dilution ventilation, mercury containment, local exhaust ventilation, and sound work practices.

SUMMARY OF INFORMATION OBTAINED

An opening conference was held during which the objectives of the program were discussed with IMC representatives. Information on mercury controls was obtained from meetings with the technical supervisor and plant engineer. Area and personal monitoring of workers in the mercury cell room was conducted by the CTA team. Historical information on air and biological monitoring was obtained.

PLANT DESCRIPTION

The IMC Chemicals Group, Chlor-Alkali Plant, located in Orrington, Maine, produces caustic soda, chlorine, chloropicrin, and muriatic acid. The plant has been in operation since 1967 and operates 24 hours/day, 7 days/week. Sixty-two people are employed at the plant, of which approximately 30 (including operators, maintenance personnel, and supervisors) are directly involved in chlor-alkali production. The facility consists of a brine system, mercury cell room, warehouse, maintenance building, offices, storage tanks, and a small chemical manufacturing building (Figure 1). The cell room is constructed of steel and concrete beams, transite siding, and concrete floors. Major renovations made for mercury control were the installation of a Pura-siv^{R} mercury vapor removal system and modifications to the end boxes of the cells for reducing the escape of mercury vapor.

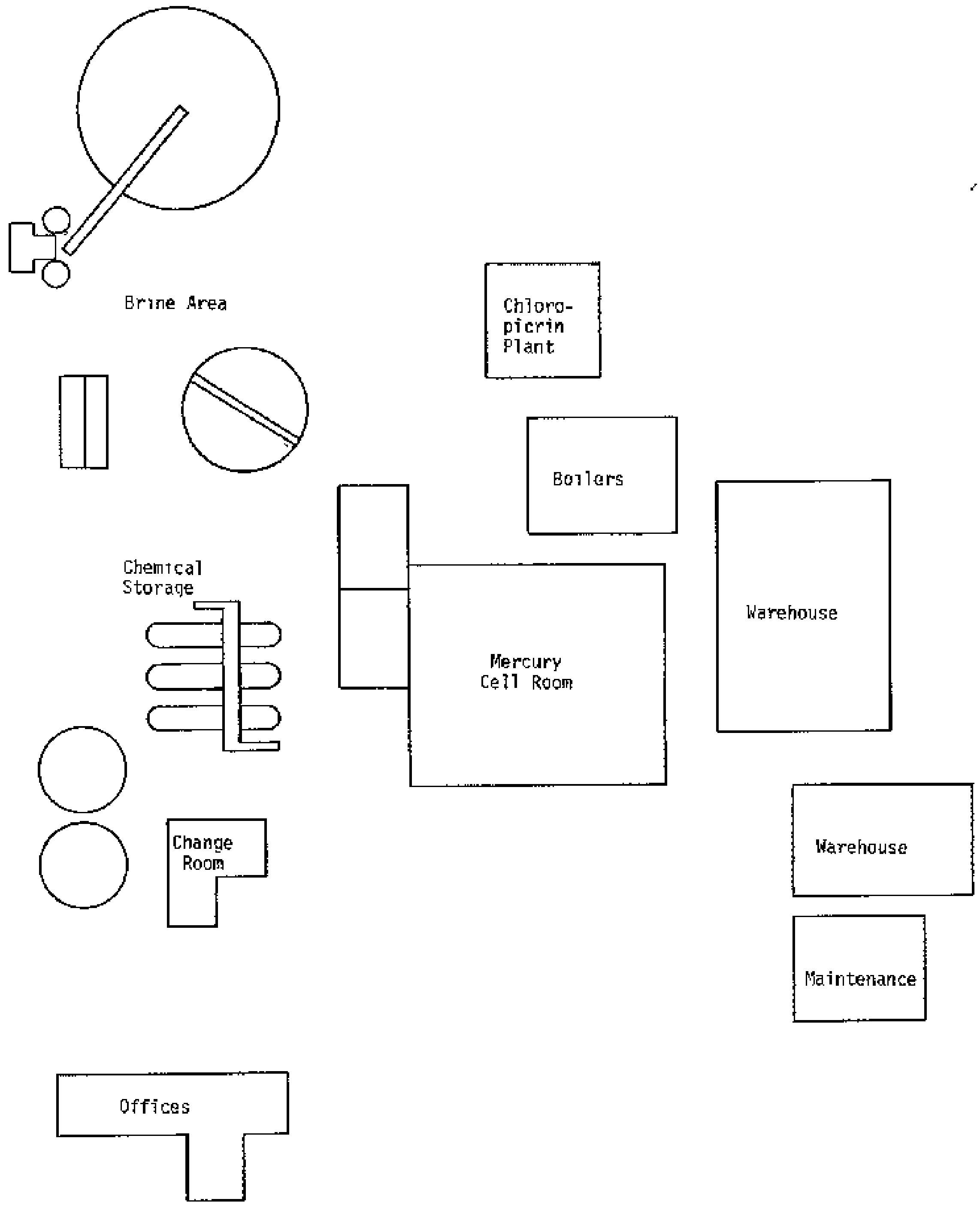

Figure 1. IMC Plant Layout.

PROCESS DESCRIPTION

BRINE SYSTEM

The brine used for the chlor-alkali electrolytic process is made by saturating water with solar salt (rock salt). The rock salt is moved by front-end loader to a hopper. A bucket conveyor moves the salt from the hopper into a saturator. Spent (weak) brine from the process is pumped up through the saturator. The saturated brine is then chemically treated and clarified to remove impurities. After clarification, the brine is pumped through a series of filters and on to the mercury cells for use in the process.

MERCURY CELLS

The electrolytic mercury cell is a steel channel sloped down at an angle of approximately 7 degrees. It is covered with a sheet of either rubber or Teflon. Inside the steel channel are several sets of screen-type anodes that are positioned under the cover by copper posts. Rubber seals are used to prevent leakage around the posts where they penetrate the cover. The depth of the anode in the mercury cell is controlled by adjusting the position of the copper posts. Anode depth must be adjusted constantly to optimize the electrolytic reaction taking place in the cell. A computer system actuates a positioner that adjusts the anode depth. At the lower (outlet) end of the mercury cell there is an outlet box for removal of the brine solution, a decomposer (a cylindrical reaction vessel approximately 4-1/2 feet high and 3 feet in diameter) for the removal of hydrogen and caustic soda, and a mercury pump for returning the mercury to the high (inlet) end of the mercury cell.

Mercury, which acts a cathode, flows along the cell bottom at a specified depth below the anode. The brine solution is introduced to the inlet end of the cell and flows between the anode and the mercury cathode. Voltage is applied between the anode and the mercury through large electrical buslines. The current causes an electrolytic reaction in which the chlorine ions in the solution lose an electron and the sodium ions gain an electron. Chlorine gas bubbles out of the solution and flows out of the cell through a collection header located at the inlet end of the cell. The sodium combines with the mercury to form an amalgam that flows down towards the outlet box at the outlet end of the cell. The heavy sodium amalgam flows below the weak brine. A submerged weir in the outlet box is situated so that only the amalgam can flow past it. Weak brine is decanted off the top of the stream through a drain pipe and is returned to the brine system. The amalgam passes through the outlet box into the decomposer where it reacts with water to form caustic soda and hydrogen gas. This is an exothermic electrochemical reaction that is driven by the potential that exists between the amalgam and a graphite packing on the inside of the decomposer. The concentration of the caustic soda produced is controlled to approximately 50 percent by regulating the flow of water into the decomposer. A minimum level of caustic is maintained in the vessel.

PRODUCT FLOW

The caustic produced is drained from the decomposer and then filtered, cooled, and stored. Hydrogen leaves the decomposer through the top and passes through a condenser to remove mercury vapor. The gas flows from the condenser to a Pura-siv^{R} unit, a molecular sieve manufactured by Union Carbide that is designed to reduce the mercury vapor concentration in the hydrogen stream from 6 to 8 milligrams per cubic meter (mg/m^3) down to 0.25 mg/m^3. After passing through the sieve, the hydrogen is burned in the plant's boilers or is used for producing muriatic acid. The chlorine gas from the cells is cooled, dried, liquefied, and stored.

The mercury, stripped of sodium in the decomposer, flows to a centrifugal pump used to return the mercury to the inlet end of the cell for reuse in the electrolytic process.

MERCURY CONTROL TECHNIQUES

CONTAINMENT

Inlet and Outlet Box Water Flush

The inlet and outlet boxes of the electrolytic cell are both sources for the potential escape of mercury vapor. At these points, mercury that is heated in the electrolytic process passes in and out of the cell by flowing through submerged weir-type gates. Maintaining water over the mercury in these boxes helps suppress mercury vaporization. However, as the water is heated due to contact with the mercury, mercury vapor may escape more readily. This problem has been solved by installing recirculating, chilled water systems--one for the inlet boxes (Figure 2) and one for the outlet boxes (Figure 3). Each system consists of a surge tank, a 240-gallon per minute pump, a chiller unit, and a manifold piping system that circulates water to each cell in parallel. Water from the chiller enters one side of the box, flows over the mercury, and exits through the other side of the box. The system supplies 20-30 C (68-86 F) water over the mercury at all times.

Mercury Addition Pig

When mercury must be added to the cell, it is added through the inlet box by using a mercury "pig." The pig is a 40-gallon tank mounted on a cart (Figure 4). It contains up to 52 flasks of mercury with 3-4 inches of water over it. The pig is lifted by crane and positioned over the inlet box of the cell to be filled. A rubber hose from the pig is set into the inlet box. Mercury flows by gravity through a valve and into the cell. Mercury addition is measured by using a rod graduated in units equal to 76-pound mercury flasks.

Covers, Seals, and Gaskets

The mercury cells at this facility have continuous, two-ply rubber covers. The covers are manufactured by B.F. Goodrich and are designed to last as long

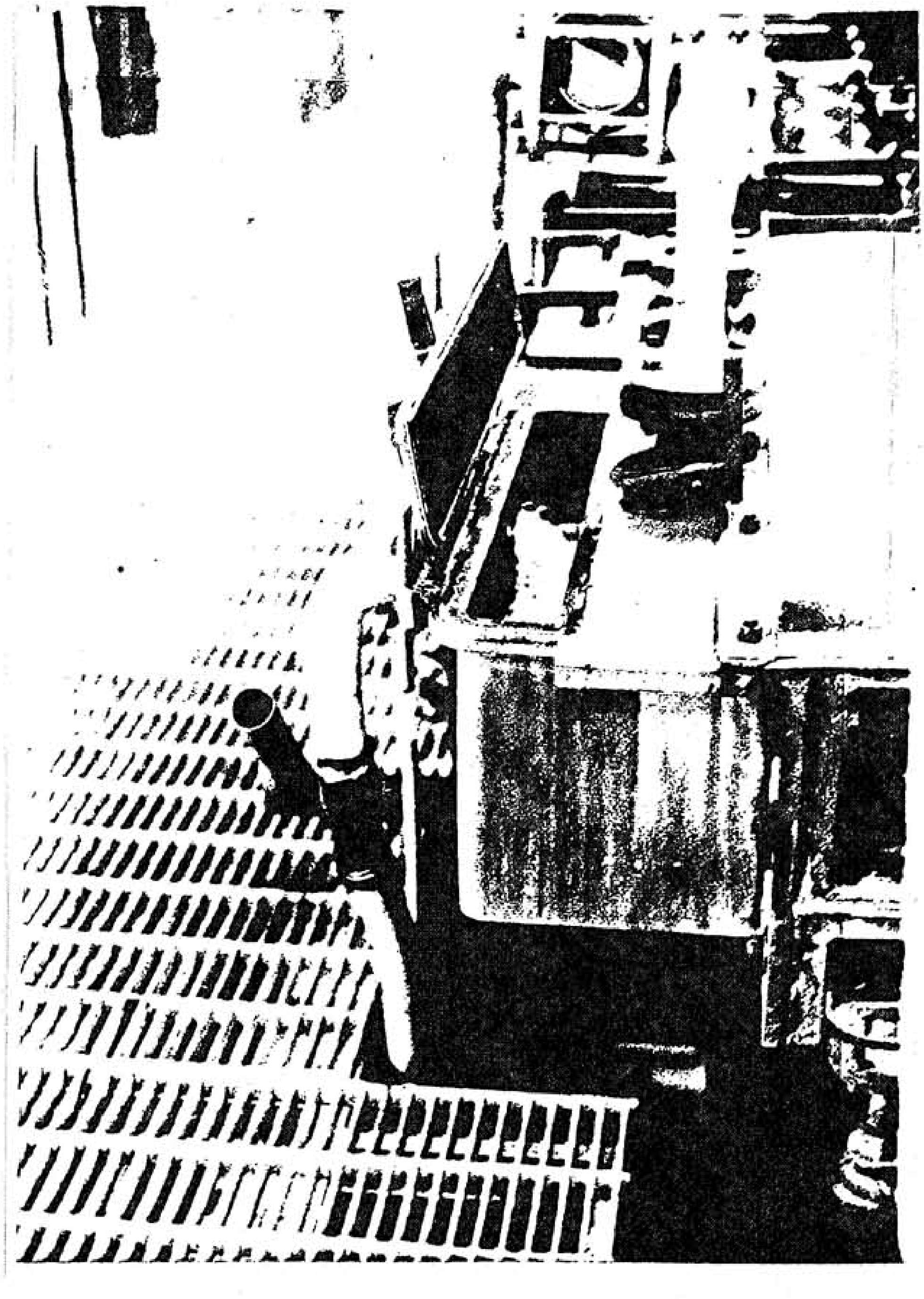

Figure 2. Inlet Box with Lid Open Showing Water Flow.

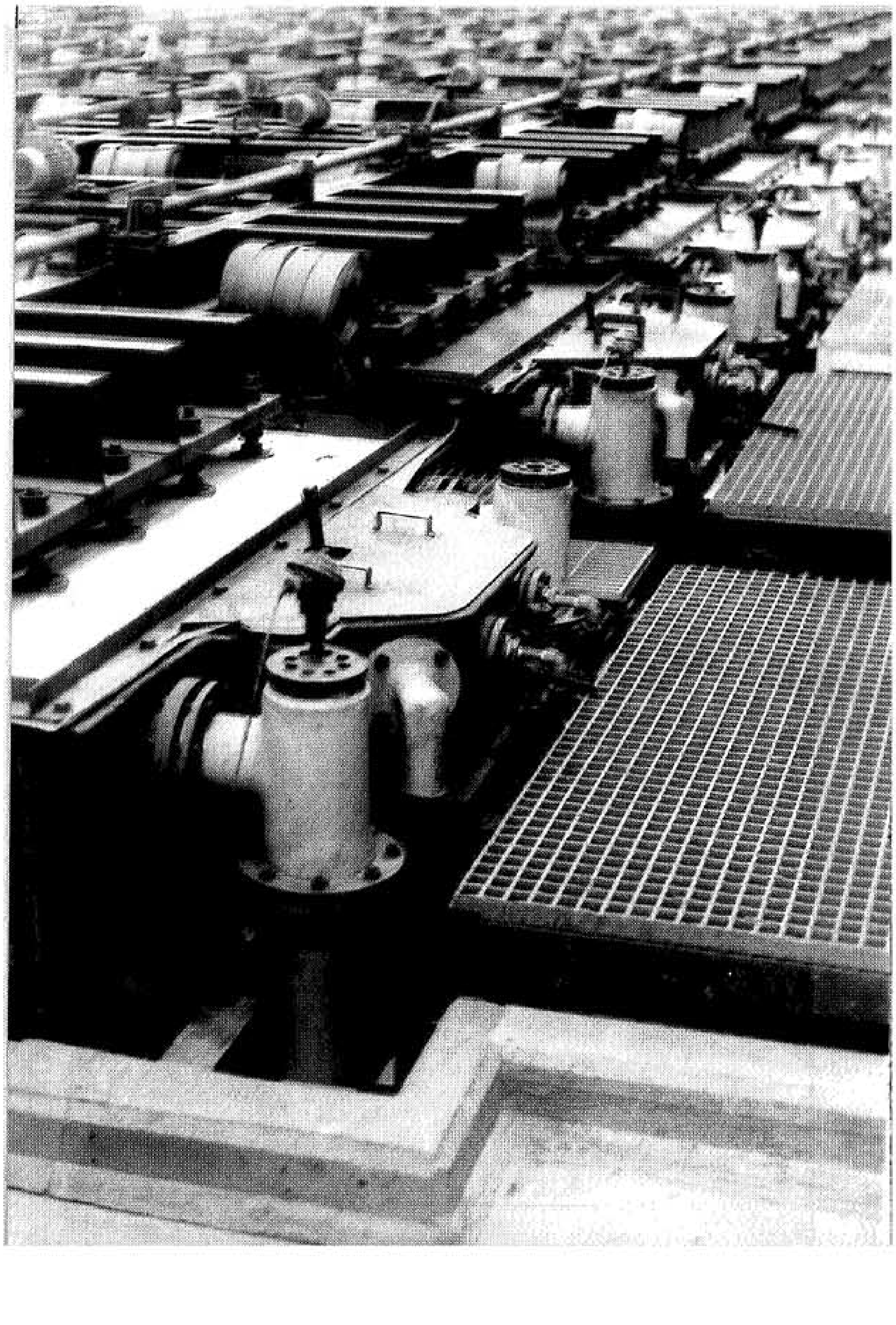

Figure 3. Outlet Boxes.

Figure 4. Mercury Addition "Pig."

as the anodes (approximately 18 months). Although there is little possibility of mercury vapor escaping from the cell because of the vacuum created by the chlorine gas removal system, the covers provide an effective seal that reduces mercury vapor emission when starting up or shutting down a cell. The copper anode posts are sealed with rubber gasketing material at the points where they penetrate the rubber cover. Plant engineers are currently process testing the use of clear Teflon cell covers. They are more expensive than the rubber covers but are expected to last longer.

The mercury system on each cell has compressed asbestos gaskets at pipe and pump connections. The plant is gradually changing over to nonasbestos materials. These gaskets effectively prevent mercury leaks during operation; however, leaks periodically develop during shutdown because of contraction at pipe flanges due to cooling.

Floor Coatings

To reduce the potential for mercury to permeate the cement floors, the plant has applied a 1/4-inch coating of epoxy resin (extended with a fine aggregate) over the first floor of the cell room. The coating, manufactured by either Conchem or Permachem, is applied by troweling it on like cement.

Cracks between floor section joints are filled with an epoxy compound containing a finer aggregate. This compound has a higher elasticity than the floor coating and allows for expansion and contraction between floor sections. This prevents cracks that might otherwise develop. The compound is available from the same manufacturers who make the floor coating.

LOCAL EXHAUST VENTILATION

To further reduce the potential for mercury vapor escaping from the inlet and outlet boxes on the cells, the boxes have been designed with ventilated enclosures. Each box has a steel cover over it with access doors for mercury addition and removal. This enclosure has an exhaust air takeoff that leads to an exhaust manifold connected to the other cells. The air is exhausted by a 1,500 cubic feet per minute (cfm) compressor located on the north side of the cell room. The original system was exhausted through a roof stack. Environmental concerns about emission of mercury vapor into the ambient air prompted the company to install a Pura-siv[R] mercury removal system similar to the one used to remove mercury from the hydrogen product stream (Figure 5). By removing mercury from the air stream, plant representatives feel that they have also indirectly reduced mercury vapor levels in the workplace. This is because the air exhausted through the stack may have been contaminating the supply air that entered the building.

The components of the air treatment system, including cooling, separation, and adsorption units, are illustrated in Figure 6. The Pura-siv[R] Mercury Adsorption Unit, manufactured by Union Carbide, is a dual, molecular sieve designed to operate with one sieve (adsorber) in service and the other sieve in regeneration. During operation, mercury in the air stream is adsorbed in the sieve through a proprietary process. During regeneration, heated 204 C (400 F) "low mercury content" gas is passed back through the sieve, vaporizing the collected mercury and carrying it through a cooler and a Peterson centrifugal separator. The liquid mercury is recovered and reused in the process.

Testing of the unit by both plant engineers and a private contractor showed that effluent mercury concentrations of 0.2 mg/m^3 were achieved with influent concentrations of 9-10 mg/m^3 during a typical 24-hour operating run. The direct effectiveness of this unit as a workplace control for worker exposure to mercury vapor has not been investigated by the plant.

DILUTION VENTILATION

The design of the mercury cell room permits the movement of a large volume of air past the mercury cells. The cell room building is a double-peaked structure with a large, open basement below the cell level (second floor) and a high ceiling above the cell level. There are vents along the roof (Figure 7) and vents and removable wall panels along the walls of the building. Air movement in the cell room is achieved through convection currents resulting from the heat of the mercury cells. The temperature differential between the hot air above the cells and the cooler outside air

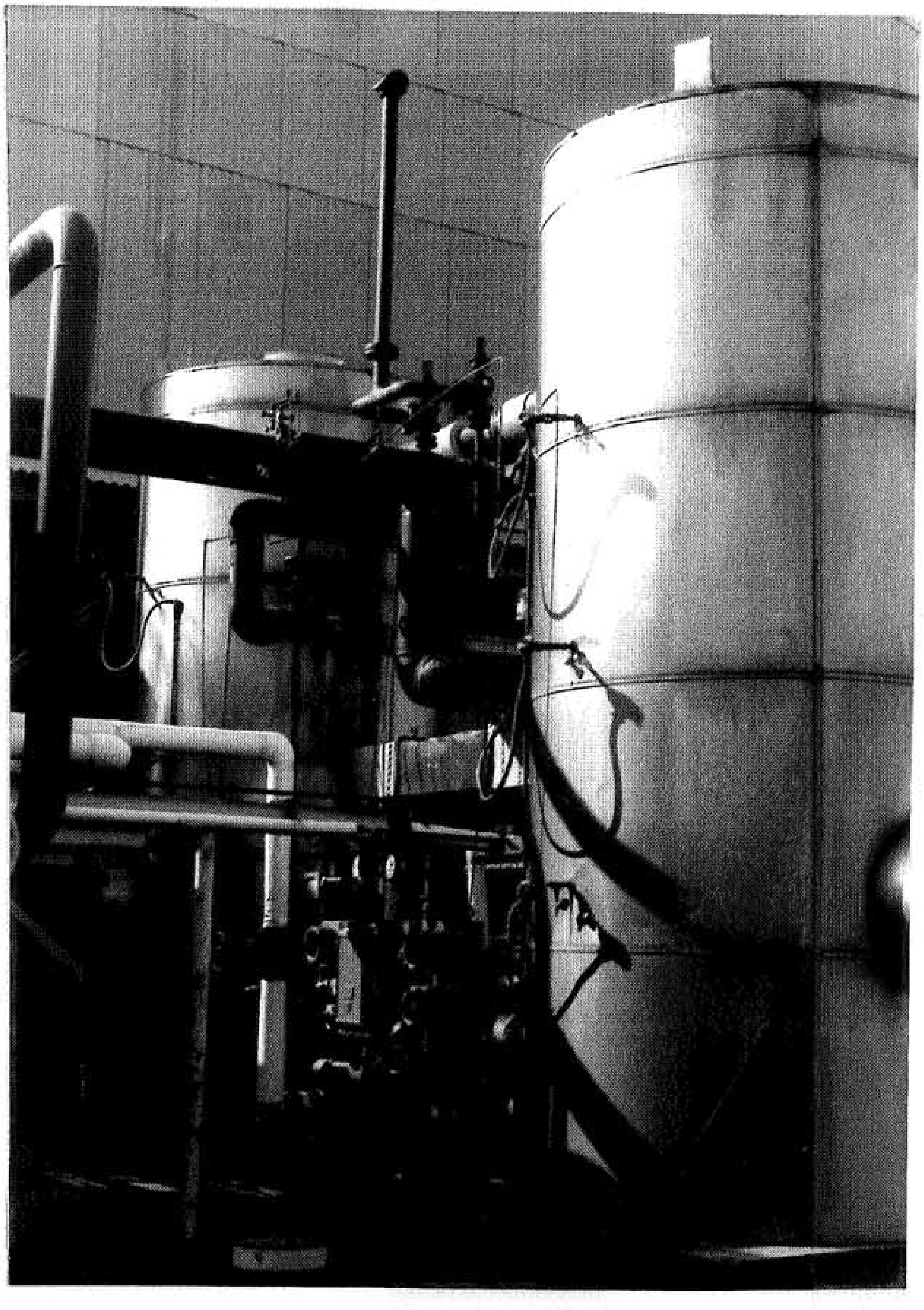

Figure 5. Pura-siv[R] Mercury Removal System.

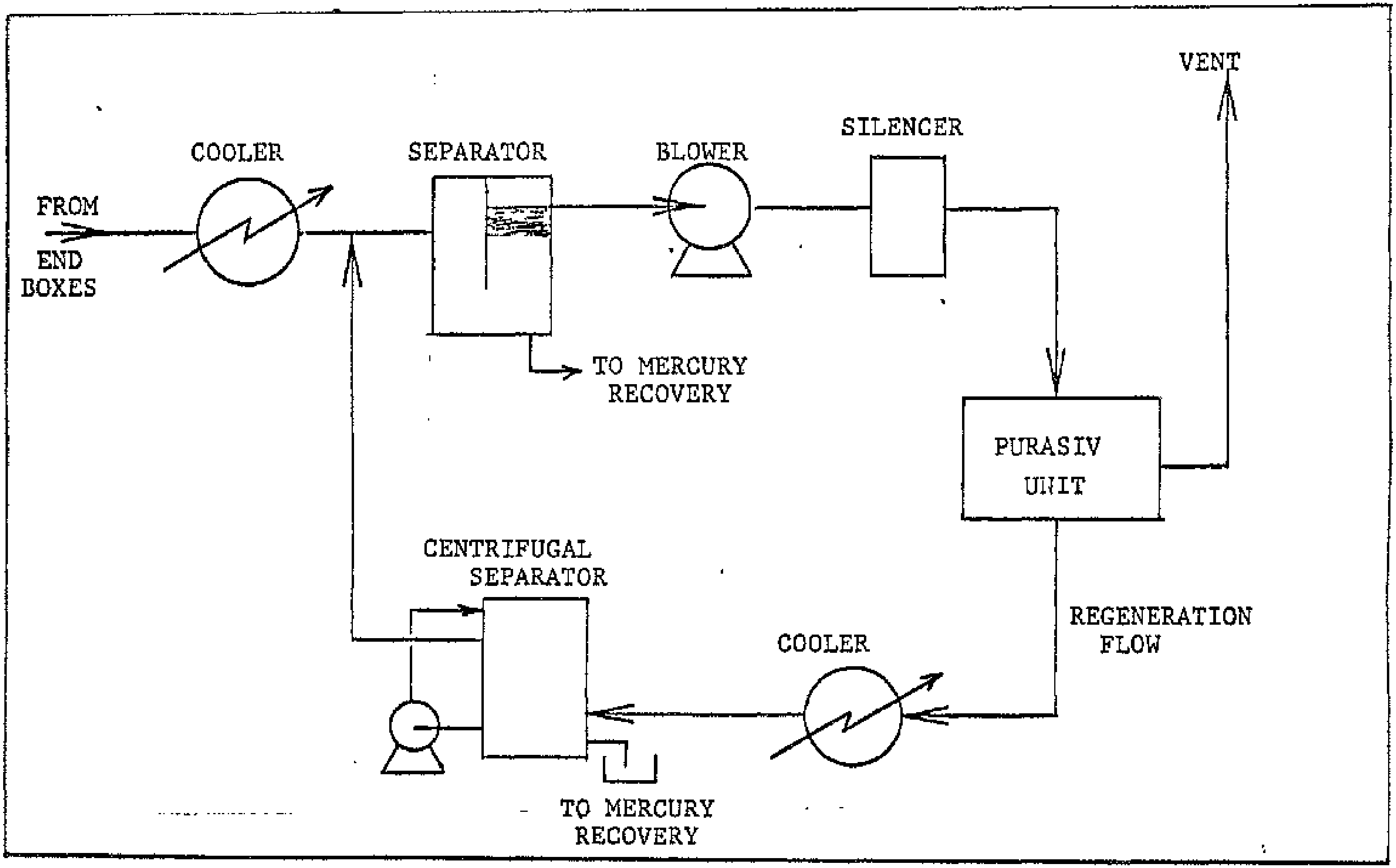

Figure 6. Air Treatment System for Mercury Removal.

Reference: Diagram from paper presented by A.L. MacMillan (IMC) at Chlorine Institute's 23rd Plant Managers Seminar, New Orleans, Louisiana, February 6, 1980.

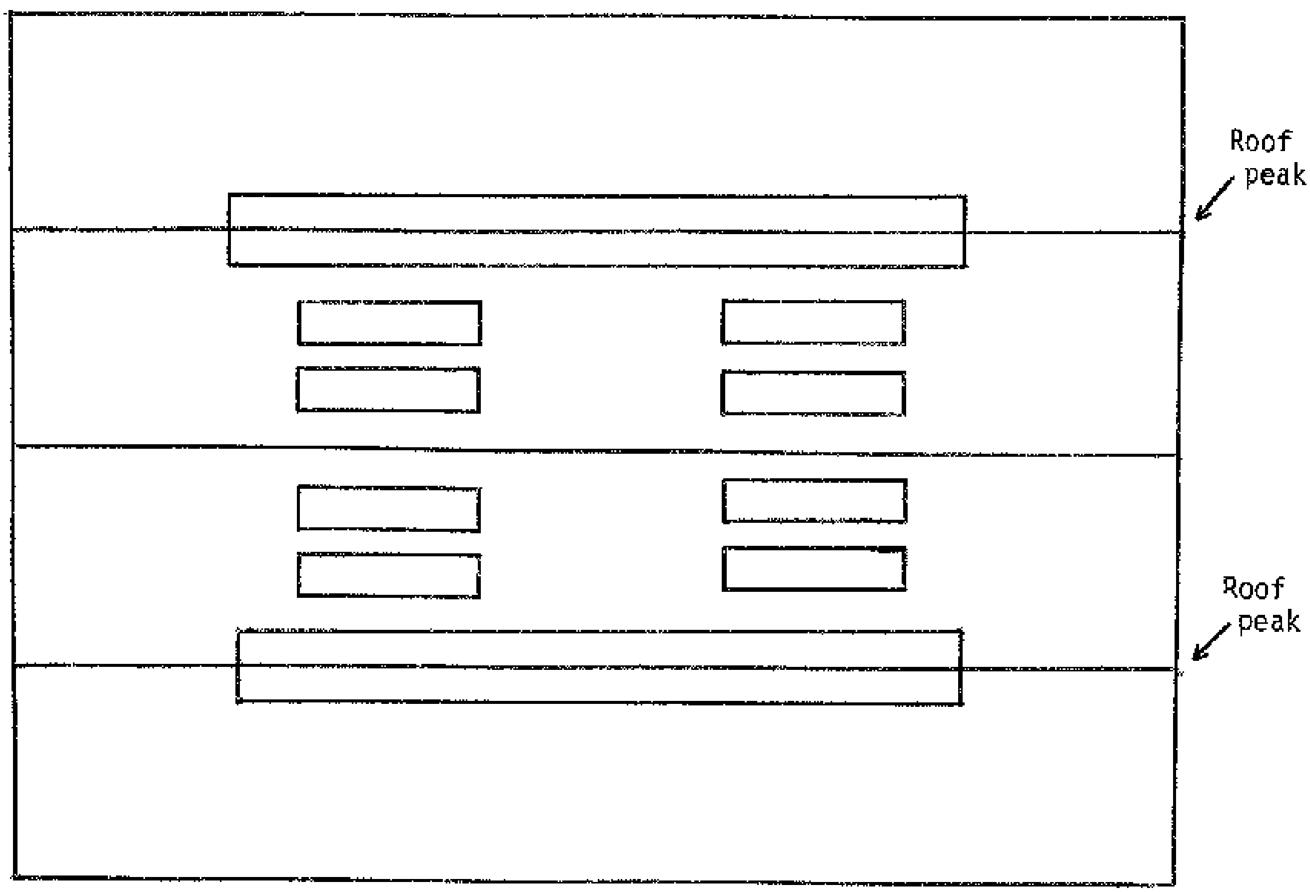

Figure 7. Diagram of Cell Room Roof Showing Position of Ventilators.

causes the hot air to rise up though the roof vents. Cooler outside air in turn flows in through the side vents (opened in the winter) or through the side panel openings (opened in the summer). Air movement between the two floors of the building is achieved through the use of Fiberglas grating installed on the walkways of the cell level. The flow of air into the building is very noticeable when standing in front of a wall vent or open panel.

A ventilation study conducted by the plant engineer in 1975 showed that the average air velocity through the roof vents was 225 feet per minute. The total open area of the roof vents is 1,180 square feet. The airflow through the building was therefore calculated to be 265,500 cfm. Total air volume of the cell room is 885,000 cubic feet; thus the air in the cell room is theoretically changed approximately every 3.3 minutes. This ventilation study was conducted in April and the cell room side panels were still closed for the winter. During the study, the outside air temperature was 11.6 C (53 F), barometric pressure was 751 mmHg, and wind speed was 10 miles per hour.

PERSONAL PROTECTIVE EQUIPMENT

Procedures for the donning of equipment and clothing are followed by employees at this plant for protection from exposure to mercury. Cloth work clothing is changed daily and may not be worn home. Street clothing must be kept in the "street" side of the change house and work clothing in the "work" side of the change house. Rubber shoes and boots are worn by cell room workers. These are kept in the boot room of the change house.

Employees are not required to wear respirators on a routine basis. Respirators are worn for activities that involve maintenance on open cells, visual checks of end boxes, sampling of solutions in end boxes, flushing cells, and cleanup and control of mercury leaks. Mercury is usually covered with water or brine solution during these activities. MSA, Comfo-II, half-facepiece, dual, chemical cartridge respirators (not approved by NIOSH), are used for these activities. The cartridges contain Mersorb® (MSA) as the primary adsorption medium for mercury vapor.

Work activities in which the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 0.1 mg/m^3 as an 8-hour time-weighted average (TWA) could be exceeded requires the use of a self-contained breathing apparatus. These activities include any work involving uncovered mercury such as cleaning cells.

WORK PRACTICES

Practices and procedures have been implemented to reduce employee exposure to mercury vapor and to contact with liquid mercury. These are described as follows:

- Women of child-bearing capability are not assigned to areas that have a potential for mercury exposure.
- Food, beverages, tobacco products, and unapplied cosmetics are prohibited in areas where mercury exposure is possible. These areas include the cell house and the utility area.
- Shower facilities are provided at this plant. Employees should shower at the end of each shift or upon overt exposure to mercury. Any saturated clothing should be removed immediately after contamination, and the person should shower.
- Careful attention is given to the washing of hands, forearms, face, and neck before eating, drinking, or smoking.
- Personal belongings such as rings, watches, combs, and wallets should not be brought into contact with mercury.
- Spills and leaks of mercury are cleaned up immediately using a vacuum cleaner designed for mercury removal (Hako Mercury Vacuum, American Cleaning Equipment). This area is washed down with water.
- Mercury is stored in closed containers and kept in a locked storage area.

MONITORING PROGRAMS

Biological Monitoring

The biological monitoring program at this plant consists of monthly urinalyses to determine the concentration of mercury. Although only the cell operators have duties that involve direct exposure to mercury on a regular basis, brine operators, control room operators, supervisors, and maintenance workers participate in the monitoring program. Spot samples, rather than 24-hour composite samples, are collected. If an employee's urine-mercury concentration reaches or exceeds 0.250 milligrams per liter (mg/L), it is brought to the attention of the employee and the supervisor. The supervisor working with the employee then takes the following actions:

- checks respirator fit on the employee
- checks work practices and personal hygiene practices to determine if the employee is guarding against contamination.

If an employee's urine-mercury concentration exceeds 0.400 mg/L on two successive analyses, the employee is removed from the mercury environment until the urine-mercury concentration falls below 0.300 mg/L. Plant representatives have determined that feedback from the supervisor to the employee regarding work practices and respirator fit, following detection of elevated urine-mercury concentration, has been an effective control in reducing employee exposure to mercury.

Recent plant records of biological monitoring show that current control strategies are effective in maintaining workers' exposure below the acceptable limit set by the plant (0.250 mg/L). The most recent plant results of urine-mercury monitoring are presented in Table 1.

TABLE 1

Biological Monitoring Data
Reported on 3/14/82

Employee	Job Classification	Urine-Mercury Concentration (mg/L)
A	Utility Operator	N.D.*
B	Cell Maintenance Worker	0.096
C	Cell Maintenance Worker	0.062
D	Cell Operator	0.134
E	Valve Repair Worker	N.D.
F	Loading Operator	0.080
G	Control Room Worker	N.D.
H	Day Relief Operator	0.061
I	Shift Supervisor	0.032
J	Brine Operator	0.024

*None Detected.

The highest urine-mercury concentration detected was in the cell operator's sample. These results reflect observed worker activities in that cell operators spend more time in the cell room than do other workers.

Air Monitoring

Air sampling and analysis to determine the TWA concentration of mercury vapor is conducted by the plant laboratory on a regular basis. When the plant began operation in 1967, samples were collected using impingers and a solution of potassium permanganate and sulfuric acid as the collection medium. In 1979, the sampling method was changed to collection on Hopcalite solid sorbent tubes. Grab sampling is also conducted using a mercury vapor detector (Bacharach MV-2); however, the strong magnetic fields created by the electrolytic cells may make this method unreliable.

Samples are collected regularly at 13 specified locations throughout the cell room. In the most recent plant air monitoring survey (February 1982), sample concentrations at the 13 locations ranged from 0.003 to 0.086 mg/m^3, with an average of 0.023 mg/m^3. Plant historical air monitoring data were reviewed during the survey and are summarized in Table 2.

TABLE 2

Summary of TWA Area Concentrations of Mercury Vapor (mg/m^3)

Sample Date	Range	Average
4/78	0.003-0.055	0.028
8/78	0.022-0.347	0.102
1/79	0.006-0.050	0.028
2/79	0.010-0.072	0.030
7/79	0.017-0.085	0.040
2/82	0.003-0.086	0.023

Medical Program

Each new employee is given a medical examination by a consulting physician. Reexaminations are performed annually. The biological monitoring program is part of the medical program; biological monitoring data for each employee are given to the physician prior to the examination.

Training Program

Each new employee assigned to work in an area that has a potential for exposure to mercury is to be trained in the following:

- the hazards of mercury
- the symptoms of mercury poisoning
- personal hygiene requirements
- housekeeping and handling of mercury
- protective equipment required.

This indoctrination is followed by yearly, general training sessions that emphasize the elements of the initial training session.

SURVEY DATA

Personal and area samples for mercury vapor were collected during the survey using sampling pumps and Hopcalite as the adsorption medium. For personal samples, the Hopcalite tube was attached to the collar of the employee. The flow rates, set at 75 ml of air per minute, were determined using a buret (soapbubble meter) both before and after sampling. Analyses of samples were done by flameless atomic absorption. Sample results are presented in Table 3.

TABLE 3

Results of Personal and Area Monitoring for Mercury Vapor

Employee/Location	Full-Shift TWA Concentration (mg/m^3)	
	3/25/82	3/26/82
Area - S.W. corner of plant on railing (J)*	0.008	--
Area - Cell 7/South (I)	0.007	0.009
Area - Cell 21/North (D)	0.018	0.029
Area - Control Room (N)	0.003	0.002
Employee A - Maintenance Operator	0.006	0.009
Employee B - Cell Room Operator	0.022	--
Employee C - Cell Room Operator	--	0.004
Area - Cell 18 North (A)	--	0.037

*Letter in parentheses indicates plant sampling point identified in Figure 8.

Area daily TWA concentrations ranged from 0.002 to 0.037 mg/m^3. Area sampling results during the survey are in general agreement with recent plant air sampling results. Personal exposure concentrations ranged from 0.004 to 0.022 mg/m^3. The OSHA PEL for mercury vapor is 0.1 mg/m^3 (as a TWA).

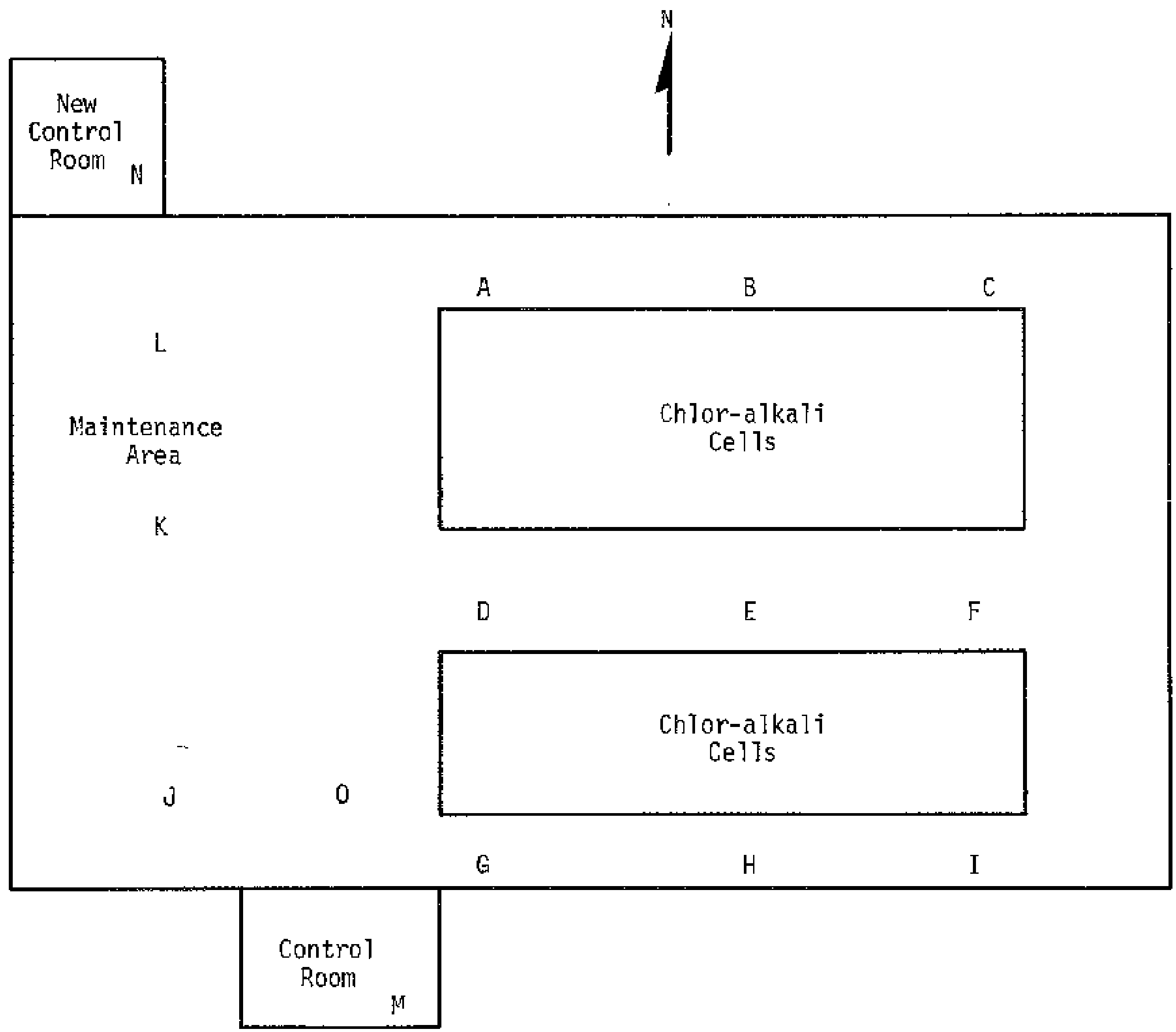

Figure 8. IMC Cell Room Layout Showing Sampling Locations.
Reference: IMC

Personal sampling results were similar to area sampling results. This may be an indicator of effective work practices in that significant contamination of employees' work clothing is not occurring at this facility. Work clothing that has become contaminated with liquid mercury usually causes higher personal exposure to mercury vapor than would be indicated by area sampling concentrations.

Personal sampling results of cell operators are indicative of typical exposure to mercury vapor because they include all routine activities for which a potential for exposure to mercury exists. These activities include taking samples of cell solutions and opening cell inlet and outlet boxes. Maintenance workers are occasionally exposed to mercury vapor concentrations in excess of cell room background levels. These occasions include maintenance work on open cells and cleaning cell bottoms. Respirators are worn for both of these activities. Maintenance workers did not perform any activities associated with increased exposure to mercury during this survey.

Air samples were also obtained using high-flow sampling pumps and particulate filters (Millipore AA, mixed-cellulose ester filter, 0.8-micrometer pore size). These samples were obtained to verify previous sampling data collected at this facility by NIOSH in which mercury was detected on Millipore AA filters. The results of this sampling showed that mercury was detected on the four samples collected. The amount of mercury trapped on the AA filters ranged from 0.26 micrograms (ug) to 1.09 ug. Mercury was not detected ($<$0.001 ug) on blank AA filters. The sampling and analytical method used does not differentiate between mercury vapor and mercury particulate. Based on observation of the chlor-alkali process, it is unlikely that particulate mercury was present. Consequently, it is assumed that the AA filter matrix collects mercury vapor from the sampled air.

CONCLUSIONS AND RECOMMENDATIONS

Based on sampling results and review of historical data, IMC has been achieving mercury vapor concentrations below the OSHA PEL of 0.1 mg/m^3 (as a TWA). The nature of the mercury electrolytic cell allows for numerous potential mercury vapor emission points. The plant has addressed this problem by containing the mercury throughout the process and by covering hot mercury with water. Local exhaust on the inlet and outlet boxes provides for removal of mercury vapor at its source.

Exposure to mercury vapor, which manages to escape into the workplace air, is minimized due to sound work practices and natural dilution ventilation. Housekeeping is a high priority at this facility, as is demonstrated by general plant cleanliness and the absence of any visible mercury on the lower floor of the cell room.

The Pura-siv[R] mercury removal system, installed for control of release of mercury vapor into the ambient air, is a control that may have applications for mercury removal from recycled workplace air.

The plant has continued to reduce its mercury vapor concentrations since its startup. This has resulted from a continuous effort in developing new controls for isolating mercury or reducing worker exposure to mercury in the air. The historical results of both urine-mercury levels and mercury vapor concentrations illustrate the value of developing and refining an integrated mercury control program.