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Report EPS 3-AP-75-6

Air Pollution
Control Directorate
March 1976

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AIR POLLUTION EMISSIONS AND CONTROL TECHNOLOGY. CHLOR-ALKALI INDUSTRY

by

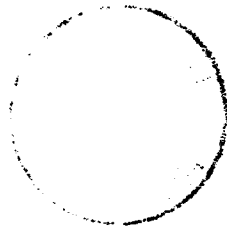
P.L. Marsh and W.H. Sullivan

Chemical Process Sources Division
Abatement and Compliance Branch
Air Pollution Control Directorate



Report EPS 3-AP-75-6

March 1976



ABSTRACT

The Canadian chlor-alkali industry is examined and the atmospheric mercury emissions from the industry are evaluated together with the technology available to control these emissions.

Mercury emissions from the mercury cell process can be eliminated by conversion to either the diaphragm or membrane cell process. The technical and economic aspects of all three processes are discussed in detail. Currently available techniques to contain mercury emissions from plants using the mercury cell process are also examined.

RÉSUMÉ

Le présent rapport traite de l'industrie canadienne du chlore et évalue ses émissions de mercure dans l'atmosphère, de même que des techniques disponibles pour les restreindre.

Les émissions de mercure provenant des électrolyseurs au mercure peuvent être éliminées en utilisant des cellules à diaphragme ou à membrane. Les aspects techniques et économiques des trois procédés y sont expliqués en détail. On y étudie aussi les techniques actuellement disponibles pour arrêter les émissions attribuables aux électrolyseurs au mercure.

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1 INTRODUCTION

1.1 Scope

This study pertains to air pollution control in the manufacture of chlorine and sodium or potassium hydroxide. The industry manufacturing these products is generally known as the chlor-alkali industry. Information on the size and growth of the industry are presented. Various plant processes are described with emphasis on process factors associated with atmospheric emissions. Emission control technology is assessed with regard to effectiveness and cost.

The report presents the situation at the time of writing because criteria for emission regulations should reflect current conditions. For this reason emission rates and costs presented are prevailing values, where possible.

1.2 Purpose

The primary purpose of this report is to provide the technical information necessary for the development of effective national emission regulations for atmospheric mercury emissions from the chlor-alkali industry. For this purpose a chlor-alkali plant is defined as a stationary source, subject to both national emission regulations and guidelines that may be published by the Governor in Council as required by the Clean Air Act of 1971.

1.3 Information Sources

Information was gathered by a comprehensive literature search. Of particular value in the preparation of this report were publications prepared by the U.S. Environmental Protection Agency during the development of regulations for the American chlor-alkali industry. Information was also received from chlor-alkali manufacturers through the Canadian Chemical Producers' Association. Manufacturers of pollution control equipment and materials also provided information, as did those companies which design and engineer chlor-alkali cells and systems. Valuable information was also derived from monthly reports submitted by mercury cell plants to Environment Canada's Water Pollution Control Directorate and from the Atmospheric Emissions Questionnaires completed by Canadian chlor-alkali plants in 1974.

2 INDUSTRY DESCRIPTION

2.1 History and Growth

In the 1890's the Ontario People's Salt and Soda Company (1) located at Kincardine, Ontario, began the first Canadian chlor-alkali operation, which was followed in 1901 by the Canadian Electro-Chemical Company, Limited (1) at Sault Ste. Marie. However, these early attempts to make chlorine and caustic soda were short-lived. It was not until 1911 that the Canadian Salt Company near Windsor, Ontario, began what was to be the first operation to produce chlorine and caustic soda on a regular basis (2). The Riordon Company in Merritton, Ontario was next, in 1916, with an operation using

36 Allen Moore cells to provide chemicals for the bleaching of its wood pulp (1). All plants up to 1935 used the diaphragm cell process.

The oldest existing plant is the mercury cell chlor-alkali plant of Canadian Industries, Limited at Cornwall, Ontario, which began operation in 1935. The Hooker plant in Vancouver, British Columbia, which began operation in 1957, is Canada's oldest operational diaphragm cell plant. Today the industry has grown to 18 plants, 10 using the mercury cell the remainder using the diaphragm cell. Together they produce a total of 3500 tons of chlorine per day. Table 1 lists the age, location and capacity of all currently operating plants. Table 2 is a similar summary of plants which have ceased operation. The geographical distribution of Canadian chlor-alkali plants is presented in Figure 1.

The growth of the Canadian chlor-alkali industry since 1911 is shown in Figure 2. It will be noted that while diaphragm plant capacity continues to increase, mercury cell plant capacity has peaked and is currently showing a downward trend. Dow Chemical has switched over completely to the diaphragm cell process; Canadian Industries, Limited has shut down its Hamilton mercury cell plant and is moving into chlor-alkali production by the diaphragm cell process with their new plant at Becancour, Quebec, which started operation in September, 1975. The change by Reed Paper, Limited from the mercury cell process to the new membrane cell process was completed in late 1975. The recent introduction of commercial membrane cells is expected to have a strong influence on the development of the chlor-alkali industry.

2.2 Markets

At present, the pulp and paper industry is the largest single user of both chlorine and caustic soda. Large quantities of both chemicals are required for multi-stage bleaching processes and caustic soda is used in chemical pulping. In 1971 about 50% of the chlorine and caustic soda produced in Canada went to this industry.

The production of industrial chemicals such as vinyl chloride and chlorinated solvents also involves large quantities of chlorine and caustic soda. In 1971, 47% of the chlorine and 35% of the caustic produced was used for these purposes.

The remaining chlorine and caustic soda is used in such industries as mining, smelting and refining, soap and detergent manufacture, municipal waterworks and in textile dyeing and finishing. Table 3 is a summary of the consumption and uses of chlorine and caustic soda (4).

3 INDUSTRIAL PROCESSES

3.1 General

When two electrodes are immersed in an electrolyte solution, such as brine, and an electric current is passed between them, the electrolyte is decomposed. This process is known as electrolysis and the assembly of electrodes, solution and containing vessel is referred to as an electrolytic cell. If the brine is a solution of sodium chloride, the products of electrolysis are chlorine and caustic soda (sodium

TABLE 1 CHLOR-ALKALI PLANTS IN CANADA, 1975 (3)

Company	Plant location	Year on line	Nominal capacity (tons/day)	
			Chlorine	Caustic soda
Mercury cell plants				
Aluminum Company of Canada	Arvida, Que.	1947	79	89
American Can of Canada Ltd.	Marathon, Ont.	1952	36	40
Canadian Industries Ltd.	Dalhousie, N.B.	1963	88	99
Canadian Industries Ltd.	Cornwall, Ont.	1935	110	123
Canadian Industries Ltd.	Shawinigan, Que.	1936	85	96
Canso Chemicals Ltd.	Pt. Abercrombie, N.S.	1970	68	77
Domtar Chemicals Ltd.	Lac Quevillon, Que.	1961	88	99
FMC Chemicals Ltd.	Squamish, B.C.	1965	99	111
Prince Albert Pulp Co. Ltd.	Saskatoon, Sask.	1964	96	108
Standard Chemical Ltd.	Beauharnois, Que.	1949	342	386
Reed Paper Ltd. [†]	Dryden, Ont.	1962	33	37
Total nominal capacity			1124	1265
Diaphragm cell plants				
Dow Chemical of Canada Ltd.	Fort Sask., Alta.	1966	614	692
Dow Chemical of Canada Ltd.	Sarnia, Ont. (Plant 1)	1958	403	454
Dow Chemical of Canada Ltd.	Sarnia, Ont. (Plant 2)	1973	556	626
Hooker Chemicals*	Vancouver, B.C.	1957	282	318
Hooker Chemicals*	Nanaimo, B.C.	1964	86	96
Hooker Chemicals*	Brandon, Man.	1968	99	112
Canadian Industries Ltd.	Becancour, Que.	1975	383	431
Total nominal capacity			2423	2729

* Division of Canadian Occidental Petroleum Ltd.

† Converted to membrane process in 1975.

TABLE 2 PAST CHLOR-ALKALI PLANTS IN CANADA*

Company	Plant location	Year on line	Year off line	Nominal capacity (tons/day)	
				Chlorine	Caustic soda
Mercury cell plants					
Canadian Industries Ltd.	Hamilton, Ont.	1965	1973	93	105
Dow Chemical of Canada Ltd.	Thunder Bay, Ont.	1966	1973	88	99
Dow Chemical of Canada Ltd.	Sarnia, Ont.	1948	1973	164	185
Dow Chemical of Canada Ltd.	Sarnia, Ont.	1970	1973	300	338
Dryden Chemical Ltd.	Dryden, Ont.	1961	1975	35	38
Diaphragm cell plants (since 1911)					
Canadian International Paper	Temiskamang, Ont.	1920	1967	10	11.2
Canadian Salt Co.	Windsor, Ont.	1911	1954	100	11.2
Domtar Chemicals Ltd.	Cornwall, Ont.	1922	1971	10	11.2
Eddy Forest Products Ltd.	Espanola, Ont.	1947	1971	20	22.4
Riordon Co. Ltd.	Merritton, Ont.	1916	(about) 1925	Unknown	Unknown

* The assistance of the many people who provided information on companies no longer in operation is acknowledged. Information was also obtained from Reference 1.

LEGEND:

- 1 Hooker Chemicals, Nanaimo, B.C.
- 2 FMC, Squamish, B.C.
- 3 Hooker Chemicals, Vancouver, B.C.
- 4 Dow, Fort Saskatchewan, Alta.
- 5 Prince Albert Pulp, Saskatoon, Sask.
- 6 Hooker Chemicals, Brandon, Man.
- 7 Dryden Chemicals, Dryden, Ont.
- 8 American Can, Marathon, Ont.
- 9 Dow, Sarnia, Ont. (2 Plants)
- 10 Domtar, Lac Quevillon, Que.
- 11 C.I.L., Cornwall, Ont.
- 12 Standard Chemical, Beauharnois, Que.
- 13 C.I.L., Shawinigan, Que.
- 14 Alcan, Arvida, Que
- 15 C.I.L., Dalhousie, N.B.
- 16 Canso Chemicals, Pt. Abercrombie, N.S.
- 17 C.I.L., Becancour, Que.

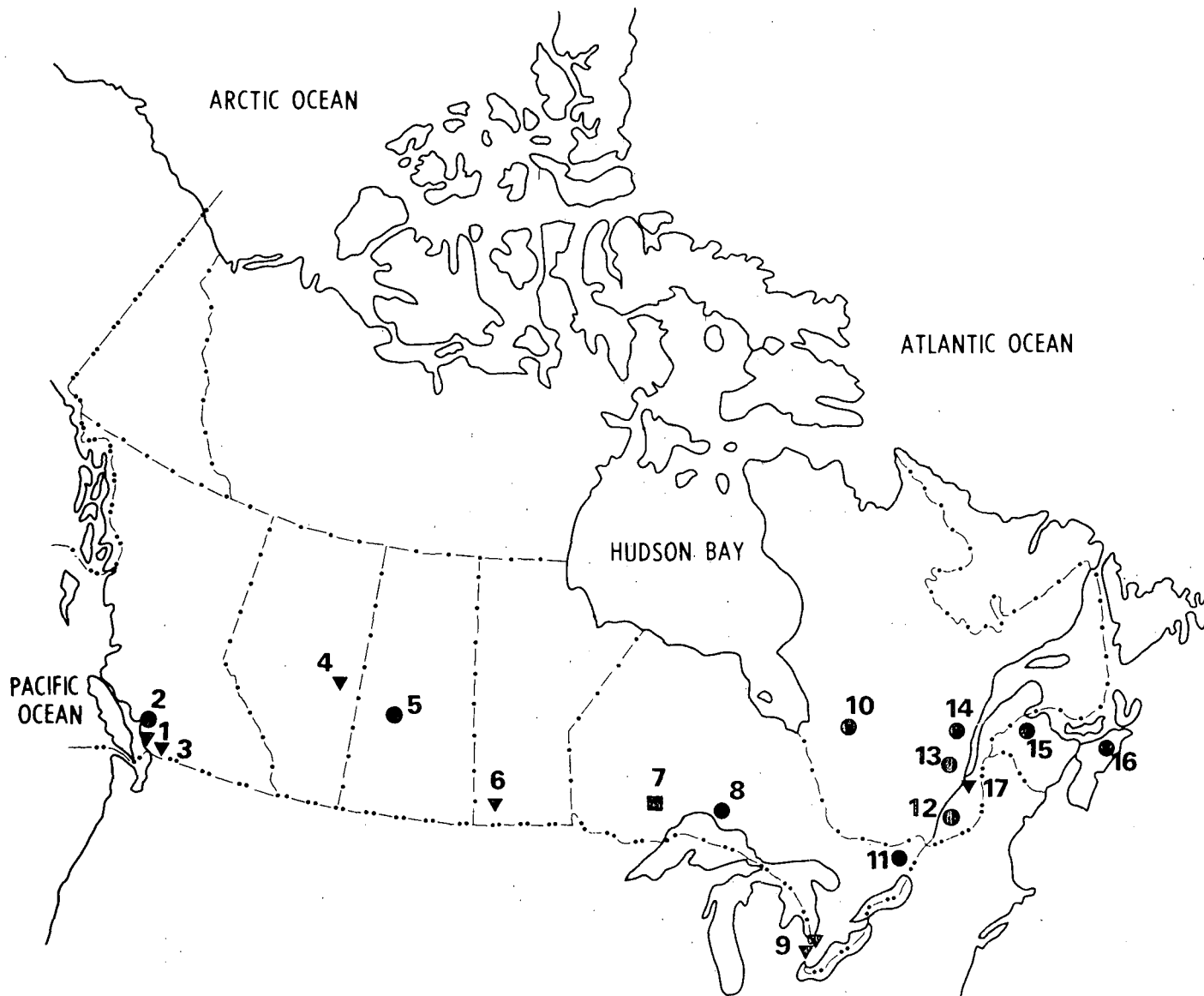


FIGURE 1 CANADIAN CHLOR-ALKALI PLANTS

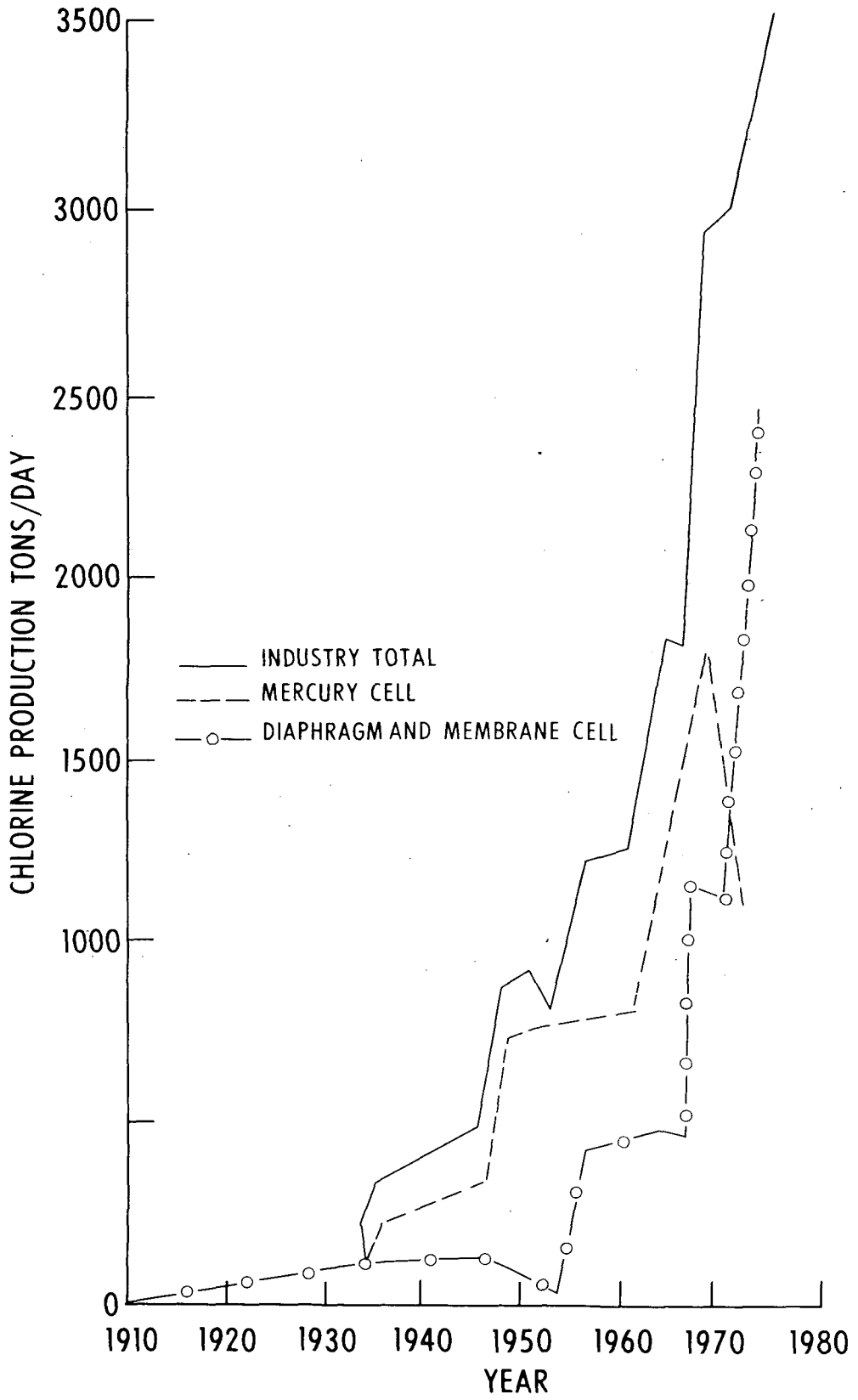


FIGURE 2 CANADIAN CHLORINE PRODUCTION

TABLE 3 CONSUMPTION OF CHLORINE AND CAUSTIC SODA IN CANADA, 1971 (5)

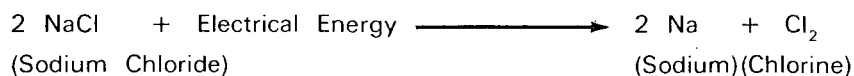
Industry	Chlorine		Caustic	
	tons/yr	% of total consumption	tons/yr	% of total consumption
Pulp and paper	420 005	50.3	548 640	50.8
Industrial chemicals	393 285	47.1	378 000	35.0
Mining, smelting and refining	6 680	0.8	14 040	1.3
Soap and detergents	10 020	1.2	48 600	4.5
Municipal waterworks	4 175	0.5		
Petroleum refining	nil	nil	16 200	1.5
Plastic and synthetic resins	nil	nil	20 520	1.9
Miscellaneous	835	0.1	54 000	5.0
TOTAL	835 000¹		1 080 000²	

1 Includes net import of 1 000 tons/yr.

2 Includes imports of 137 000 tons/yr.

hydroxide). If potassium chloride is used in place of sodium chloride, the products are chlorine and caustic potash. The feed material for the Canadian chlor-alkali industry is predominantly sodium chloride.*

A simple electrolytic cell is shown in Figure 3. In this cell the positively charged anode and negatively charged cathode are suspended in a brine solution. Electric current passes between the electrodes and the brine is decomposed to its constituent elements, sodium and chlorine:



The highly reactive sodium formed at the cathode will immediately react with water to form caustic soda and hydrogen:

* Throughout the report all data are based on a sodium chloride feed. For all practical purposes the data can be applied to potassium chloride.

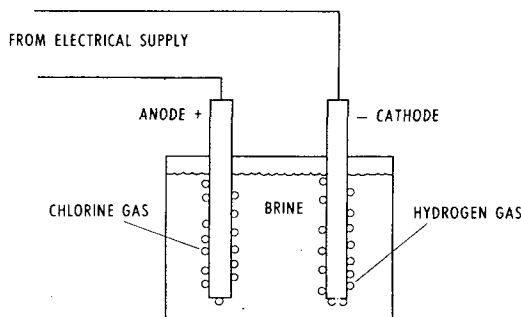
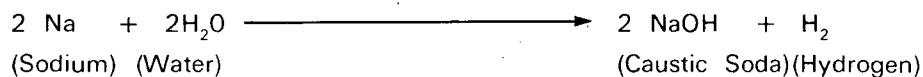
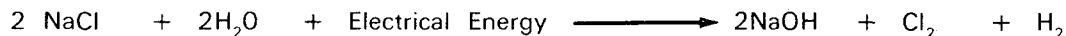


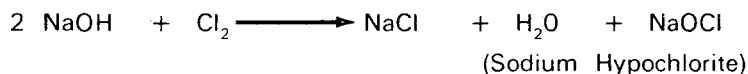
FIGURE 3 ELECTROLYTIC CELL



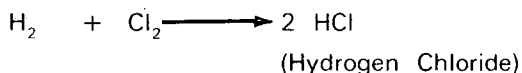
The net reaction is therefore:



In this simple cell it is possible for the products to mix and react. For example chlorine and caustic will react to form sodium hypochlorite:



Chlorine and hydrogen can react with explosive violence to form hydrogen chloride:



To preserve the desired products, chlorine and caustic soda, cells have been developed to prevent mixing. The essential difference between the various commercial processes for the manufacture of caustic soda and chlorine from brine is the manner in which the cells are designed to prevent this mixing. All commercial cell designs provide for continuous withdrawal of the product and continuous feeding with brine or salt.

The cell types most widely used are the mercury cell and the diaphragm cell. In the mercury cell the cathode is formed by a stream of mercury flowing continuously across the base of the cell. The sodium formed at the cathode reacts with the mercury to form sodium amalgam. This amalgam is removed from the cell and prevents the sodium from reacting with the chlorine liberated at the anode. The sodium amalgam is subsequently reacted with water to form caustic soda and hydrogen. In the diaphragm cell, a permeable diaphragm separates the anode and cathode, preventing chlorine from coming into contact with caustic soda or hydrogen.

A third cell type, developed recently, is the membrane cell, in which the physical separation of chlorine from caustic soda is achieved by an ion exchange membrane. This membrane is permeable

to sodium ions, but impermeable to the other ions and molecules present. All three types of cell are described in more detail in subsequent sections of this report.

Until recently the choice of cell has been between the mercury and diaphragm type. Many factors must be considered in determining the preferred cell type for any given circumstance. These include:

- *Caustic Purity.* Caustic from mercury cells is pure and concentrated. Caustic soda from diaphragm cells is dilute and contains much residual salt. If this caustic solution is concentrated by evaporation, most of the salt is precipitated, but the final solution still contains about 1% salt. For most uses of caustic soda, a 1% salt content poses no problems. If a caustic of higher purity is needed, methods are available to remove the salt, but processing costs increase accordingly.
- *Energy Requirements.* A diaphragm cell requires less electrical energy than a mercury cell of the same production capacity, but this advantage may be offset by the extra energy needed to concentrate the weaker caustic product from a diaphragm cell. The total energy cost for each process will depend upon the cost of electrical power and steam. These costs may be very different from one circumstance to another.
- *Capital Cost.* Generally the capital cost of small capacity plants is less for mercury cell plants than for diaphragm cell plants. The 'break-even' point occurs in the range of 200 tons - 400 tons chlorine per day.
- *Cost of mercury pollution control.* This has become a significant factor in the selection of cell technology.
- *Availability of Salt.* The availability, at an economic cost, of solid salt to saturate the brine is a requirement of the mercury cell process.

The membrane cell is a recent development and it is too early to judge the validity of claims for operational advantages. Successful industrial operation must be experienced before such a judgement can be made; however, current reports suggest that membrane cells will produce caustic soda of a purity similar to mercury cell caustic, and of greater strength than diaphragm cell caustic.

3.2 The Mercury Cell Process

The process design of all mercury cell chlor-alkali plants presently operating in Canada, is fundamentally the same. Differences exist because plants must accommodate for factors such as climate and variation in feed quality. Over the years, developing technology and operational experience have resulted in further variations in process design, but the basic process has remained unchanged. Figure 4 is flow diagram of a typical process scheme and a typical mercury cell is depicted in Figure 5.

Feed material for the process is common salt (sodium chloride). Salt feed enters a dissolver where the salt is contacted with weak brine solution recycled from the electrolyzer. The brine leaving the dissolver is a saturated solution. Insoluble impurities in the brine are removed by settling and subsequent filtration of the settler underflow. After leaving the settler the pH of the brine is adjusted to between 2.5-5, by the addition of hydrochloric acid. It is then heated to about 50°C before entering the electrolyzer. A bleed stream from the brine circuit may be treated to remove undesirable contaminants, such as vanadium, chromium, molybdenum, iron and magnesium. The nature and degree of such treatment depends upon the quality of the feed salt. The brine leaving the dissolver

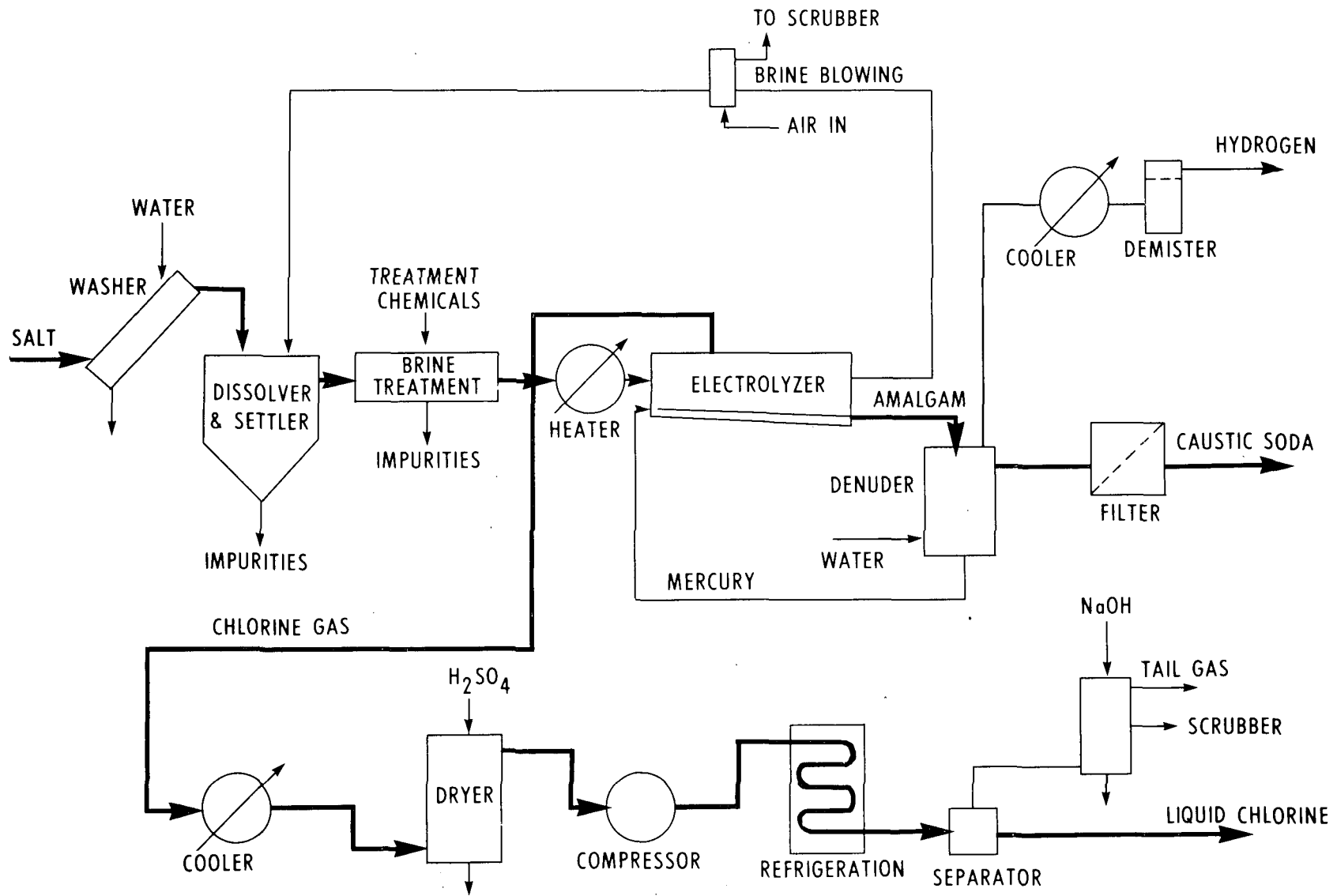


FIGURE 4 FLOW DIAGRAM, MERCURY CELL PROCESS

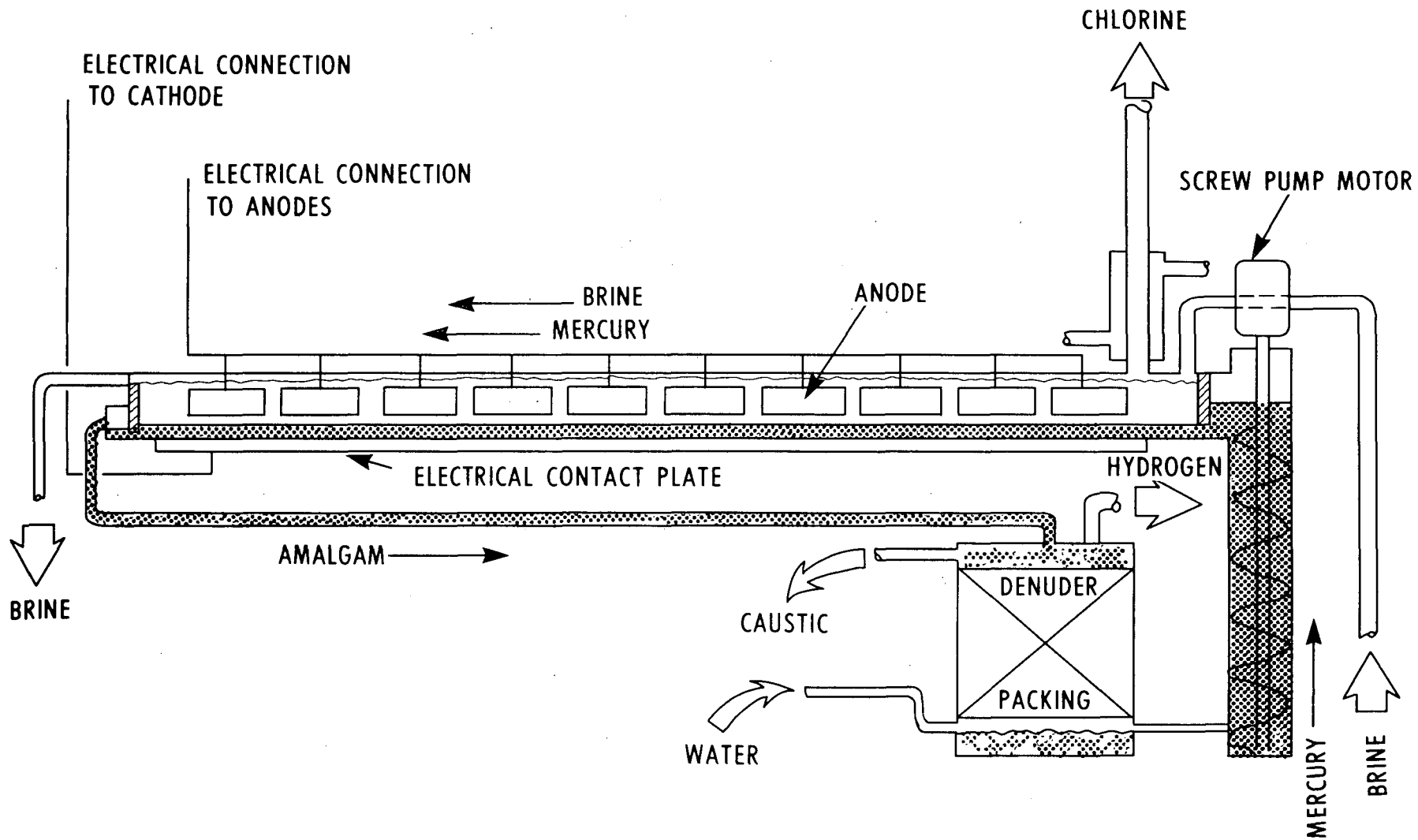


FIGURE 5 MERCURY CATHODE CELL

is a saturated solution. Insoluble impurities in the brine are removed by settling and subsequent filtration of the settler underflow. After leaving the settler the pH of the brine is adjusted to between 2.5-5, by the addition of hydrochloric acid. It is then heated to about 50°C before entering the electrolyzer. A bleed stream from the brine circuit may be treated to remove undesirable contaminants, such as vanadium, chromium, molybdenum, iron and magnesium.

In passing through the electrolyzer the salt is electrolytically decomposed to sodium and chlorine, and the salt content is lowered to about 14%. The depleted brine leaving the electrolyzer is acidified and air blown (or vacuum stripped) to remove dissolved chlorine. It is then neutralized with caustic soda and recycled to the dissolver.

The chlorine formed in the electrolyzer is about 99% pure (dry basis by volume). It contains hydrogen and, when carbon anodes are used, carbon dioxide as the major impurities. The chlorine is dried by cooling and demisting, followed by scrubbing with concentrated sulphuric acid. It is then liquefied by cooling and compression. Before venting to the atmosphere, the residual gaseous impurities, containing some uncondensed chlorine, are passed through a tail gas scrubber, where contact with caustic soda solution removes the chlorine.

The sodium formed in the electrolyzer combines with the mercury cathode to form sodium amalgam which flows to the denuder, where it is contacted with water to form caustic soda, hydrogen and mercury. Water flow to the denuder is controlled to produce a 50% solution of caustic soda. This solution is filtered, cooled and stored in product tanks. The mercury from the amalgam is recycled to the electrolyzer.

Hydrogen released from the denuder is contaminated with mercury. This mercury is removed by cooling the hydrogen stream, first with water then with refrigerant, after which mercury droplets are removed by a demister. Further mercury vapour removal may be accomplished by adsorption on a molecular sieve or activated charcoal.

3.3 The Diaphragm Cell Process

There are many differences in the design of the diaphragm cells currently being operated; however, three basic features, are common to all diaphragm cells: an anode compartment, a cathode compartment and a porous diaphragm separating these compartments. The purpose of the diaphragm is to prevent the products of electrolysis from coming into contact and reacting. Most diaphragms are composed of asbestos fibre, deposited on steel cathodes. The cathodes are usually made from wire mesh or perforated plate and the diaphragm is situated on the cathode surface closest to the anode. Anodes have traditionally been made of graphite but recently metal anodes have found wide acceptance. Metal anodes have a life of up to 7 years (6), whereas graphite anodes wear away and must be replaced within several months.

A sectional drawing of a cell based on a Hooker design is shown in Figure 6. In this type of cell, the anodes are set in lead contained in the concrete cell base. The surface of the lead between

the anodes is covered with a mastic sealer which also serves as an electrical insulator. The cathode is in the form of fingers, projecting from the cell wall. These fingers are hollow and are formed from steel mesh coated with the porous asbestos diaphragm. The cavity inside the cathode and the space between the double wall of the cell to which it connects, form the cathode compartment of the cell. The liquor level in the cathode compartment is maintained below that in the anode compartment by means of an inverted U-bend outlet pipe. A concrete dome encloses the cell. The chlorine outlet is located on the top of the dome and the brine inlet on the sloping side. The hydrogen outlet passes through the side wall of the cell to permit hydrogen to leave the cathode compartment.

Figure 7 is a flow diagram of the diaphragm cell process. Brine is fed into the anode compartment of the cell which is operated at a higher liquid level than the cathode compartment. This difference in level causes a slow flow of solution from the anode compartment, through the diaphragm into the cathode compartment. This flow prevents the migration of hydroxyl ions into the anode compartment preventing any reaction between chlorine and caustic soda. However, the flow of brine into the cathode compartment results in dilution of the caustic soda solution produced there.

The liquor leaving the cell typically contains about 12% sodium hydroxide and 16% sodium chloride together with small amounts of other impurities. For some captive uses, the cell liquor can be used without further treatment, but for most uses the high salt content and low caustic strength of the liquor cannot be tolerated. It is normal practice to evaporate the liquor in a triple effect evaporator to a sodium hydroxide concentration of 50%. During this concentration process most of the salt crystallizes and is removed in a separator. The salt concentration in 50% caustic soda produced in this manner is about 1% and, if necessary, can be reduced by further processing. The most commonly used purification method is liquid/liquid extraction of the caustic with anhydrous ammonia which reduces the salt content to as low as 0.05%.

Hydrogen from diaphragm cells is not contaminated with mercury and can be vented or used without further processing. The chlorine is processed in the same way as that from mercury cells.

It can be seen that the diaphragm cell has intrinsic disadvantages.

- Because brine flows from the anode compartment through the diaphragm into the cathode compartment, the caustic formed in the cathode compartment is weakened and contaminated with sodium chloride.
- The diaphragm in an operating cell deteriorates and must be replaced, necessitating cell shutdown.

3.4 The Membrane Cell Process

In membrane cells, an ion exchange membrane replaces the asbestos diaphragm. This membrane allows sodium ions to pass from the anode compartment to the cathode compartment, but is almost totally impervious to chloride and hydroxyl ions. Because chloride ions cannot pass from the anode compartment to the cathode compartment and there is no flow of liquid through the membrane,

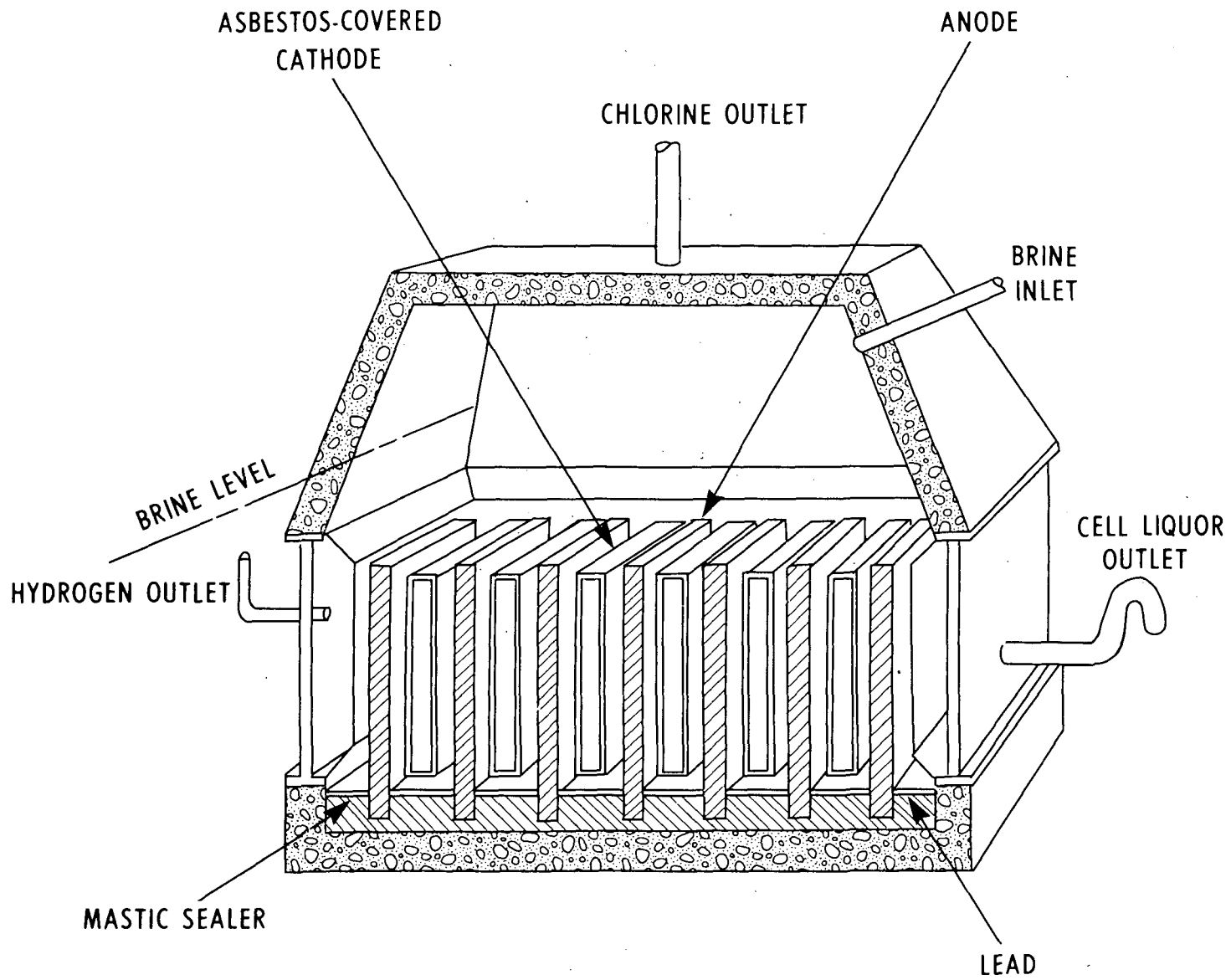


FIGURE 6 DIAPHRAGM CELL

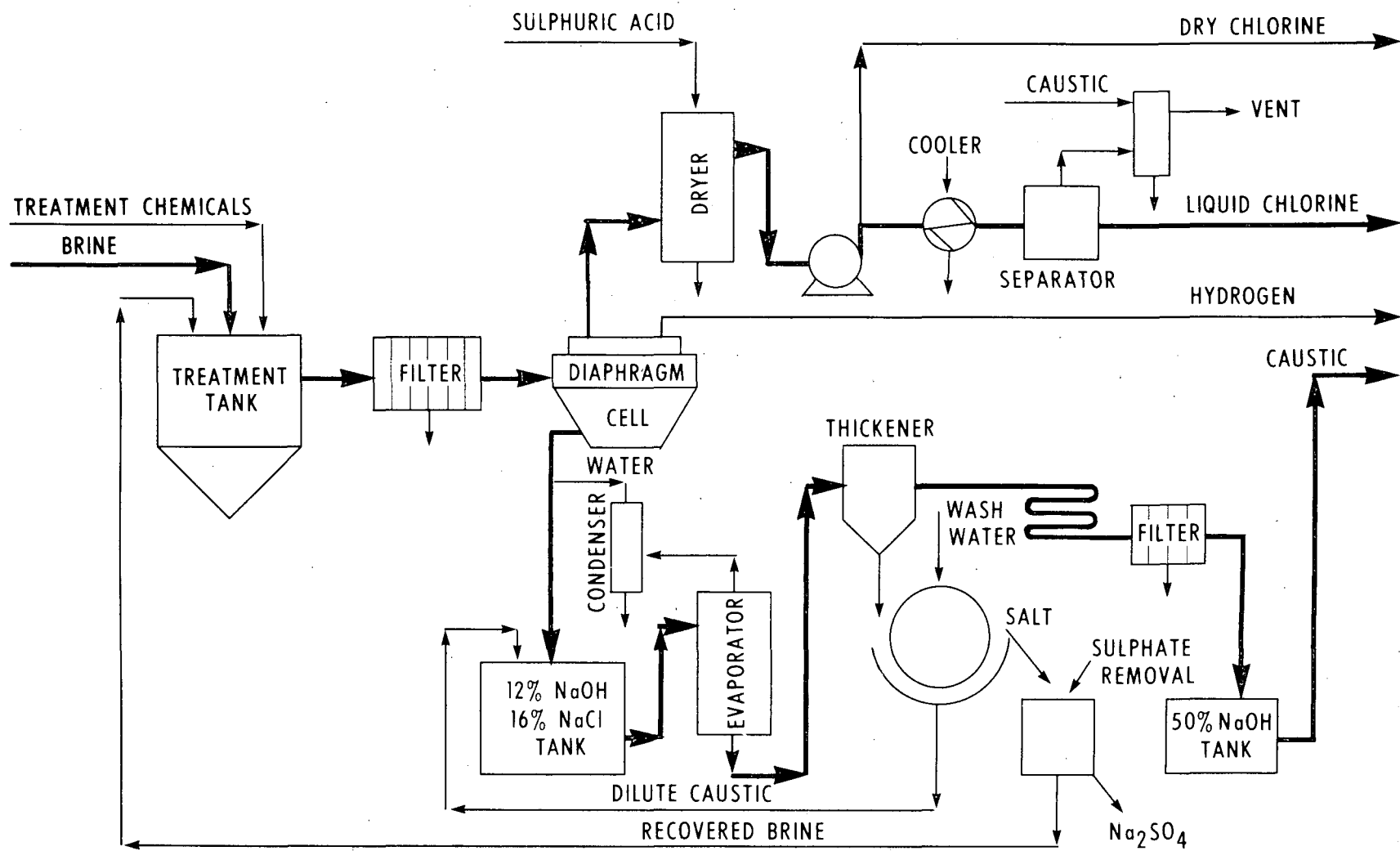


FIGURE 7 FLOW DIAGRAM, DIAPHRAGM CELL PROCESS

the caustic soda solution formed in the cathode compartment is largely salt free. The operating life of membranes has yet to be proved under commercial conditions, but is thought to be several years. Current evidence suggests that the membrane cell overcomes the major weaknesses of the diaphragm cell.

During the past few years DuPont has developed a family of perfluorinated ion exchange membranes which are now commercially available under the trademark "Nafion".* Some members of the Nafion family have the properties required for use in chlor-alkali cells. The membrane material has the excellent chemical inertness characteristic of its cousin polytetrafluoroethylene (PTFE). The properties of Nafion have been described by Grot, Munn and Walmsley of E.I. DuPont de Nemours and Company (7).

Membrane cells are now commercially available for plant capacities up to 300 tons of chlorine per day. Hooker, who market membrane cells, have in progress the engineering for a 250 ton per day membrane cell plant of their own (8) and have supplied membrane cells to Reed Paper, Limited to replace the mercury cells at their Dryden, Ontario plant. The Hooker (MX) membrane cells are currently capable of producing 12% sodium hydroxide containing very little sodium chloride. When evaporated to a concentration of 50% sodium hydroxide, the product has a salt content of about 0.2% and contains no chlorate. This purity is considered adequate for the manufacture of rayon.

Saturated brine flows to the anode compartment of the cell. Electrolysis of the brine depletes it by 10%-15% before it leaves the cell. The depleted brine is resaturated with solid salt and recycled to the cell. Water is fed into the cathode compartment at such a rate that the concentration of the effluent caustic soda solution is maintained at about 12% sodium hydroxide. Efforts to increase this concentration result in an increasing tendency for hydroxyl ions to diffuse through the membrane into the anode compartment. Although the cells now commercially available are limited to producing 12% caustic soda, it is probable that improved cell and membrane technology will achieve greater concentrations.

In construction and configuration, membrane cells are similar to diaphragm cells. Membranes, however, are in sheet form and must be supported in a manner different from asbestos diaphragms. Membrane cells utilize metal anodes and steel cathodes.

3.5 Process Comparison

3.5.1 Cell Design and Development. In comparing chlor-alkali processes, it is important to keep in mind that the industry is experiencing very rapid technology development. Comparisons that are now valid may not have been so several years ago and may no longer be so in future years.

In all types of cells, advantage has been taken of the development of construction materials, such as plastics and titanium, which can withstand the aggressive chemical environment of wet chlorine and chlorinated brine. The development of semiconductor rectifiers has improved the electrical efficiency of cell operation and has enabled larger capacity cells to be operated without increasing the cell room voltage to undesirable levels. All types of cells can benefit from the use of dimensionally stable metal anodes, which have recently been developed.

* Registered trade mark

Mercury cell technology has been developed to a high degree and has less potential for improvement than diaphragm and membrane cell technology. The environmental problems of operating mercury cells create a negative stimulus to their technological development. Until recently, the development of the diaphragm cell progressed very slowly. It is likely that the present rapid rate of development will continue and produce cells with higher efficiency and longer diaphragm life. The membrane cell has just been introduced to the commercial scene. It is reasonable to assume that technological development will lead to cells which produce stronger caustic and have better electrical efficiency.

3.5.2 Products. The hydrogen produced by all three cell types is greater than 99.8% pure. The only significant difference is that hydrogen from mercury cells contains a small amount of mercury.

Chlorine purity is best from the mercury cell. Chlorine gas from membrane and diaphragm cells contains 1%-2% oxygen which is largely absent from mercury cell chlorine. There is, however, little difference in the quality of the liquified chlorine, since any oxygen present emerges in the tail gas stream. The significant difference in product quality is in the caustic soda produced by the different cells. The mercury cell produces 50% caustic soda. The diaphragm cell produces weak caustic containing a massive salt impurity. The purity can be improved by liquid/liquid extraction with anhydrous ammonia. Membrane caustic soda is fairly weak and is less pure than mercury cell caustic; however, membrane caustic is of adequate purity for essentially all present requirements.

Table 4 summarizes the product quality of the three cell types. The 'future' column of the table presents the ultimate situation expected to result from the development of membrane cell technology.

3.5.3 Energy Requirements. The theoretical minimum voltage for the electrolysis of brine is 2.3 V. In practice the optimum voltage achieved is 4.4 V for mercury cells and 3.8 V for diaphragm cells. The major power losses are attributable to irreversible reactions occurring at the electrode surfaces and to the ohmic resistance of the electrolyte and current conductors (9); consequently, the power efficiency of an electrolysis plant is about 50%. To produce 50% caustic the diaphragm and membrane processes require additional energy in the form of steam for evaporation of the caustic solution. Table 5 presents a breakdown of the energy requirements for the various cell types. It will be noted that the electrical power consumption of the membrane and diaphragm processes is considerably less than that of the mercury cell process, but in terms of overall energy required to produce 50% caustic, the mercury cell process has the lowest energy demand.

3.5.4 Raw Materials. The cheapest form of sodium chloride is brine obtained by solution mining or from natural sources. The diaphragm cell process most readily accepts brine as the raw material. In both the mercury and membrane cell processes, depleted brine from the cells is recirculated and reconcentrated by the addition of solid salt, a prerequisite for these two processes. When brine is used as the feedstock for the mercury cell process, the spent brine is reconcentrated by recycling through the salt cavern. Diaphragm cell plants are normally located at a brine source, such as a brine well. The location of mercury cell plants is generally determined by product use or market, since solid salt can be

TABLE 4 COMPARISON OF PRODUCT QUALITY (9)

	Technology						Composition		
	Mercury 1974	Diaphragm		Membrane		1974			Future
		Without caustic purification	With caustic purification	1974	Future				
Caustic from cell	50	12	—	12	20	NaOH	% W		
	0.01	16	—	0.07	0.01	NaCl	% W		
Caustic after concentration to 50%	50	50	50	50	50	NaOH	% W		
	30	10 000	1 000	3 000	500	NaCl	ppm		
	200	1 200	1 200	1 200	1 200	Na ₂ CO ₃	ppm		
	1	800	5	800	800	NaClO ₃	ppm		
	10	100	100	100	100	Na ₂ SO ₄	ppm		
	0.1	—	—	—	—	Hg	ppm W		
Hydrogen gas	99.9	98.9-99.9		99.8-99.9			% V		
	0.01	—		—		Hg	ppm		
Chlorine gas dry basis	99-99.4	97-97.5		97-97.5		Cl ₂	% V		
	0.1	1-2		1-2		O ₂	% V		
	0.1-0.4	0.1-0.4		0.1-0.4		H ₂	% V		
	0.2-0.5	0.2		0.2		CO ₂	% V		
	0.2	0.2		0.2		N ₂	% V		

TABLE 5 ENERGY CONSUMPTION PER TON OF CHLORINE PRODUCED

Cell parameters	Unit	Cell type				
		Mercury		Diaphragm		Membrane
		1974	1974	Future	1974	Future
Optimum cell voltage	V	4.4	3.8	3.5	4.1	3.8
Current efficiency	%	96	96	96	95	96
Power consumption (dc)	kWh	3450	3000	2750	3250	3000
Steam consumption	kWh	-	2100	1750	2800	1100
Total energy	kWh	3450	5100	4500	6050	4100

shipped to any location. With regard to feed, the diaphragm cell process is the most flexible, because it will accept salt feed in solution, or in solid form.

3.5.5 Production Costs. The costs of producing chlorine and caustic soda can be grouped into four major areas; raw materials, energy and services, maintenance, and amortization of the capital investment. The unit cost of electrical power, steam, and raw materials varies considerably, depending on such factors as location and plant capacity. It is therefore difficult to reliably compare the costs of producing chlorine from the different types of cell; however, a paper presented to the Chlorine Bicentennial Symposium (9), analyzed production costs for a plant producing 500 tons chlorine/day. The data are presented in Table 6. The 1974 data demonstrate how the cost advantage can shift from one process to another. For example, 50% regular grade diaphragm cell caustic can be produced at a lower cost than mercury cell caustic; however, if caustic with a very low salt content is required, 50% mercury cell caustic is less expensive.

It can be seen that, in general, the cost of producing chlorine by the three processes is similar; although, under various circumstances, any one of the processes might be the most economic. Production costs are sufficiently close that the choice of process is often determined by other factors.

4 ATMOSPHERIC EMISSIONS

Most emissions are common to both the mercury cell and the diaphragm cell. These include chlorine, hydrogen, carbon dioxide and carbon monoxide. Few problems are associated with controlling emissions of chlorine, carbon dioxide and carbon monoxide. The dangerous properties of chlorine are well

TABLE 6 PRODUCTION COSTS (\$ Per ton of chlorine produced, based on 500 ton/day plant)

Process parameters	Process						
	Mercury	Diaphragm (brine) without caustic purification		Diaphragm (brine) with caustic purification		Membrane 10 % Caustic 20% Caustic	
		1974	1974	Future	1974	Future	1974
Raw materials							
Salt	24	14	14	14	14	24	24
Chemicals	5	3	2	5	5	3	3
Subtotal	29	17	16	19	19	27	27
Energy electrical & services	45	37	34	37	34	38	37
Steam	-	12	10	16	14	16	6
Water	2	3	3	3	3	3	2
Subtotal	47	52	47	56	51	57	45
Maintenance	8	8	7	9	9	8	7
Capital cost	32	32	32	37	37	33	30
TOTAL COST	116	109	102	121	116	125	109

Unit costs assumed:

Electrical Power @ 1.2¢ per kWh
 Steam @ \$4.00 per ton
 Brine @ \$8.00 per ton NaCl
 Salt @ \$14.00 per ton NaCl

recognized and precautions are taken to prevent the buildup of harmful concentrations. Carbon dioxide and carbon monoxide are present in such low quantities that their disposal does not constitute a pollution problem. Hydrogen from diaphragm cells can be vented without treatment. On the other hand hydrogen from mercury cells is saturated with mercury which must be removed before the hydrogen is vented.

Mercury emissions are peculiar to the mercury cell process, and are the major air pollution problem in the chlor-alkali industry. Atmospheric emission sources include the hydrogen stream, the end-box ventilation stream, the cell room and the tank vents. It is possible to remove mercury from most streams; however, because of the large volume involved, the cell room ventilation is not amenable to treatment. Emissions from this source can only be controlled by following procedures to prevent mercury from discharging into the cell room atmosphere.

Only the diaphragm process uses asbestos. It is used to form the cell diaphragm and is a potential health hazard. This hazard is recognized and working conditions are regulated to protect workers' health. Atmospheric emissions can be minimized by treating asbestos-contaminated streams before venting to the atmosphere.

5 MERCURY EMISSION SOURCES

5.1 Emission Sources and Magnitude

5.1.1 General. In the mercury cell process, the mercury acts as the cathode and as a medium to transport sodium from the electrolyzer to the denuder. Because no mercury is consumed, there should be no depletion of the initial cell inventory. In practice, however, mercury is lost from the system by the following routes.

- As an impurity in the products.
- In atmospheric emissions.
- In liquid effluents.
- In solid wastes.

Permeation into the fabric of the buildings and theft have also been suggested as means by which mercury might be lost from the process.

Lost mercury is replaced by adding fresh mercury to the cells from time to time. The total mercury lost by the various routes should equal the quantity of mercury added to the cells to maintain a uniform mercury inventory.

In 1973 Canadian producers and Environment Canada cooperated in an attempt to compare measured mercury losses with the amount of mercury consumed by the plants. The results of this comparison, for the twelve-month period ending August 1974, were presented at a seminar on the Chemical Industry and the Environment (10) and are summarized in Figure 8. Of the 104 000 lb mercury consumed in the one-year period, more than half could not be accounted for. Current reports from the

industry indicate that this poor accountability has not improved. The magnitude of the unaccounted losses must be considered when assessing the reliability of reported losses to the atmosphere.

The cell room ventilation air, the end-box vent and the hydrogen vent are believed to be the principal sources of atmospheric mercury emissions. In the survey completed by Environment Canada in September 1974, the cell room ventilation was reported to be the largest emission source, accounting for 5600 lb mercury/yr. Emissions from the hydrogen vent and end-box vent were 1270 lb/yr and 735 lb/yr respectively. Miscellaneous emission sources were responsible for reported losses of 800 lb/yr. The total reported discharge to the atmosphere of 8400 lb mercury/yr is an apparent improvement on that of 12050 lb/yr reported in 1973 (Fig. 8).

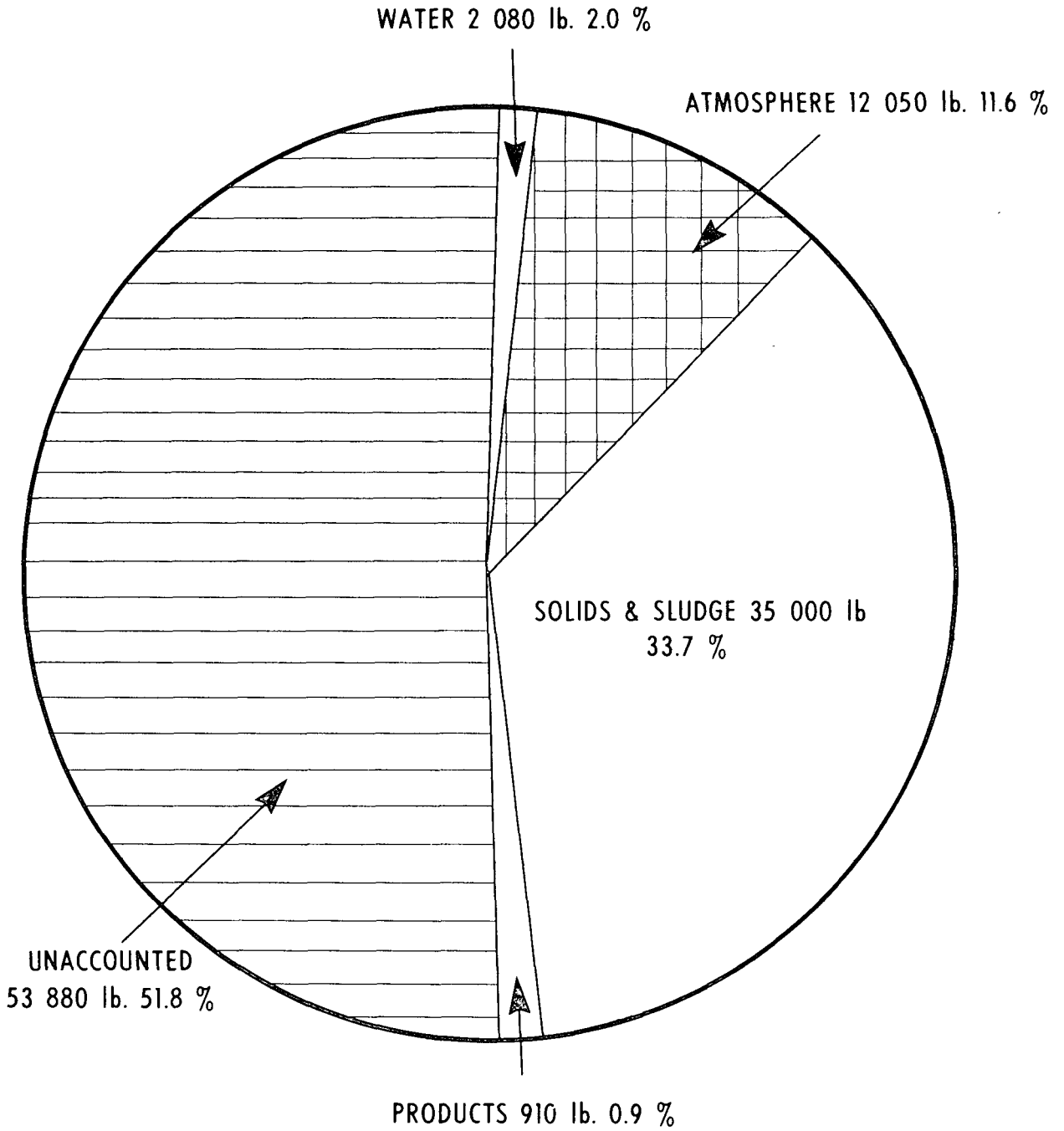
Surveys of the ambient air quality at four mercury cell plants, have been carried out by Environment Canada (11). Samples of 10-minute duration were taken along boundaries downwind from the plant. The average mercury concentrations detected ranged from $0.25 \mu\text{g}/\text{m}^3$ - $2.5 \mu\text{g}/\text{m}^3$. The highest single sample was $10.8 \mu\text{g}/\text{m}^3$. Normal background levels are less than $.01 \mu\text{g}/\text{m}^3$. Because emissions occur at low elevations close to the roof level of the cell room buildings, a reliable computation of emission rates cannot be made from these ambient concentration measurements. The surveys clearly demonstrate that mercury is emitted from the chlor-alkali plants in sufficient quantity to create ambient concentrations at the plant boundaries which are high enough to cause concern for public health.

5.1.2 Cell Room Emissions. In all but one of the Canadian chlor-alkali plants, the electrolytic cells are located in a building commonly referred to as the cell room, which is ventilated both to keep mercury concentrations below the threshold limit value of $50 \mu\text{g}/\text{m}^3$ and to keep the cell room temperature at a tolerable level. The amount of air required for ventilation varies seasonally with geographic location, cell design and the age of the plant. The ventilation air expelled from the cell room is the source of the greatest atmospheric mercury emission, responsible for a reported discharge of 5600 lb annually.

Mercury enters the cell room atmosphere as a result of a number of operations or conditions such as.

- end-box sampling procedures;
- removal of mercury sludges from end-boxes,
- cell and mercury pump leaks;
- hot hydrogen leaks;
- cell maintenance and rebuilding operations;
- other maintenance work which exposes the internal surfaces of pipes and equipment;
- accidental mercury spills;
- cell failure and other unusual circumstances.

Treatment of the ventilated air is difficult because the volumetric flow rate is very large. There appears to be no commercially available technology to remove mercury from the air ventilated from a cell room. Careful plant operation and good housekeeping are necessary to minimize emissions



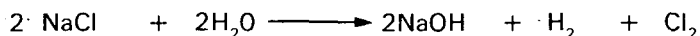
TOTAL Hg CONSUMED 104 000 lb.
CHLORINE PRODUCED 425 000 tons

12-MONTH PERIOD ENDING JULY/AUG. 1973

FIGURE 8 REPORTED MERCURY LOSSES FROM CHLOR-ALKALI PLANTS

5.1.3 Hydrogen. The hydrogen by-product stream originates at the denuder or decomposer where the sodium-mercury amalgam produced in the electrolyzer is decomposed by water to form caustic soda solution and hydrogen.

For each mole of chlorine produced there is one mole of hydrogen generated:



At 0°C this represents 286 m³ hydrogen/ton chlorine.

The hydrogen leaving the denuder is saturated with mercury at about 100°C. If this stream were vented without treatment, atmospheric emissions would amount to at least 140 lb mercury/100 tons of chlorine produced. It is potentially the largest single emission source; however, all Canadian plants treat the hydrogen and emissions are much less than this potential maximum.

5.1.4 End-box. Typically a cell has a weak end-box at the point where the mercury enters and a strong end-box at the point where the amalgam leaves. Most cells are designed so that suction is applied to these boxes; only three out of eleven plants are not designed to operate in this manner. The end-box ventilation stream, as the name suggests, originates at this source.

The function of the end-box is best illustrated if the circuit of the mercury is traced from the exit to the entrance of the cell. Mercury leaves the cell as sodium-mercury amalgam. It first enters the brine or dirt box where the brine is separated from the mercury. Here, about once a shift, any dirt such as carbon or mercury sludge, which floats on the mercury surface, is removed with a screen ladle, hence the name dirt box. The amalgam next enters what is commonly referred to as the strong end-box which serves both as a sample and inspection port, and as a seal to prevent hydrogen from leaking from the denuder. Suction is applied to remove any hydrogen which may have escaped into the box, thereby diluting it to below the explosive limit.

After passing through the denuder the mercury enters the weak amalgam end-box which serves as an inspection port and which may, depending on the design of the cell, also act as a place for insertion of graphite denuder grids and as a grid shaker port. Here again suction is applied to remove any hydrogen which may have escaped into the box.

This end-box ventilation stream joins the strong end-box stream and the combined stream is subsequently treated.

5.2 Miscellaneous Mercury Emission Sources

5.2.1 Caustic Receiving Tank Vent. Usually caustic is transferred from the denuder to a caustic receiving tank. Mercury is lost to the atmosphere by evaporation of dispersed mercury from the caustic surface. One plant estimates emissions from this source to be 0.6 lb/day/100 tons of chlorine.

5.2.2 Mercury Retort Vent. Mercury recovered from the process may be purified by distillation on site and recycled to the cells. The rate of mercury loss will depend on the design and operating

conditions of the retort. No information is available on the degree of mercury emissions from this source.

5.2.3 Weak Brine Air Blowing. Chlorine is stripped from the weak brine by passing the brine down a packed tower through which air is drawn counter-current. After leaving the tower, the stripping air is scrubbed with caustic soda, to remove chlorine before venting. In the course of this procedure the stripping air could pick up mercury from the brine and convey it to the atmosphere.

5.2.4 Fugitive Sources.

5.2.4.1 Locker Room. Workmen, in their daily routine, come into contact with mercury. Some ends up in the locker room on shoes and clothing and, through evaporation, becomes a source of mercury emissions.

5.2.4.2 Caustic Soda Filtration. Caustic is filtered to remove suspended mercury. The filter precoat and equipment become contaminated with mercury. In the course of operating and cleaning the filter, mercury-contaminated materials are exposed and give rise to atmospheric emissions.

6 CONTROL METHODS

6.1 Cell Room Emissions

It is impractical to remove mercury from cell room ventilation air, because of the large volume of air involved (60 000 cfm-750 000 cfm). Mercury emissions from this source can be controlled only by preventing mercury vapour from entering the cell room atmosphere.

The vapour pressure of mercury at ambient temperatures is sufficiently high that exposure of a mercury surface will result in contamination of the ambient air. This effect is accentuated by the tendency of mercury to form globules which, when mercury is spilled, result in a small quantity of mercury presenting a very high surface area for evaporation. Similarly there will be contamination of the atmosphere if mercury-contaminated equipment or waste materials are not stored in sealed containers until decontaminated or impounded. To minimize contamination of the cell room atmosphere rigorous cleaning and housekeeping procedures must be observed.

Hydrogen diffuses readily through small apertures; consequently, a faulty gasket or loose joint on a pipe or vessel containing hydrogen may result in a large volume of gas leaking to the atmosphere. Because hydrogen from the cells is mercury saturated, any hydrogen leaking to the atmosphere conveys mercury with it. To control mercury emission associated with hydrogen leaks, the hydrogen system should be checked frequently and any leaks immediately corrected.

The U.S. Environmental Protection Agency has formulated a list of procedures to minimize emissions from the cell rooms of chlor-alkali plants. This list is given in the Appendix. In their National Emission Standards for Mercury, the U.S. Environmental Protection Agency assumes that an emission rate of 1300 g/day will occur from the cell room of plants in which their recommended procedures are followed. This figure is based on a hypothetical plant capacity of 500 tons chlorine/day.

In February 1975, Environment Canada participated in discussions with a team of experts from the Japanese chlor-alkali industry who presented emission data for a particular Japanese plant. The mercury emission from the cell room of this plant was given as 0.357 g/ton caustic soda. This corresponds to a rate of about 200 g/day for a plant producing 500 tons chlorine/day.

In late 1975, emission tests were carried out at two Canadian mercury cell chlor-alkali plants. The average mercury emissions from the cell room were found to be about 320 g and 3800 g/100 tons of chlorine produced.

6.2 Hydrogen and End-Box Streams

6.2.1 General. The hydrogen and end-box streams are similar in that both are contained gases contaminated with mercury. Hydrogen leaves the denuder at about 100°C saturated with mercury vapour at a concentration of 2300 mg/m³. End-box streams, which are primarily air are not saturated and therefore carry less mercury. These streams must be treated separately due to the possibility of an explosion if treated together. They are both amenable to the same mercury emission control technology.

6.2.2 Condensation. The hydrogen leaving the electrolyzer is saturated with water vapour and mercury vapour. If the hydrogen is cooled mercury will condense reducing the concentration of mercury in the gas. Figure 9 shows the equilibrium mercury concentration in air as a function of temperature. Mercury removal by condensation is widely practiced to reduce the mercury content of both the hydrogen and end-box vent streams. The most common cooling device is the shell and tube heat exchanger. Plant service water is used to cool the gas to a temperature typically in the range of 27°C-49°C. Additional cooling with brine can reduce the gas temperature to about 3°C, at which time the surface of the heat exchanger is approaching 0°C, the temperature at which the system will malfunction due to icing of the tubes.

A second method of mercury removal by condensation employs direct contact coolers. Two classes of cooling media are used: water and aqueous solutions such as brine. When water is used, cooling is limited to about 3°C, but much lower gas temperatures are attainable with brines. In a typical brine system brine is cooled with a refrigerant in a shell and tube heat exchanger to -12°C. The chilled brine is passed through a packed tower counter-current to the hydrogen or end-box. The gas temperature is reduced to -11°C and the mercury content to the equilibrium value, 0.6 mg/m³. For a plant producing 100 tons chlorine/day, an emission rate as low as 14 lb/yr can be achieved. The brine, saturated with mercury, is fed to the cells.

6.2.3 Mist Elimination. In an indirect cooling system mercury condenses from the gas as small droplets. Some of the droplets coalesce and can be removed by passing the gas through a knockout pot, but some of the condensed mercury remains in the gas stream as a fine mist. This mist can be removed by a mist eliminator. Commercial mist eliminators remove entrained droplets by passing the gas stream through fibre pads, or through converging-diverging nozzles.

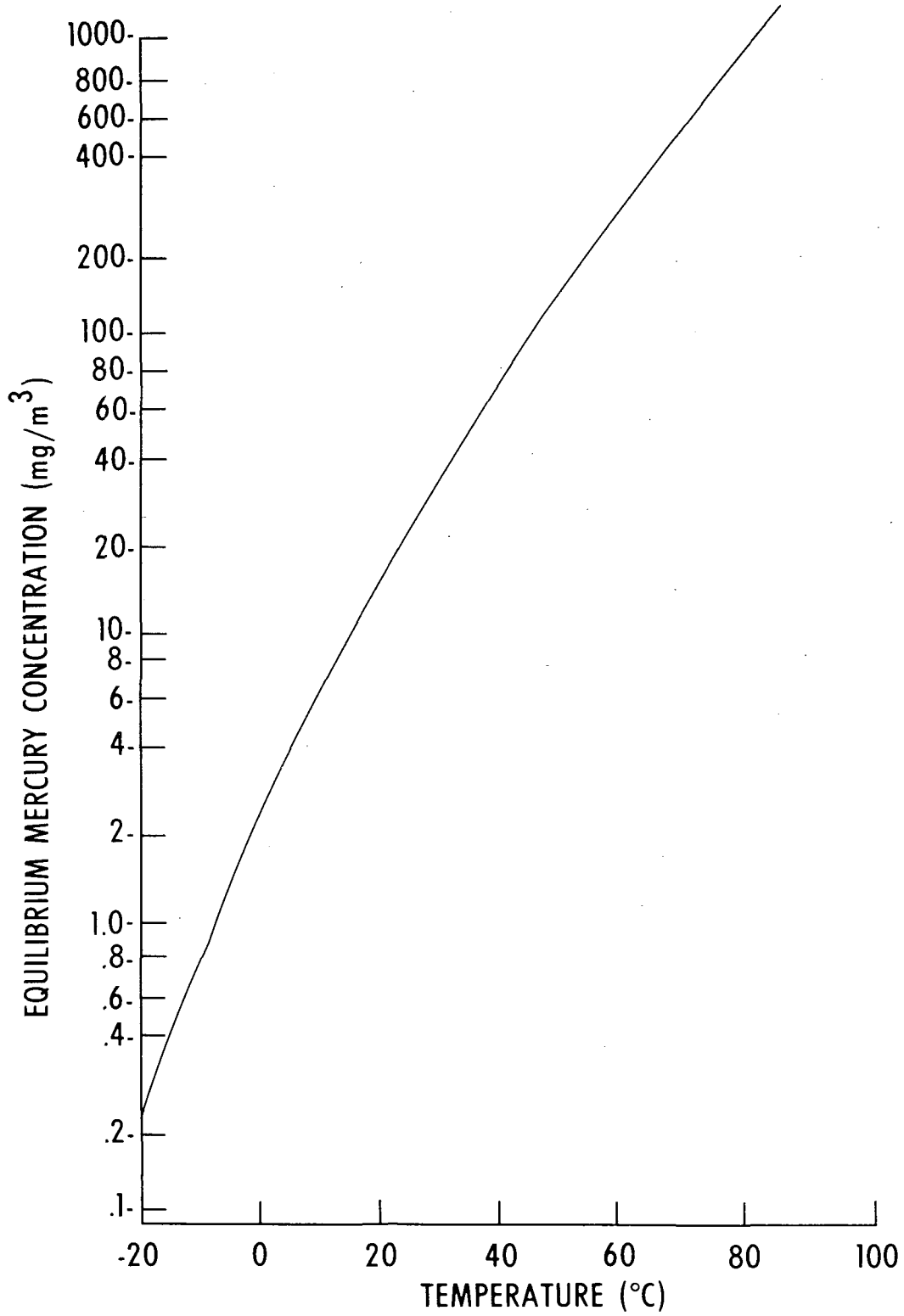


FIGURE 9 EQUILIBRIUM MERCURY CONCENTRATION AS A FUNCTION OF TEMPERATURE

The efficiency of the mist eliminator has a dramatic effect upon the final mercury content of the gas. Figure 9 shows that at 38°C, saturated gas contains about 53 mg/m³ mercury. If this gas is cooled to 4.5°C the equilibrium concentration will fall to about 3 mg/m³, and about 50 mg/m³ of mercury will condense from the gas.

Table 7 shows the calculated final mercury content of the gas after demisting for a range of mist eliminator efficiencies.

When direct contact cooling is used to condense mercury there is generally less need for mist elimination from the hydrogen or end-box streams. In a packed tower, the mercury droplets impinge upon the packing and are carried away in the liquid coolant.

TABLE 7 MERCURY CONTENT OF GAS AFTER DEMISTING

Mist eliminator efficiency (%)	Mercury content after demisting (mg/m ³)
100	3
80	13
50	28
0	53

6.2.4 *Adsorption With Activated Carbon.* Adsorption systems which utilize activated carbon to remove mercury from gases are commercially available. The carbon is usually impregnated with either sulphur or iodine to make it specifically active toward mercury vapour. Mercury removal to concentrations as low as .01 mg/m³ or 1 ppb by volume can be achieved (12). One Canadian plant reports a mercury concentration of .01 mg/m³ from such a system. A typical system has a fixed bed of activated carbon 3 ft-5 ft deep and operates with a gas velocity through the bed of about 20 fpm (12). The effectiveness of the carbon is severely reduced by condensation of water in the bed. To prevent condensation, the gas streams, which are water saturated, are first heated to a few degrees above their dew point.

Under favourable conditions, the activated carbon will adsorb more than 20% of its weight in mercury (12). When the carbon bed has reached its practical working capacity, the mercury concentration of the gas leaving the bed will increase rapidly. At this stage, the spent carbon bed is dumped and replaced with a charge of new activated carbon. Mercury can be recovered from the spent carbon by retorting but the carbon cannot be reused for adsorption. To achieve reasonable operating

cycles and to optimize operating costs, activated carbon systems are used only after most of the mercury has been removed from the gas stream by cooling and demisting.

6.2.5 Adsorption with Molecular Sieve. Molecular sieve adsorbents have been widely used in the chemical industry for several years, but have only recently been used for the containment of air pollutants. Molecular sieves are crystalline zeolites which have the basic formula $M_2/nO \cdot Al_2O_3 \cdot x SiO_2 \cdot yH_2O$, where M is a cation of n valence, x is an integer usually greater than 2, and y an integer which can vary greatly. The crystal structure of zeolites is typically honeycombed with cavities connected to each other by pores of uniform size. These pores act like sieves with respect to gas molecules, allowing only molecules smaller than the pore diameter to diffuse into the crystal.

An adsorption system using a molecular sieve has been developed to remove mercury from the hydrogen and end-box streams of chlor-alkali plants. The system called the Purasiv-Hg* molecular sieve was developed by Union Carbide. No Canadian plants use the molecular sieve system, but it has been adopted by several plants in the United States. A unit went on stream at the Sobin chlor-alkali plant in August 1972 (13), and has since performed extremely well. The effluent hydrogen has been reported to contain less than $2 \mu\text{g}/\text{m}^3$ mercury (14), which is equivalent to .0001 lb/100 tons chlorine produced at the Sobin plant. An evaluation of this unit's performance in September 1974, indicated that there is no apparent deterioration of the adsorbent. The adsorbent manufacturers now expect that the life of the adsorbent will be in excess of 5 years (5).

A flow diagram of a typical molecular sieve system is shown in Figure 10. The hydrogen stream has been used in this example but the arrangement for the end-box stream is similar. Hydrogen from the primary cooler, typically at 38°C , is compressed to about 2-3 psig and, after passage through a knockout pot, is cooled with chilled brine. The gas from the cooler passes through a mist eliminator and enters the bottom of an adsorption tower. Two adsorption towers are used. As one becomes saturated with mercury, a second fresh tower can be brought on line to replace it. The saturated adsorbent is regenerated by heating a portion of the mercury-free effluent gas and passing it downwards through the bed of spent adsorbent. The hot gas strips the mercury from the adsorbent and cold gas is passed through the bed to cool it to operating temperature (16). The design of these units usually provides for the beds to alternate duty every 24 h. A typical cycle for an adsorbent bed would be 24 h adsorbing, 9 h regenerating with hot gas and 15 h cooling. This cycle is automatically controlled by a cycle timer. The units may be supplied skid mounted and can be connected with little plant-down time.

6.2.6 Chemical Scrubbing. No chemical scrubbing systems are currently used in Canada; however, systems are in use in the United States.

A system, recently developed in the United States, used an equimolar solution of sodium chloride and sodium hypochlorite. For optimum mercury removal the scrubbing medium required close pH control which was difficult to maintain. For this reason the system was converted to use depleted brine in the scrubber (17).

A second system is reportedly available which solves the problem of pH control. This system employs a dilute solution of sodium hypochlorite with a large molar excess of sodium chloride. It has been

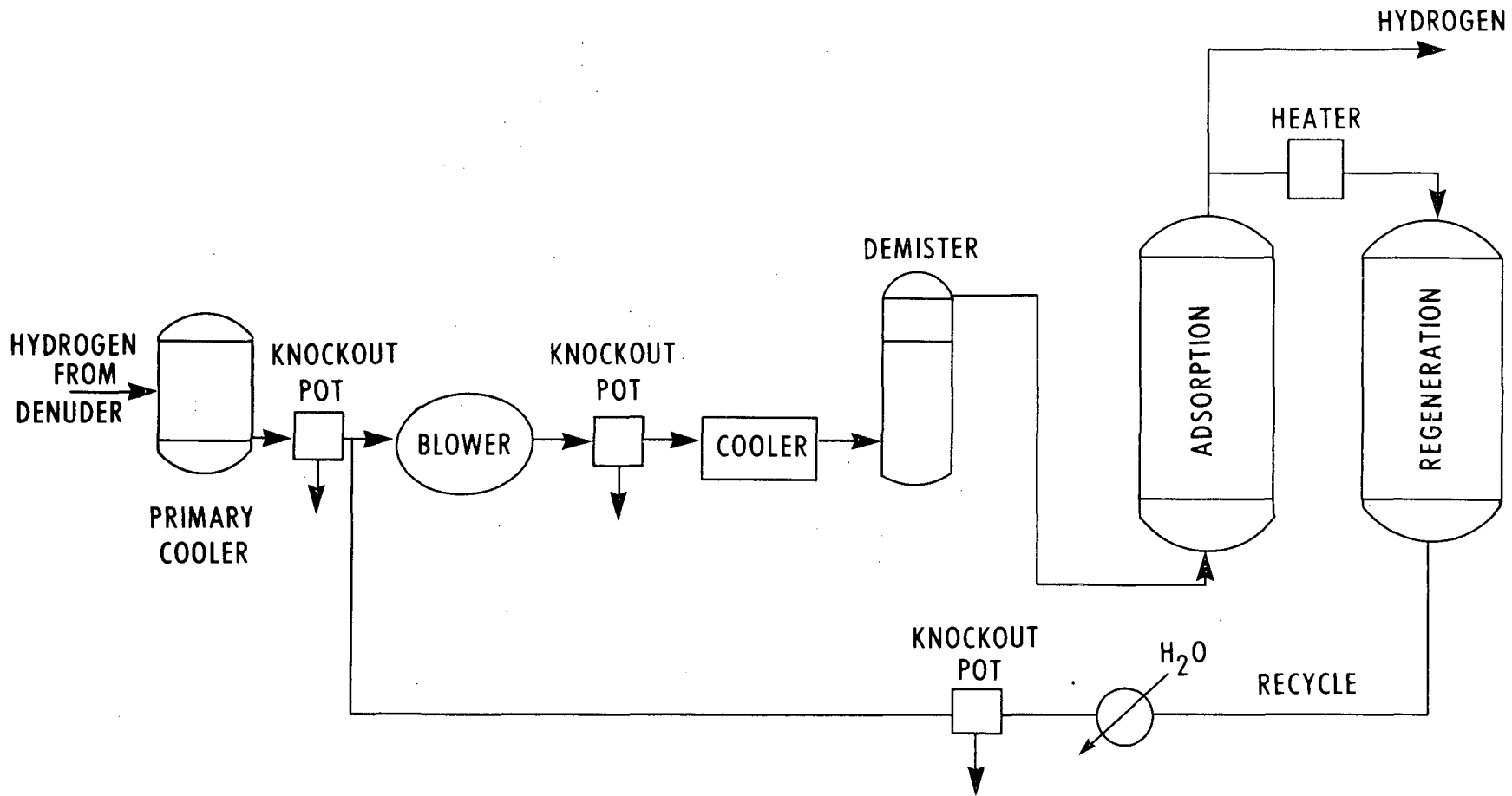
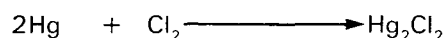


FIGURE 10 PURASIV SYSTEM

tried twice in the United States and a collection efficiency of 95%-99% has been reported. It is estimated that mercury emissions for the combined hydrogen and end-box streams from this system would range from 0.2 lb - 0.8 lb/day for a 100 ton/day plant.

6.2.7 Calomel. The Calomel process, developed by Akzo Zout Chemie Nederland B.V., is based upon the reaction of mercury in the hydrogen or end-box streams with a slight excess of chlorine to produce mercurous chloride or calomel according to the reaction:



The calomel is deposited on the inert packing of a reactor. Generally, the pressure drop across the reactor is less than 1 in. water column. The gas leaving the reactor is saturated with calomel which has a volatility about 1/200 that of mercury. The system has a long operating cycle and needs cleaning only once or twice per year. To recover the mercury, the reactor contents can be retorted, or leached with chlorinated brine which may then be returned to the cell brine circuit.

It is claimed that the small excess of chlorine which remains in the gas stream is tolerable if the gas is to be vented. If it is necessary to produce chlorine-free hydrogen, the chlorine can be removed by passing the hydrogen through an adsorber. A flow diagram of the Akzo calomel process is shown in Figure 11. The suppliers claim that the system is capable of reducing the mercury concentration of the treated stream to less than 60 ppb by volume (about $540 \mu\text{g}/\text{m}^3$) (18) or about .03 lb/100 tons chlorine produced. This concentration is determined by the equilibrium concentration of calomel in the gas at the temperature at which the gas leaves the reactor. The equilibrium concentration is shown as a function of temperature in Figure 12 which is based on the data of Akzo Zout Chemie.

Akzo report that they have four mercury cell plants operating with the calomel process. The first full size calomel unit has been operating since September 1971.

6.3 Mercury Control by Process Change

There is no control technology available to eliminate atmospheric mercury emissions from mercury cell chlor-alkali plants. Mercury emissions can be eliminated, however, if mercury cell plants are converted to, or replaced by a process that does not use mercury, i.e. the diaphragm cell process, or the membrane cell process. The conversion or replacement of mercury cell plants is expensive, but two Canadian producers have chosen this option. Dow Chemical Canada, Limited has closed down all its mercury cell plants and replaced them with a single diaphragm cell plant. Reed Paper Limited, is currently converting its mercury cell plant to the membrane process. Both companies have indicated that the changes were made to eliminate mercury pollution from their plants.

The membrane process seems to be the more attractive option for process conversion, since use can be made of both the rectifier and the brine system from the mercury cell process. In converting from the mercury to the diaphragm process the brine system must be changed, but the same rectifier may be used.

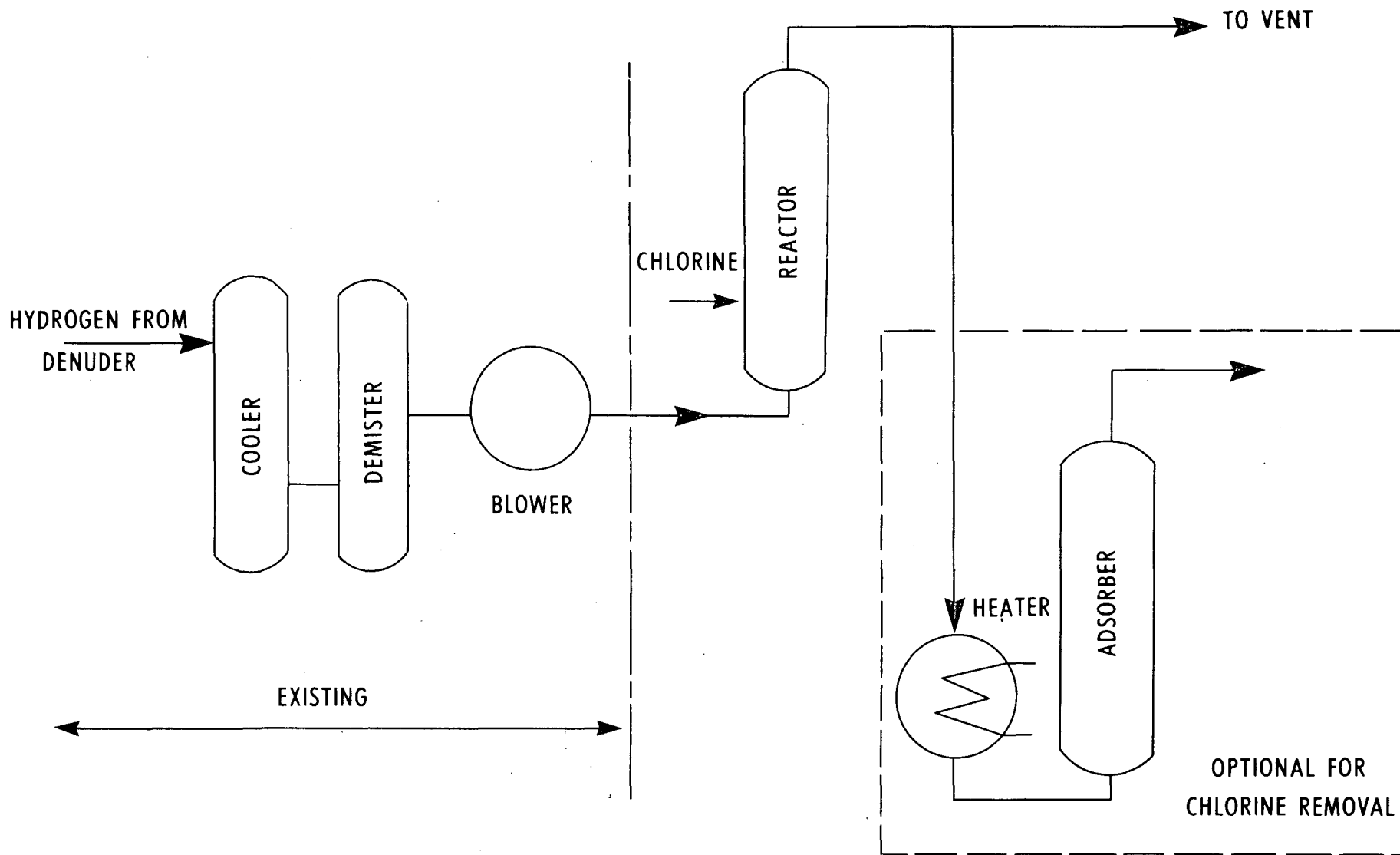


FIGURE 11 CALOMEL PROCESS

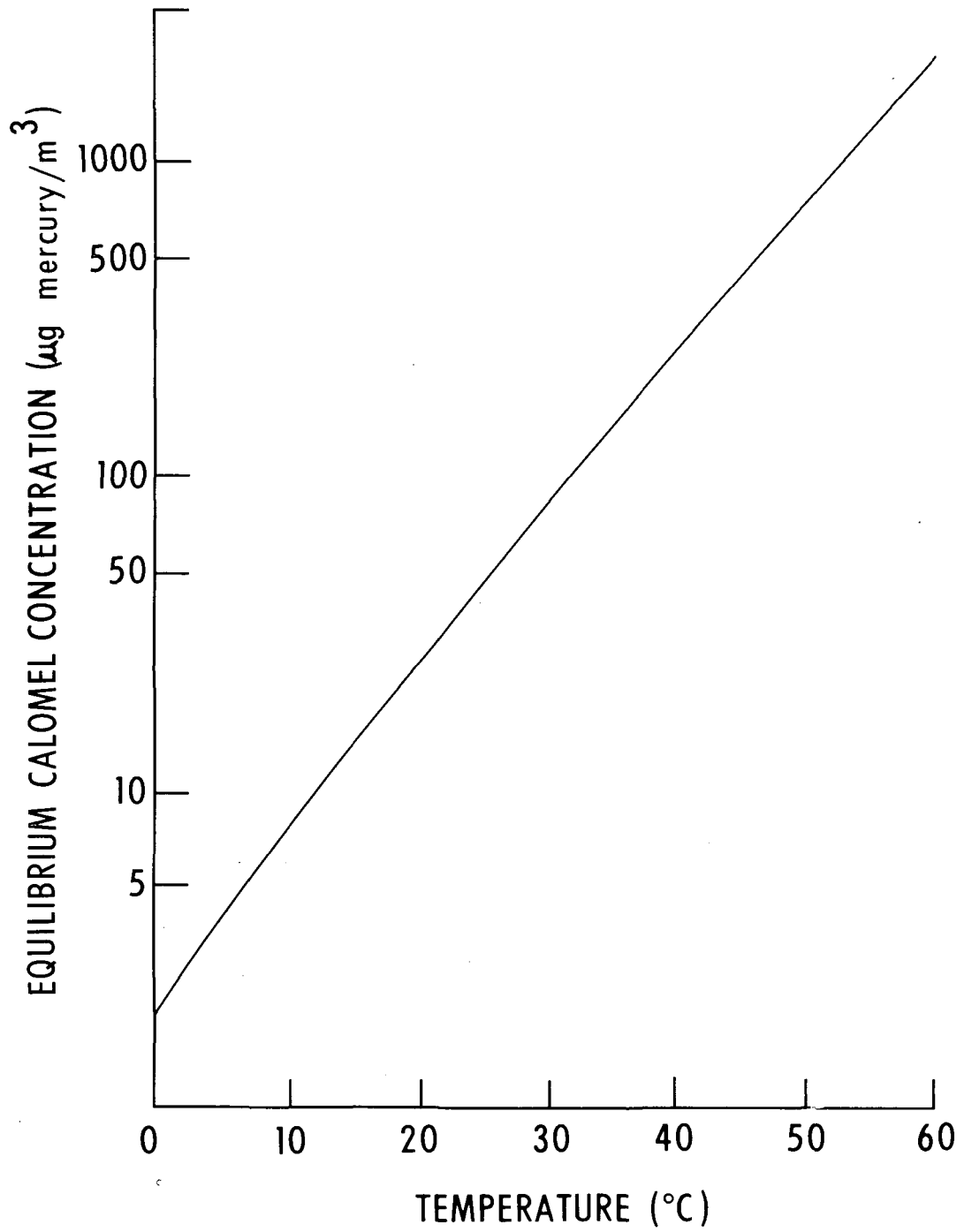


FIGURE 12 EQUILIBRIUM CONCENTRATION OF CALOMEL

6.4 Review of Mercury Control Technology

Process replacement is the only way in which mercury emissions can be eliminated. The absence of available demonstrated techniques to remove mercury from cell room air, results in the inevitable emission of mercury when mercury cells are operated. Techniques to remove mercury from the hydrogen and end-box streams have been described. A review of these techniques follows.

Both adsorption techniques reviewed are very effective for the treatment of the end-box and hydrogen streams. The carbon adsorbent must be removed from the process when it becomes mercury saturated and the mercury removed by retorting. Handling and retorting the carbon creates a potential for air pollution, but this can be kept to low levels. Since it is not possible to completely remove mercury from the carbon by retorting, the disposal of the solid residue presents the possibility of further pollution. The molecular sieve system has no secondary pollution problems, since the adsorbent is cyclically regenerated and the recovered mercury recycled.

The level of mercury removal by condensation is limited to the equilibrium concentration of mercury at the temperature of the cooled gas. The gas streams emitted are saturated with mercury. When atmospheric temperature is below the gas temperature, some mercury vapour may be condensed from the gas as it is emitted. Mercury droplets formed by this condensation may fall to the ground. Studies of the snow cover around five Swedish chlor-alkali plants indicated that there was in fact mercury fallout from the plants (19). If particulate fallout is to be avoided it is necessary to remove mercury to levels below those obtained by condensation techniques.

The calomel process is somewhat similar to the condensation techniques. The effluent gases are saturated with mercurous chloride and particles of solid mercurous chloride could form if the gas were discharged into very cold air. Because of the low volatility of calomel the mercury fallout from the calomel process would likely be less than with condensation systems. Further, the mercury would be deposited as mercurous chloride, which is of low toxicity (20). It is not known if mercurous chloride would be assimilated into the food chain.

From a pollution aspect the replacement or conversion of mercury cell plants is the most effective control measure. The molecular sieve system is the best available mercury containment system.

6.5 Cost of Pollution Control

The cost of air pollution control for Canadian mercury cell plants is difficult to estimate with precision. Costs will be influenced, in each particular case, by such factors as layout of existing equipment, climatic considerations, plant capacity and design of associated equipment. No attempt has been made to develop accurate hypothetical costs. Instead, a summary of approximate costs is presented, based upon information from equipment manufacturers, chlor-alkali plant operators and published material. In some cases different sources produced conflicting costs. In these cases the judgement of the authors has generally been biased towards the higher cost. Costs have been adjusted to a June 1974 cost base.

The capital and operating costs of the different control methods are presented in Table 8 together with mercury emission rates typical of the methods listed. In preparing this table, it has been assumed that the plants are equipped with primary water-cooled systems for both the hydrogen and end-box streams.

TABLE 8 COSTS OF CONTROLLING HYDROGEN AND END-BOX STREAMS IN A TYPICAL MERCURY CELL PLANT, (100 TONS CHLORINE/DAY)

Control method	Capital cost (\$x1000)	Annual operating cost (\$x1000)	Typical emission rate lb/day mercury
Conversion to membrane or diaphragm cell process	10 000	nil	nil
Secondary cooling with mist elimination	167	66	0.6
Cooling and mist elimination followed by activated carbon	252	91	<0.04
Cooling and mist elimination followed by molecular sieve	330	115	<0.04
Chemical scrubbing (hypochlorite)	248	75	0.5
Calomel	67	nil	0.1

NOTE: The above costs do not include the cost of a primary cooler.

The cost of converting all present Canadian mercury cell plants to either diaphragm or membrane cell operation is estimated to be about \$100 million.

The cost to the Canadian industry to reduce the combined hydrogen and end-box emissions to less than 0.04 lb/day/100 tons of chlorine would be about \$2.5 million based upon selection of the molecular sieve system. A similar level of containment is possible with activated carbon systems. The cost of reducing cell room emissions is difficult to estimate, but could total several million dollars for the ten plants concerned.

7 SURVEY OF CANADIAN MERCURY CELL PLANTS

7.1 General

A questionnaire survey of the Canadian mercury cell chlor-alkali industry was carried out in 1974. The questionnaire was sent in two sections, one dealing with technical aspects of the industry the other with economic aspects. Response to the technical section was very good with all questionnaires returned within the time allotted. Returns of the economic section, were not as readily forthcoming.

None of the plants treat cell room emissions in any way. All plants cool the hydrogen and end-box vent to condense mercury. Some plants effect further mercury removal by secondary cooling, demisting and carbon adsorption. None of the Canadian plants use the molecular sieve, calomel or chemical scrubbing techniques to remove mercury. A summary of the technology used is given in Table 9. The data presented in the subsequent sections are based on information reported in the questionnaire.

TABLE 9 CURRENT METHODS OF MERCURY EMISSION CONTROL IN CANADIAN CHLOR-ALKALI PLANTS

Control equipment	Number of plants	
	Hydrogen	End-box
Primary cooling		
Indirect	9	6
Direct	1	2
Secondary cooling		
Indirect	7	3
Direct	2	0
Tertiary cooling		
Indirect	2	0
Direct	0	0
Mist elimination	5	4
Charcoal adsorber	2	2
Other	0	0

7.2 Hydrogen Stream

The hydrogen originating at the denuder of the mercury cell is saturated with mercury which must be removed. The most common method of treatment involves cooling the hydrogen to condense mercury. In fact, all ten mercury cell plants use this method either alone or as part of a process sequence. The final gas temperature after cooling ranges from a high of 16°C to a low of -11°C.

Plants cool hydrogen using either shell and tube heat exchangers (indirect contact) or towers in which the hydrogen comes into direct contact with the coolant (direct contact). Five plants follow this cooling with mist elimination to remove condensed mercury droplets. Two plants have charcoal adsorbers as final treatment.

Emission factors per 100 tons of chlorine produced, range from a high of 1.35 lb for the least controlled plant, to an average reported low of .029 lb for the two plants having charcoal adsorbers.

Three plants are planning to add better pollution abatement equipment. Of these, two are considering lower temperature cooling, the other either the calomel or molecular sieve process.

Total mercury emitted each year in Canada in the hydrogen stream, as reported in the questionnaires, is 1200 lb.

7.3 End-Box Stream

Not all mercury cell designs incorporate end-box ventilation; three Canadian plants do not. The remaining seven plants cool the end-box ventilation air to condense the mercury present, either as the only emission control, or as part of a pollution control sequence.

Four plants have mist eliminators to remove the condensed droplets and two have charcoal adsorbers as a final stage of treatment.

The end-box volume per 100 tons of chlorine produced ranges from a minimum of 250×10^3 scf to a maximum of 1.2×10^6 scf. Mercury emissions per 100 tons of chlorine for plants without charcoal adsorbers range from 0.13 lb-0.52 lb. Two plants have charcoal filters and their emissions are substantially lower, averaging .015 lb/100 tons of chlorine produced.

The total mercury emission to the atmosphere from this source, as reported in the questionnaires, is 800 lb/yr.

7.4 Cell Room

All but one Canadian mercury cell plants have cell rooms. Although the high ventilation rates are designed to keep the ambient mercury concentration in the cell room air, below the threshold limit value (TLV) of $50 \mu\text{g}/\text{m}^3$, the survey indicates that in one plant the mercury concentration in the cell room exceeded the TLV. None of the plants treat the cell room ventilation stream to remove mercury.

Ventilation rates in cell rooms range from 60 000 scfm-750 000 scfm. The reported mercury concentration in the ventilation air ranges from 20 $\mu\text{g}/\text{m}^3$ - 100 $\mu\text{g}/\text{m}^3$. The average reported rate of mercury emission from the cell room is 1.5 lb/100 tons of chlorine produced. The highest reported emission rate from this source is 11 lb mercury/100 tons chlorine and the lowest is 0.4 lb/100 tons chlorine. The largest emission from any cell room was reported as 1400 lb mercury/yr. The total reported emission from the cell rooms of all the plants is 5600 lb/yr. Reported values are in most cases based on assumptions and inference. Emission tests have indicated that the estimated emission rates are probably lower than actual emission rates.

8 BEST AVAILABLE TECHNOLOGY

There is no technology available that will completely eliminate mercury emissions from mercury cell chlor-alkali plants. It is impractical to remove mercury from cell room ventilation gases because of the large volume of air involved. The only way to reduce mercury emissions from the cell room ventilation stream is to prevent mercury vapour entering the cell room atmosphere. The good housekeeping practices described in the Appendix will limit mercury emission by cell room ventilation air. Technology such as activated carbon adsorption and molecular sieve adsorption is available to contain mercury emissions from the hydrogen stream, the end-box, the storage tanks and retort vent gases.

The emission limits attainable with the above control technology are shown in Table 10.

TABLE 10 EMISSION RATES ATTAINABLE BY USE OF BEST AVAILABLE TECHNOLOGY (21)

Source	Mercury emissions (lb/100 tons chlorine)
Hydrogen gas stream	0.02
End-box vent	0.02
Cell room vent	1.0
Storage tank and retort	0.02

Use of these control technologies would reduce mercury emissions from the Canadian chlor-alkali industry to about 4000 lb mercury/yr.

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APPENDIX RECOMMENDED HOUSEKEEPING PRACTICES*

* U.S. Environmental Protection Agency, *Control Techniques for Mercury Emissions from Extraction and Chlor-Alkali Plants*, pp. 3-30, Publication No. AP-118.

The following housekeeping practices for minimizing the various mercury emissions within the cell room are recommended. Adherence to these practices will result in a sizeable reduction of the mercury vapour concentration in the ventilation effluent from the cell room.

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 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 should be 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 in 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 vapour outlet with a connection to the end-box ventilation system. The connection should be under a slight negative pressure so that all vapours flow into the end-box ventilation system.
10. Unless vapour-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 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 for mercury removal.
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. During cleaning, all cells should have any mercury surface covered continuously with an aqueous medium. When the cells are disassembled for overhaul maintenance, 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.

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