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JOURNAL REVIEW

Losses of Mercury from Chlorine Plants: A Review of a Pollution Problem

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The problem of mercury losses from chlorine plants is reviewed. The mercury material balance is difficult to establish because mercury escapes from the process by a number of routes. Some of the reasons for the mercury emissions are explored, and some problems involved in the measurement of mercury in various effluents are discussed.

A number of mercury containment processes for specific streams have already been proposed, but the need for an integrated mercury recycle policy still exists.

SCOPE

Over the past two years there has been much concern and discussion over environmental pollution by industrial discharges of mercury. This article attempts to review the mercury problem from the process engineering point of view. The particular situation that we examine in detail is that of a mercury-cell chlorine plant. Such plants have been the largest contributors to mercury pollution in the chemical industry.

Although chlorine plants should not consume any mercury in the process, steady losses from the mercury inventory have been the universal experience over the years. One reason this situation persisted so long is that a direct determination of the mercury material balance is extremely difficult. Although a complete and detailed measurement of the mercury losses is not available, we present some estimates of mercury flows with various effluent streams. We discuss some of the causes of these losses as well as possible reasons that they have eluded quantitative detection.

In any case, it is clear that mercury loss from a chlorine process does occur by various routes and in several forms. The containment and recovery of this mercury presents a challenging problem to the chemical engineer. A number of schemes for mercury separation from effluent streams have been proposed. We present a short review and evaluation of these processes.

We hope that this exposition will not only put the mercury problem into perspective but also provide an illustrative example that can help solve or prevent similar loss problems in other industries.

CONCLUSIONS AND SIGNIFICANCE

There appears to be adequate evidence that environmental mercury pollution can be quite dangerous and that industrial discharges, particularly from mercury-cell chlorine plants, contribute to environmental mercury levels. Thus, it is incumbent on chlorine producers to reduce greatly their mercury losses. Economic considerations also lead to this conclusion.

A rational, integrated recycle policy for mercury containment requires first of all that one know where the mercury is escaping and in what quantities. This question has not been resolved very precisely. Difficulties in sampling and analysis arise not only from the nature of the process but also from the unusual physical and chemical properties of mercury, properties that cause the losses in the first place. It is clear that a better understanding of mercury chemistry is needed, not only to understand why it is escaping from the plant but also to devise effective control technology.

Most of the processes that have been proposed for mercury containment consider only a single effluent stream. They do not recognize the interactions of that stream with the rest of the process. For example, recycling a mercury-bearing liquid to the brine from a filter backwash may cause a buildup in the brine of some minor contaminant such as iron. This buildup will require more frequent cleaning of the electrolysis cells. A shutdown for cleaning causes large temporary losses of mercury to the air, to the brine, and to the brine sludges. Thus the net result of filtration for mercury containment might be greatly increased mercury losses. Another shortcoming of some proposed control processes is that they introduce foreign chemicals to the plant which may just result in substituting one pollution problem for another. In spite of all the processes that have been offered for mercury removal from effluents, there is still a need for more sophisticated recycle methods that contain the mercury effectively and economically and that can be integrated into a complete, well-coordinated chlorine process.

The implication of the mercury problem for other chemical plants is clearly that process engineers must be aware of the material balances of all chemicals in a process, both at the design stage and in plant operation. Particularly where toxic chemicals are involved, the safest and most economical policy is to include containment procedures in all stages of the development and design of a process, such that these procedures will be optimized with respect to total plant operation.

THE MERCURY POLLUTION PROBLEM

Early in 1970 the public in this country was made aware of a newly discovered pollution problem by reports of high levels of mercury in freshwater fish at various locations in the United States and Canada. Concentrations of the element in some lakes and rivers and particularly in the fish were detected to be unnaturally high. This discovery took place 15 years after a similar crisis occurred in Japan and shortly after the problem also arose in Sweden. The experience in Japan, in particular, showed that environmental mercury can be dangerously toxic.

Governmental authorities and the scientific community immediately mounted a concerted effort to piece together all that was known about environmental mercury at the time (Stahl, 1969; Rehfus et al., 1970). Clarification of the detailed aspects of mercury chemistry and of its effects on the biosphere were needed, detection methods had to be improved, and a technology for mercury containment by industry had to be developed. Before these problems could even be well formulated, however, two other questions had to be answered, at least partially. The sources and ultimate destination of the environmental mercury had to be identified.

WHERE DOES THE MERCURY COME FROM?

Consumption and uses of mercury have been rising steadily over the past 30 years. Worldwide production in 1968 was approximately 9×10^6 kg, of which the U.S. used about 2.6×10^6 kg or roughly 30%. This domestic consumption, as reported by the Bureau of Mines, was distributed as indicated in Table 1.

On the basis of that year's consumption in the United States, the sources of mercury were distributed as shown in Table 2.

From these two tables one can see that only 18% rather than the possible 74% of the total consumption was actually recycled. Most of the remaining amount was unaccounted for and presumably lost to the environment.

There are, of course, other significant sources of environmental mercury in addition to those listed in Table 1. As much as 10^3 metric tons of mercury may be going

TABLE 1. U.S. CONSUMPTION OF MERCURY IN 1968

Dissipative uses	%	10^5 kg
Pulp and paper	1	0.26
Pharmaceuticals	1	0.26
Catalysts	2	0.52
Dental	4	1.06
Agriculture	5	1.32
Paints	13	3.43
Subtotal	26	6.9
Potentially recyclable uses		
Electrical	27	7.1
Laboratory	3	0.8
Measurement and control	11	2.9
Chlorine—caustic soda	33	8.7
Subtotal	74	19.4
Total	100	26.3

TABLE 2. RELATIVE DISTRIBUTION OF COMMERCIAL MERCURY SOURCES

Source	% of total
Imports	22
Government stockpiles	24
Domestic mining	36
Recycled metal	18

into the U.S. atmosphere each year through the burning of coal (Billings and Matson, 1972). Open roasting or smelting of huge volumes of material in metallurgical operations may transport large quantities of mercury to the air when the ores contain finite concentrations of mercury minerals (Kangas et al., 1971). Natural geological processes obviously play a significant role as well, releasing large undetermined amounts of mercury to the atmosphere and surface waters. Although the magnitude of the latter contribution is difficult to estimate for determining natural levels of environmental mercury, the data in Tables 1 and 2 provide an indication of the major sources and estimates of the rates of mercury flow into the environment resulting from industrial activity. The other primary questions that must be considered involve the routes followed by mercury through the biosphere and its effects on ecological systems.

WHERE DOES THE MERCURY GO?

A number of questions have been raised regarding the form the metal takes once in the environment and particularly whether it ends up as an unreactive compound or not. If the mercury does become labile, what are its ultimate effects on living organisms? Some of these phenomena can be understood in terms of the metal's known chemistry (see Appendix); however, most of the interaction mechanisms are not yet understood. At this point, we shall make only a few general observations and historical comments, these being representative of much more detailed discussions found in the literature (Wallace et al., 1971; Jones, 1971; Anon., 1971a). To determine the toxicity of mercury in its various chemical forms has been the focus of most biological investigations in the past.

Inorganic mercury, and especially the metallic form, is much less poisonous than its organic compounds. The former is eliminated relatively rapidly by the body. The latter, as a true protoplasmic poison, is absorbed very strongly in the heart, liver, kidneys, and most of all in the brain and medula where it attacks the whole nervous system and results, in many instances, in death (McAlpine and Shukuro, 1958; Kurland et al., 1960; Batigalli, 1960).

To determine how much mercury levels have risen with increased industrial activity is a difficult task. Early data are scant because appropriate methods of analysis were not developed until recently. Studies conducted in Sweden show a marked rise in mercury concentrations in seed-eating and predatory birds since 1940. In 1958 levels between 2 and 200 ppm were detected in the liver and kidneys of dead birds. However, there is evidence that some species (such as swordfish) have always contained some mercury, and this should be taken into account by those imposing regulations; what is high for one species may be natural for another.

Although the link between industrial mercury losses and environmental pollution is debatable on a number of points, there exists a definite correlation between mercury levels in freshwater fish and local industrial mercury emissions (Kleinert and Degurse, 1972; Konrad, 1971). Furthermore, mercury concentrations found in fish are much higher than those in the ambient water. Researchers claim that such mercury is mostly in the form of methyl mercury, even where the mercury originated in some other form. Supposedly mercury in the environment is converted into the methyl form by some bacterial action and is eventually transported and concentrated by the aquatic food chain. It is clear that biological methylation is quite possible in many ways, but to the best of our knowledge no definite evidence is available to establish under what conditions this does occur in nature.

Unfortunately, methyl mercurials are the most toxic of the element's compounds. The classical example of methyl mercury poisoning is the case of the Minamata Bay tragedy in Japan in 1955 (Kurland, 1960). The source of the pollution was a polyvinyl chloride plant which used a mercury catalyst. Almost 50 fish-eaters died, and at least 100 were severely poisoned. Cases of human poisoning have also resulted from the use of mercury chemicals in agriculture, particularly as seed dressings.

INDUSTRIAL MERCURY POLLUTION

The answers to these two general questions regarding mercury pollution, then, are that large amounts of mercury are disbursed into the environment by industrial activity, and that under some circumstances this environmental mercury can be quite dangerous. On the basis of these conclusions, authorities in state and federal agencies have established regulations concerning discharges of mercury to the environment. Because of our ignorance of the many complexities of mercury chemistry in natural systems, these regulations are somewhat arbitrary but hopefully conservative.

From Table 1 one can see that the largest single user of mercury was the chlorine industry. Only 270,000 kg or 31% of the mercury going into the chlor-alkali industry in 1968 was dedicated to new cell requirements for startup; the rest was apparently lost in the process and reaching the environment in one way or another. Even from an economic standpoint such a large loss is clearly undesirable. For the market price which prevailed at the time, it amounted to a $9 million cost to the industry, which, being about 2% of the total product value, could have been of critical importance to plant profitability. Where loss rates are so high, efficient recovery, although difficult, may render economic benefits quite aside from the additional social implications of mercury pollution.

For the chemical engineer working in a process industry which discharges significant amounts of mercury to the environment, the challenge presents itself to identify the causes of the loss and to devise appropriate remedial measures for limiting the mercury emissions in an economical way. In this review we investigate some of the causes for mercury losses from chlorine plants as well as the obstacles to their identification, and we discuss briefly the technology which has been developed for containing the mercury. The purpose of the review is to present a relatively complete picture of an unfortunate industrial pollution problem. Perhaps there are some lessons to be learned from this situation that will help the chemical process industries to identify and contain potentially dangerous emissions and to avoid such environmental crises in the future.

MERCURY LOSSES FROM CHLORINE-CAUSTIC SODA PLANTS

A significant number of plants in the U.S. chlorine-caustic soda industry use the mercury-cathode process (35% in 1968) rather than the diaphragm cell process. It is this portion of the chlorine industry which was consuming one-third of the total U.S. mercury demand in 1968. The mercury process is preferred under certain conditions because it renders directly products of higher purity than does a diaphragm cell.

The process consists in the electrolysis of a concentrated solution of sodium chloride in a cell where the cathode is a flowing stream of mercury and graphite is the usual anode. The primary product is chlorine, which is evolved at the anode. The mercury stream leaves the cell as amalgamated sodium [Hg(Na)] and passes to a decomposer where, upon reaction with water, hydrogen gas and 50% sodium hydroxide solution are the products obtained. The mercury is then recycled to the electrolysis cell. The depleted brine is reloaded with salt, treated for impurities, and returned to electrolysis. The chlorine, caustic, and hydrogen streams usually undergo some further processing as final products although the hydrogen in many cases is discharged to the atmosphere.

In summary, the process can be described by the following set of reactions:

$$NaCl + x\,Hg^\circ \rightarrow 1/2\;Cl_2\uparrow + Na\,(Hg)_x, \text{ and}$$
$$Na\,(Hg)_x + H_2O = NaOH + 1/2\;H_2\uparrow + x\,Hg^\circ,$$

for an overall reaction

$$2\,NaCl + 2\,H_2O = 2\,NaOH + H_2 + Cl_2\,.$$

A flow diagram of the process is presented in Figure 1, and typical operating conditions for electrolysis are indicated in Table 3 (MacMullin, 1962).

At this point we recognize that although the simple flow sheet shows no mercury consumption, the use of mercury to make up for operational losses is well known (MacMullin, 1962; Sommers, 1965; Chlorine Institute, 1971) and has always been taken into account in the economic analysis of new plants. For example, the following are the raw material requirements in the list of specifications of a commercial unit per 10^3 kg of Cl_2 produced:

NaCl	1.7×10^3 kg
Graphite	4.2 kg
Concentrated HCl	7.5 kg
Mercury	0.28 kg

This stated requirement of mercury per 10^3 kg of chlorine produced is consistent with the ratio of the total mercury consumption rate in the industry to the total mercury-cell chlorine capacity in 1968. Its value, which is the rate of mercury addition to the electrolysis cell needed to maintain a steady mercury inventory, had been established by years of operating experience. For a 10^5 kgCl$_2$/day plant, this mercury consumption corresponds to a loss of 28 kg/day. Because of the magnitude of the mercury inventory, losses of this size are detectable only over a period of months (Cowley et al., 1966).

In order to reduce the mercury losses from a chlorine plant in an efficient and effective way, one must first identify where these losses occur. Figure 1 shows a number of major product and effluent streams, any one of which may transport mercury from the process. Let us consider these streams in some detail to establish the most likely routes for mercury losses.

1. *Hydrogen gas stream.* Hydrogen is formed in the decomposer where temperatures of 100°C or higher exist. Since the hydrogen has direct contact with mercury, and the latter has a finite vapor pressure, the exiting gas stream can carry large amounts of mercury vapor. Table 4 gives the hydrogen gas stream capacity for mercury in a 10^5 kg Cl$_2$/day plant on the basis of equilibrium concentrations corresponding to various gas temperatures.

One can see that if hydrogen were leaving at 100°C it would have the capacity for as much as 100 kg Hg/day in a 10^5 kg Cl$_2$/day plant. Such high levels have in fact been measured by Balla and Kalman (1969). However, that is the extreme case. In practice, the hydrogen streams from the decomposers are generally passed through heat exchangers to condense the mercury vapor. If the hydrogen is not used in another process it is vented to the atmosphere at a temperature of about 30°C, depending upon the available cooling water temperature. The condensed mercury is collected and recycled to the cells. If effective condensation is accomplished, very little mercury should escape by this route, but the potential for loss is certainly present.

TABLE 3. BRINE CONDITIONS IN A TYPICAL CHLORINE CELL

	Inlet	Outlet
Temperature, °C	50	70
NaCl, g/l	305	270
Available Cl$_2$, g/l	0.03	3.0
*p*H	4	2.5-3

TABLE 4. EQUILIBRIUM CONCENTRATION OF MERCURY VAPOR IN GASES AND THE FLOW RATE OF MERCURY IN A SATURATED H$_2$ STREAM

T, °C	Equilibrium concentration, g/Hg m^3 (STP)	kg Hg/day with H$_2$ for $\frac{10^5 \text{ kg Cl}_2}{\text{day}}$
0	0.00217	0.068
10	0.00575	0.18
20	0.0142	0.45
30	0.0326	1.0
40	0.0714	2.3
50	0.1488	4.7
60	0.2965	9.4
80	1.043	33
100	3.206	100

2. *End box fumes.* In newer plants there is a positive ventilation system on the ends of the electrolysis cells for venting the hydrogen which is produced by contact of the amalgam with the water seal. These vents are expected to carry mercury out by the same mechanism as does the hydrogen stream. However, because gas temperatures are much lower, the gas-metal contact less intimate, and the volume of the fumes somewhat smaller, the potential losses by this stream should be considerably lower than with the hydrogen, particularly if the gases are cooled further before venting.

3. *Cell room ventilation air.* Especially when cells are opened for inspection and repairs, evaporation losses may be significant; the volume of circulated air in the cell room can be so high that losses by evaporation could be considerable.

4. *Sodium hydroxide.* Because this product stream comes into intimate contact with hot mercury, it can carry mercury from the cells, particularly by droplet entrainment. However, because many customers impose rigid mercury level specifications on caustic, an effort is made to remove most of the mercury by filtration.

5. *Washing water from cell rooms.* Due to occasional spilling of mercury, some metal reaches the cell room sump and may be suspended or even dissolved in the waste water. This erratic amount may be lost to the environment.

6. *Brine.* This could be another major route for mercury losses because of the solubility of metallic and oxidized mercury in chloride solutions. Periodic purging of the brine loop is required, and this stream, along with any brine leaks or spills, can carry mercury from the cells.

7. *Solid wastes.* Recycled brines are treated for removal of impurities after resaturation with salt. The treatment consists of precipitation by *p*H adjustment of calcium, magnesium, and iron ions, among others. Insoluble gypsum is purged from the brine saturator and is a

second source of solid waste. These precipitates can entrain a quantity of mercury-containing brine or even coprecipitate mercuric ions or flocculate suspended mercury droplets. If such deposits are rejected as brine sludges without any processing for mercury recovery, significant losses may occur here.

8. *Chlorine.* It is possible that mercuric chloride in entrained brine droplets may be carried out of the electrolysis cell by the chlorine. Prior to liquefaction the chlorine is dried with concentrated sulfuric acid and filtered. Thus, any mercury losses by this route should end up in the waste diluted sulfuric acid.

MEASUREMENT OF MERCURY LOSSES

To determine the exact amount of mercury that actually escapes with each one of the effluent streams is a difficult task. Sampling and analysis present formidable problems. In addition to chemical problems in the determination of very low mercury concentrations, one encounters in several streams the problem of getting a representative sample of a heterogeneous system. And not only do conditions vary from plant to plant, but within a particular plant the mercury flows probably vary dramatically with fluctuations in operating conditions. Even if one could obtain complete and correct data for all streams at steady state operation, these figures may bear little relation to the average rate of mercury loss. Departures from normal operation may cause temporary losses by one stream or another to be extremely high. These are problems that are inherent in the determination of a material balance in a chemical plant, particularly for a minor component. They can be overcome only by a considerable experimental effort both in the plant and in the laboratory.

Any attempt to measure the mercury content in the various effluent streams requires an accurate method for quantitative analysis. Not only must the method be sensitive, but it must also be adaptable to the type of sample to be analyzed. In the case at hand, one must deal with gas, liquid, and solid streams and with a variety of chemical environments. Very seldom will concentrations be higher than 50 μg Hg/ml for liquids or solids or 0.5 mg/l for gases; usually they will be much lower. Under such circumstances many of the conventional analytical techniques, not being sufficiently sensitive, must be abandoned.

Fortunately, in the case of mercury, a number of very sensitive analytical techniques have been developed in recent years. These include neutron activation analysis, various types of spectrophotometry, mass spectrometry, and several types of electrochemical analysis for the element and gas chromatography for organomercurials. Although each of these methods has played a role in the study of mercury pollution, the method which is by far the most convenient and suitable for plant studies because of its speed, flexibility, and sensitivity is the flameless atomic absorption (AA) spectrophotometric method. In the usual procedure, mercuric ions in solution, formed by oxidation and dissolution of the sample if necessary, are reduced to the metallic state by $SnCl_2$; Sn (II) is oxidized to Sn (IV). The mercury is then easily removed by vaporization into a carrier gas, such as nitrogen and air, and passed through an optical cell where its atomic absorbance is measured. A spectrophotometer is calibrated with standard mercury solutions. Stripping of all the metal can be completed in less than 2 to 5 minutes with the proper gas flow rate. The analysis has a minimum resolution of 2 ppb with ± 5% relative error under the worst conditions.

Although there is available such an accurate and convenient method for mercury analysis, there remain two major problems, aside from representative sampling, that can lead to erroneous results in the measurement of mercury losses. One is related to the determination of mercury in a hydrogen stream; the other is related to the loss of mercury from extremely dilute solutions.

LOSS OF MERCURY FROM DILUTE SOLUTIONS

In many cases it is critical to determine the concentration of mercury with high accuracy. When one uses the AA flameless method with a normally sensitive instrument (such as most commercial AA units), with a flow rate of about 5 l/min as a good compromise for fast analysis and reproducibility, and with an absorption cell 10 cm in length, as little as 3 μg of Hg will give an absorbance of 75%. With the use of expanded scales, 0.1 μg will give a reliable response. Since a convenient sample volume to be treated is 60 ml, these figures imply measurable concentrations between 1.6 and 50 ng/ml if we take 1 ml as the smallest aliquot measurable with accuracy. (If one has samples of concentrations higher than 3 μg/ml, the sample can be diluted to the range where the response from the instrument falls on a convenient scale.) In general, sample solutions and standards will be on the order of 1 μg/ml, while the final solution to be treated will have, at most, 1/60 of that concentration. In short, one is forced to work with very dilute solutions during the course of the analysis.

We have observed that even those samples containing 1 μg Hg/ml appeared to be losing mercury during analysis. When a 1 μg/ml standard, prepared with $Hg(NO_3)_2$ or $HgCl_2$ in HCl and HNO_3, was analyzed repeatedly by taking aliquots from an uncovered volumetric flask, the measured absorbance decreased by 50% within 6 minutes of the first measurement. However, constant readings of ± 3% were obtained when the standard was made much more acidic and the flask was kept closed. This indicates that appreciable Hg^0 may form and evaporate from the solution.

From current literature and from private communication, it was known that this had been the experience of many. T. Y. Toribara et al. (1970) conducted experiments on mercury loss from solution where they traced the mercury with Hg^{203}. Their explanation of the phenomenon involves either the formation and escape of minute amounts of Hg^0 by action of small amounts of reducing agents on Hg(II), or reduction only to Hg(I), which for kinetic reasons will not be reduced by the $SnCl_2$ currently used in most flameless analyses. Hg^0 has a vapor pressure at room temperature of 0.27 N/m^2, and its aqueous solubility is 20 μg/l at 20°C. Reduction to Hg^0 of only 1% of a 2 ppm Hg sample will saturate the solution, but at equilibrium the gas phase in contact with it will contain 23 μg/l. If the air above the solution is well circulated, it is easy to see how mercury can evaporate from solution. Toribara recommends having small amounts of an oxidizing agent such as $KMnO_4$ present to stabilize the solution. Concentrated nitric acid should also be effective in preventing the escape of mercury from dilute samples.

One must also beware of mercury adsorption on tubing and vessel walls in this regard, particularly those made of plastic or soft glass.

SAMPLING FROM GASEOUS STREAMS—ABSORPTION OF MERCURY VAPORS IN ACIDIC PERMANGANATE

The accepted practice for sampling gaseous streams for mercury analysis is to pass the gas through a strong oxidizing solution and subsequently to analyze this solution for mercury by flameless AA. Although different agents have been used, an acidic permanganate solution has been most frequently recommended. The typical composition of such an absorbing solution is 1% $KMnO_4$ w/v and 10% H_2SO_4 v/v.

There is no doubt that this permanganate solution is strong enough to oxidize the amount of mercury usually found in industrial gaseous streams or ambient air, but application of this procedure to any specific gas under extreme conditions may present unexpected problems. For instance, in the sampling from a hydrogen stack in a chlorine plant, the presence of entrained droplets of mercury and failure to capture them may render values lower than the actual mercury content. If the distribution of droplets along the stack cross-section is very irregular, sampling may not be representative; and if droplets are present at all, they have to be broken or else they will not be oxidized by the permanganate in a very short contact time. Adhesion of liquid mercury to the sampling probe may also be a problem. In fact, it has been found in sampling from hydrogen that measured mercury concentrations are generally much lower than expected. Measurements less than the vapor equilibrium concentration have been obtained even though liquid mercury was observed to be present in great profusion. A few laboratory experiments were conducted to explore this phenomenon.

Experiment A. Air or hydrogen was passed through a pool of mercury at a controlled flow rate. Volumetric flow rates were measured with a rotameter calibrated for each gas. The concentration of mercury in the gas stream was measured directly with a 1-cm optical cell in the AA spectrophotometer by extrapolation of the absorbance obtained with known liquid standards. Then the gas stream was passed through a permanganate solution for a given time period, and the latter was analyzed for mercury. The results appear in Table 5. The results were not entirely reproducible, but they do show that the two separate analyses generally agreed for air, whereas mercury levels determined in the hydrogen stream were consistently lower by the permanganate method than by direct measurement.

Experiment B. A second experiment was done in which a known volume of gas was passed through a similar pool of mercury and then through a bed of copper wire. The latter was intended to remove entrained droplets of mercury; under such conditions the maximum concentration of mercury should be the equilibrium value. The gas was then bubbled through two gas washing bottles in series, both of which contained 50 ml of a permanganate absorbing solution. Three different cases were studied: first 0.5% w/v $KMnO_4$ and 10% v/v H_2SO_4; second, 1% w/v $KMnO_4$ and 10% v/v H_2SO_4; and third, 2% w/v $KMnO_4$ and 12.5% v/v H_2SO_4. The mercury content after absorption was determined twice for each bottle; one aliquot of each sample was pretreated by digestion, and a second was not. Digestion consisted of the addition of 10 ml of a concentrated H_2SO_4/HNO_3 (1:1) mixture to a 10 ml aliquot. Results are given in Table 6.

Both experiments indicate that the absorbing permanganate solution works more efficiently with air than with hydrogen. Results show better absorption in experiment B than in A, even with air; the improvement may be attributed to the removal of entrained mercury droplets and to lower mercury concentrations in general relative to the concentrations in experiment A.

TABLE 5. RESULTS OF MERCURY ABSORPTION STUDY A

	Relative concentration (1)	Relative concentration (2)	% recovered by permanganate, (1)/(2) × 100%
Air stream	119	106	102
	49.0	48.0	102
	41.6	65.8	63
	106.5	111	97
	58.4	103	56.5
	121	121	100
H_2 stream	23.4	45.2	51.8
	12.8	41.2	31.2
	15.2	30.3	50.2
	10.0	48.6	20.7
	20.5	32.6	63
	19.2	28.6	67

(1) Concentration determined in the $KMnO_4$ solution.
(2) Concentration in $KMnO_4$ solution expected from direct optical measurements for 100% absorption.

TABLE 6. RESULTS OF MERCURY ABSORPTION STUDY B

Solution		Mercury recovery* (%) Bottle First	Second	Total
Deficient permanganate (0.5% w/v) Untreated samples	Air	75.6	24.2	99.8
	H_2	55	25	80
Deficient permanganate (0.5% w/v) Digested samples	Air	75.6	25.2	99.8
	H_2	64.2	35.8	100
Regular permanganate (1% w/v) Digested samples	Air	99.3	0.7	100
	H_2	94.4	3.6	98
Strong permanganate (2% w/v) Digested samples	Air	100	0	100
	H_2	99	1	100

* Total Hg absorbed = 150μ g.

One can see that even with an enormous excess of permanganate, on the basis of stoichiometric requirements not all of the mercury is absorbed in one gas washing bottle. Also, the analyses yield higher concentrations when the samples are digested. The reason for this phenomenon might be the formation of Hg(I) in the presence of H_2. It is known, as discussed in the Appendix, that Hg(II) can be reduced homogeneously by molecular hydrogen and that such a reaction might very well be catalyzed by acidic permanganate. Although this reaction is not expected to proceed below 65°C, further research in this area is required.

On the basis of these observations the following recommendations concerning gas sampling are offered:

The permanganate should be more concentrated than that currently in use. 2% w/v in $KMnO_4$ seems to be adequate.

Great care should accompany sampling from hot gases or from those very concentrated in mercury.

The method is not reliable where entrained droplets are present unless about three bottles in series are used (50 ml of each).

Long periods of sampling should not be used; any impurity that might consume permanganate will contribute to lower the effectiveness of the solution as the permanganate concentration decreases.

THE MERCURY MATERIAL BALANCE

As a result of the many difficulties associated with the sampling and analysis of various mercury-bearing streams in a chlorine plant, there has been no complete experimental mercury balance established which accounts for all the mercury known to be lost from the process. At least no such balance has been reported in the open literature. One suspects that it was the lack of such a definitive balance that stood in the way of more effective mercury control technology prior to 1971.

In spite of the uncertainties, several tentative estimates of the mercury material balance have been offered, and these are presented in Table 7.

One can see in Table 7 that there are large discrepancies among the various authors for certain individual streams. This is to be expected because none of them had access to complete and extensive data. The figures in the table are based on only scattered measurements and a great deal of speculation. In Chapman's figures, for instance, the total was known from consumption rates, but hurried, incomplete, and unreliable measurements from one day's sampling made some arbitrary allocation of this amount to the various streams necessary. It is quite possible that the average flows with brine sludges or to the cell room air may be higher than indicated and the average hydrogen losses somewhat lower.

The resolution of the differences in Table 7 is somewhat academic at this point. The data under consideration refer to operating conditions in 1970 and earlier. The advent of water quality standards and subsequently of air pollution standards relevant to mercury emissions has forced major modifications of mercury-cell chlorine plants such that nearly all effluent streams are being recycled or processed in some way for mercury removal. The net effect of these modifications on total mercury consumption and loss remains to be determined over the next year or two. The effectiveness of the control measures is already indicated, however, by a sharp drop in mercury purchases by the chlorine industry.

In spite of the fact that the mercury problem is apparently being solved without the benefit of a quantitative mercury balance, it should be instructive to examine why the mercury material balance has been so elusive. One fallacy in the calculation of the material balance is to assume that the plant operates in a steady state such that the mercury input rate always equals the rate of outflow. For example, when the current to a cell is turned off, the chlorine in solution can attack the mercury cathode to form soluble mercuric chloride in the brine. This will raise mercury levels in the sludges considerably. Similarly, opening of a cell for cleaning or the occurrence of hot hydrogen leaks can cause temporary but large mercury flows to the ventilation air.

Another fallacy in some mercury balance attempts is to assume that the hydrogen being vented from the plant carries little if any mercury in excess of the equilibrium amount at the exit temperature. The actual mercury content of this stream depends upon the physical configuration of the gas coolers and the conduit. The reason for this can be seen from a few simple calculations.

ANALYSIS OF THE HYDROGEN COOLER

We can imagine as an approximation the hydrogen cooler to be a simple shell and tube heat exchanger with sufficient cooling water that the water temperature remains constant at, say, 20°C. Suppose that the hydrogen stream enters at 80°C and leaves at 30°C. If we assume that the major resistance to heat transfer lies in the gas phase, the product of the gas film heat transfer coefficient h_g and the surface area A may be calculated from the heat exchanger design equation (Bird et al., 1960).

$$h_g A \approx UA = w_g \hat{C}_{pg} \ln \left[\frac{T_{g1} - T_L}{T_{g2} - T_L} \right] \tag{1}$$

or

$$\left[\frac{h_g A}{w_g \hat{C}_{pg}} \right] = \ln \left[\frac{80 - 20}{30 - 20} \right] = 1.79$$

Now, because of its very high surface tension, mercury is very difficult to condense unless it has a favorable nucleation site. Suppose there is no such nucleation site except on the tube walls. Therefore, the rate of condensation will be determined by the rate of mass transfer to the tube walls.

The rate of mass transfer to the tube walls is governed by an equation analogous to Equation (1). In particular, for dilute gas mixtures:

$$\rho\, k_g A = w_g \ln \left[\frac{\omega_{\mathrm{Hg}1} - \omega_{\mathrm{Hg}}{}^{*}}{\omega_{\mathrm{Hg}2} - \omega_{\mathrm{Hg}}{}^{*}} \right] \tag{2}$$

or

$$(\omega_{\mathrm{Hg}2} - \omega_{\mathrm{Hg}}{}^{*}) = (\omega_{\mathrm{Hg}1} - \omega_{\mathrm{Hg}}{}^{*}) \exp \left[-\frac{\rho\, k_g A}{w_g} \right] \tag{3}$$

Eliminating (A/w_g) from Equation (3) by use of Equation (1), we obtain

$$(\omega_{\mathrm{Hg}2} - \omega_{\mathrm{Hg}}{}^{*}) = (\omega_{\mathrm{Hg}1} - \omega_{\mathrm{Hg}}{}^{*}) \exp \left[-1.79 \frac{\rho\, k_g \hat{C}_{pg}}{h_g} \right] \tag{4}$$

Now, according to the Chilton-Colburn analogy between heat and mass transfer, there is a relationship between k_g and h_g (Bird et al. 1960). In particular, by substitution of the standard dimensionless group definitions, we obtain

$$\left[\frac{k_g\, \rho\, \hat{C}_{pg}}{h_g} \right] = \frac{Sh\; Pr}{Nu\; Sc} = \frac{j_D Re Sc^{1/3} Pr}{j_H Re Pr^{1/3} Sc} = \left(\frac{Pr}{Sc} \right)^{2/3} \tag{5}$$

if $j_D = j_H$.

If we use the properties of hydrogen gas and estimate the diffusivity of mercury vapor in hydrogen from kinetic theory, we can estimate the (Pr/Sc) ratio to be about 0.28. Substituting Equation (5) with this value into Equation (4), we obtain

$$\frac{(\omega_{\mathrm{Hg}2} - \omega_{\mathrm{Hg}}{}^{*})}{(\omega_{\mathrm{Hg}1} - \omega_{\mathrm{Hg}}{}^{*})} = \exp\,[-0.76] = 0.47 \tag{6}$$

Thus, if $\omega_{\mathrm{Hg}1}$ is the saturation value at 80°C and $\omega_{\mathrm{Hg}}{}^{*}$ is that at 20°C, the exit vapor concentration will be, according to Table 4, 0.5 g/m^3 rather than 0.033 g/m^3, the equilibrium value at the exit temperature 30°C.

This is a very rough calculation, but it shows qualitatively that the mercury condensers may operate very inefficiently in this system if provision for effective nucleation and mechanical separation of mercury is not made. In actual practice the mercury vapor may remain supersaturated, or it may form a mist of small droplets in the gas stream if homogeneous nucleation can be accomplished. In either case, large quantities of mercury in excess of the equilibrium value can be carried out of the

TABLE 7. MERCURY LOSSES FROM CHLORINE PLANTS. VALUES ARE IN kg Hg/DAY FOR A 10^5 kg Cl_2/DAY PLANT

Stream	Johnson and Bouveng (1970)	Wallace et al. (1971)	Chapman (1970)
Hydrogen	3-10	0.3	20-25
Sodium hydroxide	0.1-2	0.3	0.25
Brine sludges	0.3-5	14	0.5-1.5
Wash waters	1.1	7.5	0.5-2
End box fumes vent	—	—	2.5-5
Cell room ventilation	1.7-2.7	0.9	0.5-1.5
Others	—	7	0.5
Total	5-20	30	27-32

plant by the hydrogen stream. It was this reasoning along with the direct observation of a large amount of liquid mercury in a hydrogen stack that lead to the large hydrogen stream value given by Chapman in Table 7.

MERCURY RECOVERY PROCESSES

After governmental authorities, the public, and chlorine producers became aware of the magnitude of the mercury pollution problem, all efforts were directed to restrain the losses of the metal to the environment by whatever means were available. Among the immediate targets were mercury-containing fungicides for agricultural uses, the paper industry, some polymer producers, and the chlorine industry. The amounts of mercury involved in the former three industries were not very large or particularly vital so that the safest action was to eliminate or to substitute for mercury. Most of the attention was therefore focused on the chlor-alkali plants that used the mercury process.

Similar crises had taken place in Japan and Sweden long before the United States and Canada realized the existence of the problem; hence, most of the new mercury recovery technology came from these countries. The problems of mercury containment had not been completely solved, however. Not all forms of emissions had received equal attention; some of the proposed processes were too expensive; new research in the biological areas raised the need of imposing still more stringent regulations; and last of all, very few of the proposed treatment processes allowed economical recovery of mercury, at least not without consuming other materials in the extraction process. Probably the sole exception to this latter statement is the mechanical recovery of mercury from hydrogen streams where filters and condensers were used (Jones, 1971; Chapman, 1970; Johnsen and Ullman, 1970; Bouveng and Ullman, 1969).

As an initial step in the chlorine industry, all side streams containing mercury were segregated, washing waters from cell rooms were collected, and sludges and slurries purged from the brine purification system were contained in settling basins rather than being discharged to the environment. Similarly, filters and condensers removed a good part of the mercury from hydrogen streams and cell fumes. These procedures halted the direct discharge of mercury to rivers and public water systems and substantially reduced emissions to the atmosphere. The problem remained to dispose safely of collected waters and to recover the mercury in a useful form. A number of separation and recovery processes have been subsequently proposed. The processes available for extracting mercury from various process streams and effluents are summarized below.

MERCURY RECOVERY FROM GASEOUS STREAMS

As indicated above, losses of mercury vapors to the atmosphere are a substantial part of the total loss from chlorine plants. The loss due to cell room ventilation can be reduced by properly handling of spills and leaks. Hydrogen and cell fumes can be treated in a number of ways. In principle, the same procedures can be applied to mercury-bearing gas streams of any kind except where the gas can react with the materials used. Most processes have been designed to treat the hydrogen stream where mercury levels and losses are the greatest.

As previously presented in Table 4, the equilibrium concentration of mercury in the gas phase changes dramatically with temperature. The hydrogen gas leaves the decomposer at about 100°C which would mean a capacity at equilibrium of 100 kg Hg/day. On the basis of 10^5 kg Cl_2/day (20 m^3 STP H_2/min) a reduction in temperature to 10°C from 80°C will bring the equilibrium concentration in the vented hydrogen stream down to 0.0057 g/m^3 from 1.043 g/m^3 or the hypothetical mercury flow from 33 kg/day to 0.18 kg/day.

On this basis, cooling has been the most common form of gas treatment. However, as we have already shown, simple cooling may not be sufficient to reduce the mercury content in the gas stream to its equilibrium level. In the absence of an appropriate wettable surface that will provide nucleation sites, mercury will remain as supersaturated vapor or will condense in the form of very fine drops that might be carried up the stack by the hydrogen. Rough terminal velocity calculations show that droplets as large as 100 μm in diameter can be easily entrained.

Chipley, Jensen, Reynolds, Inc. produces the Platecoil heat exchanger which, on the basis of an intricate geometry, attempts to provide the nucleation sites required. A possible problem with this type of condenser is a pressure drop larger than the process can tolerate. Expensive compressors may then be required. The latter have been used in Sweden to enhance condensation.

A second alternative, Monsanto's Brink mist eliminator (Brink, 1963; Brink et al., 1964) is being used by many U.S. chlorine plants. It consists of a packing of glass fibers, and the manufacturers generally claim a 100% collection of particles larger than 3 μm. The Brink has been tested and used successfully in a variety of other mist applications, but its performance with mercury does not appear to be as good as with water, probably because glass is not a surface wettable by mercury. A similar design with a metallic packing that amalgamates with mercury would probably be much more efficient but also more expensive.

A third strategy consists in adsorption of mercury by activated charcoal. Adsorption is greatly enhanced by impregnation with silver, potassium iodide, or any other substance that will react with mercury (Stock, 1934; Dreibelbis and Joyce, 1965; Manes, 1965, 1968; Park, 1966; Logan, 1966). Although in some instances (such as adsorption on silver) the substrate can be regenerated by heating to around 400°C, this method has not received wide acceptance in the chlorine industry. The process is too expensive, the regeneration process with mercury recovery is not very well established, and water vapor may interfere.

An effective approach to gas treatment consists in absorbing mercury with a strongly oxidizing aqueous solution so as to bring it into solution in the mercuric state. One example is the use of acidic permanganate in the same fashion as is done for analytical purposes. The use of permanganate, however, implies introduction of a completely foreign stream into the system, and subsequent recovery of the metal from the loaded solution and reagent regeneration will require additional processing systems.

A more attractive alternative is to use sodium hypochlorite (NaOCl) as the oxidizing agent. It has reportedly been used already for a few processes where hydrogen had to be purified for use in the preparation of hydrogenated fats or foodstuffs, or in catalytic reactions where the catalyst was subject to mercury poisoning (Parks and Baker, 1969; Parks and Fittinghoff, 1970). The system has been installed recently for mercury removal by at least one chlor-alkali plant and found to be highly efficient. The loaded solution can be recycled directly to the electrolysis cells for reduction of the mercury although this procedure may induce a buildup of mercury in the depleted brine and thus in the brine purification sludges. This latter phenomenon must be taken into account in any processing of the hydrogen, cell fumes, or brine that involves recycling because the lowering of the losses from one stream may be reflected by an increase in those from another stream. In general, increasing the degree of recycling in a plant will also require more frequent purging from the brine loop in order to maintain satisfactory steady state operation. This implies another source of mercury-laden effluent, the brine purge.

RECOVERY OF MERCURY FROM LIQUID STREAMS

In a chlorine plant there are various liquid streams with which mercury can escape. The caustic and cell room washing water contain primarily suspended droplets of elemental mercury which can be recovered via filtration on precoat filters (Anon., 1970). However, the depleted brine and consequently the brine sludges (and any purge) contain mercuric ions, mostly in the form of the tetrachloride complex $Hg\,Cl_4^{2-}$ due to the high chloride concentration. Again, there are a number of ways to go about recovering the mercury.

Mercuric ion can be chemically reduced from aqueous solutions with a variety of agents. Ventron Corporation, for instance, offers a process in which sodium borohydride ($NaBH_4$) is used to reduce mercury at very low levels such as those found in waste water (Rosenzweig, 1971). Alkali metals, hydrazine, Sn^{2+}, Zn, Sn, NH_2OH, H_3PO_2, HCHO, and glycerine are among other reducing agents that can be used. However, the high cost of reactants and the possible creation of new pollution problems related to discharge of the reaction products are factors working against this approach. One also has the problem remaining of recovering the elemental mercury.

The possibility of direct reduction with sodium amalgam presents itself as a clean way to recover dissolved mercury ions in that no foreign reagents are required (Yokota, 1968). This reaction, however, may not be efficient at low mercury concentrations without good mixing, and there are the problems of removing elemental mercury from the aqueous and gaseous effluents once again. Hydrogen reduction itself may be an interesting possibility. In any case, it must be recognized that schemes involving less exotic reducing agents will require some preliminary concentration of the mercury because the reduction potential is too large for very dilute solutions and because rates and reaction efficiencies face transport limitations.

A second alternative for mercury removal from solution that accomplishes a concentration as well is to precipitate directly an insoluble metal salt, either with or without further processing. Raising the *p*H of the solution will render HgO, which can be removed by filtration. The idea of precipitation as HgS with Na_2S or H_2S is also along these lines, although equilibrium solubilities of sulfide complexes may limit the possible extent of the separation (Barnes et al., 1967). Recovered precipitates can be subsequently redissolved with sodium hypochlorite (NaO Cl) and then be treated with a reducing agent or be recycled to the electrolysis cells. The latter procedure, however, can impose a strain on the process by raising the concentrations of trace impurities in the brine. The high price of reagents in these processes is a major drawback, not to mention that some of them require considerable labor.

A third approach is to exploit the presence of the charged mercury species in solution and to extract them with ion exchange resins (Gardiner and Munoz, 1971). A few cation exchangers have been reported to be quite successful in extracting ionic mercury (Högfelt and Muhammed, 1970). Chuveleva et al. (1970) studied the carboxylic acid resin SG-1 taking advantage of the highly stable acetate-Hg(II) complex. However, such treatments have little application in brines, where, because of the high chloride concentration, mercury exists as the $Hg\,Cl_4^{2-}$ anion. This observation brings us to the most successful of the processes in use so far: those which use anion exchangers and chelating resins.

Q-13 is a proprietary anion exchanger developed in Sweden (Fuxelius, 1970). It adsorbs mercury very efficiently, but it is blocked by anions such as $O\,Cl^-$, $SO_3^=$ and $SO_4^=$. Ajinomoto Inc. from Japan offers a chelating resin that operates at *p*H 6-10 and which reduces mercury concentrations in brines from 15 to 0.01 ppm. The metal can be recovered by destructive distillation, but the resin is damaged by strong oxidizing agents such as Cl_2 and $O\,Cl^-$ as well as by strong alkali solutions.

A Swedish process currently in use at Aktiebolaget Billingsfors-Langed integrates the Q-13 with another resin, Q-sorb (Anon., 1971b). The latter is used as a final polishing agent and is discarded when completely loaded so that the mercury is not recovered. Osaka Soda, Japan, has in use a process very similar to this Swedish one. It has been used by many Japanese chlor-alkali plants for more than five years.

A more recent development in the anion exchanger field is the use of a silicon-containing cationite obtained from metallurgical slag (Ionesca and Tudorache, 1971). Also, a number of patents have been issued describing the use of quaternary ammonium cross-linked resins for mercury adsorption (Crain and Judice, 1965; Scholten and Prielipp, 1963; Calkins et al., 1963). It is very probable that this is the structure of the Japanese and Swedish resins mentioned above.

In general, all of these resins are damaged by strong oxidizing agents, which are present in the system under consideration. Total recovery of mercury, without destruction of the resin, is possible in very few cases. Mercury is usually recovered by destructive distillation, but this procedure is not efficient. In most cases the resins are used until their chemical capacity is reached, and then they are discarded.

RECOVERY OF MERCURY FROM SOLIDS

Treatment of solids for mercury removal generally consists of dissolution with an oxidizing agent, such as hypochlorite, followed by a reduction step that will yield metallic mercury. Such an oxidation step has been developed for the extraction of mercury from low-grade cinnabar ores (HgS) by the reaction $HgS + 4OCl^- \rightarrow HgCl_4^= + SO_4^=$ which shows a critical dependence on *p*H, the optimum being around 6 (Parks and Baker, 1969). Another process for hydrometallurgical extraction of mercury from ores by electrolytic oxidation has been developed recently by the U.S. Bureau of Mines (Scheiner et al., 1970). The chemistry and technology involved in these processes should be relevant to the digestion of brine sludges to prepare the mercury for further processing in the liquid phase.

The question of whether the solids should be processed depends on what the mercury content is. One must ask first whether the solid waste is an economic ore for mercury and then, if not, whether there is a safe disposal site which obviates the need for mercury removal.

AN INTEGRATED RECYCLE STRATEGY

From Table 5, approximate though it may be, we may conclude that there are in fact three major categories of mercury-bearing effluents from a chlorine plant: gas streams, liquid streams, and solid waste. The distribution of the escaping mercury among the three phases is not well established because of difficulties in representative sampling and accurate analysis. Neither is it yet known to what extent the discharges in any particular form are detrimental to the environment. Nevertheless, the chlorine industry has been faced with the fact that its various mercury emissions must be reduced to very low levels.

First, the discharges to rivers and lakes had to be curtailed. Next, very stringent atmospheric emission limits were imposed. In some places there exist regulations controlling the disposal of mercury-bearing solid wastes as well.

The response of the industry to these regulations has been somewhat fragmented, this being the result largely of the press of short-term deadlines. It is unfortunate that, instead of attacking one effluent at a time, one could not optimize the mercury recycle strategy for an entire plant. To do this effectively, one would need not only an accurate picture of the mercury material balance but also a good understanding of the complex interactions among the various process streams.

Of the processes described for mercury recovery from individual effluent streams, practically every one suffers from the shortcoming that it solves only a very narrowly defined problem. In removing the mercury from one particular stream, a process may well be creating several other disposal problems. It has not been recognized very explicitly that modification of one part of a process will generally affect all other parts.

In meeting the requirements of government regulations, the industry has been forced to patch together a number of these individual separation processes to ensure that effective mercury containment is achieved. It is doubtful that such an approach, even though successful, yields a solution that is very close to the optimum; there certainly remains room for improvement in the area of mercury recovery technology.

From our review of the mercury loss problem, we can state some rather general criteria for an economically as well as environmentally attractive solution:

1. Most of the mercury loss should not only be contained but also recovered and recycled to the electrolysis cell to minimize make-up requirements.
2. Recovery processes and procedures should be devised to treat gaseous, liquid, and solid effluents, and these processes should be coordinated to recognize their mutual interactions through the central process.
3. Recovery processes should use as few foreign reagents as possible to minimize the generation of additional effluent streams.
4. Recycling procedures should be highly selective for mercury so that undesirable contaminants will not disrupt steady operation of the plant, disturbances and shut-downs being recognized as a major cause of mercury losses.

This list of criteria is intended as a supplement to the usual rules of economic process design.

In a subsequent paper (Caban and Chapman, 1972) we propose an integrated mercury recycle scheme that attempts to satisfy these criteria.

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NOTATION

A = heat transfer area, m^2
$\hat{C}_{pg}$ = molar heat capacity of gas stream, J/kg·K
h_g = film heat transfer coefficient of gas stream, J/m^2·s·K
j_D = Chilton-Colburn j-factor for mass transfer, dimensionless (Bird et al., 1960)
j_H = Chilton-Colburn j-factor for heat transfer, dimensionless (Bird et al., 1960)
k_g = film mass transfer coefficient in gas phase, kg-moles·m/s
Pr = Prandtl number, dimensionless
Re = Reynolds number, dimensionless
Sc = Schmidt number, dimensionless
Sh = Sherwood number, dimensionless
T = temperature, K
U = overall heat transfer coefficient, J/m^2·s·K
w_g = mass flow rate of gas, kg/s
ρ = density of fluid, kg/m^3
ω_{Hg} = mass fraction of mercury vapor in gas stream, dimensionless
ω_{Hg}^* = equilibrium mass fraction of mercury vapor in gas at the temperature of the tube wall, dimensionless

Subscripts

g = gas stream
L = cooling liquid
1 = entrance condition
2 = exit condition

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APPENDIX. SOME RELEVANT ASPECTS OF MERCURY CHEMISTRY

To understand some of the problems associated with mercury pollution and to consider the possibilities for a better method for the recovery of mercury, we should take a look at the chemical behavior of the metal in its various forms.

Mercury is the 80th element in the periodic chart with an atomic weight of 200. It appears in nature together with zinc and cadmium, and with their common nd^{10} $(n+1)$ s^2 configuration these are the last of the transition metals. Listed below are some of the physical properties of mercury.

Ionization potentials	1st	10.43 eV
	2nd	18.65 eV
	3rd	34.3 eV
Melting point		−38.87°C
Boiling point		357°C
Heat of vaporization		14.7 kcal/g mol
Standard potential, E^0, for $Hg^{2+} + 2e \rightarrow Hg^0$		+0.854V

The most stable of the oxidized species is the mercuric. Most mercurous compounds are unstable, and there is no evidence of a mercury (III) chemistry.

Mercury forms compounds with most of the nonmetals, particularly with oxygen, sulfur, phosphorus, seleneium and all the halogens. The stereochemistry of these is mainly two-coordinate, linear, and four-coordinate, tetrahedral.

Most $Hg\ X_2$ compounds ($X =$ F, Cl, Br, etc.) are strongly covalent molecular substances which are practically undissociated in aqueous media. For the halogens the $Hg\ X_3^-$ and $Hg\ X_4^=$ species are readily formed, this being the case for other anions like CN^- as well. The oxide HgO is suspected to be formed from the hydroxide $Hg(OH)_2$, which is only slightly soluble and an extremely weak base. The oxide de-

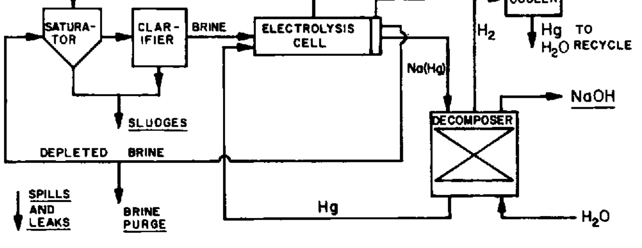


Fig. 1. Flow diagram of a mercury cell chlorine-caustic soda plant.

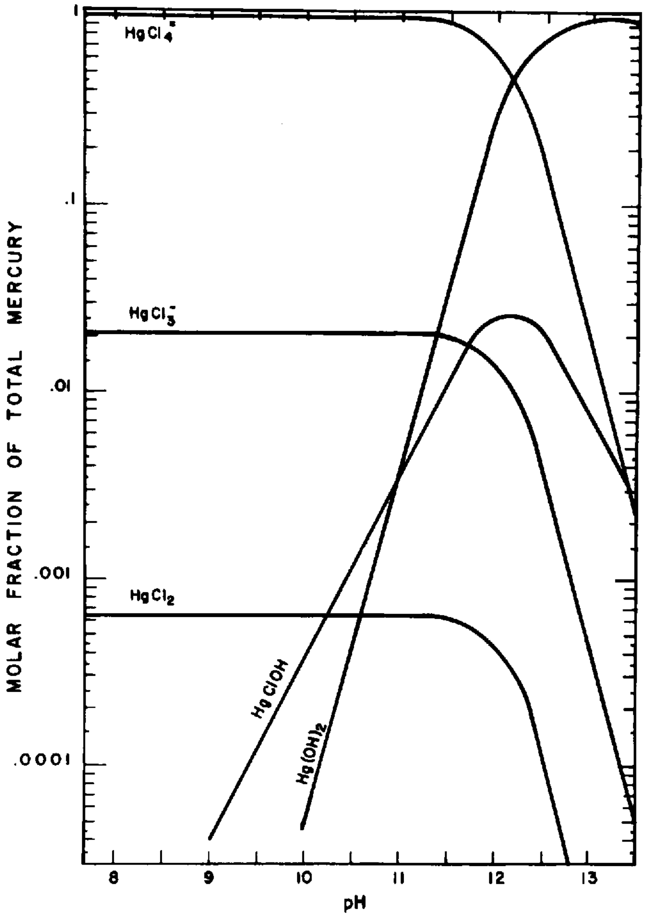
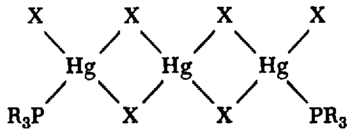


Fig. 2. The relative distribution of mercuric ion species in 4.63 M NaCl at 25°C as a function of pH.

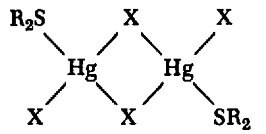
composes at about 400°C rendering the metal and molecular oxygen (Cotton and Wilkinson, 1966).

A wide variety of organic compounds can be formed and are known as organo-mercurials (Whitmore, 1921). These are the toxic substances of such concern today.

Mercury will also complex with neutral Lewis bases (that is, substances capable of donating a pair of electrons) such as amines, phosphines, and arsenes. Those formed with the latter two are more common and have structures of the form



where R represents an alkyl group. Such structures can be even more highly bridged, whereas dialkyl sulfides give only complexes of the form



With en (ethylenediamine), mercuric ion forms the complex $[Hg(en)_3]^{2+}$, which is one of the few cases where mercury appears in the octahedral form (Cotton and Wilkinson, 1966).

The mercuric ion can be reduced by many reagents, but the novel reduction by CO and by H_2 in the presence of perchlorate ions, as reported by Halpern (1956) and Halpern and Korinek (1956) deserves special attention. The reaction proceeds homogeneously at temperatures as low as 60°C, having the Hg_2^{2+} ion as an intermediate.

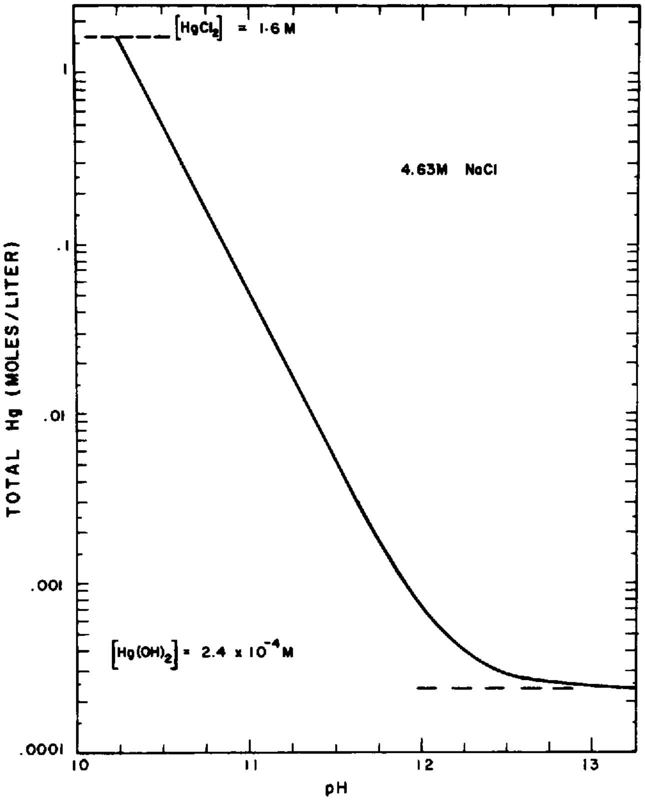


Fig. 3. The solubility of mercury (II) in 4.63 M NaCl at 25°C as a function of pH. Solid phase is Hg(OH)2.

For the special case of mercury behavior in brines at chlorine plants, we can focus our attention on mercuric chloride and hydroxide species. Equilibrium constants at 25°C for these are as follows (Butler, 1964; Civiatta and Grimaldi, 1968):

$Hg^{2+} + Cl^-$	$= HgCl^+$	6.5×10^6
$HgCl^+ + Cl^-$	$= HgCl_2$	3.02×10^6
$HgCl_2 + Cl^-$	$= HgCl_3^-$	7.1
$HgCl_3^- + Cl^-$	$= HgCl_4^{2-}$	10
$Hg\,ClOH + OH^-$	$= Hg(OH)_2 + Cl^-$	5.9×10^3
$Hg\,Cl_2 + OH^-$	$= Hg\,ClOH + Cl^-$	2.75×10^4
$Hg\,(OH)_2$ aq	$= HgO\,(OH_2)_{solid}\ K_S =$	2.4×10^{-4}

From these values and the assumption of unit activity coefficients, one can calculate the relative concentrations of the different species in 4.63 M NaCl (270 g/l). This should be the distribution of mercuric species in the depleted brine of a chlorine plant and is presented in Figure 2 as a function of *p*H. Similarly, the total mercury concentration at which HgO precipitates is presented in Figure 3.

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