EURO CHLOR

representing the European Chlor-Alkali Industry

A Major Group within CEFIC

To - VS Executive Board 1/5/94

EURO CHLOR

REPORT OF THE TASK FORCE

CONSIDERING

THE PHASE-OUT OF MERCURY CELLS BY 2010

OCTOBER 1993

CTL010001

Avenue E. Van Nieuwenhuyse 4, Box 2 - B-1160 BRUSSELS
Telephone: 02/676 72 11 Telex: 62444 CEFICB
Telefax: 02/676 73 01

1 SUMMARY

Mercury is a ubiquitous environmental pollutant with numerous sources - both natural and anthropogenic - and a complex biogeochemical cycle. Natural sources of mercury include volcanoes, geysers and hot springs; mineral ores; and ground-water, surface waters and the oceans. Anthropogenic sources include smelting and refining of mercury-containing ores, waste incineration, combustion of fossil fuels and a variety of manufacturing processes.

Mercury exerts its ecological effects through the process of bioaccumulation and is toxic to most organisms at relatively low environmental concentrations. It can form a variety of chemical compounds (both organic and inorganic) in combination with carbon, chlorine, nitrogen and other chemical elements. Once released into the environment, mercury and mercury compounds can undergo chemical transformation through photolytic, microbial and/or chemical mechanisms.

The most toxic forms of mercury are organic mercury compounds, in particular, methyl mercury.

Due to the persistence of mercury in the environment, the mercury released in previous years can continue to affect air and water quality for years after cessation of the activities that initially released the material. For this reason the present day mercury concentrations in the environment continue to rise.

From studies in Sweden there is some evidence that decreasing pH due to acid rain is a factor increasing the mercury concentrations in the environment. Research also indicates that under conditions of low pH, more mercury is able to undergo methylation.

Against this background, industrial discharges of mercury have, for many years, been stringently regulated.

Current data estimates that approximately 71% of worldwide emissions of mercury are due to anthropogenic sources. The single largest source of mercury emissions is fossil fuel combustion, at approximately 31% of the total emissions of 20665 tonnes for 1983.

In comparison to this, the European chlor-alkali industry released 25 tonnes of mercury to the environment in 1992. Mercury emissions per tonne of chlorine capacity have been reduced by 86.5% since 1977. This improvement has been brought about by significant capital investments and by the industry's commitment to environmental improvement.

The European chlor-alkali industry comprises about 25% of the world installed capacity, most of it in mercury cell technology. Several cellrooms have undergone conversion from mercury technology in recent years. These decisions have been based on the sound economics of individual cases amidst a background of increasing environmental performance standards.

Certain plants due to the age and condition of equipment coupled with local environmental scenarios have found that the most favourable route by which upgrading of plant standards can be achieved is via conversion to either membrane or diaphragm technology. Cost savings such as energy and waste handling were taken into account, but in many cases the driving force was the requirement of significant capital spending in order to uprate standards.

Many mercury plants are however already operating to proposed 1996 standards and have installed a range of mercury recovery/treatment equipment. If the best available technology was installed in all current mercury plants in Europe then mercury emissions would be reduced by 44% to 14 tonnes a year and it can be expected that new technology in years to come will further reduce this figure.

On analysis of all the facts, the decision to phase-out all mercury cellrooms by 2010 on an environmental basis must surely be questioned. At 0.07% of the most conservative estimate of global mercury emissions, the industry does not constitute a major source of mercury pollution.

Since the overall aim is to reduce the impact of industry on the environment then each situation should be assessed on an individual plant basis. Greater benefits may be achieved in many cases by diverting the capital into projects requiring more pressing environmental solutions. Prioritisation of the environmental improvement to be brought about by the available capital will not, in many cases, lead to the conversion from mercury to membrane. It would be unfortunate if pressures were unreasonably brought to bear on this conversion process, such that the capital was diverted from much larger problems, some of which will be very amenable to significant improvement.

Thus it can be concluded that all cases should be taken on their merits and that blanket requirements for conversion to membranes may prevent the overall improvement to which the industry is committed.

2 INTRODUCTION

For more than 2000 years mercury has been put to a wide variety of uses by man and a public awareness has gradually developed that some aspects of its use can give rise to toxic hazards. Serious effects were identified outside the EC in the 1960's and early 1970's. The main incidents arose (1) from the consumption of fish containing a high level of methyl mercury as a result of an industrial effluent containing methyl mercury, and (2) from the consumption of grain treated with alkyl mercury fungicides and intended for use as seed. Specific classes of organic mercury compounds are the major toxic forms of mercury.

As a result of these incidents, which caused a large number of deaths and disablements, many government authorities and international agencies have reacted sharply and have set very stringent standards on the discharge of all forms of mercury. This reaction has been promoted by evidence that mercury can be converted into the methyl form under certain conditions. However, reverse reactions are known to occur and so it seems probable that some sort of equilibrium becomes established. Since mercury is widespread in the environment and is generally not found in the organic form it would appear that conditions do not, in general, favour its formation.

The European chlor-alkali industry comprises about 25% of the world installed capacity, most of it in mercury cell technology. The industry has worked closely together for a number of years in connection with the environment issue, having jointly set out to establish lower levels of loss to the environment and hence increase the margin of security. Facilities have been set up to monitor future progress. The industry intends to maintain an active role, and to assist in the understanding and reasonable and controlled improvement of the situation.

3 GLOBAL MERCURY EMISSIONS

Very considerable confusion surrounds the estimates of mercury released to the environment, in particular that arising from natural sources. Literature published in 1990/91 suggests that the figures derived in the 1970's were incorrect by an order of magnitude. For example, a recent report quotes mercury releases from volcanic activity to be 20 t/yr compared to a 1970's estimated that such activity formed the largest portion of a natural release totalling 150 000 t/yr. A further example of confusion is a 1987 UNEP (Assessment of the State of Pollution of the Mediterranean Sea by Mercury and Mercury Compounds, Athens 1987) report quoting a natural atmospheric emission of 26 820 t/yr compared to a 1993 OECD (OECD Cooperative Risk Reduction Activities for Certain Dangerous Chemicals : Mercury - Draft Status Report, March 12, 1993) report quoting 2500 t/yr.

Taking the most pessimistic median values from the OECD report gives Table 3.1.

Table 3.1

Worldwide Emissions of Mercury to Air, Soil and Water 1983 (te/yr) (median values)

Source	Atmosphere	Water	Soil
Coal combustion	2075	1800	2585
Metal production	130	20	40
Refuse incineration	1160		
Waste water		300	400
Wood combustion	180		
Metal mining		75	
Urban refuse			130
Commercial wastage			685
Manufacturing		1160	
Agricultural waste			850
Logging waste			1100
Sewage sludge		160	
Mine tailings			1675
Smelter wastes			165
Sub Total	3545	3515	7630
Natural Sources	2500	1010	2465
TOTAL	6045	4525	10095

20665

4 EFFECTS ON MAN AND NATURE

Whilst the mining of mercury and the uses of mercury in agriculture and industry have undoubtedly fallen over the last decade, the concentration of mercury, particularly in fresh water lakes far removed from industrial activity has been increasing.

The most credible theory for this is unrelated to increasing or decreasing anthropomorphic mercury uses. There is a large natural cycle of mercury arising from volatilisation, transport and deposition. The residence time in the atmosphere has been estimated from 6 days to 2 years. These significant lifetimes would result in the potential for deposition of atmospheric mercury at thousands of kilometres from the source and imply that atmospheric mercury may be relatively homogeneously distributed in the troposphere. Most atmospheric emissions are of the elemental form but the oxidative nature of the atmosphere has the ability to convert this elemental form into

more oxidised states that have higher solubilities. That fraction of soluble mercury will eventually be precipitated into surface waters. Atmospheric kinetics indicated that the presence of the acidifying species SO_2 and NO_x in cloud systems will favour the removal of mercury from the atmosphere through wet deposition. Hence, increasing acid rain will result in more deposition of soluble mercury in lakes. Moreover, low pH and low alkalinity in lakes enhanced by the acid rain effect has been shown to make more mercury available for methylation. In addition such freshwater lakes have often comparatively high dissolved organic carbon contents, predominantly humic and fluvic acids, mobilising mercury in the aquatic system and forming methyl mercury. Conversely, the abundant and thus constant mercury concentration in the oceans (approximately 70 million tonnes), the buffering effect of the salinity and the oxygen-poor environment of many industrial coastal waters (leading to the geological sink of precipitated mercuric sulphide) results in a very low conversion of elemental mercury to methyl mercury in open water systems such as the North Sea.

Moreover, acidic precipitation will by itself dissolve and weather further mineral-bound mercury thus increasing the burden on the lakes. Finally, methyl mercury itself is volatile and can therefore be volatilised, transported and re-precipitated.

The focus on methyl mercury is important because this is the largest source of mercury entering the human body. Ingestion can take place by a variety of pathways but the most significant route is via fish. Fish consumption by man accounts for about 50% of his total intake and for 90% of the methyl mercury intake. Ingested methyl mercury compounds are almost completely absorbed by man and excreted very slowly. If absorbed in large enough quantities they cause irreversible damage to the central nervous system. Methyl mercury is recognised as the most hazardous form of mercury in the environment. The World Health Organisation (WHO) have laid down a Permitted Tolerable Weekly Intake figure of 0.3 mg/per person/per week, of which not more than 0.2 mg should be in the methyl form. Typical dietary intake for Western Europeans is in the range of 0.07-0.15 mg/per person/per week.

In the absence of mercury bearing effluents, freshwater fish typically contains 0.2 ppm mercury. Certain predatory species (eg Bass, Pike) may contain up to 0.5 ppm. Marine fish and shellfish in North Sea coastal waters, in the absence of effluent streams, currently average 0.15 ppm mercury, whereas mercury bearing effluents raise the mean level to about 0.3 ppm, with individual samples reaching 1.0 ppm. It is pertinent to relate this to the experience at Minamata Bay where the mercury in sediments rose to over 2000 ppm and in fish to 50 ppm. During the period 1959 to 1972 the mercury in fish in Minamata Bay dropped to about 0.4 ppm without any significant change in the mercury content of the sediments. This strongly suggests that the high level of mercury in fish in the bay were due directly to the input of organic mercury in industrial effluents rather than to the mercury contained in the sediments.

Mercury is thought to have little effect on microbes and plankton. Most aquatic life is exposed to methyl mercury due to the natural bacterial action. Similarly little effect is shown on aquatic plants. Indeed some plants such as water hyacinth and duckweed are known to remove mercury from waste water and some interest has been shown in their environmental potential. Terrestrial plants absorb mercury from the soil, although effects are mediated by the strong absorption of mercury by soil. Only very high mercury concentrations have been shown to inflict any damage. Bio-accumulation is uncommon, with mushrooms (strictly a fungus and not a plant) being the exception to the rule with accumulation factors of up to 100.

Toxicity research to date indicates that direct mercury toxicity to both aquatic and terrestrial invertebrates is unlikely.

Neither terrestrial nor marine mammals have been well-studied. Tuna are known to bio-accumulate large quantities of mercury. This appears to be no different for coastal tuna than deep sea tuna. Bird studies have shown no effects, other than a particular epidemic associated with seed-eaters eating a very heavily contaminated crop dressed with a now-banned fungicide in the 1970's.

The UNEP Report on Pollution of the Mediterranean Sea stated:

"High body levels have been observed in many species in polluted and unpolluted areas. Past discharges of large amounts of mercury from chlor-alkali and petrochemical plants (approx 10 MT/year) have locally increased the mercury concentration in the biota. Organisms living within a range of 10 to 20 km from the discharges have mercury levels 1000 to 10 000 times about background levels, **but any adverse effects on marine biota observed could not be attributed to the higher mercury concentrations but rather appear to be due to the release of other wastes discharged simultaneously.** Discharges of such magnitude should not occur any more in the Mediterranean because increasingly stringent controls and changes in process technology have led to a marked reduction in industrial mercury discharges, but the release of mercury from past discharges will keep levels in marine ecosystems high for many years."

5 MERCURY FROM CHLOR-ALKALI PRODUCTION

5.1 The Process

Chlorine is produced commercially by the electrolysis of brine, co-producing sodium hydroxide and hydrogen. Potassium hydroxide is also produced by electrolysis of potassium brine.

Today, three technologies are in operation around the world - the diaphragm process, the mercury process and the membrane process. The European industry has most experience with the mercury process, in use since 1892. Historically, this was developed because of its advantages over the rival diaphragm process:

→ the quality of the caustic soda
→ the quality of the chlorine
→ the energy consumption

In this technology, the electrolytic decomposition of the alkali chloride salt requires two essential parts - an electrolyser and a decomposer.

In the electrolyser an aqueous solution of the salt is electrolysed, making use of a permanent anode and a flowing mercury cathode. Chlorine gas is collected at the anode and alkali metal (sodium or potassium) is deposited at the surface of the mercury cathode, in which it is dissolved to form a liquid amalgam.

In the decomposer the amalgam is decomposed with water to form alkali hydroxide and hydrogen gas.

A closed circulation of mercury is maintained through both the electrolyser and the decomposer. The alkali chloride salt is chemically purified and recycled through the electrolyser, with the depleted brine either disposed of, or much more commonly, re-strengthened by addition of salt.

5.2 Current Mercury Emissions

In this process, emissions of mercury to the environment can come from:

- the products : - entrainment in hydrogen
  - alkalis;
- the waste water streams;
- gaseous process vents;
- the ventilation of the cell rooms.

Table 5.1 shows how these figures have evolved for the Euro Chlor companies over the last 15 years.

Table 5.1

Mercury Emissions from Euro Chlor Cell Rooms (g Hg/te Cl_2)

	1977	1985	1992
Products	5.5	1.6	0.7
Aqueous discharges	9.4	2.2	0.5
Process exhaust	4.9	1.7	0.9
Cell room ventilation	6.8	2.6	1.5
TOTAL	26.6	8.1	3.6

With an installed chlorine capacity of 7 million tons in Europe this equates to a total environmental emission of 25 tons of mercury in 1992. In addition approximately 100 tes of mercury was buried either in salt mines or specially prepared concrete-encapsulated pits. This mercury in mainly in the
form of inactive mercury sulphide or is contaminated pipework, equipment or filter aid. Such mercury has no route to the outside environment and is not considered to be an emission.

5.3 Total Industry Emissions by 2010

The improvements made over the last fifteen years have been substantial. Nonetheless, the industry believes that further reductions in mercury discharges are achievable. This will be brought about through a combination of plant closures, selective conversions to other technologies and improvements to mercury containment by appropriate capital investment.

An examination of the technologies available together with learning experience from recent improvements suggests that a total usage of 2 g/te Cl_2 will be achievable by 2010.

At a mercury emission rate of 2 g/te capacity, the European chlor-alkali plants will reduce their total emissions to:

7.0 million tes x 2 g Hg/te capacity = 14 te/yr

(cf 1985 = 56 te/yr; 1977 = 186 te/yr.)

Based on the data in Table 3.1 this represents 0.1% of the anthropomorphic global mercury emissions.

6 THE ECONOMIC CASE

Much has been said about the technological simplicity of changing from mercury technology to membrane technology and the comparatively low costs of doing so; equally as much has been said about the difficulty of so doing and the prohibitive costs associated with it. Not surprisingly, technology suppliers will tend to play down the costs and play up the benefits - producers will tend to do the opposite. For this study, wherever possible, independent surveys such as the Chem Systems 1992 report, have been used and the data corroborated against known plant performance. Three areas have been addressed:

1. The capital cost of investment
2. The savings to be gained from the investment
3. The ability of the industry to fund the investment

6.1 Capital Cost of Investment

In an earlier document, Euro Chlor estimated the capital cost of conversion of an average size mercury plant (say 100 000 te/yr) to its equivalent membrane plant to be approximately 700 ECU/te Cl_2 capacity. At today's exchange rates this equates to DM 1400/te Cl_2 capacity. Recent analyses by member companies, based on both in-house costings and suppliers' quotes, as well as independent market intelligence reports have shown this figure still to be accurate. Chem Systems quote a figure of DM 1500/te.

The mercury cell capacity within Europe is approximately 7 million tonnes. The cost to the industry of involuntarily converting this capacity will therefore be:

7 000 000 x 1400 DM or DM 10 billion.

It is further shown in Section 5.4 that through voluntary environmental improvements to which the industry will commit, mercury losses to air and water will be reduced to 14 te/yr by the same date. Therefore the capital cost of reducing this small emission, (which represents less than 0.07% of the total annual emission of mercury to the environment) is: DM $\frac{10\ 000\ 000\ 000}{14\ 000}$/kg Hg

or DM 700 000/kg mercury.

6.2 Operating and Fixed Cost Savings

To obtain a comparison of the differences in operating costs between mercury cells and membrane cells, independent sources have been used wherever possible. Corroboration of the data has been possible through comparison with member companies' experience.

* Chem Systems Ltd have published leader and laggard data for mercury cell plants valid to Q3 1992. For this study the leader data has been chosen based on the belief that over the next ten years or so only the best performing, lowest cost mercury cell rooms will remain in service.

* Costs for the membranes cell plant have been based on an unpublished survey by SRI, but modified to reflect European power prices (the figure used by Chem Systems has been adopted) and the power usage has been adjusted to reflect member company experience. In addition, since SRI is based on mid-91 prices, inflation of 5% has been added to bring both sets of data to a comparable base line.

* The resulting comparisons are shown in Table 6.1.

* Table 6.1

Comparison of Mercury and Membrane Technology Costs

	DM/te Cl_2	
	Mercury Cells	Membrane Cells
Brine	57.0	57.0
Chemicals	31.0	55.7
Power	273.6	223.9
Total Variable Cost	361.6	336.6
Steam	2.4	20.8
Water	3.7	2.9
Liquefaction	9.7	10.6
Others	0.4	7.0
Operating Labour & Materials	16.6	15.1
Maintenance Labour & Materials	61.5	44.7
Supervision	3.3	2.9
* Total Fixed Cost	97.6	104.1
Direct Cash Cost of Production	459.2	440.6

Exchange rates $ = DM 1.6

Electricity usage : Mercury cells 3361 KWh/te Cl_2
Membrane cells 2750 KWh/te Cl_2

Power price : DM 81.4/MWh

* Assumed that mercury cell plant has the "best" mercury reduction technology.

6.3 Investment Returns

The average capacity in Europe is very close to 100 kt/yr of chlorine; this capacity is the basis for the following economic considerations:

The estimated cost for mercury - membrane conversion is 700 ECU/ton of chlorine, so the total investment cost for the above capacity is:

700 x 100 kt = 70 MECU

Using an exchange rate of ECU/DM = 2, we have:

70 x 2 = 140 MDM

Normally, for this kind of plant, the depreciation is based on 10 years, this means: 14.0 MDM/year.

The reduction of the total direct operating cost with the mercury - membrane conversion is 18.6 DM/ton.

For 100 kt/yr of capacity the saving is:

100 kt/y x 18.6 DM/t = 1.86 MDM/yr

ie the recovery is 1.86 - 14.0 = -12.14 MDM/yr
and the payback is $\frac{140}{1.86}$ = 75 years

6.4 Sensitivity Analysis

Membrane suppliers are actively working on reducing the voltage of their membranes. This will reduce the power consumption. They are also known to be researching membranes to produce 50% NaOH. If successful this will obviate the need for steam for evaporation (it will also however increase electrical power consumption).

An assumption can be made that, overall, power consumption will reduce by 10% and steam usage will be reduced to mercury cell levels.

Hence, increased saving is 22.4 + (20.8 - 2.4) DM/te
= 41 DM/te Cl_2

Total Direct savings = 41 + 18.6
= 60 DM/te Cl_2

For 100 000 te/yr plant:

Savings = 100 x 60 MDM/yr
= 6.0 MDM/yr

Payback = $\frac{140}{6.0}$ = 23.3 yrs

Learning curve theory might suggest that capital costs will reduce in real terms over the period by say 30% (opposing this is the possibility of an EC energy tax which would lead to reduced current density operation and thus increased capital charges).

However, accepting 30% reduction in capital would give a capital cost for a 100 ktpa plant of 98 MDM. Depreciation at 10% = 9.8 MDM/yr.

The savings in operating and fixed costs of 6.0 MDM/yr would still not cover the increased depreciation charges although the payback would be reduced to 16.4 yrs.

7 CONCLUSIONS

1) European chlor-alkali producers have significantly reduced levels of emissions of mercury to the environment over the last 15 years.

2) Potential exists to make further substantial reductions over the next 15 years.

3) Mercury emissions from European chlor-alkali plants are already an insignificant proportion of the total global mercury emissions from both human and natural causes.

4) The huge investment to replace mercury cells with membrane cells cannot be justified on any economic grounds.

5) There is no sustainable environmental argument to justify the necessary investment.

APPENDIX A

Potential Mercury Emissions

The following indicative figures have been arrived at without any attention to the cost or time implications for their implementation. The values indicate what is believed to be possible to achieve by 2010, provided the plants had the assurance that they would be able to run beyond that date to recoup the investment.

a) Mercury in Products

The technology for filtering mercury from caustic is known and available. From 1992 returns, 26 out of the 68 responding plants achieved less than 0.2 g/te Cl_2.

Similarly, technologies are being exploited to treat hydrogen and achieve levels of less than 0.1 g/te Cl_2.

It is concluded that an achievable target for the industry for this category would be less than 0.2 g Hg/te Cl_2 capacity.

b) Mercury in Waste Water

For closed cycle plants, technology exists for treatment of purge brine streams and waste water systems.

In 1991, 32 plants recorded returns of less than 0.05 g Hg/te Cl_2.

However, it is impossible for waste brine plants to achieve this standard. This is acknowledged in the EC Mercury in Waste Water Directive (EEC 82/176) where a factor of 10 is applied between waste brine and resaturation systems.

Therefore, 0.10 g/te is suggested as the target, with the assumption that resaturation plants will do better than this to allow for higher figures from waste brine plants.

c) Mercury in Process Exhaust

31 plants out of 70 achieved less than 0.05 g/te Cl_2 in 1991. A target figure for 2010 is suggested at 0.1 g Hg/te Cl_2 for all plants. Technology exists.

d) Mercury in Cell Room Ventilation

The situation varies considerably from plant to plant. In the northern half of Europe plants tend to be enclosed; in the south they are frequently in the open air. Where they are enclosed with forced circulation, filtration is possible. Cell rooms relying on natural convection, of which there are many, cannot filter their air. Ambient temperature also plays a major role in the performance.

From 1992 returns, 34 cell rooms out of 68 calculated emissions of less than 1.5 Hg/te Cl_2 in their ventilation air. This is suggested as the target for 2010.

e) Summary

If these targets are accepted, the potential emissions to the environment in 2010 will be reduced to:

	g Hg/te Cl_2
a) Products	0.2
b) Aqueous waste	0.1
c) Process exhaust	0.1
d) Cell room ventilation	1.5
TOTAL	**1.9**

It should be noted that the Paris Commission requires that the sum of c), d) plus the hydrogen contribution to a) should be less than 2 g Hg/te Cl_2 by 31 December 1996, unless an undertaking has been given that the plant will convert to membrane cells no later than 2000.