

CONTROL OF MERCURY IN EFFLUENTS FROM CHLORINE PLANTS

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ABSTRACT

Background information as to the environmental effect of discharges of mercury is provided. The information has justified a programme, outlined in the paper, for reducing mercury in products, waste waters and vented air from chlorine plants using the mercury process. The strict separation of the waste waters and certain technical measures creates possibilities of reducing the discharges effectively. An 80 per cent reduction of the mercury in effluents was achieved, for example, by substituting indirect forced cooling of the hydrogen for the traditional direct cooling and returning the condensate to the head of the amalgam decomposers. The major cause of discharge of mercury with vented air was found to be leaking hot hydrogen in the cell room.

Different principles for the polishing of the final effluent and for the removal of mercury from the caustic soda produced are described.

INTRODUCTION

Mercury has recently been found to give rise to environmental problems of a very complex nature. The element appears to have been a part of man's environment during all time. Sea water and precipitation normally contain mercury in the order of 0.1 mg/m³ (ppb). It will not stay outside the ecological systems on land and in water as organisms tend to become enriched in mercury from their surrounding medium. Marine fish will consequently contain some 0.02–0.1 mg/kg (ppm) wet weight and freshwater fish 0.1–0.2 mg/kg or slightly more.

Westöö¹ was able to prove that mercury is present in fish essentially as methyl mercuric complexes. Jensen and Jernelöv² demonstrated that aquatic micro-organisms are capable of converting available inorganic mercury into the methyl mercuric ion and, under certain conditions, also into the water-immiscible, volatile dimethyl mercury.

The presence of mercury in the environment in dependence on natural factors has not a static but a highly dynamic character. The modes by which the transport takes place in the environment as a whole are known only fragmentarily, as are the possible sources and sinks. The available information is consistent with the assumption—at least as a working hypothesis—that the main part is transported either as water-soluble monomethyl or as volatile dimethyl mercury. *Figure 1* summarises this as yet partly hypothetical transport system in a simplified way.

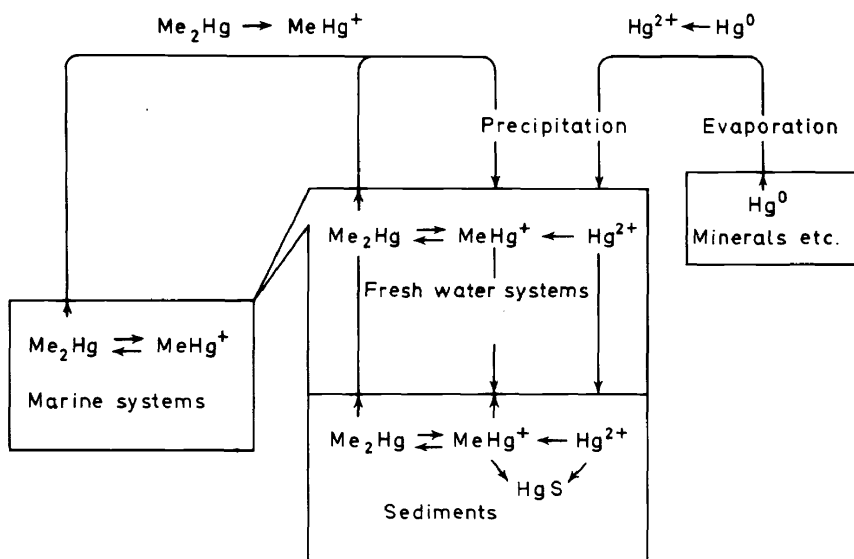


Figure 1. Tentative scheme of the circulation of mercury

The toxicity of mercury depends on whether its state is metallic, mono- or divalent inorganic, or organic in different forms. Meaningful discussions of the toxicological aspects of different uses of mercury will therefore require that the particular species under consideration is clearly defined. Methyl mercury complexes act by destroying the function of cells of certain brain centres in an irreversible way. Numbness of limbs, restricted range of vision, incoherent speech and motional disturbances are early symptoms of poisoning by methyl mercuric compounds. Paralysis and death will follow in severe cases. The poisoning has a cumulative aspect. Healthy cells may take over the function of damaged cells. The symptoms may not become manifest until a continuous addition of methyl mercuric compounds, e.g. through contaminated fish, has finally reduced the stock of healthy cells below the number required for proper physiological function.

The activity of man has increased the quantity of biologically available mercury in the environment, locally to high levels. Diffuse discharges related to urbanisation and technical development in general, and point discharges from specific industrial activities, have been contributory factors. The impact of a discharge on an ecological system is indicated by the resulting levels of methyl mercury in certain organisms. Stationary species, e.g. the commercially important northern pike³ (*Esox lucius*) have proved to be valuable indicator organisms for aquatic systems. The impact will depend not only on the quantity of mercury discharged but to an important extent also on its physical and chemical state and on the properties of the effluent. Factors related to the ecological characteristics of the discharge area will sometimes enhance, sometimes reduce, the effect of a discharge in terms of elevated concentrations of methyl mercury in a chosen biological indicator. The use of phenyl mercuric acetate for the control of microbial growth in pulp

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and paper mills thus gave a very high 'yield' of methyl mercury in fish, while the corresponding yield of the very substantial quantities of inorganic mercury originating from the chlorine plants was comparatively moderate in the majority of instances. There are cases known where the industrial discharges have had no apparent effect at all. There are several lakes in Sweden, on the other hand, where other sources than precipitation are virtually absent, although the concentration of methyl mercury in fish is high enough to justify its being classified as unfit (cf. below) for consumption.

THE SWEDISH SITUATION

The first Swedish reports indicating mercury to be a serious environmental hazard date from the late fifties. Analyses of a large number of certain ground-feeding birds and their predators, which had been found paralysed or dead, indicated the cause to be poisoning by mercury. The link between the observation that, for instance, the peregrine falcon (*Falco peregrinus*) was close to extinction and the use since 1940 of methyl mercuric derivatives for seed dressing was clearly established⁴. Figure 2 shows analyses of feathers

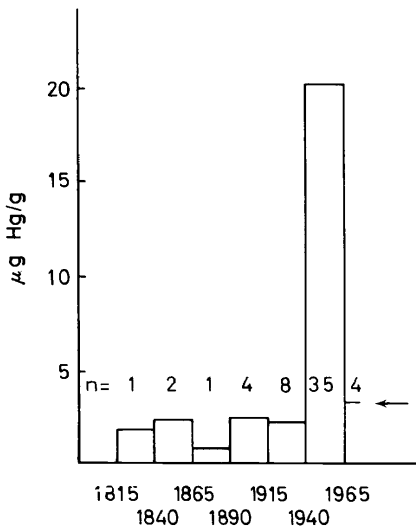


Figure 2. Mercury in the feathers of a female goshawk (*Accipiter gentilis*). After Johnels *et al.*⁵

of Swedish specimens of the goshawk (*Accipiter gentilis*)⁵. The effect of the introduction of methyl mercuric compounds in seed dressing formulations around 1940 and its legally enforced replacement by the 'environmentally labile' methoxyethyl mercuric acetate in 1966 is fairly obvious. The pioneers in this early, at first much disputed, work are indeed worth mentioning: K. Borg (Professor, Institute of Veterinary Medicine, Stockholm), A. Johnels (Professor, Museum of Natural History, Stockholm), E. Rosenberg

(naturalist and author, Örebro), and T. Westermarck (Professor, Department of Nuclear Chemistry, Royal Institute of Technology, Stockholm).

It was proven beyond doubt in early 1965 that the presence of mercury in industrial effluents might result in elevated concentrations of mercury in fish downstream from the point of discharge. Concern and worry became acute when this observation was combined with the finding soon afterwards that virtually all mercury in fish is present as a methyl mercuric complex irrespective of whether the origin is metallic, inorganic or organic^{1, 3}. There was simultaneously a breakthrough of information on the so-called Minamata disease⁶, of which a large number of persons in the Japanese city of Minamata died or were permanently disabled from eating fish contaminated with methyl mercuric compounds of industrial origin. There was then only one conclusion possible: the use of mercury for industrial or other purposes involves an obvious risk of environmental poisoning and must therefore be made subject to severe restrictions.

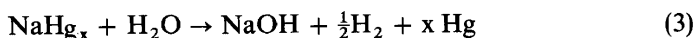
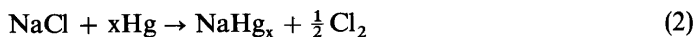
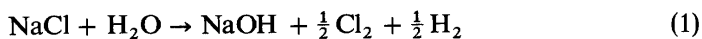
The first result was an almost immediate ban on the use of phenyl mercuric acetate in the pulp and paper industry, as this compound had been found drastically to increase the concentration of mercury in down-stream fish, in some cases up to 5–10 mg/kg wet weight⁵. Commercial fishing of specified species was later prohibited in any lake, stream or coastal water where the concentration of mercury in the particular species exceeded 1 mg/kg wet weight. The prohibitive measures were combined with a recommendation not to consume freshwater fish more than once a week.

Another result was the demand that the chlorine industry (at the time producing c. 250000 tons of chlorine per year) should take such technical measures that the little known, though probably very large, discharges of mercury (or, from a technical point of view, losses) were drastically reduced.

The chlorine industry and the Swedish Water and Air Pollution Research Laboratory had already agreed that the existing situation should be surveyed in a joint effort when the Swedish Environment Protection Board, late in 1966, officially requested that the chlorine industry should in future efficiently prevent discharges of mercury to the environment. The survey was to be combined with the planning of proper technical measures. The present paper will report the experience gained as a result of this agreement.

PROCESS DESCRIPTION

When chlorine and sodium hydroxide (caustic soda) are produced electrolytically by the mercury process, the net reaction (1) is divided into two stages (2, 3) taking place in separate process units. A typical flow sheet is shown in *Figure 3*. Parallel streams of saturated sodium chloride (brine,



300–310 g/l) and mercury (as mobile cathode) enter a primary cell with anodes of graphite. The cell is usually operated at 4.3–4.8 V. The concentration of the brine is reduced to 260–270 g/l during the passage through the cell. The

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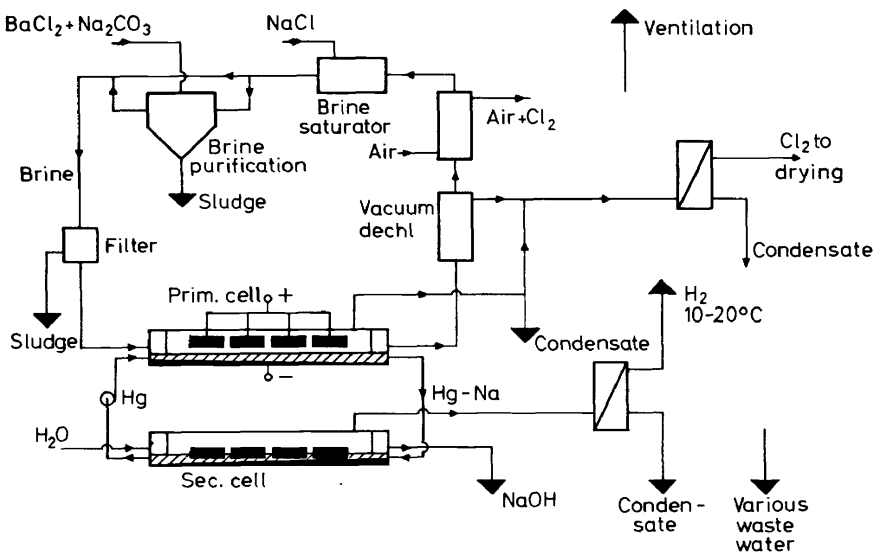


Figure 3. Discharges of mercury from a chlorine plant

sodium amalgam formed in the electrolysis is brought into reaction counter-currently with water in the separate, secondary cell (denuder) to give sodium hydroxide and an equivalent amount of hydrogen. The denuder is arranged for either horizontal or vertical flow and short-circuited with graphite elements. It is normally run to produce a 50 per cent caustic soda. The denuded mercury is returned to the primary cell by pumping. The brine circulates in a closed system from which water is normally lost only by evaporation and with the sludges formed in refining operations. The brine, after leaving the cell, is taken under vacuum for dechlorination and is subsequently aerated for removal of residual chlorine. It is saturated and then treated with sodium carbonate and barium chloride to remove impurities such as iron, alkaline earth metals and sulphate. When rock salt is used for brine make-up, the whole volume has to be treated, while only 10–20 per cent of the cycled brine is removed for treatment when the raw material is evaporated salt. After filtering to remove graphite particles and after adjustment of the pH the brine is ready for a new cycle.

The chlorine which is liberated directly in the primary cell and on vacuum dechlorination is cooled, dried with sulphuric acid and liquefied. The chlorine removed by aeration is converted into hypochlorite by absorption in lime or caustic soda. The caustic soda leaving the denuder is partially cooled and is then ready for delivery.

Equipment installed about ten years ago was designed for cell loadings up to 180 kiloamp. This corresponds to an annual production of *c.* 1.800 tons of chlorine per cell. The rectifier technology has since improved considerably, and cells with an annual capacity of 3.000 tons or more are now available on the market^{7, 8}.

ORIGIN OF MERCURY LOSSES: GENERAL CONSIDERATIONS

A review of the literature indicates that mercury losses of the order of 150–200 g/ton (metric) of chlorine have been considered, uncritically, to be quite normal or even small^{9, 10}. A recent report states that the U.S. chlorine industry consumed an average of 0.5 pound of mercury per ton of chlorine at the time when alarm went up in the spring of 1970, making countermeasures an immediate necessity¹¹.

The literature contains no useful information as to the distribution of losses between the different waste waters and products obtained in the process. The review gave the impression that proper consideration had not been paid to the question of whether the losses could be avoided or not. This indifference is rather remarkable, as the figure quoted above could correspond to an annual loss of as much as *c.* 5 per cent of the cell inventory.

The different points from which mercury is emitted in a traditional chlorine plant are indicated by broad arrows in *Figure 3*. Beside emissions which can be attributed to defined process stages, mercury is also emitted with waste waters from various cleaning operations and with the air passed through the plant for the purpose of ventilation.

The precise measurement of the quantity of mercury lost from a chlorine plant involves considerable practical difficulties. One reason is obviously that the existing plants were designed at a time when the control of losses was largely disregarded. The necessity for adequate facilities for flow measurement and sampling had not been foreseen. Installation of the required equipment afterwards, once the need had arisen, was in many cases a difficult matter. As a consequence the following survey of the mercury losses and of the measures taken to reduce them has to be based not only on actual measurements but also on judgment and on more or less approximate estimates. For convenience, all data will be given as grammes of mercury per produced metric ton of chlorine, unless otherwise stated.

CHLORINE SYSTEM

A small quantity of mercury (<1 g/ton) follows the chlorine leaving the primary cell. Part of this can be attributed to a carry-over of brine which normally contains some dissolved mercury, while the rest appears to result from a reaction between chlorine and metallic mercury in the vapour phase. The major part of the mercury and the brine will come down with the aqueous condensate separating in the conduits. The quantity reaching the drying and liquefaction systems will be insignificant provided that the condensate is withdrawn.

BRINE SYSTEM

The brine appears to contain 3–5 ppm of mercury when the cell performance is normal. This seems to correspond to an equilibrium concentration. The mercury is then present essentially as the tetrachloro complex HgCl_4^{2-} , at least when free chlorine is present. The concentration will increase considerably when the cell operation is disturbed or stopped by short-circuiting or interruption of energy supply. Unless brine is discharged as such for some

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reason, mercury can only escape from the brine system with the sludges obtained from precipitation and filtering. As the soluble tetrachloro complex is very stable at the chloride concentration in question and when free chlorine is available, mercury can be precipitated from brine only in the presence of impurities which form stronger, insoluble complexes or, in reduced form, when the dechlorination has been extensive. This may occur to some extent in the precipitation step, especially when rock salt is used for brine make-up. The sludge formed in the treatment of rock salts with sodium carbonate and barium chloride will in fact be rather rich in mercury. Analyses of deposits from the brine clarifiers in a plant using rock salt gave values of 8–15 g of mercury per kg of dry solids. The quantity of mercury thus lost (the sludge was previously discharged with the waste water) is subject to variations but for some types of salt may be of the order of 50 g/ton. When evaporated salt is used, the quantity of mercury removed by precipitation will be small, on the other hand, and seldom exceeds 2 g/ton of chlorine. The sludge obtained on filtering of the clarified brine before this is pumped back to the primary cell consists mainly of graphite. The solid phase is practically free from mercury.

HYDROGEN SYSTEM

The hydrogen formed when the sodium amalgam decomposes will leave the denuder saturated with mercury. As its temperature will be 70–100°C, the quantity of mercury leaving the cell system in this way will be appreciable, as appears from *Table 1*. The quantity lost will depend finally on how far

Table 1. Mercury in hydrogen from chlorine plants

Temp. °C	mg Hg/Nm ³ H ₂	g Hg/t Cl ₂	Temp. °C	mg Hg/Nm ³ H ₂	g Hg/t Cl ₂
0	2.19	0.68	40	77.4	24
10	5.85	1.8	50	170	53
20	14.5	4.5	60	370	115
30	34.2	10.6	70	824	250

the mercury is cooled and how the condensate is handled after being collected from the coolers.

Water of environmental temperature (0–20°C) was previously used for the hydrogen cooling in most Swedish mills. The resulting temperature of the emitted hydrogen would then normally be 10–30°C. As over-saturation was found to be practically negligible, the loss of mercury varied between 2 and 11 g/ton, with an annual average of about 5 g/ton.

The separation of the metallic mercury formed on cooling of the hydrogen from the simultaneously condensed water presents problems which previously were largely overlooked. The metal condenses partly as small, very stable droplets with little tendency to coalesce. They sediment slowly and will therefore pass conventional equipment for gravity separation fairly

easily. As the condensed water is strongly alkaline (pH *c.* 12), the metallic mercury is readily oxidised when air is allowed to enter. When direct cooling is employed, the efficiency of mercury separation will be reduced further because of the larger volume of water which then has to be handled.

The exact measurement of the quantity of mercury lost with the condensate from the hydrogen coolers encounters the difficulty of sampling a system containing two phases which differ widely in density. Continuous samplers, especially those of pneumatic type, are usually inadequate for the purpose. Manual sampling will therefore be necessary in most instances. Values obtained from 24-hour survey (sampling every hour) have accordingly varied considerably, indicating losses from *c.* 25 up to 75 g/ton of chlorine. There is no doubt, however, that the condensate from the hydrogen coolers is one of the most important sources of mercury losses.

CAUSTIC SODA SYSTEM

The caustic soda contains finely dispersed metallic mercury which, above levels of *c.* 5 ppm, may be observed as a greyish haziness. Part of the mercury settles in the conduits and subsequently, very slowly, in the storage tanks. The quantity settled reflects to some extent the degree of dispersion: only particles above a certain minimum size will settle out within a reasonable time. With normal times of storage at the production site, the separation achieved in the tanks will be restricted.

The mercury content of the caustic soda produced at the eight Swedish plants operating in 1967 was estimated by analysing sixteen samples from each mill. The results are summarised in *Table 2*. Half of the samples were

Table 2. Mercury in caustic soda from Swedish chlorine plants

Plant	Hg in NaOH, mg/l		Average	
	I	II	I	II
A	1.7 - 4.0	1.8 - 3.3	2.5	2.2
B	1.8 - 3.6	2.1 - 3.2	2.8	2.6
C	0.6 - 1.5	0.6 - 1.1	1.1	0.8
D	0.07- 0.33	0.07- 0.33	0.22	0.20
E	6.0 -10.7	4.7 - 9.8	8.1	6.4
F	1.6 - 6.2	0.9 - 2.1	3.6	1.5
G	5.0 -12†	4.1 -18.8†	13.6	12.2
H	0.05- 0.27	0.15- 0.34	0.19	0.24

I: Sample collected after the denuder

II: Sample collected at tap for delivery

† Operational disturbance during sampling period

collected in the cell room and the rest at the tap station for delivery to tank wagons or from an equivalent point. As is evident from the table, there are considerable differences between the mills, while the caustic soda from each particular mill shows only moderate variations in mercury content.

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The differences displayed in the table seem to be due to several factors, such as cell loading, type and size of denuder and concentration of caustic soda produced. The mercury lost with the product will thus vary from 0.4 up to 15–20 g/ton of chlorine when there are no operational disturbances.

OTHER WASTE WATERS

A certain quantity of mercury-containing waste water arises on cleaning of cells and cell room facilities, on reactivation of denuder graphite, from equipment for recovery of mercury in waste amalgam ('cell butter') and the like. The mercury may be present both in metallic and in oxidized form in these waste waters. The total quantity will be very variable, in dependence on local practice. When unnecessary spillage is avoided to an acceptable extent, and when the sewers are equipped with satisfactorily dimensioned gravity traps for metallic mercury, it appears not to exceed 10 g/ton of chlorine when mill operation is normal.

VENTILATION SYSTEM

The cell rooms of chlorine plants have to be well ventilated in order to keep the temperature at an agreeable level and to prevent hazardous concentrations of mercury vapour. Up to 500.000 m³ of air per hour may thus pass the cell room in a plant making 100 tons of chlorine per day. An exact measurement of the quantity of mercury escaping through the ventilation system is obviously difficult. Of the measurements previously reported from Swedish mills, only two were fairly satisfactorily carried out. The reported data indicated losses of the order of 15–25 g/ton.

Several factors influence the quantity of mercury emitted via the ventilation system. The temperature of the cells and of the cell room floor, the type of mercury pump used, operational disciplines concerning mercury spillage, are all contributory factors.

It has been assumed more or less automatically that spillage of mercury on floors and gangways are of major importance for the concentration of mercury in ambient air. This seems not to be the case, however. A test using marked droplets of mercury placed in various parts of the cell room indicated that the rate of evaporation is very slow under the prevailing conditions. Evidence of this is that a droplet might remain on the hot cell lid for a long time. Oxidation of the metal surface to mercurous or mercuric chloride by the action of free chlorine would be a rational explanation of this phenomenon. Although spills of mercury provide an indication of poor operational discipline and inadequate routines, they cannot apparently account for more than a part of the losses with ventilation air.

It was further found that the quantity of mercury absorbed by concrete floors with no cracks is limited. One study gave a value of the order of 60 kg per 1.000 square meters. Large quantities are found locally where cracks are frequent (*Figure 4*).

Available information indicates that leaky packings and joints which

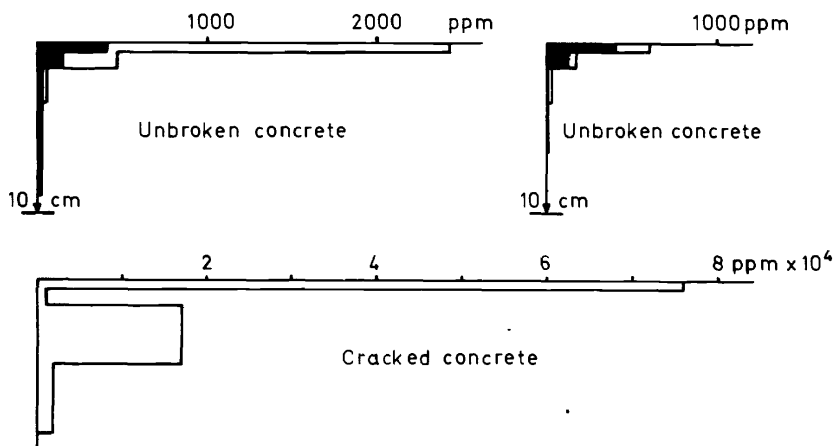


Figure 4. Mercury in the cell room floors of chlorine plants. Solid areas represent mercury soluble in dilute hydrochloric acid.

allow hot hydrogen to escape are the major sources of mercury in ambient air. It may be mentioned that measurements in one mill showed that *c.* 20 per cent of the losses to the ventilation system originated from the mercury pumps serving the cells of the older section of the cell room.

MAIN SEWERAGE

It has hitherto been the traditional practice that all waste water (including cooling water, which constitutes more than 90 per cent of the total water consumption) is combined in one sewer for transport to the receiving lake or stream. Partial separation of sewers may occur in some mills. This will be due to local conditions of a practical character rather than to anticipation of the need to treat the effluents. During the described survey work it was observed by actual measurements that the quantity of mercury discharged by the main sewer exceeded the combined quantities found in the separate waste streams making up the final effluent. This finding could be explained partly by the practical difficulties in sampling waste waters containing metallic mercury which proceeds slowly along the bottom of the sewer. Temporarily installed weirs for flow measurements would block this stream of mercury, so that it would escape sampling and be unaccounted for. The chief reason appeared to be that the metallic mercury escaping into the main sewer was there brought into contact under highly turbulent conditions with other effluents containing chlorine. Oxidation and subsequent dissolution of mercury would take place. The quantity of mercury lost with the waste water, as accounted for inside the mill, increased in one instant by no less than 40 per cent through oxidative leakage from metallic mercury in the main sewer. In this connection it should be noted in addition that leaky joints of old sewerage provide an excellent opportunity for the escape of metallic mercury.

INTERNAL MEASURES FOR REDUCING MERCURY LOSSES

The work which has now been carried out in the Swedish mills to reduce the losses began with the planning of the necessary internal measures. The first step was to separate the sewerage system in order to reduce the volume of waters requiring special treatment. The principle applied is that uncontaminated cooling water, constituting more than 90 per cent of the total effluent, the waste waters, normally carrying chlorine, and the spent sulphuric acid from the chlorine dryers, should be discharged separately from the mercury-containing effluents. It is of special importance that effluents containing free chlorine are not brought into contact with metallic mercury.

The various effluents containing mercury have to be characterized with their compatibility with different procedures for final treatment. If pre-treatment of a particular effluent by, for instance, separate neutralization is required, the necessary facilities have then to be provided. Depending on the local conditions, the construction work necessary for this separation of sewers may in some instances be complicated and costly, and in others a fairly simple undertaking.

The internal measures otherwise taken are illustrated schematically in Figure 5 and may be summarized as follows.

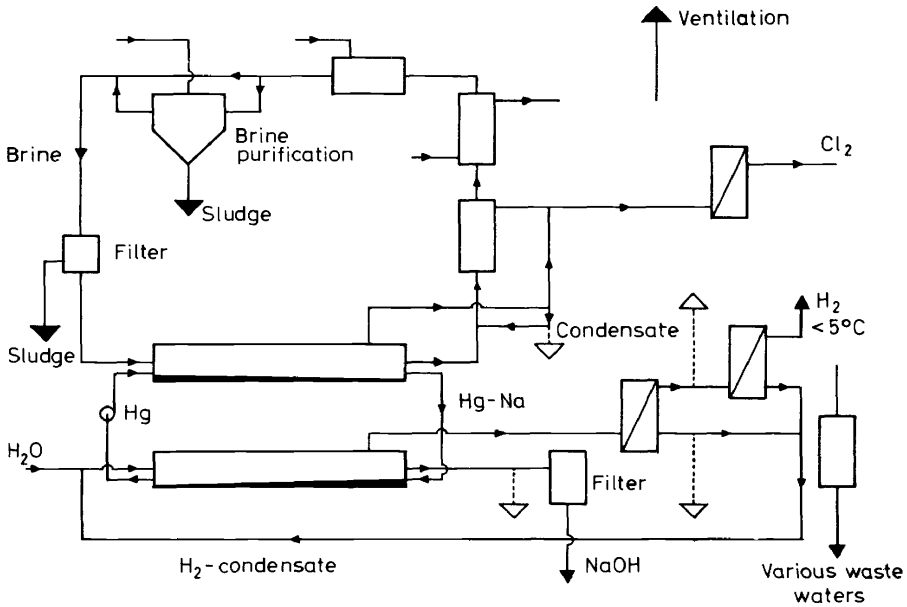


Figure 5. Discharges of mercury from a revised chlorine plant

CHLORINE SYSTEM

The small quantity of mercury lost with the condensate formed in the chlorine conduits may be recovered simply by returning the condensate to

the brine, either before or after the vacuum dechlorinator. Optimizing a maximum mercury recovery and a minimum volume of returned condensate with respect to the necessity for maintaining the water balance in the brine system seems to be achieved most conveniently by the installation of a tube cooler inclined backwards. This will allow monitoring of the volume of returned condensate. The negligible quantity of mercury remaining will be removed in the drying system.

BRINE SYSTEM

The mercury-containing sludge formed on treatment of the brine with precipitating chemicals is bulky and difficult to dewater. The properties improve considerably on addition of a sludge conditioner of synthetic type. For mills using rock salt, it seems profitable to install equipment, e.g. a filter press, for sludge dewatering and subsequent recovery of the contained mercury. This is most certainly not the case in plants using evaporated salt, however. There it seems most suitable to thicken the sludge and then introduce it in the system for treating the cell room effluent and similar waste waters.

The graphite-containing filter sludge is too low in mercury to be a pollutant from that point of view. The main disadvantage of discharging this sludge is its tendency to settle out in the receiving water.

The potential build-up of water in the brine system is a critical problem in a chlorine plant based on the mercury process. It was previously common practice to correct a lack of balance simply by discharging a suitable volume of brine. This practice must, of course, be abandoned. A minimizing of additions of water when adjusting the pH and a monitored removal of chlorine condensate will be necessary. A further possibility is to choose a procedure for the final treatment of the effluents which is capable of handling brine as well.

The brine system of some mills may have to be redesigned in order to eliminate any discharges of brine on major operational failures. This is the more important as the mercury concentration may be exceptional on such occasions.

HYDROGEN SYSTEM

The Swedish mills have equipped their hydrogen systems with coolers capable of reducing the temperature of the emitted hydrogen to below +5°C. Indirect cooling is used throughout. The condensate may then be returned to the denuders as feed water. In two mills the denuders are equipped with precoolers for direct return of a major part of the condensate with the contained mercury. This has the obvious advantage of reducing the quantity of mercury which is recovered and handled externally. According to reports, the return of the condensate involves no problems from an operational point of view. In one mill producing *c.* 100 tons of chlorine daily, the simple measure of returning the condensate brought down the annual losses of mercury with the waste water from, in rough figures, 1.000 to 200 kg.

CAUSTIC SODA

The Swedish authorities now require that marketed caustic soda shall not contain more than 0.5 mg of mercury per litre. This is achieved by filtering the caustic soda through precoat disc filters. Special grades of carbon have to be used as precoat. If the filtration is done at the proper temperature, a product of excellent quality will result. The spent filter medium is washed free of caustic soda and the mercury may then be recovered by distillation.

Data from recent installations indicate that the production of caustic soda with 0.2–0.3 mg of mercury per litre will meet no difficulties, except that the screens for supporting the precoat tend to corrode faster than is quite acceptable. A further reduction will require the use of two filters in series.

TITANIUM ANODES

It seems that several of the Swedish chlorine producers are now studying whether or not it will be technically and economically feasible to substitute titanium anodes for the traditional anodes made of graphite. Besides appearing to be a technical asset generally speaking, the use of titanium anodes would have considerable advantages in the discussed respect. Dismantling of cells for cleaning would have to be done less frequently and the graphite sludge would be eliminated from the brine filtration. It may further be assumed that the chlorine would carry less impurities.

CELL ROOM SEWERAGE

Mercury losses not directly related to the process systems occur through spillage in the routine maintenance of the cells or when the cells are dismantled for cleaning and repair. Apart from accidental leaks, equipment for reactivation of graphite from denuders and for wet recovery of mercury from wastes, such as solidified amalgam (cell butter) from cell boxes, are other sources of mercury losses. The sewerage system is normally equipped with traps of water-seal type for recovery of 'loose' metallic mercury. It has been found by inspection of the sewers succeeding these traps that they are in many instances either under-dimensioned or function unsatisfactorily in other respects.

It has been clearly demonstrated in several mills that the quantity of mercury accidentally leaving the process systems can be very much reduced if the cell room routines are overhauled and if the cell design is suitably modified with respect to details known to be subject to leakage. The provision of adequate equipment for operations in which spillage readily occurs, e.g. the removal of cell butter and the replacement of denuder elements, will bring further improvements and help to raise the attention of the personnel. The overall costs for the latter activities are difficult to assess but seem to be moderate, or may even be balanced by the improved recovery of mercury.

Further improvements have been the replacement of the traditional, usually more or less corroded, concrete floor channels by V-shaped channels lined with epoxy resin or PVC. The numerous small mercury traps in the sewerage have been omitted in favour of a single, amply dimensioned

sedimentation tank making possible an efficient removal also of finely dispersed mercury.

The old cracked concrete or asphalt floors of the cell rooms are being repaired and covered with epoxy resin or PVC wherever possible. The use of hoses with self-closing valves has helped to reduce the volume of waste water originating from various cleaning operations.

LOSSES WITH VENTILATION AIR

The losses with the ventilation system depend, as has been pointed out, on several factors, some of which are difficult to control by simple measures. Reports indicate that the various measures taken hitherto may have cut these losses by some 50 per cent or more.

The caustic soda and hydrogen systems are of special interest in this connection. Leakages involving hot hydrogen are equivalent to costly losses of mercury. It is obvious that many traditional cell designs are inadequate in this respect. The desire to cut down mercury discharges will prompt efforts to design as far as possible closed constructions. The plant operators will, in addition, have to improve their watch that gaskets and tubings etc. are tightened or replaced before the need becomes acute.

The various measures discussed above may often be difficult to develop in an existing mill, designed before discharges of mercury were recognized as an environmental hazard. The situation differed in the ninth Swedish chlorine plant which went on stream during 1969. The possibility of keeping the mercury discharges at an extremely low level were carefully considered from the very start of the design work. As a result, the calculated losses with waste water are less than one gramme of mercury per ton of chlorine. The estimated remaining losses of mercury after instituting the possible internal measures are summarized in *Table 3*.

Table 3. Losses of mercury from a reconstructed chlorine plant

Source	g of Hg/t of Cl ₂	Remarks
Chlorine	<0.5	
Hydrogen	1	Cooling to +5°C
Caustic soda	<1	After filtering
Brine, precipitation sludge	<2	Evaporated salt used
Brine, graphite sludge	nil	
Hydrogen condensate	0	Returned to denuder
Other effluents	<0.5	After final treatment
Ventilation system	variable	

EXTERNAL MEASURES

Properly carried out internal measures will leave a fairly small volume of mercury-containing effluent. The value 0.5–1 cubic metre per ton of chlorine

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has been quoted for some mills. Considerable deviations due to local conditions may occur, however. The average mercury concentration will be of the order of 5 mg/l according to available data, but variations may be expected.

The Swedish authorities require that the final effluent is treated for removal of mercury. Several alternative forms for such treatment exist. All of them appear to allow a reduction down to 0.1–0.3 mg of mercury per litre of treated effluent under practical conditions.

There are three fairly obvious basic principles for the removal of mercury:

- (a) Conversion to the metallic form by reduction and subsequent separation, using filtering or stripping techniques.
- (b) Oxidation followed by separation on an ionic exchange resin.
- (c) Precipitation, possibly combined with flocculation and separation by gravity settling or flotation.

Reduction of mercury and separation of the metal on a disc filter using activated carbon as precoat is reported to work quite satisfactorily in the recently constructed plant referred to. There is a choice of reducing agents, but lack of data on operational conditions makes comparison impossible. The principle was tried in an older plant but with little success. The effluent to be treated contained too much solid and semi-colloidal matter, probably emanating from corroded concrete and the like, to permit reasonably long filter cycles.

Mercury may be absorbed on an ion-exchange resin at high chloride concentrations or on a cation exchange resin at low concentrations. Cationic exchange has been practised on a pilot scale in one Swedish plant. It operates quite well under normal conditions but obviously involves certain problems. Pretreatment by filtering will be required. Facilities must be available for catching larger accidental spills of brine to prevent an uncontrolled displacement of absorbed mercury from the resin. The mercury-rich eluate obtained in the regeneration cycle will have to be treated in some way. It has been claimed that the eluate can be returned to the system for brine purification, but the claim has been questioned.

An attempt has been made in one or two places to minimize the volume of water used for cleaning etc. The water is bled into the brine purification system. This method is most probably not practical in the long run for obvious reasons.

Processes based on precipitative removal of mercury can be made robust and reliable but do not appear to be very sophisticated. The use of sodium sulphide as precipitant and ferric chloride as flocculant has been studied at our Institute. This combination has the advantage that any excessive sulphide will be oxidised and thus give rise to no problems: $2\text{Fe}^{3+} + 3\text{S}^{2-} \rightarrow 2\text{FeS} + \text{S}$. The process has the further advantage that waste waters which are highly concentrated with respect to brine can be handled provided that the pH is controlled satisfactorily. Optimum pH is around 8.5.

The volume of sludge obtained will be of the order of 0.3–0.5 litre per cubic metre of treated effluent. The addition of synthetic flocculants will improve the mechanical properties of the sludge considerably. If it is found unpractical to recover the rather small amount of mercury involved, the sludge may be partially dewatered and placed under ground in a way that does not allow air to enter.

DIAPHRAGM CELLS

During the early part of the work reported in this paper, it was discussed whether or not the mercury process should be abandoned and the corresponding capacity raised in the form of plants based on the diaphragm process. This drastic alternative was studied carefully. The negative attitude of industry was summarized in a report on this subject to the authorities as follows:

- (a) the mercury process will offer the better possibilities of technical development,
- (b) the mercury process is more acceptable in Sweden with respect both to construction and operation costs,
- (c) the diaphragm process provides a caustic soda which may not be accepted for certain uses,
- (d) the discharges of mercury can be reduced by technical measures to a level which appears to be acceptable from the environmental point of view.

The industrial position appears to have been accepted by the authorities. All new developments in the Swedish chlorine industry are thus planned for the mercury process.

CONCLUSION

The mercury losses of the chlorine industry present a spectacular case of some pedagogical value. It may be assumed that large, and largely unnecessary, losses of valuable process chemicals are a feature which is not unique to this particular industry.

There are no available data of the actual costs for the cleaning-up programme. They seem to have been unexpectedly low in a few cases and quite high in others, depending on whether the local conditions were favourable or not. The costs have been balanced by the reduced costs for replenishment of the mercury stock, at least partly. A more important economical factor is possibly the resulting increase of operational efficiency. It has been claimed, rightly or wrongly, that the modernization of equipment and the rationalization of routines forced upon the chlorine industry have increased the practical capacity to a significant extent.

The 'memory' of the previous discharges, that is their effect on the environment, is expected to vanish only slowly in certain areas and at a noticeable rate in others. Urbanisation as a diffuse source of mercury contamination may always be apparent. The point sources, locally giving rise to hazardous levels of mercury in certain organisms, are seemingly eliminated by moderate efforts once the practical problems have been properly identified.

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