



EUROPEAN COMMISSION

**Integrated Pollution Prevention and Control (IPPC)**

**Reference Document on Best Available Techniques in the  
Chlor-Alkali Manufacturing industry**

**December 2001**



## EXECUTIVE SUMMARY

This reference document on best available techniques in the chlor-alkali industry reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface which describes the objectives of the document and its use.

### The chlor-alkali industry

The chlor-alkali industry is the industry that produces chlorine ( $\text{Cl}_2$ ) and alkali, sodium hydroxide ( $\text{NaOH}$ ) or potassium hydroxide ( $\text{KOH}$ ), by electrolysis of a salt solution. The main technologies applied for chlor-alkali production are mercury, diaphragm and membrane cell electrolysis, mainly using sodium chloride ( $\text{NaCl}$ ) as feed or to a lesser extent using potassium chloride ( $\text{KCl}$ ) for the production of potassium hydroxide.

The diaphragm cell process (Griesheim cell, 1885) and the mercury cell process (Castner-Kellner cell, 1892) were both introduced in the late 1800s. The membrane cell process was developed much more recently (1970). Each of these processes represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode. Currently, 95% of world chlorine production is obtained by the chlor-alkali process.

The geographic distribution of chlor-alkali processes world-wide differs appreciably (production capacity of chlorine):

- western Europe, predominance of mercury cell process (June 2000): 55%
- United States, predominance of diaphragm cell process: 75%
- Japan, predominance of membrane cell process: >90%

The remaining chlorine production capacity in western Europe consists of (June 2000) diaphragm cell process 22%, membrane cell process 20% and other processes 3%.

Chlorine production since the 1940s has risen enormously, on the back of the burgeoning demand for plastics, notably PVC and polyurethanes. The production of chloroaromatics (e.g. chlorobenzene for phenol synthesis), propylene oxide (chlorohydrin process), solvents containing chlorinated hydrocarbons, and inorganic chlorine compounds are also important factors behind the increased use of chlorine after 1940. The chlorine production of a country is an indicator of the state of development of its chemical industry.

Global production capacity of chlorine in 1995 was about 44 million tonnes, the EU accounting for about 24% of that capacity. In June 2000 the chlorine production capacity in western Europe was 11.3 million tonnes. Of world chlor-alkali capacity, 65% is concentrated in three regions; North America, western Europe and Japan. After a fall at the beginning of the 1990s, production in western Europe now seems to be stabilised at around 9 millions tonnes per year (9.2 million tonnes in 1999).

The chlor-alkali sector in Europe has developed over time and is scattered geographically. The inevitable co-production of chlorine and sodium hydroxide in almost equal amounts has always been a problem for the chlor-alkali industry. Both products are used for very different end uses with differing market dynamics and it is only by rare chance that demand for the two coincides. Europe is approximately in balance in chlorine, and has traditionally been the world's second largest exporter of caustic; currently it is a net importer.

Chlorine is largely used in the synthesis of chlorinated organic compounds. VCM for the synthesis of PVC still remains the driver of chlor-alkali production in most European countries.

Chlorine is difficult to store and transport economically and it is therefore generally produced near consumers. More than 85% of the chlorine produced in EU is used on the same or adjacent sites for other chemical processes.

Sodium hydroxide is usually supplied as a 50% aqueous solution and can be stored for long periods and readily transported (rail, road and ship). The main areas of application of sodium hydroxide today are:

- chemicals: synthesis of organic or inorganic compounds
- metallurgy, alumina/aluminium industry
- pulp and paper industry
- textile industry
- soaps, surfactants
- water treatment
- consumer products.

### **Inputs and pollutant outputs**

Some inputs and pollutant outputs from the chlor-alkali industry are common to all processes. Others are specific to the cell technology used, the purity of the incoming salt and the specifications of the products.

The inputs are primarily salt and water as feedstock; acids and chemical precipitants used to remove impurities in the input brine or output chlorine/caustic soda; cooling agents (CFCs, HCFCs, HFCs, ammonia, etc.) for liquefying and purifying the chlorine gas produced. The chlor-alkali process needs huge amounts of electricity and electrical energy is a major input.

The main pollutant outputs which are common to all three electrolytic processes are chlorine gas emissions to air, free oxidants to water, spent acids, cooling agents, and impurities removed from the input salt or brine.

The pollutant of most concern from the chlor-alkali industry is mercury, which is specific to the mercury cell technology. Due to the process characteristics, mercury can be emitted from the process through air, water, wastes and in the products. The total mercury emission to air, water and products from chlor-alkali plants in western Europe was 9.5 tonnes in 1998, ranging from 0.2-3.0 g Hg/tonne of chlorine capacity at the individual plants.

The majority of mercury losses occur, however, in the various process wastes. For 1997, OSPARCOM reported 31 tonnes of mercury in solid wastes not recycled. Mercury in solids disposal plant-by-plant were in the range of 0-84 g Hg/tonne chlorine capacity in 1998, as reported by Euro Chlor (see Annex C to this document).

At present some 12000 tonnes of mercury are contained in mercury cells used for chlorine production in the EU. When the plants are converted or shut down, this mercury has the potential to be released into the global environment. Currently, there is no European Union policy or legislation on how to deal with this huge amount of pure mercury.

The main issue with the diaphragm technology is asbestos. Both the potential exposure of employees to asbestos and releases of asbestos to the environment are of concern.

Historical mercury and PCDD/Fs contamination of land and waterways from mercury and diaphragm chlor-alkali plants is a big environmental problem at some sites. The contamination is due to fallout of mercury and historical disposal of graphite sludges, from the use of graphite anodes, and other wastes on and around the plant sites.

The membrane cell process has inherent ecological advantages over the two older processes, as it does not use mercury or asbestos, and it is the most energy efficient process. Despite these advantages, the change of technology to membrane cells has been slow in western Europe because most existing chlorine plants were installed in the 1970s with a plant life of 40-60 years and there has been no need for new production capacity. Nor has there been a legislative drive to change technology.

With the inputs/outputs of the chlor-alkali sector, it is also relevant to point out the special importance of safety aspects related to production, handling and storage of chlorine.

### Conclusions about best available techniques (BAT)

BAT for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT. The total energy use associated with BAT for producing chlorine gas and 50% caustic soda is less than 3000 kWh (AC) per tonne of chlorine when chlorine liquefaction is excluded and less than 3200 kWh (AC) per tonne of chlorine when chlorine liquefaction and evaporation are included.

#### *All cell plants*

Best available techniques for the manufacture of chlor-alkali include the following measures:

- Use of management systems to reduce the environmental, health and safety risks of operating a chlor-alkali plant. The risk level should tend to zero. The management systems will include:
  - training of personnel
  - identification and evaluation of major hazards
  - instructions for safe operation
  - planning for emergencies and recording of accidents and near-misses
  - continuous improvement including feedback and learning from experience.
- A chlorine destruction unit designed to be able to absorb the full cell-room production in the event of a process upset until the plant can be shut down. The chlorine absorption unit prevents emissions of chlorine gas in the event of emergencies and/or irregular plant operation.

The absorption unit should be designed to lower the chlorine content in the emitted gas to less than 5 mg/m<sup>3</sup> in the worst case scenario.

All chlorine-containing waste gas streams should be directed to the chlorine absorption unit. The chlorine emission level to air associated with BAT during normal operation is less than 1 mg/m<sup>3</sup> in the case of partial liquefaction and less than 3 mg/m<sup>3</sup> in the case of total liquefaction.

No systematic discharge of hypochlorite to water should take place from the chlorine destruction unit.

- Minimising consumption/avoiding discharge of sulphuric acid by means of one or more of the following options or equivalent systems:
  - on-site reconcentration in closed loop evaporators
  - using the spent acid to control pH in process and waste water streams
  - selling the spent acid to a user that accepts this quality of acid
  - returning the spent acid to a sulphuric acid manufacturer for reconcentration.

If the sulphuric acid is reconcentrated on-site in closed loop evaporators, the consumption can be reduced to 0.1 kg of acid per tonne of chlorine produced.

- Minimising the discharge of free oxidants to water by applying:
  - fixed bed catalytic reduction
  - chemical reduction
  - any other method with equally efficient performance.

The emission level of free oxidants to water associated with BAT is less than 10 mg/l. The overall environmental impact should be considered when the destruction method is chosen.

- Use of carbon tetrachloride-free chlorine liquefaction and purification processes.
- Hydrogen should be used as a chemical or as fuel in order to conserve resources.

### *Membrane cell plants*

Best available techniques specific to membrane cell plants include the following measures:

- Minimising the discharge of chlorate and bromate to water by applying:
  - acid conditions in the anolyte (pH 1-2) to minimise the formation of chlorate ( $\text{ClO}_3^-$ ) and bromate ( $\text{BrO}_3^-$ )
  - chlorate destruction in the brine circuit to remove chlorate before purging.

The acidity of the anolyte is a design parameter of membrane cell plants and cannot be adjusted without affecting the operation of the membrane cell. If this is not the chosen, option a chlorate decomposer may be necessary to remove chlorate before purging. The chlorate level associated with BAT in the brine circuit is 1-5 g/l and the associated bromate level is 2-10 mg/l (note that the bromate level depends on the bromide level in the salt).

- Appropriate handling of spent membranes and gaskets.

### *Mercury cell plants*

Best available techniques specific to mercury cell plants is considered to be conversion to membrane cell technology.

During the remaining life of mercury cell plants all possible measures should be taken to protect the environment as a whole. The best performing mercury cell plants are achieving total mercury losses to air, water and with products in the range of 0.2-0.5 g Hg/tonne of chlorine capacity as a yearly average. The majority of mercury losses are in the various wastes from the process. Measures should be taken to minimise current and future mercury emissions from handling, storage, treatment and disposal of mercury-contaminated wastes. Decommissioning of mercury cell plants should be carried out in a way that prevents environmental impact during and after the shutdown process as well as safeguarding human health. Chapter 4.2 gives more details about available techniques for prevention and/or reduction of emissions, handling and treatments of wastes, energy use, decommissioning of mercury cell plants and conversion to membrane cell technology.

### *Asbestos diaphragm cell plants*

Best available techniques specific to asbestos diaphragm cell plants is considered to be conversion to membrane cell technology or, when the energy use criterion is fulfilled, the use of non-asbestos diaphragms.

During the remaining life of asbestos diaphragm cell plants all possible measures should be taken to protect the environment as a whole. Chapter 4.3 gives more details about available techniques for prevention and/or reduction of emissions, wastes and energy use in asbestos diaphragm cell plants.

## PREFACE

### 1. Status of this document

Unless otherwise stated, references to “the Directive” in this document means the Council Directive 96/61/EC on integrated pollution prevention and control.

This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available techniques (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

### 2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term “best available techniques”, are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community’s industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term “best available techniques” is defined in Article 2(11) of the Directive as “the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.” Article 2(11) goes on to clarify further this definition as follows:

“techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

“available” techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

“best” means most effective in achieving a high general level of protection of the environment as a whole.



Furthermore, Annex IV of the Directive contains a list of “considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention”. These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

### **3. Objective of this Document**

Article 16(2) of the Directive requires the Commission to organise “an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them”, and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that “the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive.”

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

### **4. Information Sources**

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

### **5. How to understand and use this document**

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit

conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapters 1 and 2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapter 3 provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapter 4 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapter 5 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in chapter 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

Edificio Expo-WTC, C/Inca Garcilaso, s/n, E-41092 Seville, Spain

Telephone: +34 95 4488 284

Fax: +34 95 4488 426

e-mail: [eippcb@jrc.es](mailto:eippcb@jrc.es)

Internet: <http://eippcb.jrc.es>

---

# Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry

<b>EXECUTIVE SUMMARY .....</b>	<b>I</b>
<b>PREFACE .....</b>	<b>VI</b>
<b>SCOPE.....</b>	<b>XIV</b>
<b>1 GENERAL INFORMATION .....</b>	<b>1</b>
1.1 Industrial and economical development of the chlor-alkali sector .....	1
1.2 Industry size and geographic distribution of chlor-alkali production sites in Europe .....	3
1.3 Technologies in use .....	4
1.4 Consumption of chlorine .....	5
1.5 Consumption of sodium hydroxide .....	6
1.6 Chlorine/sodium hydroxide: a delicate balance .....	7
1.7 Consumption of hydrogen .....	7
1.8 Environmental relevance of the chlor-alkali industry .....	7
<b>2 APPLIED PROCESSES AND TECHNIQUES .....</b>	<b>9</b>
2.1 The mercury cell process.....	12
2.1.1 The mercury cathode electrolyser and decomposer .....	13
2.1.2 Decomposition of the amalgam.....	14
2.2 The diaphragm cell process.....	15
2.2.1 Diaphragm without asbestos .....	17
2.2.2 Activated cathodes .....	17
2.3 The membrane cell process .....	18
2.4 Auxiliary processes .....	20
2.4.1 Salt unloading and storage .....	20
2.4.2 Brine purification and resaturation.....	21
2.4.2.1 Brine purification .....	21
2.4.2.2 Brine resaturation and dechlorination .....	25
2.4.3 Chlorine production, storage and handling .....	26
2.4.3.1 Dealing with impurities.....	29
2.4.3.2 The chlorine absorption unit .....	30
2.4.4 Caustic production, storage and handling .....	31
2.4.5 Hydrogen production, storage and handling .....	33
<b>3 PRESENT CONSUMPTION AND EMISSION LEVELS .....</b>	<b>34</b>
3.1 Overall consumption and emission levels of all cell plants .....	34
3.1.1 Inputs in the production line.....	36
3.1.1.1 Sodium chloride/potassium chloride.....	36
3.1.1.2 Water .....	36
3.1.1.3 Energy .....	36
3.1.1.4 Ancillary materials.....	38
3.1.2 Outputs in the production line.....	39
3.1.2.1 Emissions from the mercury cell process .....	39
3.1.2.1.1 Air emissions.....	39
3.1.2.1.2 Water emissions .....	42
3.1.2.1.3 Generation of wastes .....	44
3.1.2.1.4 Mercury contained in products.....	47
3.1.2.1.5 Mass balance calculation.....	47
3.1.2.2 Emissions from the diaphragm cell process.....	48
3.1.2.2.1 Air emissions.....	48
3.1.2.2.2 Water emissions .....	49
3.1.2.2.3 Generation of wastes .....	49
3.1.2.3 Emissions from the membrane cell process .....	50

3.1.2.3.1	Water emissions .....	50
3.1.2.3.2	Generation of wastes.....	50
3.1.2.4	Emissions from auxiliary processes .....	50
3.1.2.4.1	Emissions from salt unloading and storage .....	50
3.1.2.4.2	Emissions from the brine circuit.....	50
3.1.2.4.2.1	Air emissions .....	51
3.1.2.4.2.2	Water emissions.....	51
3.1.2.4.2.3	Generation of wastes.....	53
3.1.2.4.3	Emissions from chlorine gas production, cooling, drying, liquefaction and storage.....	54
3.1.2.4.3.1	Air emissions .....	54
3.1.2.4.3.2	Water emissions.....	56
3.1.2.4.3.3	Generation of wastes.....	56
3.1.2.4.4	Emissions from sodium and potassium hydroxide processing .....	57
3.1.2.4.5	Hydrogen processing .....	57
3.2	Historical contamination of chlor-alkali plant sites.....	57
3.3	Safety aspects of chlor-alkali plants .....	58
<b>4</b>	<b>TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BEST AVAILABLE TECHNIQUES.....</b>	<b>60</b>
4.1	All cell plants.....	60
4.1.1	Safety measures .....	60
4.1.2	The chlorine absorption unit.....	65
4.1.3	Metal anodes .....	66
4.1.4	On-site reconcentration of spent sulphuric acid .....	66
4.1.5	Treatment of waste water containing free oxidants, including bleach destruction ...	67
4.1.6	Carbon tetrachloride-free chlorine liquefaction and purification.....	71
4.2	Mercury cell plants .....	72
4.2.1	Overview of mercury emission abatement.....	72
4.2.1.1	Reduction of mercury emissions to air, including hydrogen gas .....	79
4.2.1.2	Reduction of mercury emissions to water .....	82
4.2.1.3	Removal of mercury from caustic soda.....	84
4.2.1.4	Treatment of mercury-containing wastes, including recovery of mercury.....	85
4.2.2	Conversion of mercury cell plants to membrane technology .....	88
4.2.3	Decommissioning.....	96
4.3	Diaphragm cell plants .....	98
4.3.1	Abatement of asbestos emissions and discharges.....	98
4.3.2	Application of non-asbestos diaphragm material .....	101
4.3.3	Conversion of asbestos diaphragm cell plants to membrane technology or to asbestos-free diaphragms.....	105
4.4	Membrane cell plants.....	106
4.4.1	High performance membranes .....	106
<b>5</b>	<b>BEST AVAILABLE TECHNIQUES.....</b>	<b>108</b>
<b>6</b>	<b>EMERGING TECHNIQUES .....</b>	<b>113</b>
6.1	Oxygen depolarised cathodes in modified membrane cells.....	113
6.2	Membrane for direct production of 50% caustic soda.....	116
6.3	Built-in precathode diaphragm .....	117
<b>7</b>	<b>CONCLUDING REMARKS .....</b>	<b>120</b>
	<b>ANNEX A: CHLOR-ALKALI PLANT CAPACITIES IN WESTERN EUROPE (JUNE 2000) .....</b>	<b>121</b>
	<b>ANNEX B: MONITORING OF MERCURY.....</b>	<b>125</b>
	Relevant items with regard to mercury monitoring.....	125
	Mercury monitoring of air.....	127
	Mercury monitoring of water .....	129
	Mercury monitoring of products .....	129
	Mercury accumulation in equipment and wastes .....	130

---

<b>ANNEX C: MERCURY LOSSES PLANT BY PLANT 1998 AND THE TREND 1977-1998 .....</b>	<b>132</b>
<b>ANNEX D: NATIONAL AND INTERNATIONAL LEGISLATION .....</b>	<b>136</b>
Flemish legislation concerning the Chlor-alkali industry.....	136
Summary of current German legislation relevant for the sector of Chlor - alkali industry .....	136
Italian Regulations .....	144
Dutch legislation .....	145
Austrian wastewater legislation.....	148
Regulations concerning the chlor-alkali industry in Finland.....	148
British Legislation Concerning the Chlor-Alkali Industry .....	148
European Legislation regarding Mercury containing Wastes .....	150
<b>ANNEX E: RELEVANT ADDRESSES.....</b>	<b>152</b>
<b>REFERENCES .....</b>	<b>154</b>
<b>GLOSSARY OF TERMS AND ABBREVIATIONS.....</b>	<b>161</b>

---

## List of tables

Table 1.1: Distribution of processes and capacities of chlor-alkali plants in western Europe (June 2000) ..	4
Table 2.1: Main characteristics of the different electrolysis processes .....	11
Table 2.2: Example of brine specifications for the membrane process operating at a current density up to 4 kA/m <sup>2</sup> .....	23
Table 2.3: Possible trade-off in chlorine gas liquefaction .....	28
Table 3.1: Overview of inputs and outputs of the chlor-alkali manufacturing processes .....	35
Table 3.2: Comparison of typical energy use by the mercury, diaphragm and membrane cell chlor-alkali technologies, assuming production of 50% caustic soda and before liquefaction of chlorine ...	37
Table 3.3: Consumption and use of chemical auxiliaries in chlor-alkali plants using a brine recirculation process .....	38
Table 3.4: Waste generation and final treatment at Akzo Nobel Bohus in 1998/99 .....	46
Table 3.5: Yearly waste generation and final treatment at Hydro Polymers AB .....	46
Table 3.6: Releases into water from the brine circuit using a recirculation process .....	51
Table 3.7: Application of carbon tetrachloride in the chlor-alkali industry in western Europe .....	55
Table 4.1: List of some preventative and corrective or emergency measures to avoid accidents at loading areas of a chlor-alkali plant .....	62
Table 4.2: List of some preventative and corrective or emergency measures to avoid accidents associated with storage of liquid chlorine .....	63
Table 4.3: Overview of measures, corresponding mercury levels and emissions from the Hydro Polymers (Stenungsund, Sweden) mercury cell chlor-alkali plant in 1997. ....	77
Table 4.4: Overview of measures, corresponding mercury levels and emissions from the Akzo Nobel (Bohus, Sweden) mercury cell chlor-alkali plant in 1997. ....	78
Table 4.5: Treatment possibilities for mercury-containing wastes .....	85
Table 4.6: Some available techniques with typical performances for treatment of mercury containing wastes .....	86
Table 4.7: Data from the conversion of the Borregaard chlor-alkali plant to membrane technology .....	93
Table 4.8: Comparison of reported conversion costs .....	94
Table 6.1: Precathode technology at CHLORALP (Le Pont de Claix-France) .....	119

---

## List of figures

Figure 1.1: Development of chlorine production in western Europe .....	1
Figure 1.2: Chlorine production in western Europe in 1999.....	2
Figure 1.3: Geographic distribution of chlor-alkali plants within the European Union 1999 .....	3
Figure 1.4: Comparison of the total chlorine capacity by technology between western Europe, United States and world-wide.....	5
Figure 1.5: Chlorine applications in western Europe .....	6
Figure 2.1: Flow diagram of the three main chlor-alkali processes .....	10
Figure 2.2: Simplified scheme of chlorine electrolysis cells.....	11
Figure 2.3: Flow diagram of mercury cell technology .....	13
Figure 2.4: Mercury cells with horizontal decomposer.....	14
Figure 2.5: Mercury cells with vertical decomposer.....	15
Figure 2.6: Typical diaphragm electrolysis cell.....	16
Figure 2.7: Flow diagram of integration of membrane or mercury and diaphragm processes .....	17
Figure 2.8: Diagram of a membrane process .....	19
Figure 2.9: Exploded view of a monopolar membrane electrolyser.....	19
Figure 2.10: View of a membrane cell room equipped with bipolar electrolyzers.....	20
Figure 2.11: Possible lay-out for the brine purification system used in membrane process.....	22
Figure 2.12: View of chelate resin towers in a secondary brine purification system .....	24
Figure 2.13: View of polishing filters in a secondary brine purification system.....	24
Figure 2.14: The flow of chlorine from the electrolyzers to storage .....	26
Figure 2.15: View of caustic production and storage .....	31
Figure 2.16: The flow to storage of caustic soda from the different technologies .....	32
Figure 3.1: Solid waste sources in the mercury process.....	45
Figure 4.1: Schematic diagram of a catalytic reduction fixed bed reactor process .....	69
Figure 4.2: Mercury plant conversion to membrane technology.....	89
Figure 4.3: Example of handling of asbestos from Dow in Stade (Germany).....	101
Figure 6.1: The influence of oxygen depolarised cathodes on the electrode potentials, NaCl.....	113
Figure 6.2: Principle of the Gas Pocket Electrode for pressure compensation .....	114
Figure 6.3: Structure of Fx-50 membrane producing 50% caustic soda .....	116
Figure 6.4: The built in precathode diaphragm operating principle.....	117

---

## SCOPE

This document relates to the chlor-alkali industry in the context of Annex 1 of Directive 96/61/EC, namely:

Section 4.2: Chemical installations for the production of basic inorganic chemicals:

- a) Chlorine
- c) Sodium hydroxide and potassium hydroxide

The processes involved in the production of chlorine and caustic solution by the electrolysis of brine cover:

- the unloading and storage of salt
- the purification and resaturation of brine
- the different electrolytic processes
- the process engineering of caustic solution concentration, purification, storage and loading
- the process engineering of chlorine cooling, drying, purification and liquefaction before storage and loading
- the process engineering of hydrogen cooling, purification and compression before storage and loading.

In addition to covering the basic manufacturing activities, this document addresses the following substances, in Annex III of the Directive, which are associated with those activities and which could have an effect on emissions or pollution:

Relating to air:

- 5. Metals and their compounds (in particular mercury)
- 7. Asbestos (suspended particulates, fibres)
- 8. Chlorine and its compounds
- 13. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans

Relating to water:

- 1. Organohalogen compounds and substances which may form such compounds in the aquatic environment
- 7. Metals and their compounds (in particular mercury)

Environmental and safety items not specifically related to the chlor-alkali sector are not covered in the document e.g. environmental aspects of cooling systems, emissions related to storage and handling of feedstock or special agents used as precipitants.

The high toxicity of chlorine is a major factor in the chlor-alkali industry, so the document does address:

- safety management procedures
- control of handling and loading and
- prevention of chlorine losses.



# 1 GENERAL INFORMATION

## 1.1 Industrial and economical development of the chlor-alkali sector

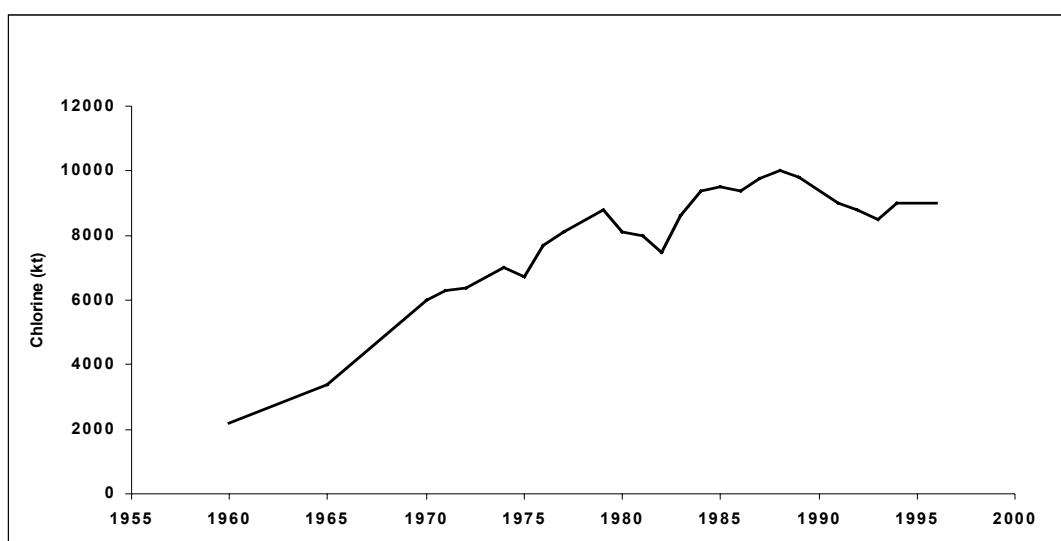
In 1800, Cruickshank was the first to prepare chlorine electrochemically. The process was, however, of little significance until the development of a suitable generator and of synthetic graphite for anodes in 1892. These two developments made possible the electrolytic production of chlorine, the chlor-alkali process, on an industrial scale. About the same time, both the diaphragm cell process (Griesheim cell, 1885) and the mercury cell process (Castner-Kellner cell, 1892) were introduced. The membrane cell process was developed much more recently (1970). Currently, 95% of world chlorine production is obtained by the chlor-alkali process. [Ullmann's, 1996]

Since 1970 graphite anodes have been largely superseded by activated titanium anodes in the diaphragm and mercury cell processes. The newer membrane cell process uses only activated titanium anodes. [Ullmann's, 1996]

Production of chlorine was very low in the 1800s and chlorine was only used for bleaching. In 1887, annual world production was 115 tonnes [Le Chlore, 1996]. Chlorine production since the 1940s has risen enormously, on the back of the burgeoning demand for plastics, notably PVC [J. Ind. Ecology, 1997] and polyurethanes. The production of chloroaromatics (e.g. chlorobenzene for phenol synthesis), propylene oxide (chlorohydrin process), solvents containing chlorinated hydrocarbons, and inorganic chlorine compounds are also important factors behind the increased use of chlorine after 1940.

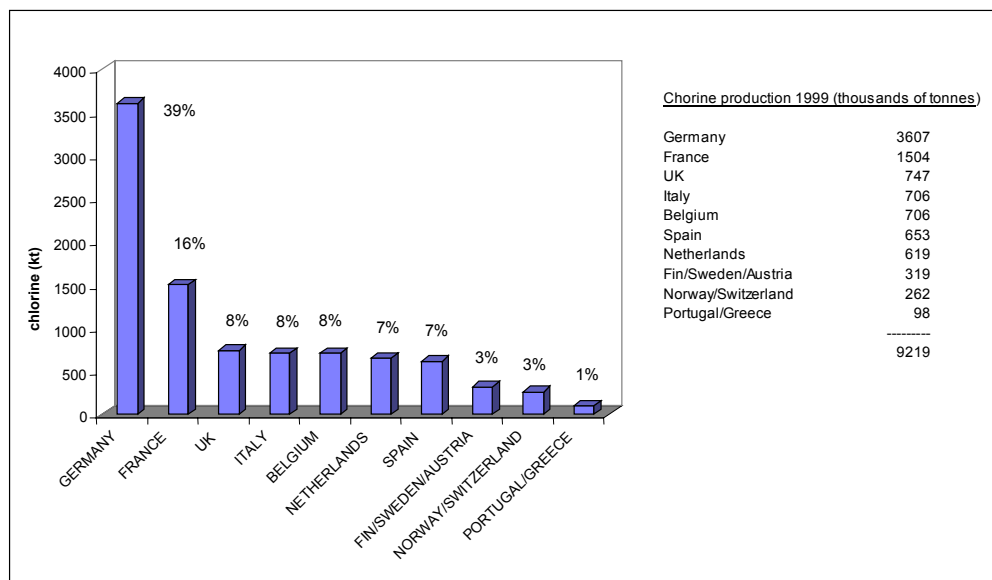
After a fall at the beginning of the 1990s, production in western Europe now seems to be stabilised at around 9 millions tonnes per year (9.2 million tonnes in 1999). This placed it behind the United States, with production of 11.2 million tonnes in 1994, but ahead of Japan, with 4.2 million tonnes production capacity in 1995. The world-wide chlorine production was 38 million tonnes in 1994. The global demand for both chlorine and caustic has been forecast to increase, although mainly in Latin America and Asia.

Figure 1.1 gives an overview of how production has developed since 1960 in western Europe.



**Figure 1.1: Development of chlorine production in western Europe**  
[Le Chlore, 1996]

Figure 1.2 shows the annual chlorine production in western Europe per country in 1999. Denmark and Luxembourg do not have any chlor-alkali plants and Ireland, with only 6000 tonnes production capacity, is not shown. In June 2000, there were 79 chlorine production plants corresponding to 93 process units in 15 west European countries (EU countries, Switzerland and Norway). A detailed list is given in Annex A.



**Figure 1.2: Chlorine production in western Europe in 1999**

[Euro Chlor]

Sustained growth in the USA and Europe resulted in expansion to meet demand. Although there have been some fluctuations, utilisation of plant capacity has remained at between 80% and 95% in both areas since the late 1980s. At the moment there is no overcapacity and new plant investment seems to be under way [Euro Chlor report, 1997]. Global production capacity of chlorine in 1995 was about 44 million tonnes, the EU accounting for about 24% of that capacity. Of world chlor-alkali capacity, 65% is concentrated in three regions; North America, western Europe and Japan [Beal, 1995].

The chlor-alkali process is one of the largest consumers of electrical energy. The chlorine production of a country is an indicator of the state of development of its chemical industry.

The total value of western European chlor-alkali sector production is 3 billion euros, according to [SRI Consulting, 1997]. SRI Consulting estimates that the turnover in 1995 generated by chlor-alkali related products amounted to some 230 billion euros, that is about 60% of the turnover of the west European chemical industry.

Euro Chlor estimates that there are 46000 employees involved in the direct production of chlorine in the EU. When chlorine derivatives and chlorine-dependent industry are included the number of employees is approximately two million.

## 1.2 Industry size and geographic distribution of chlor-alkali production sites in Europe

Chlor-alkali production sites in Europe are shown on a map in Figure 1.3. Compared to the same industry in the United States, the average plant size is smaller and in general the cost for the main raw materials, salt and electricity, are significantly higher. The chlor-alkali sector in Europe has developed over time and is scattered geographically. [SRI Consulting, 1997].



Figure 1.3: Geographic distribution of chlor-alkali plants within the European Union 1999

Since chlorine and caustic soda are co-products produced in almost equal amounts, the distribution of the caustic soda manufacturing industry is essentially the same as the chlorine manufacturing industry.

### 1.3 Technologies in use

The main technologies applied for chlor-alkali production are mercury, diaphragm and membrane cell electrolysis, mainly using sodium chloride as feed or to a lesser extent using potassium chloride for the production of potassium hydroxide. Other electrochemical processes in which chlorine is produced include the electrolysis of hydrochloric acid and the electrolysis of molten alkali-metal and alkaline-earth-metal chlorides, in which the chlorine is a by-product, but these account for less than 3% of the total chlorine production capacity.

Table 1.1 shows the distribution of the chlorine production processes in west European countries, indicating the number of installations and the annual capacity of chlorine production.

west European countries	Mercury process		Diaphragm process		Membrane process		Other processes		TOTAL
	number of inst.	capacity (kt)	number of inst.	capacity (kt)	number of inst.	capacity (kt)	number of inst.	capacity (kt)	capacity (kt)
AUSTRIA					1	55			55.0
BELGIUM	5	662			1	120	1 (HCl)	50	832.0
FINLAND	1	40			1	75			115.0
FRANCE	7	874	3	560	2	232	1 (Na)	20	1686.0
GERMANY	13	1762	3	1446	4	844	3 (HCl)	230	4282.0
GREECE	1	37							37.0
IRELAND					1	6			6.0
ITALY	9	812			1	170			982.0
NETHERLANDS	1	70	1	140	2	414			624.0
NORWAY			1	130	2	50			180.0
PORTUGAL	1	43			2	46			89.0
SPAIN	9	761.5			1	40			801.5
SWEDEN	2	220			1	90			310.0
SWITZERLAND	3	103.5							103.5
UK	3	856	2	220	4	105			1181.0
<b>TOTAL</b>	<b>55</b>	<b>6241</b>	<b>10</b>	<b>2496</b>	<b>23</b>	<b>2247</b>	<b>5</b>	<b>300</b>	<b>11284.0</b>

NB: Any one plant can have more than one cell technology installed

**Table 1.1: Distribution of processes and capacities of chlor-alkali plants in western Europe (June 2000)**

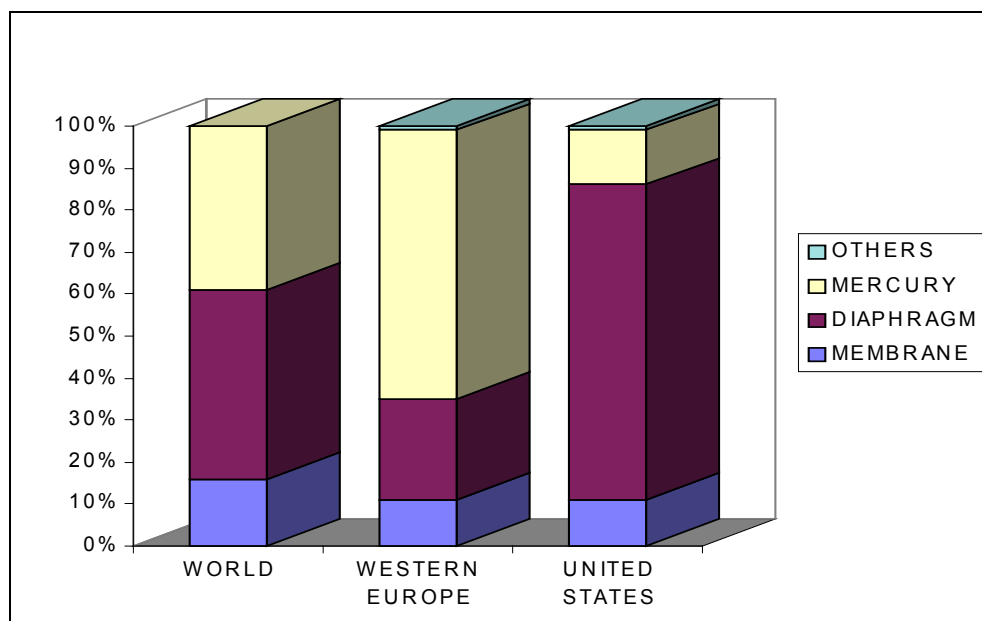
[Euro Chlor]

Where caustic soda production is concerned, an alternative route to the electrolysis of sodium chloride is the lime-soda process. Today, this process is not considered as a profitable operation in Europe compared with the electrolysis of sodium chloride. The situation seems to be different in the USA, where mineral deposits of natural carbonate exist.

The geographic distribution of processes world-wide differs appreciably:

- western Europe, predominance of amalgam process (June 2000): 55%
- United States, predominance of diaphragm process: 75%
- Japan, predominance of membrane process: >90%

Figure 1.4 gives a more general picture comparing the division of total chlorine capacity by technology in the United States, western Europe and in the world.



**Figure 1.4: Comparison of the total chlorine capacity by technology between western Europe, United States and world-wide**

[Lindley, 1997]

Since 1975, the membrane cell process has been developed to a high degree of sophistication. It has ecological advantages over the two older processes and has become the most economically advantageous process in recent years. Despite these advantages, the change of technology to membrane cells has been slow in western Europe because most existing chlorine plants were installed in the 1970s with a plant life of 40-60 years and there has been no need for new production capacity. Nor has there been a legislative drive to change technology.

## 1.4 Consumption of chlorine

Chlorine is largely used in the synthesis of chlorinated organic compounds. VCM for the synthesis of PVC still remains the driver of chlor-alkali production in most European countries.

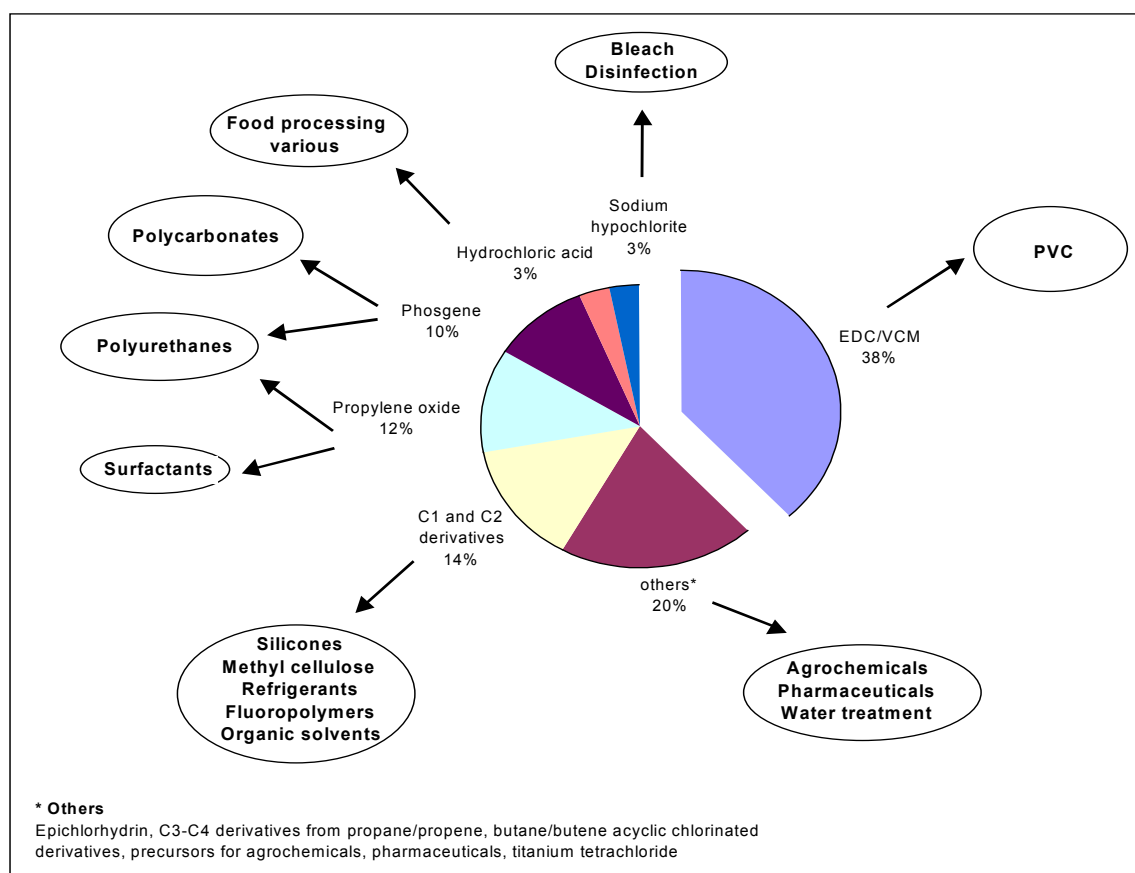
Chlorine is difficult to store and transport economically and, therefore, chlorine is generally produced near consumers. When other solutions cannot be found, chlorine is transported by pipe, road and rail.

The uses of chlorine can be divided into:

- **organic uses**, which account for about 80% of consumption:  
synthesis of VCM, chloromethane, phosgene, organic chlorinated solvents such as trichloro-ethene, tetrachloro-ethene, oxygenated derivatives, precursors or intermediates for the synthesis of pesticides or pharmaceutical products.
- **inorganic uses**, which account for about 15% of consumption:  
synthesis of sodium hypochlorite, hydrochloric acid, metal chlorides, bromine.
- **direct uses**, which account for less than 4% of consumption:  
water treatment, pulp and paper

Western European exports of elemental chlorine to outside the region are negligible. More than 85% of the chlorine produced in EU is used on the same or adjacent sites for other chemical processes. The production of chlorine and caustic is completely inter-related with the downstream businesses, including the PVC industry and the intermediates used to manufacture PVC. [Lindley, 1997]

Figure 1.5 shows the main applications of chlorine in western Europe.



**Figure 1.5: Chlorine applications in western Europe**

Based on [Euro Chlor report, 1997], [SRI Consulting, 1997]

## 1.5 Consumption of sodium hydroxide

Initially devised for the production of chlorine, electrolysis rapidly produced the caustic soda needed for numerous new sectors: artificial textiles, detergents, etc. The output of caustic soda is proportional to that of chlorine, in the ratio of their molecular weight ( $40.00 / 35.45 = 1.128$ ). Thus, 1.128 tonnes of caustic soda (100%) are produced by electrolysis per tonne of chlorine.

Sodium hydroxide is usually supplied as a 50% aqueous solution and can be stored for long periods and readily transported (rail, road and ship). The main areas of application of sodium hydroxide today are:

- chemicals: synthesis of organic or inorganic compounds
- metallurgy, alumina/aluminium
- pulp and paper
- textile
- soaps, surfactants
- water treatment
- consumer products.

Western Europe is a significant exporter of caustic soda to outside the region (140 million euros in 1996) [SRI Consulting, 1997].

## 1.6 Chlorine/sodium hydroxide: a delicate balance

The co-production of chlorine and sodium hydroxide in fixed proportions, 1.128 tonnes of caustic (as 100% NaOH) per tonne chlorine produced, has always been a problem for the chlor-alkali industry. Both products are used for very different end uses with differing market dynamics and it is only by rare chance that demand for the two coincides. Depending on which demand is dominant, either can be regarded as a by-product and the price varies accordingly. Price fluctuations can be extreme: in the spot market in cases of oversupply, caustic prices can be as low as \$ 20-30 per tonne whereas, in short supply, prices can be \$ 300 and higher per tonne [Euro Chlor report, 1997].

Chlorine itself is difficult to transport long distances; however it can be, and is, readily exported as EDC, a precursor for PVC. Caustic soda is a globally traded commodity. Because of the favourable economics of production in the US Gulf (cheap electricity, salt and ethylene) the USA is the largest exporter of EDC and caustic soda. Europe is approximately in balance in chlorine, and has traditionally been the world's second largest exporter of caustic; currently it is a net importer. Australia (alkali for the alumina industry) and south-east Asia (EDC and caustic) are the main importing areas.

New capacity in the Middle East and south-east Asia may upset these traditional trade patterns. Moreover, chlorine growth in Europe is likely to be lower than in most other parts of the world. Whilst globally the chlorine growth may average 2-3% per year over the next 10 years, it is forecast to be less than 1% per year in Europe.

## 1.7 Consumption of hydrogen

Hydrogen is also a co-product of the electrolysis of brine (28 kg for 1 tonne of chlorine). Hydrogen is generally used on-site as a combustible or sent as a fuel to other companies. It can also be used on integrated sites for certain applications in particular because of its high purity: synthesis of ammonia, methanol, hydrochloric acid, hydrogen peroxide, etc.

## 1.8 Environmental relevance of the chlor-alkali industry

Inputs and pollutant outputs from the chlor-alkali industry are quite specific to the cell technology used, the purity of the incoming salt and the specifications of the products. Because of the huge amount of electricity needed in the process, energy can be considered as a raw material. The chlor-alkali process is one of the largest consumers of electrical energy.

Historical mercury and PCDD/Fs contamination of land and waterways from mercury and diaphragm chlor-alkali plants is a big environmental problem at some sites.

For many years, the mercury cell has been a significant source of environmental pollution, because some mercury is lost from the process to air, water, products and wastes. Inorganic mercury can be metabolised to form highly toxic methyl mercury by anaerobic bacteria, and this organic mercury is bio-accumulated<sup>1</sup> in the food chain.

It is recognised that the main part of the mercury losses is in the different wastes from the process. Considerable emissions of mercury can also occur with run-off water. The soil at many

---

<sup>1</sup> In the 1950s a chemical plant producing acetaldehyde discharged a spent catalyst containing organic mercury into Minimata Bay, Japan. A number of people (mostly fishermen) became seriously ill and some were disabled. This event was at the origin of environmental regulations in Japan and caused changes into mercury free technologies in some industrial sectors.

sites is contaminated with mercury due to deposition of diffuse emissions and/or historical disposal of mercury contaminated wastes. The mercury leaks from the soil and ends up in the run-off water. Another big entry is the 'Difference to Balance'. The annual mercury balance for a site is never zero. This is because mercury accumulates in plant equipment and structures during the life of the plant.

The chlor-alkali industry was the largest domestic user of mercury in the years 1989 to 1990 in the USA and this could be expected to be the same in Europe [J. Ind. Ecology, 1997]. Based on the European Atmospheric Emission Inventory of Heavy Metals and Persistent Organic Pollutants [UBA (D)-TNO report, 1997] in the 15 EU countries, the highest emitters of mercury to air in 1990 include: coal burning electric utilities (highest figure of 90.5 tonnes), municipal and hazardous waste incinerators and cement industry (37.7 tonnes). Chlor-alkali emissions to air are reported to be 28.4 tonnes. A USEPA report, dated 1998, identifies the same sources of emissions: municipal waste incinerators, medical waste incinerators, hazardous waste incinerators and industrial boilers. In addition, certain manufacturing processes, most notably chlor-alkali and cement plants, are listed although their emissions are substantially lower than those of incineration sources.

According to Euro Chlor, the total mercury emission to air, water and products from chlor-alkali plants in western Europe was 9.5 tonnes in 1998, ranging between 0.2-3.0 g Hg/tonne of chlorine capacity at the individual plants.

Decision 90/3 of 14 June 1990 of the Commission for the Protection of the Marine Environment of the North-East Atlantic (PARCOM<sup>2</sup>) recommends that existing mercury cell chlor-alkali plants should be phased out as soon as practicable. The objective is that they should be phased out completely by 2010.

As regards the diaphragm technology, due to the potential exposure of employees to asbestos and releases to the environment, the use of good practices is needed and some efforts are being made to replace the asbestos with other diaphragm material.

With the inputs/outputs of the chlor-alkali sector, it is also relevant to point out the special importance of safety aspects related to production, handling and storage of chlorine.

---

<sup>2</sup> Since 1992 OSPARCOM. Publications can be found at <http://www.ospar.org>



## 2 APPLIED PROCESSES AND TECHNIQUES

In this chapter the applied processes and techniques are qualitatively described. Chapter 3 covers the quantitative aspects of consumption and emission levels.

The chemical, thermodynamic and kinetic principles are not explained. For this, reference is made to literature relevant to the subject [Ullmann's, 1996] or [Kirk-Othmer, 1991].

The chlor-alkali industry produces chlorine and caustic solution (sodium or potassium hydroxide) simultaneously by means of decomposition of a solution of salt in water. Along with the chlorine and the caustic solution, hydrogen is produced. An industrial chlor-alkali production unit comprises a series of operations, structured as shown in Figure 2.1.

In the chlor-alkali electrolysis process, a chloride-salt solution is decomposed electrolytically by direct current. Most of the time sodium chloride is used in the process in western Europe and less frequently potassium chloride (about 3-4% of the chlorine production capacity). Other processes such as the electrolysis of hydrochloric acid or the electrolysis of molten sodium chloride are applied, but these only account for about 3% of total chlorine production capacity in Europe.

The electrolysis of molten sodium salts which is applied to obtain sodium and for which chlorine is only a co-product is described in the BAT Reference document on non-ferrous metals, as sodium is an alkali metal.

There are three basic processes for the electrolytic production of chlorine, the nature of the cathode reaction depending on the specific process. These three processes are the diaphragm cell process (Griesheim cell, 1885), the mercury cell process (Castner-Kellner cell, 1892), and the membrane cell process (1970). Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode [Ullmann's, 1996].

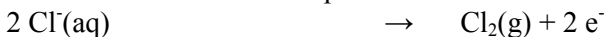
The basic principle in the electrolysis of a sodium chloride solution is the following:

- At the anode, chloride ions are oxidised and chlorine ( $\text{Cl}_2$ ) is formed.
- At the cathode: In the mercury process a sodium/mercury amalgam is formed and hydrogen ( $\text{H}_2$ ) and hydroxide ions ( $\text{OH}^-$ ) are formed by the reaction of the sodium in the amalgam with water in the denuder. In membrane and diaphragm cells, water decomposes to form hydrogen ( $\text{H}_2$ ) and hydroxide ions ( $\text{OH}^-$ ) at the cathode.

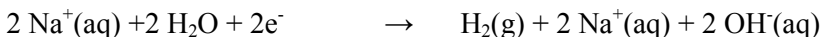
For all processes the dissolving of salt, sodium chloride, is:



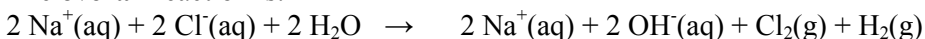
The **anode** reaction for all processes is:

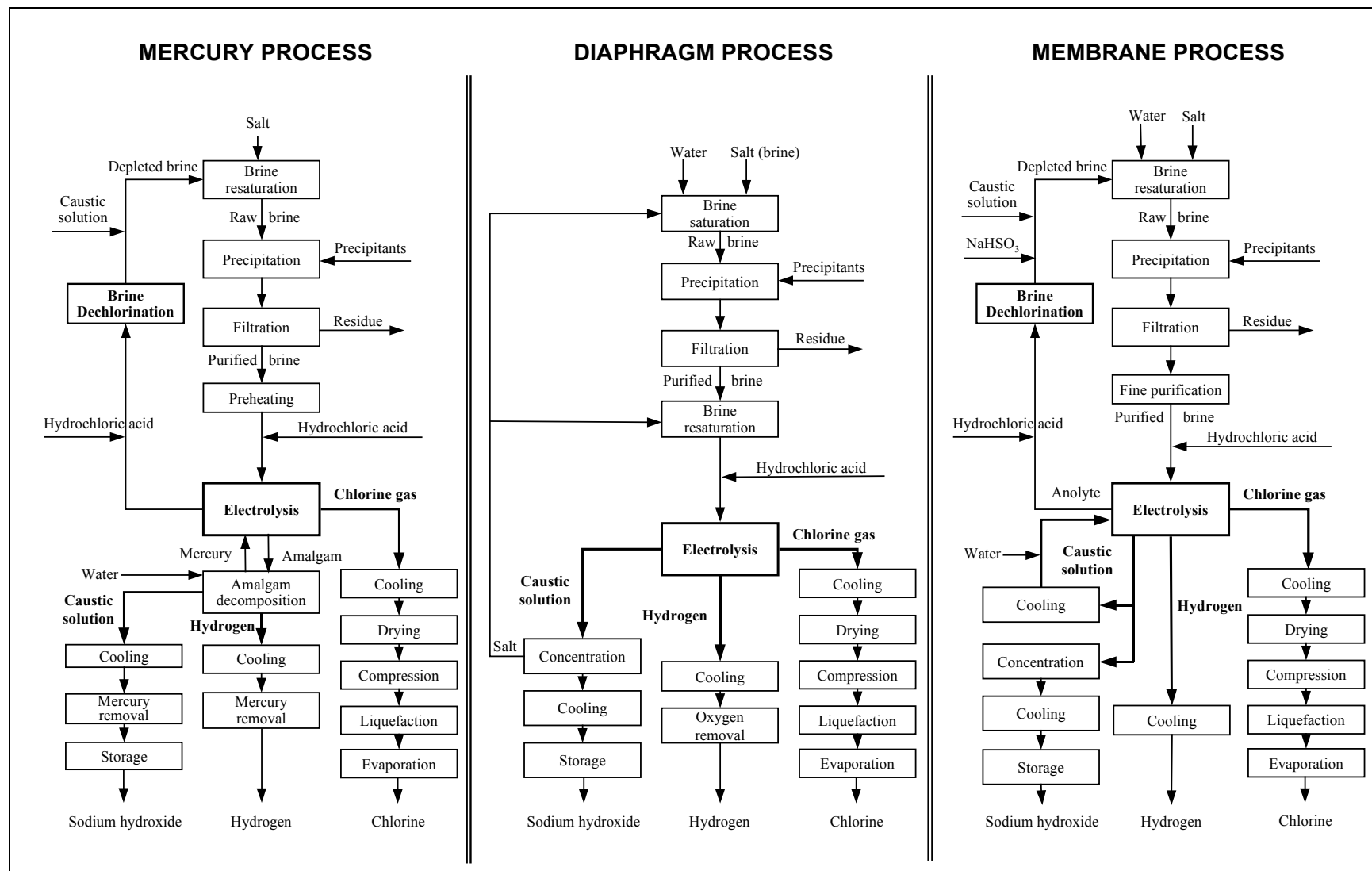


The **cathode** reaction is:



The **overall** reaction is:



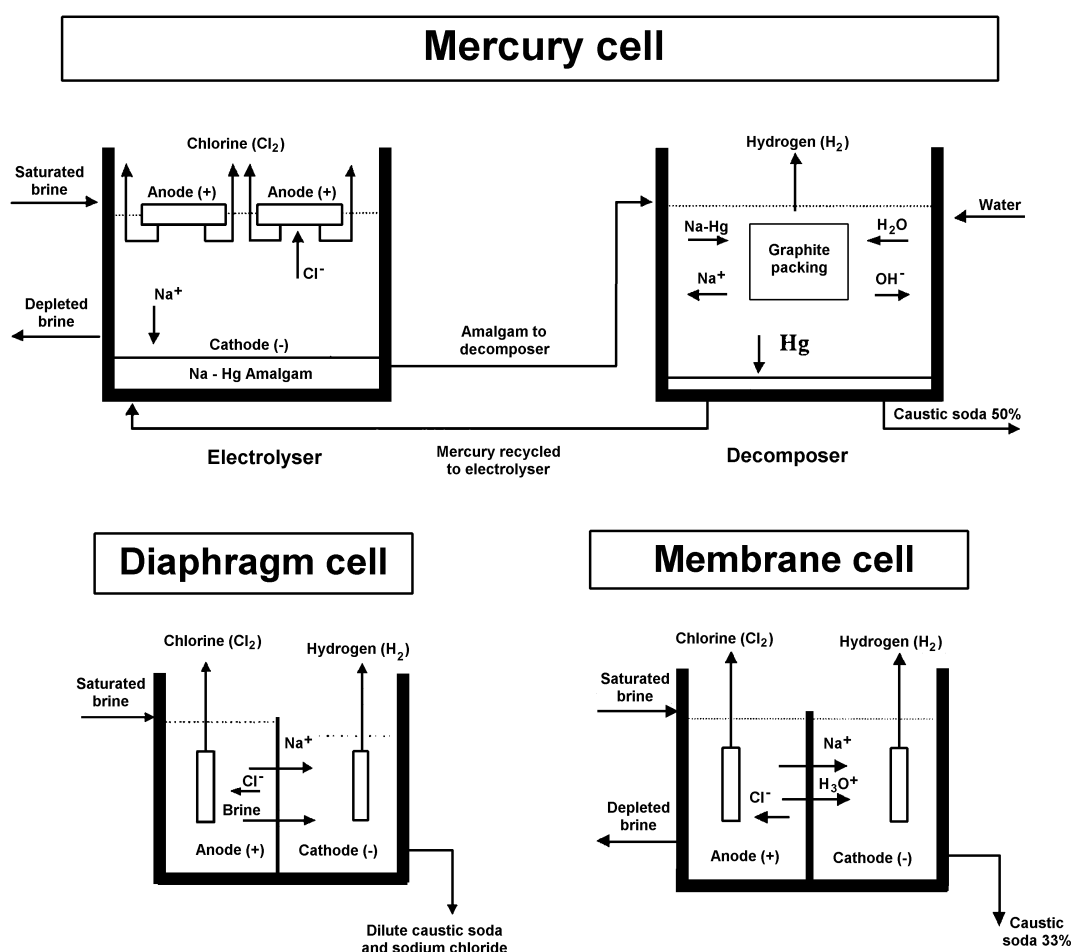


**Figure 2.1: Flow diagram of the three main chlor-alkali processes**  
based on [Kirk-Othmer, 1991], [Ullmann's, 1996]

The main characteristics of the three electrolysis processes are presented in Table 2.1.

	<b>Mercury</b>	<b>Diaphragm</b>	<b>Membrane</b>
Caustic quality	High, <30 ppm NaCl 5-150 µg Hg/l (Before treatment the Hg level is between 2.5-25 mg Hg/l)	1.0-1.5% by weight NaCl (Before treatment the NaCl content is about 18%) 0.1% NaClO <sub>3</sub> Not suitable for some applications	High, <50 ppm NaCl
Caustic concentration	<b>50%</b>	<b>12%</b> , requires concentration to 50% for some applications	<b>33%</b> , requires concentration to 50% for some applications
Chlorine quality	Contains low levels of oxygen (< 0.1%) and hydrogen	Oxygen content between 1.5-2.5%	Oxygen content between 0.5% and 2%, depending on whether an acidified electrolyte is used
Brine feedstock	Some purification required but depends on purity of salt or brine used	Some purification required but depends on purity of salt or brine used	Very high purity brine is required as impurities affect membrane performance
Variable electric load performance	Good variable electricity load performance, down to 30 % of full load possible for some cell rooms, which is very important in some European countries	Tolerates only slight variation in electricity load and brine flows in order to maintain diaphragm performance	Variable electricity load performance less than for mercury (40-60% depending on design load), affects product quality, and efficiency at lower loads

**Table 2.1: Main characteristics of the different electrolysis processes**  
after [Kirk-Othmer, 1991], [Lindley, 1997], [Ullmann's, 1996] and other sources



**Figure 2.2: Simplified scheme of chlorine electrolysis cells**  
after [Dutch report, 1998]

## 2.1 The mercury cell process

The mercury cell process has been in use in Europe since 1892 and accounted in 1999 for 58 % of total production in western Europe. As shown in Figure 2.3, the mercury cell process involves two “cells”. In the primary electrolyser (or brine cell), purified and saturated brine containing approximately 25% sodium chloride flows through an elongated trough that is slightly inclined from the horizontal. In the bottom of this trough a shallow film of mercury (Hg) flows along the brine cell co-currently with the brine. Closely spaced above the cathode, an anode assembly is suspended.

Electric current flowing through the cell decomposes the brine passing through the narrow space between the electrodes, liberating chlorine gas (Cl<sub>2</sub>) at the anode and metallic sodium (Na) at the cathode. The chlorine gas is accumulated above the anode assembly and discharged to the purification process.

As it is liberated at the surface of the mercury cathode, the sodium immediately forms an amalgam [Kirk-Othmer, 1991]. The concentration of the amalgam is maintained at 0.2-0.4% Na (by weight) so that the amalgam flows freely, 0.3% is the reference figure in [Gest 93/186, 1993]. The liquid amalgam flows from the electrolytic cell to a separate reactor, called the decomposer or denuder, where it reacts with water in the presence of a graphite catalyst to form sodium hydroxide and hydrogen gas. The sodium-free mercury is fed back into the electrolyser and reused.

The reaction in the electrolyser is:  $2 \text{Na}^+ + 2\text{Cl}^- + 2 \text{Hg} \rightarrow 2 \text{Na-Hg} + \text{Cl}_2(\text{g})$

The reaction in the decomposer is:  $2 \text{Na-Hg} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Na}^+ + 2 \text{OH}^- + \text{H}_2(\text{g}) + 2 \text{Hg}$

The brine anolyte leaving the cell is saturated with chlorine and must be dechlorinated before being returned to the dissolvers.

The sodium hydroxide is produced from the denuder at a concentration of about 50%; the maximum value reported is 73% [Ullmann's, 1996]. However, industry reports state that no plant in Europe is known to be operating above 50%.

The decomposer may be regarded as a short-circuited electrical cell in which the graphite catalyst is the cathode and sodium amalgam the anode.

For its operation, the mercury cell depends upon the higher overpotential of hydrogen versus mercury to achieve the preferential release of sodium rather than hydrogen. However, impurities that can appear on the mercury surface may lack this overvoltage protection and can cause localised release of hydrogen into the chlorine (hydrogen can form an explosive mixture (>4% H<sub>2</sub>) in chlorine or air). The presence of even trace amounts of certain metals, such as vanadium, can cause the release of dangerous amounts of hydrogen.

Mercury cells are usually operated to maintain a 21-22% (by weight) concentration of salt in the spent brine discharged from the electrolyser. This corresponds to the decomposition of 15-16% of the salt during a single pass. Further salt decomposition to a lower concentration in the brine would decrease brine conductivity, with the attendant loss of electrical efficiency.

A portion, or in some cases all, of the depleted brine is subsequently dechlorinated, resaturated with solid salt, and returned to the cell brine feed. Some facilities purge small amounts of brine solution and use new brine as make-up in order to prevent the build-up of impurities, mainly sulphate, in the brine. Figure 2.3 shows a flow diagram of the mercury cell.

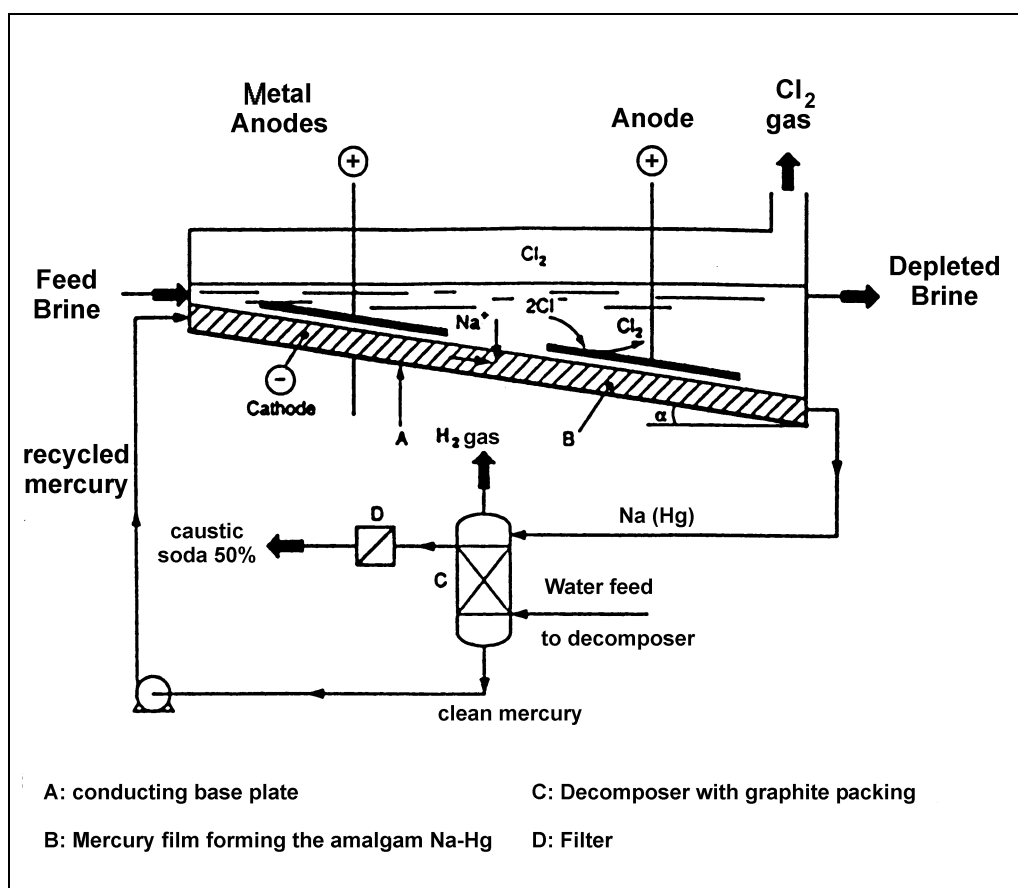


Figure 2.3: Flow diagram of mercury cell technology

### 2.1.1 The mercury cathode electrolyser and decomposer

The cell is made of an elongated, slightly inclined trough and a gas-tight cover. The trough is made of steel, and its sides are lined with a protective, non-conductive coating to prevent contact with the anolyte, to confine brine-cathode contact to the mercury surface, and to avoid the corrosive action of the electrolyte. Modern electrolyzers are 1-2.5 m wide and 10-25 m long. As a result, the cell area today can be greater than 30 m<sup>2</sup>. The size of the cells can be varied over a broad range to give the desired chlorine production rate. At the design stage, computer programs can be used to optimise the cell size, number of cells, and optimum current density as a function of the electricity cost and capital cost [Ullmann's, 1996]. The steel base is made as smooth as possible to ensure mercury flow in an unbroken film. In the event of a break in the mercury surface, caustic soda will be formed on the bare (steel) cathode, with simultaneous release of hydrogen, which will mix with the chlorine. Because hydrogen and chlorine can form a highly explosive mixture, great care is necessary to prevent hydrogen formation in the cell.

Characteristics of the cathode: The cathode is made by a shallow layer of mercury which flows from one extremity of the cell to the other because of the slight inclination from the horizontal of the cell.

Characteristics of the anode: Electrolytic cell anodes were made of graphite until the late 1960s in western Europe when anodes of titanium coated with ruthenium oxide ( $\text{RuO}_2$ ) and titanium oxide ( $\text{TiO}_2$ ) were developed. The use of  $\text{RuO}_2$  and  $\text{TiO}_2$  coated metal anodes reduces energy consumption by about 10% and their life expectancy is higher. In recent years there have been competitive developments in detailed anode geometry, all with the aim of improving gas release in order to reduce ohmic losses and increase the homogeneity of the brine to improve anode coating life.

An “end box” is attached to each end of the electrolyser. The end box incorporates compartments for collecting the chlorine gas and weirs for separating the mercury and brine streams, washing the mercury and permitting the removal of thick mercury “butter” that is formed by impurities. [Kirk-Othmer, 1991]

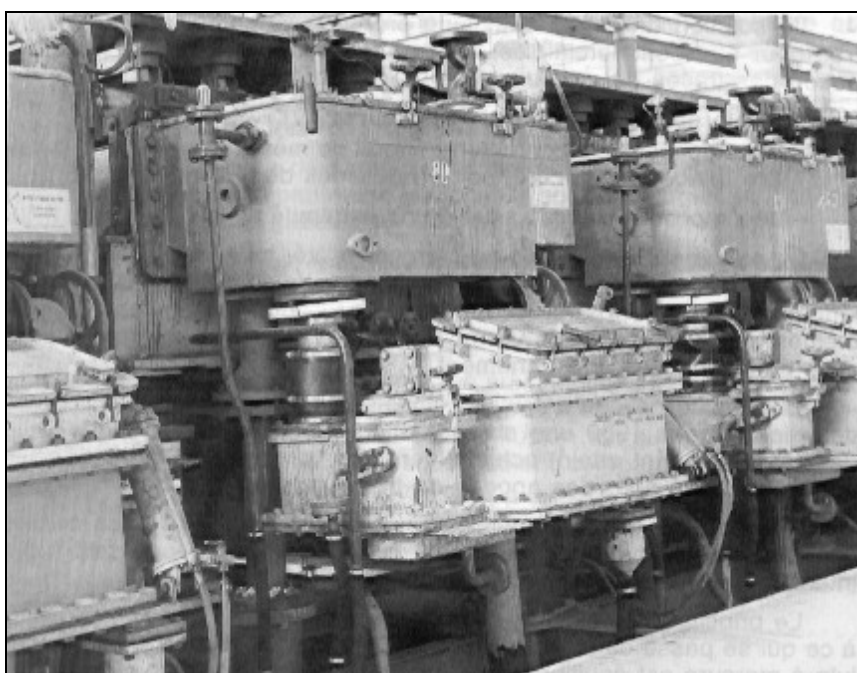
The whole electrolyser is insulated from the floor to prevent stray ground currents. Usually, several electrolyzers are placed in series by means of electrically connecting the cathode of one electrolyser to the anodes of the next electrolyser. Individual cells can be by-passed for maintenance and replacement.

The electrolyser is operated at a temperature of approximately 70-80 °C. At this temperature, the conductivity of the brine solution and the fluidity of the mercury are higher compared to operation at ambient temperature. The temperature can be achieved by preheating the saturated brine with steam and is increased in the electrolyser by the heat of resistance.

The decomposer operates at a temperature of approximately 90-130 °C, which is caused by the chemical reactions in the decomposer and the input of warm amalgam from the electrolyser.

### 2.1.2 Decomposition of the amalgam

The amalgam is decomposed in horizontal decomposers, alongside or beneath the cell (Figure 2.4) or more often, since ca. 1960, in vertical decomposers (or denuders), at one end of the cell (Figure 2.5). Industrial decomposers are essentially short-circuited electrochemical primary cells. The most common catalyst is graphite, usually activated by oxides of iron, nickel or cobalt or by carbides of molybdenum or tungsten.



**Figure 2.4: Mercury cells with horizontal decomposer**  
[Le Chlore, 1996]

The mercury process has the advantage over diaphragm and membrane cells that it produces a chlorine gas with nearly no oxygen, and a 50% caustic soda solution. However, mercury cells operate at a higher voltage than diaphragm and membrane cells and, therefore, use more energy (caustic soda concentration excluded). The process also requires a pure brine solution with little



or no metal contaminants to avoid the risk of explosion through hydrogen generation in the cell. The amalgam process inherently gives rise to environmental releases of mercury.



**Figure 2.5: Mercury cells with vertical decomposer**  
[Le Chlore, 1996]

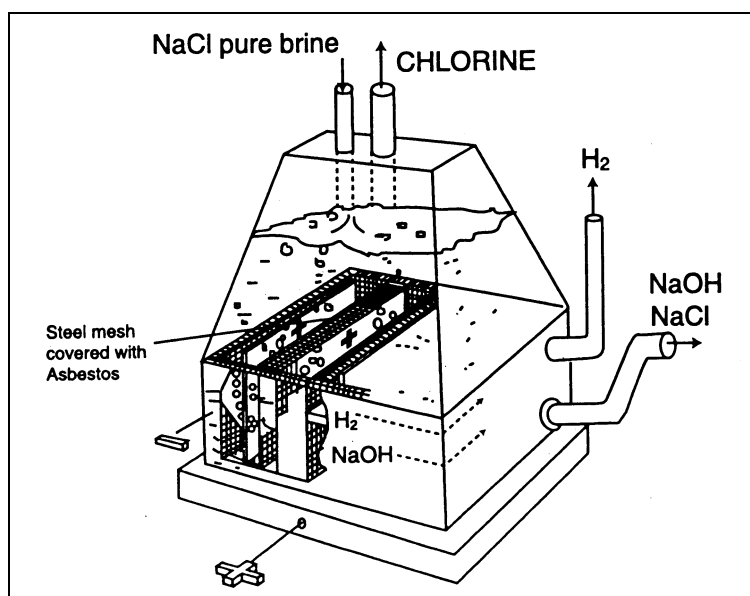
## 2.2 The diaphragm cell process

The diaphragm process was developed in the 1880s in the USA and was the first commercial process used to produce chlorine and caustic soda from brine. In North America, diaphragm cells are still the primary technology, accounting for roughly 70% of all USA production. The process differs from the mercury cell process in that all reactions take place within one cell and the cell effluent contains both salt and caustic soda. A diaphragm is employed to separate the chlorine liberated at the anode, and the hydrogen and caustic soda produced directly at the cathode. Without the diaphragm to isolate them, the hydrogen and chlorine would spontaneously ignite and the caustic soda and chlorine would react to form sodium hypochlorite ( $\text{NaClO}$ ), with further reaction to produce sodium chlorate ( $\text{NaClO}_3$ ) [Kirk-Othmer, 1991].

The diaphragm is usually made of asbestos and separates the feed brine (anolyte) from the caustic-containing catholyte. Purified brine enters the anode compartment and percolates through the diaphragm into the cathode chamber. The percolation rate is controlled by maintaining a higher liquid level in the anode compartment to establish a positive and carefully controlled hydrostatic head. The percolation rate is determined as a compromise between a low rate that would produce a desirably high concentration of caustic soda in the catholyte (which provides the cell effluent) and a high rate to limit back-migration of hydroxyl ions from catholyte to anolyte, which decreases cathode current efficiency [Kirk-Othmer, 1991].

In the diaphragm cell, saturated brine (about 25%  $\text{NaCl}$ ) is decomposed to approximately 50% of its original concentration in a pass through the electrolyser as compared to a 16% decomposition of salt per pass in mercury cells. Heating caused by passage of current through the diaphragm cell raises the operating temperature of the electrolyte to 80-99 °C.

When graphite anodes were used, the diaphragm became inoperable after 90-100 days due to plugging of the diaphragm by particles of graphite. Nowadays, all plants in the European Union use metal anodes and the lifetime of the diaphragm is over one year. Their service life has also increased because their compositions have changed. At the beginning the diaphragms were made of asbestos only and were rapidly clogged by calcium and magnesium ions coming from the brine. Asbestos was chosen because of its good chemical stability and because it is a relatively inexpensive and abundant material. Beginning in the early 1970s, asbestos diaphragms began to be replaced by diaphragms containing 75% asbestos and 25% of fibrous fluorocarbon polymer of high chemical resistance. These diaphragms, trade named Modified Diaphragms, are more stable. The polymer stabilises the asbestos, which in itself lowers cell voltage and also allows for the use of the expandable anode [Le Chlore, 1995][Ullmann's, 1996]. Chrysotile asbestos ("white asbestos") is the only form of asbestos used in diaphragm cells.



**Figure 2.6: Typical diaphragm electrolysis cell**  
[USEPA, 1995]

Both diaphragm and membrane cells for the production of chlorine and sodium hydroxide are classified as either monopolar or bipolar. The designation does not refer to the electrochemical reactions that take place, which of course require two poles or electrodes for all cells, but to the electrolyser construction or assembly. There are many more chlor-alkali production facilities with monopolar cells than with bipolar cells. The monopolar electrolyser is assembled so that the anodes and cathodes are arranged in parallel. As a result of this configuration, all cells have the same voltage of about three to four volts; up to 200 cells can be constructed in one circuit. Bipolar electrolysers have unit assemblies of the anode of one cell unit directly connected to the cathode of the next cell unit, thus minimising intercell voltage loss. These units are assembled in series.

All diaphragm cells produce cell liquor that contains ca. 11% caustic soda and 18% sodium chloride. This solution is evaporated to 50% NaOH by weight at which point all of the salt, except a residual 1.0-1.5% by weight, precipitates out. The salt generated is very pure and is typically used to make more brine. This high quality sodium chloride is sometimes used as a raw material for an amalgam or membrane process. A flow diagram of a possible integrated site is shown in Figure 2.7 on page 17.

Low concentrations of oxygen in chlorine are formed by electrolytic decomposition of water and hypochlorous acid (from the reaction of chlorine with water).



Precipitation of magnesium and calcium hydroxides on the catholyte side of the diaphragm may also create blocking problems. Hydrochloric acid is often added to the brine to remove  $\text{CO}_2$ ; it may also be added to the brine entering the anode compartment to reduce back-migration of hydroxyl ions and to suppress formation of hypochlorous acid.

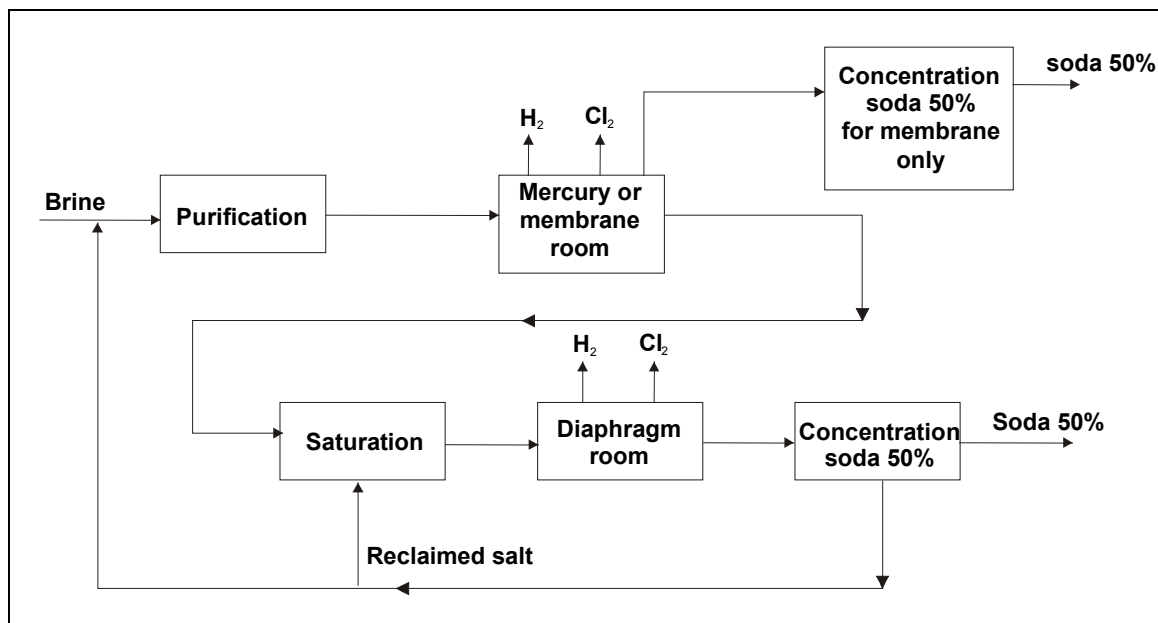


Figure 2.7: Flow diagram of integration of membrane or mercury and diaphragm processes

Diaphragm cells have the advantage of:

- operating at a lower voltage than mercury cells
- operating with less pure brine than required by membrane cells

When using asbestos diaphragms, the diaphragm process inherently gives rise to environmental releases of asbestos.

### 2.2.1 Diaphragm without asbestos

Due to the potential exposure of employees to asbestos and emissions in the environment, efforts are being expanded to replace the asbestos with other diaphragm materials.

Development of non-asbestos diaphragms started in the middle of the 1980s and some companies have now succeeded in operating with them. The basis of the material used is the same in all diaphragms developed free of asbestos, i.e. a fluorocarbon polymer, mainly PTFE (polytetrafluoroethylene). The differences lie in the fillers used and the way the hydrophobic PTFE fibres are treated and deposited in order to form a permeable and hydrophilic diaphragm (see Section 4.3.2).

### 2.2.2 Activated cathodes

Many different types of activated cathodic coating are under development in order to reduce the power consumption of the cell. These have to be robust because the powerful water jet used to remove the diaphragm from the cathode mesh can adversely affect the cathode.

An industrial application of “integrated pre-cathode” diaphragm has been conducted (full scale) and has been found to contribute to saving energy by reducing electric power consumption and

improving current efficiency. The life time of the diaphragm has also been found to be improved by introduction of the pre-cathode (see Section 0).

## **2.3 The membrane cell process**

In the 1970s, the development of ion-exchange membranes enabled a new technology to produce chlorine: the membrane electrolysis process. The first ion exchange membranes were developed at the beginning of the 1970s by Du Pont (Nafion), followed by Asahi Glass (Flemion) which installed the first industrial membrane plant in Japan in 1975 due to the pressure of Japanese environmental regulations. Non-chlor-alkali related mercury pollution in Minamata drove the authorities to prohibit all mercury processes and Japan was the first country to install the membrane process on a massive scale in the mid-1980s.<sup>3</sup>

Today, it is the most promising and fast-developing technique for the production of chlor-alkali and it will undoubtedly replace the other two techniques in time. This can be deduced from the fact that since 1987 practically 100% of the new chlor-alkali plants world-wide apply the membrane process. The replacement of existing mercury and diaphragm cell capacity with membrane cells is taking place at a much slower rate because of the long lifetime of the former and because of the high capital costs of replacement.

In this process, the anode and cathode are separated by a water-impermeable ion-conducting membrane. Brine solution flows through the anode compartment where chloride ions are oxidised to chlorine gas. The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. The demineralized water added to the catholyte circuit is hydrolysed, releasing hydrogen gas and hydroxide ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32-35% by recirculating the solution before it is discharged from the cell. The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and resaturated with salt. If needed, to reach a concentration of 50% caustic soda, the caustic liquor produced has to be concentrated by evaporation (using steam).

The cathode material used in membrane cells is either stainless steel or nickel. The cathodes are often coated with a catalyst that is more stable than the substrate and that increases surface area and reduces over-voltage. Coating materials include Ni-S, Ni-Al, and Ni-NiO mixtures, as well as mixtures of nickel and platinum group metals. The anodes used are metal.

The membranes used in the chlor-alkali industry are commonly made of perfluorinated polymers. The membranes may have from one up to three layers, but generally consist of two layers. One of these layers consists of perfluorinated polymer with substituted carboxylic groups and is adjacent to the cathodic side. The other layer consists of perfluorinated polymer with substituted sulphonic groups and is adjacent to the anodic side. To give the membrane mechanical strength, the membrane is generally reinforced with PTFE fibres. The membranes must remain stable while being exposed to chlorine on one side and a strong caustic solution on the other. The general economic lifetime of chlor-alkali membranes is approximately three years, but ranges between 2-5 years [Euro Chlor report, 1997].

Membrane cells have the advantage of producing a very pure caustic soda solution and of using less electricity than the other processes. In addition, the membrane process does not use highly

---

<sup>3</sup> There are 2 mercury plants in Japan (Toagosei Co. and Nippon Soda Co.) producing potassium hydroxide (total capacity of both: 45 000 tonnes/year) which are allowed to operate because of the high grade KOH produced which is needed for the optical glass industry. The reason why membrane technology cannot achieve the same performances, however, is not known (source: Asahi Glass Co).

toxic materials such as mercury and asbestos. Disadvantages of the membrane process are that the caustic soda produced may need to be evaporated to increase concentration and, for some applications, the chlorine gas produced needs to be processed to remove oxygen. Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly additional purification steps prior to electrolysis (see paragraph on brine purification).

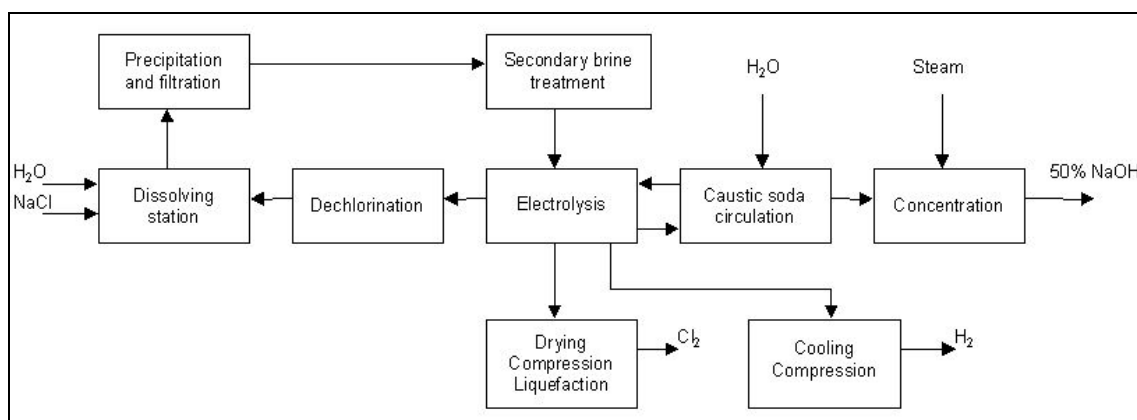


Figure 2.8: Diagram of a membrane process

Membranes cells can be configured either as monopolar or bipolar. As in the case of the diaphragm cell process, the bipolar cells have less voltage loss between the cells than the monopolar cells.<sup>4</sup> However, the number of cells connected together in the same circuit is limited.

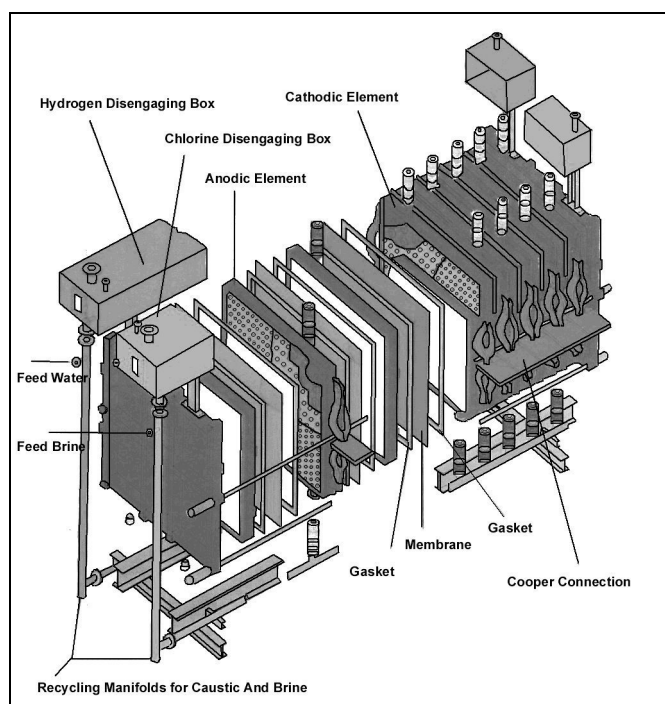


Figure 2.9: Exploded view of a monopolar membrane electrolyser

[Source: De Nora]

<sup>4</sup> It has been estimated that approximately 30 kWh are lost each year per tonne chlorine produced. Energy losses from monopolar electrolyzers are about 150 kWh per tonne chlorine produced compared to bipolar ones.



**Figure 2.10: View of a membrane cell room equipped with bipolar electrolyzers**  
(Source: Hoechst-Uhde)

## 2.4 Auxiliary processes

Apart from the cells, which remain the heart of the chlorine production line, there are other processing steps or equipment, common to amalgam, diaphragm and membrane technologies. These are:

- salt unloading and storage
- brine purification and resaturation
- chlorine processing
- caustic processing
- hydrogen processing.

### 2.4.1 Salt unloading and storage

The brine used in the mercury cell and membrane processes is normally saturated with solid salt, although some installations use solution-mined brine on a once-through basis (i.e. no brine recirculation).

Brine is generally produced by the dissolving of fresh salt in water or depleted brine from mercury and membrane processes. The basic raw material is usually solid salt: rock salt, solar salt, or vacuum-evaporated salt from purifying and evaporating solution-mined brine.

Generally the salt is stored in a sealed area equipped with a roof. Because of its high purity the vacuum salt in particular needs to be protected.

## 2.4.2 Brine purification and resaturation

### 2.4.2.1 Brine purification

As can be seen in Figure 2.1 on page 10, the brine purification process consists of a primary system for mercury and diaphragm technologies and an additional secondary system for membrane technology. This operation is needed to avoid any undesirable components (sulphate anions, cations of Ca, Mg, Ba and metals) that can affect the electrolytic process. The quality of the raw material and the brine quality requirements for each of the three technologies determine the complexity of the brine treatment unit.

#### Primary purification

##### *Precipitation*

The initial stage of purification uses sodium carbonate and sodium hydroxide to precipitate calcium and magnesium ions as calcium carbonate ( $\text{CaCO}_3$ ) and magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ). Metals (iron, titanium, molybdenum, nickel, chromium, vanadium, tungsten) may also precipitate as hydroxide during this operation. The usual way to avoid metals is to specify their exclusion in the purchase and transport specification for the salt. Sodium sulphate is controlled by adding calcium chloride ( $\text{CaCl}_2$ ) or barium salts to remove sulphate anions by precipitation of calcium sulphate ( $\text{CaSO}_4$ ) or barium sulphate ( $\text{BaSO}_4$ ). Precipitation of barium sulphate can take place simultaneously with the precipitation of calcium carbonate and magnesium hydroxide, whereas the precipitation of calcium sulphate requires a separate vessel.

##### *Filtration*

The precipitated impurities are removed by sedimentation, filtration or a combination of both. The separated filter cake is generally concentrated to 50-60% (although a figure of 60-80% is reported in the literature) solids content in rotary drum vacuum filters or centrifuges before disposal. [Ullmann's, 1996]

The purified brine should contain ideally [Ullmann's, 1996]:

Ca: <2 mg/l

Mg: <1 mg/l

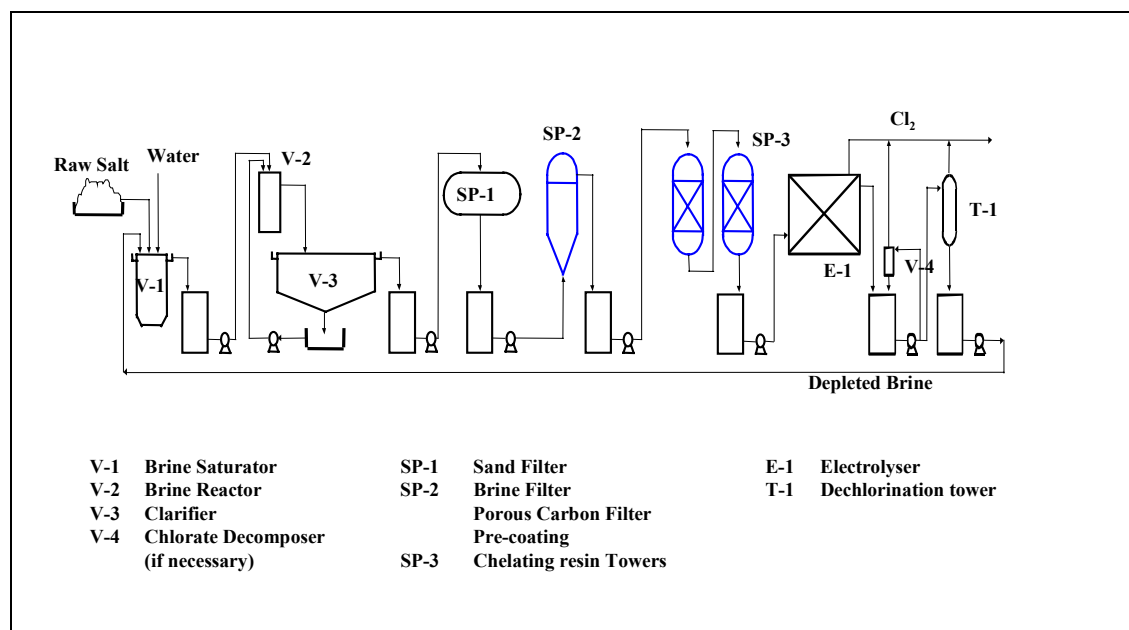
$\text{SO}_4$ : <5 g/l

#### Secondary purification: Membrane circuit

To maintain the high performance of the ion-exchange membrane, the feed brine must be purified to a greater degree than in the conventional mercury or diaphragm processes.

The precipitation step alone is not enough to reduce the levels of calcium and magnesium and additional softening is required. Figure 2.11 shows a possible lay-out for the brine purification system used in the membrane process.





**Figure 2.11: Possible lay-out for the brine purification system used in membrane process**  
(Source: Asahi Glass CO)

The secondary brine purification consists of a polish filtration step and brine softening in an ion exchange unit:

- The secondary filtration generally consists of candle-type, plate frame or pressure leaf filters (either with or without cellulose-based precoat) in order to sufficiently reduce the suspension matter and protect the ion-exchange resin from damage.
- The ion exchange chelating resin treatment is designed to decrease the alkaline earth metals to ppb level. Table 2.2 indicates the specifications required for metals,  $\text{SO}_4$  and other impurities. These specifications can vary if the users want to operate at a low current density ( $<4 \text{ kA/m}^2$ ) or at a high current density. The specifications are more stringent for high density current.
- The resin is periodically regenerated with high purity hydrochloric acid and sodium hydroxide solutions. Generally, one resin exchange column is in operation while another resin exchange column is regenerated.

A chelating resin tower must be installed, but in some cases no polishing filter is needed in the secondary brine treatment.

<b>General Table</b>					
Impurities	Unit	Upper Limit	Condition	Influence	Remarks
Ca + Mg	ppb	20		Ca: CE, Mg: V	
Sr	ppm	0.04	(SiO <sub>2</sub> =10ppm)	CE	Sr and SiO <sub>2</sub> seem to be co-precipitated within the membrane. (synergistic effect) 0.04 ppm in Sr content in purified brine is easily kept under normal operation of Chelating Resin Tower. If SiO <sub>2</sub> content is kept less than 1 ppm, then Sr is allowable up to 0.1 ppm.
SiO <sub>2</sub>	ppm	10		CE	
Ba	ppm	0.5 0.05	(Iodine=0.2) (Iodine=0.5)	CE, (V)	Ba and Iodine seem to be co-precipitated within the membrane. (synergetic effect) When SO <sub>4</sub> content is kept 6 g/l, Ba content should be 0.05ppm or less.
Iodine	ppm	0.5 0.2	(Ba=0.05) (Ba=0.5)	CE	Iodine originates from underground salt and water. If solar salt and ordinary surface water are used, Iodine content should be 0.1 ppm or less.
Fe	ppm	1		V	
Ni	ppm	0.01		V	
Heavy Metals	ppm	0.1			
Al	ppm	0.1		CE, (V)	
SO <sub>4</sub>	g/l	6		CE	We are evaluating to raise the upper limit to 8 g/l.
ClO <sub>3</sub>	g/l	20		CE	

<b>Additional Table for Plants to be operated with care</b>					
Impurities	Unit	Upper Limit	Condition	Influence	Remarks
Mn	ppm	0.1			The limit is 0.05 ppm in some plants due to caustic user needs.
Cr	ppm	1			Mainly due to caustic user needs
Cu	ppm	0.01			Mainly due to caustic user needs
Hg	ppm	10			Mainly due to caustic user needs and risk of cathode damage
F	ppm	0.5			
SS	ppm	1			Suspended Solid
TOC	ppm	1			Total Organic Carbon

CE: Current Efficiency should decrease

V: Cell voltage should increase

**Table 2.2: Example of brine specifications for the membrane process operating at a current density up to 4 kA/m<sup>2</sup>**

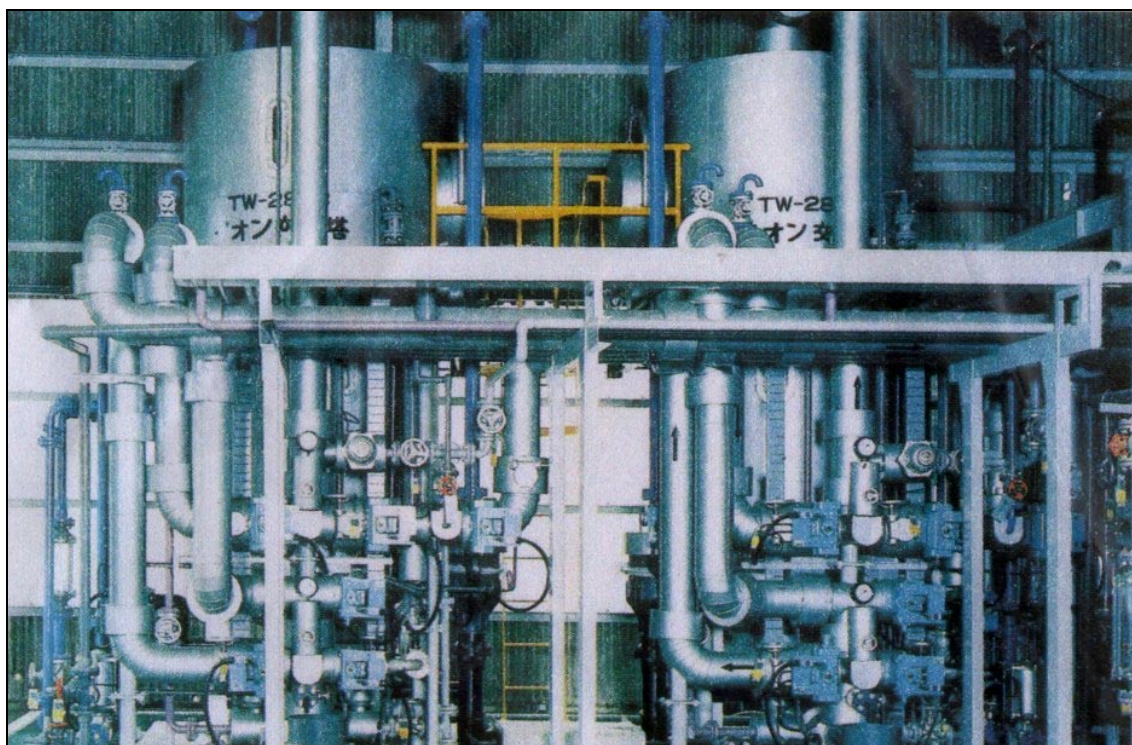
(Source: Asahi Glass Co)

### Control of nitrogen trichloride (NCl<sub>3</sub>)

Apart from sulphates and hardness ions, the brine may contain ammonium ions or organic nitrogen which are converted to nitrogen trichloride in the electrolytic cell. If concentrated in liquid form in downstream processes, NCl<sub>3</sub> may explode with disastrous results.

Nitrogen compounds in the brine is the main source of NCl<sub>3</sub>. Rock salt, in particular solution-mined salt using surface waters, will contain varying levels of ammonium and nitrate salts, whereas the use of vacuum salt in the brine recycle circuit will give very low levels of NCl<sub>3</sub>, except where ferrocyanides are added to avoid caking. Also, the water quality may vary, in particular if surface water is used. The total concentration of nitrogen compounds in the brine should be checked regularly. Chlorination at a pH higher than 8.5 or hypochlorite treatment of the brine is however, capable of destroying a large proportion of the ammonium salt impurity. [Gest 76/55, 1990]

Methods to remove NCl<sub>3</sub> from chlorine after it is formed are described in Section 4.1.6.



**Figure 2.12: View of chelate resin towers in a secondary brine purification system**  
(photograph supplied by Asahi Glass Co)



**Figure 2.13: View of polishing filters in a secondary brine purification system**  
(photograph supplied by Asahi Glass Co)



### 2.4.2.2 Brine resaturation and dechlorination

Mercury and membrane systems usually operate with brine recirculation and resaturation. There are, however, 3 waste brine mercury plants and 1 waste brine membrane plant operating in western Europe.

Some diaphragm cell lines have a once-through brine circuit, whilst others employ brine saturation using the salt recovered from the caustic evaporators.

In recirculation circuits, the depleted brine leaving the electrolyzers is first dechlorinated:

- Partially for the mercury process (leaving active chlorine in the brine keeps the mercury in ionic form and reduces the presence of metallic mercury in the purification sludge)
- Totally for the membrane process (necessary here because the active chlorine can damage the ion exchange resins of the secondary brine purification unit).

For this purpose, the brine is sent to an air blown packed column or is sprayed into a vacuum system to extract the major part of the dissolved chlorine.

No such dechlorination treatment is required for the diaphragm system since any chlorine passing through the diaphragm reacts with caustic soda in the catholyte compartment to form hypochlorite or chlorate.

For the membrane process, there is a preliminary stage of hydrochloric acid addition (to reach pH 2-2.5) in order to achieve better chlorine extraction. A further stage is also necessary to eliminate the chlorine completely; this is done by passing the brine through an activated carbon bed or by injection of a reducing agent (e.g. sulphite).

If the saturation is made with impure salt (followed by a primary purification step on the total brine flow), the pH of the brine is then brought to an alkaline value with caustic soda, to reduce the solubilisation of impurities from the salt. If the saturation is made with pure salt (with subsequent primary purification on a small part of the flow), there is no alkalisation step at that level (only in the purification phase).

Depleted brine from the mercury and membrane cells, with a concentration of 210-250 g/l, depending on the technology, current density and heat balance of the cell, is resaturated by contact with solid salt to achieve a saturated brine concentration of 310-315 g/l.

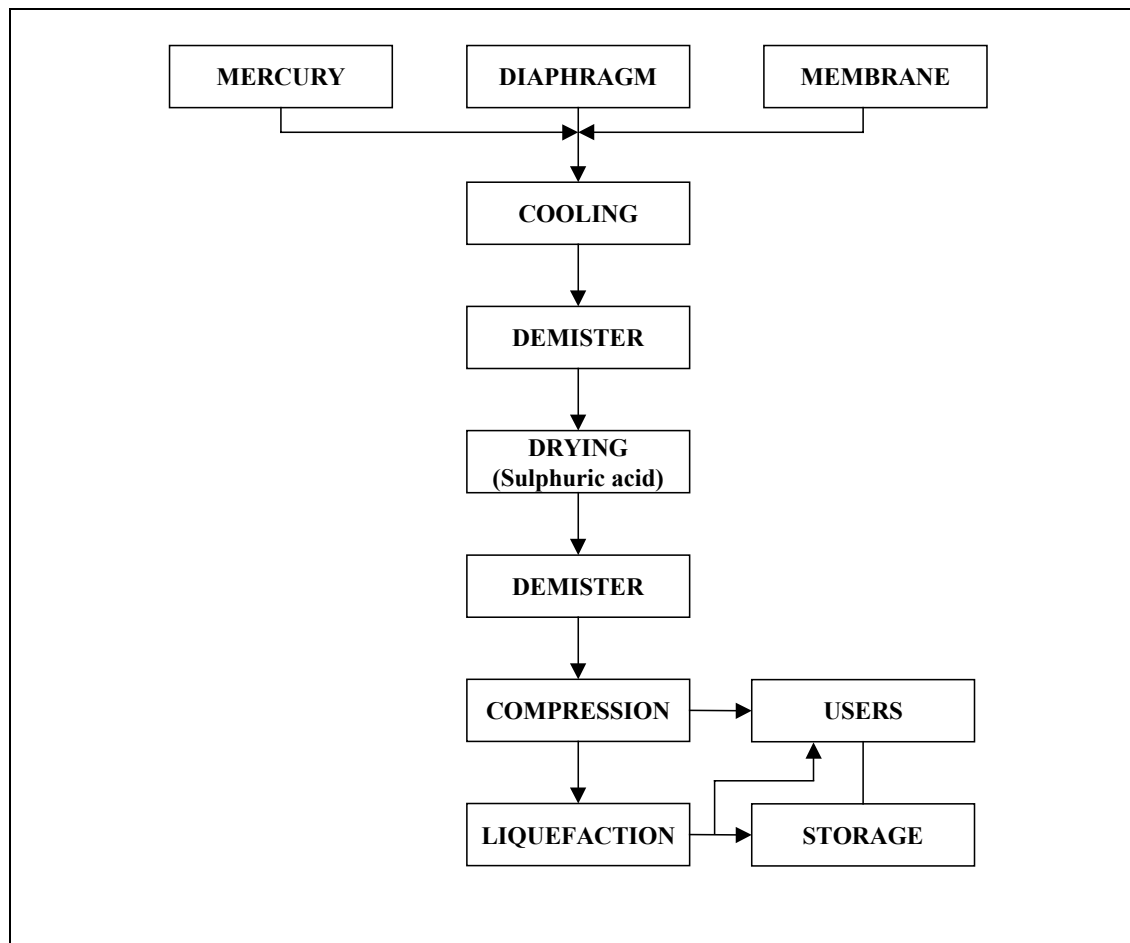
In the case of diaphragm cells, the catholyte liquor (10-12% NaOH, 15% NaCl) goes directly to the caustic evaporators where solid salt and 50% caustic are recovered together. Fresh brine can be saturated with recycled solid salt from the caustic evaporators before entering the diaphragm electrolyzers.

Resaturators can be either open or closed vessels.

The pH of the brine sent to the electrolyzers may be adjusted to an acidic value (pH 4) with hydrochloric acid in order to protect the anode coating, to keep the formation of chlorate at a low level and to decrease the oxygen content in the chlorine gas. Hydrochloric acid can also be added in the anodic compartments of membrane cells to further reduce the content of oxygen in the chlorine, especially for electrolyzers with older membranes (poorer performances). The (bi)carbonates introduced with the salt are decomposed by these acid additions, producing gaseous carbon dioxide.

### 2.4.3 Chlorine production, storage and handling

Generally, before the chlorine can be used, it goes through a series of processes for cooling, cleaning, drying, compression and liquefaction. In some applications, it can be used as a dry gas without need for liquefaction. Very occasionally it can be used directly from the electrolyzers. A general flow of chlorine from the electrolyzers to storage is presented in Figure 2.14.



**Figure 2.14: The flow of chlorine from the electrolyzers to storage**  
[Euro Chlor report, 1997]

The chlorine process usually takes hot, wet cell gas and converts it to a cold, dry gas. Chlorine gas leaving the electrolyzers is at approximately 80-90 °C and saturated with water vapour. It also contains brine mist, impurities such as N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and traces of chlorinated hydrocarbons. Electrolyzers are operated at essentially atmospheric pressure with only a few milli-atmospheres differential pressure between the anolyte and the catholyte.

#### Cooling

In the primary cooling process, the total volume of gas to be handled is reduced and a large amount of moisture is condensed. Cooling is accomplished in either one stage with chilled water or in two stages with chilled water only in the second stage. Care is taken to avoid excessive cooling because, at around 10 °C, chlorine can combine with water to form a solid material known as chlorine hydrate. Maintaining temperatures above 10 °C prevents blockages in process equipment.

Two methods are most frequently used to cool chlorine gas:

- 1) Indirect cooling through a titanium surface (usually in a single-pass vertical shell-and-tube exchanger). The resultant condensate is either fed back into the brine system of the mercury process or dechlorinated by evaporation in the case of the diaphragm process. This method causes less chlorine to be condensed or absorbed and generates less chlorine-saturated water for disposal. [Brien-White, 1995]
- 2) Direct contact with water. The chlorine gas is cooled by passing it directly into the bottom of a tower in which the packing is divided into two Sections, for 2-stage cooling. Water is sprayed into the top and flows counter-current to the chlorine. The cooling water should be free of traces of ammonium salts to avoid the formation of nitrogen trichloride. This method has the advantage of better mass-transfer characteristics and higher thermal efficiency.

Closed circuit direct cooling of chlorine combines the advantages of the two methods. The chlorine-laden water from the cooling tower is cooled in titanium plate coolers and recycled. The surplus condensate is treated exactly like the condensate from indirect cooling.

Following primary cooling, chlorine gas is demisted of water droplets and brine impurities. Impurities are removed mechanically by using special filters, or by means of an electrostatic precipitator. Chlorine is then passed to the drying towers.

### **Drying**

Chlorine from the cooling system is more or less saturated with water vapour. The water content is typically 1-3%. This must be reduced in order to avoid downstream corrosion and minimise the formation of hydrates [Brien-White, 1995].

Drying of chlorine is carried out almost exclusively with concentrated sulphuric acid [Ullmann's, 1996]. Drying is accomplished in counter-current sulphuric acid contact towers which reduce the moisture content to less than 20 ppm [Stenhammar]. Dry chlorine leaving the top of the drying tower passes through high efficiency demisters to prevent the entrainment of sulphuric acid droplets. The spent acid usually becomes a waste product or requires reprocessing if it is reused. For example, it has to be dechlorinated by air blowing and may be reconcentrated before being sold or used for effluent treatment.

### **Compression**

After drying, chlorine gas might be scrubbed with liquid chlorine or treated with ultra-violet irradiation to reduce levels of nitrogen trichloride and then it may be compressed in a variety of compressors:

- sulphuric acid liquid ring compressors at low pressures (~4 bar)
- mono- or multi-stage centrifugal compressors (5 bar or higher)
- reciprocating compressors (>11 bar)
- screw compressors (various pressures)

Because of heat build-up from compression, multistage units with coolers between stages are usually necessary. Compressor seals are generally fitted with a pressurised purge to inhibit leakage of chlorine to the atmosphere [UK Guidance note, 1993].

To avoid noise, which is quite important even for low pressures, chlorine compressors should be sound insulated.

## Liquefaction

Liquefaction can be accomplished at different pressure and temperature levels, at ambient temperature and high pressure (for example 18 °C and 7-12 bar), at low temperature and low pressure (for example -35 °C and 1 bar) or any other intermediate combination of temperature and pressure.

The chosen liquefaction pressure and temperature influence the choice of cooling media and the safety precautions necessary to operate safely. However, the efficiency of liquefaction is limited because hydrogen is concentrated in the residual gas and its concentration needs to be kept below the explosive limits.

The choice of the cooling medium in a certain stage of the liquefaction depends on the temperature of the chlorine. When the temperature is sufficiently high, water can be used as an indirect cooling medium. When the temperature is relatively low, other cooling media such as HCFCs or HFCs (indirect cooling), ammonia (indirect cooling) or liquid chlorine (direct cooling) are used.

The temperature of the chlorine gas in a certain stage depends mainly on the initial temperature and on the pressure increase during compression. A large pressure increase generally enables water cooling, but implies an increased hazard risk. Chlorine temperature has to be kept well below the point where it reacts spontaneously and uncontrollably with iron (approx. 120 °C).

Construction materials must be chosen to suit the conditions under which chlorine is being handled:

- Wet or dry
- Gas or liquid
- Temperature
- Pressure

In terms of safety, it is very important to avoid, during compression and liquefaction, any possibility of mixing chlorine with oils or greases which are reactive as regards chlorine.

Table 2.3 shows the possible trade-off between different types of chlorine gas liquefaction, cooling methods applied and safety aspects.

Liquefaction system	Cooling medium	Safety aspect	Storage
High pressure (7-16 bar) and high temperatures	Water	High precautions	Lowest energy costs but high material costs
Medium pressure (2-6 bar) and medium temperatures (between -10 and -20 °C)	Water-HCFC/ HFC or ammonia	Moderate precautions	Moderate energy and material costs
Normal pressure (~1 bar) and low temperatures (below -40 °C)	Mainly HCFC/HFC or ammonia	Precautions <sup>1</sup>	Cryogenic storage of liquid chlorine is possible. High energy and lower material costs

1. Attention must be paid to the increased solubility of other gases at low temperatures, especially carbon dioxide

**Table 2.3: Possible trade-off in chlorine gas liquefaction**  
based on [Ullmann's, 1996], [Dutch report, 1998]

## Handling and storage

Chlorine is liquefied and stored at ambient or low temperature. The liquid chlorine from the bulk tank can be used as a feedstock for on-site processes or loaded into containers, road or rail tankers. Because of the high toxicity of chlorine, the storage area must be carefully monitored and special care must be taken during loading operations.

### 2.4.3.1 Dealing with impurities

Chlorine gas from the electrolysis cells may contain impurities such as nitrogen trichloride ( $\text{NCl}_3$ ), bromine ( $\text{Br}_2$ ), halogenated hydrocarbons ( $\text{C}_x\text{H}_y\text{X}_z$ ), carbon dioxide ( $\text{CO}_2$ ), oxygen ( $\text{O}_2$ ), nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ).

Nitrogen trichloride, bromine and halogenated hydrocarbons predominantly dissolve in the liquid chlorine, whereas the non-condensable gases ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ) remain in the gas phase and increase in concentration during chlorine liquefaction. Traces of sulphuric acid, ferric sulphate, ferric chloride and/or carbon tetrachloride might also be present in the gas phase after drying and liquefaction of chlorine.

Special attention should be paid to the following impurities:

#### Water

All metals are attacked by wet chlorine with the exception of titanium and tantalum. Titanium can only be used in wet chlorine conditions; it spontaneously combusts in dry chlorine.

#### Hydrogen

All three technologies produce hydrogen which can form an explosive mixture ( $>4\% \text{H}_2$ ) in chlorine or air. Light, friction and gas depressurisation may bring enough energy to initiate the reaction at ambient temperature. Chlorine gas is analysed regularly to ensure the absence of an explosive mixture.

#### Nitrogen trichloride

Nitrogen trichloride is formed during the electrolytic production of chlorine, due to side reactions between the chlorine and various nitrogen compounds in the brine solution. 1 ppm of  $\text{NH}_3$  in brine is enough to give  $>50$  ppm  $\text{NCl}_3$  in liquid chlorine. In plants which use direct contact water cooling of the chlorine gas before drying and compression,  $\text{NCl}_3$  may also be formed if the water is polluted with nitrogen compounds [Gest 76/55, 1990].

Nitrogen trichloride is characterised by its utmost instability. Experimental results show that a concentration of  $\text{NCl}_3$  greater than 3% by weight at ambient temperature is capable of accelerated decomposition which is strongly exothermic.

$\text{NCl}_3$  has a higher boiling point than chlorine and any  $\text{NCl}_3$  present in the chlorine gas will concentrate in the liquid phase in a chlorine liquefaction process. Any evaporative handling of liquid chlorine is potentially dangerous due to the selective concentration of  $\text{NCl}_3$  in the liquid phase.

Methods to remove  $\text{NCl}_3$  from chlorine are described in Section 4.1.6.

## Bromine

The quantity of bromine present depends on the quality of the salt used. Its concentration is generally higher if chlorine is obtained by electrolysis of potassium chloride to obtain potassium hydroxide. Bromine, like water, can accelerate the corrosion of the materials.

## Non-condensable gases (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>)

There are several ways to deal with the non-condensable gases, depending on the layout of the chlorine liquefaction unit. Some are described below.

### *Dilution with air and production of weak NaOCl*

During chlorine gas compression and cooling, most of the chlorine gas is condensed. However, the non-condensable gases (H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>) increase in concentration. By diluting the remaining chlorine gas with air, the concentration of hydrogen can be kept below the explosion limit. This allows additional liquefaction of chlorine gas. The remaining gases after liquefaction (so-called "tail gas") have to be purged from the system. The tail gas still contains a significant amount of chlorine, and the gas is therefore normally led to the chlorine destruction/absorption unit.

### *Production of hydrochloric acid*

Instead of diluting the remaining gases after partial condensation of the chlorine gas, the hydrogen can be removed from the system by means of a reaction with chlorine gas in a column. This removes virtually all the hydrogen and yields gaseous hydrochloric acid, which exists harmlessly with the chlorine gas and can be recovered in a hydrochloric acid unit. The remaining chlorine gas can now safely be further condensed. The tail gases with some chlorine gas and the remaining non-condensable gases (CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>) will be passed through a hydrochloric acid unit. This solution can be chosen if HCl is a saleable product or if it can be used as a feedstock for downstream production, such as ferric chloride.

## 2.4.3.2 The chlorine absorption unit

The purpose of a typical chlorine absorption system is two-fold:

- 1) To continuously absorb chlorine gas arising in streams such as tail gas from liquefaction, air blown from waste brine or chlorine condensate dechlorination and also wet and dry maintenance headers. Up to 5%, but normally less than 1%, of the plant production is absorbed in this way.
- 2) To absorb the full cell-room production during emergency for an adequate period, usually not less than 15 to 30 minutes, to enable corrective measures to be taken or the plant to be shut down in a safe manner. Gravity-fed head tanks or pumps supplied with back-up power supplies may be used to give increased reliability and operation under power failure conditions.

The above functions could be undertaken in separate purpose-built units, providing the integrity of the systems is maintained by having back-up scrubbers. All gaseous vents contaminated or potentially contaminated with chlorine thus pass into the atmosphere through caustic scrubbing towers containing packing irrigated with caustic soda. Heat is generated by the absorption reaction and temperatures should not be allowed to increase above about 30 °C to avoid formation of sodium chlorate instead of sodium hypochlorite solution. To avoid overheating



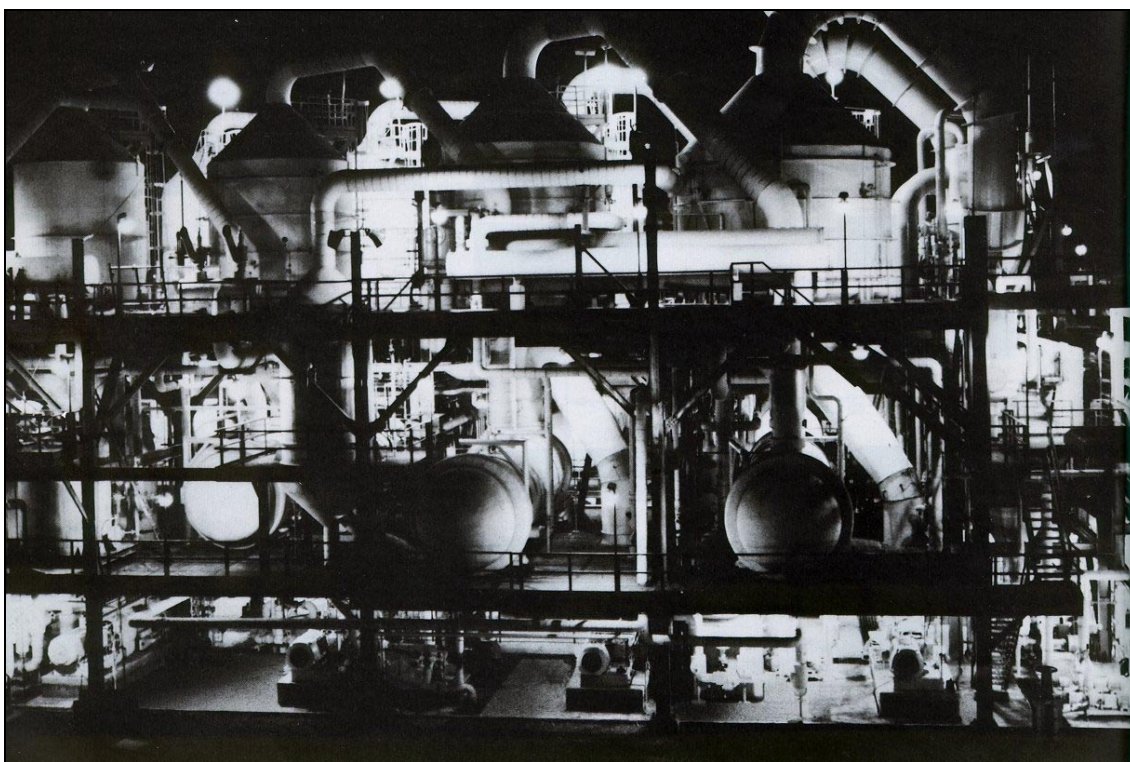
during a full-scale relief, the fresh caustic soda feed solution should not be stronger than about 12% by weight. Higher caustic concentrations can be used providing adequate cooling is installed, but there is an increased risk of solids deposition and blockage.

Tail gas from the chlorine liquefaction unit contains residual chlorine and carbon dioxide, which are absorbed in the caustic, and hydrogen, which is diluted with air to less than 4% by volume to avoid flammable mixtures.

Optimum design of scrubbing systems must include high reliability, automatic operation in emergencies, and countercurrent flow of liquid and gas to achieve low exit concentrations. If sale is not possible, efficient decomposition of the sodium hypochlorite produced into sodium chloride can be achieved using a nickel catalyst.

#### 2.4.4 Caustic production, storage and handling

Sodium hydroxide (caustic soda) is produced in a fixed ratio of 1.128 tonnes (as 100% NaOH) per tonne chlorine produced.

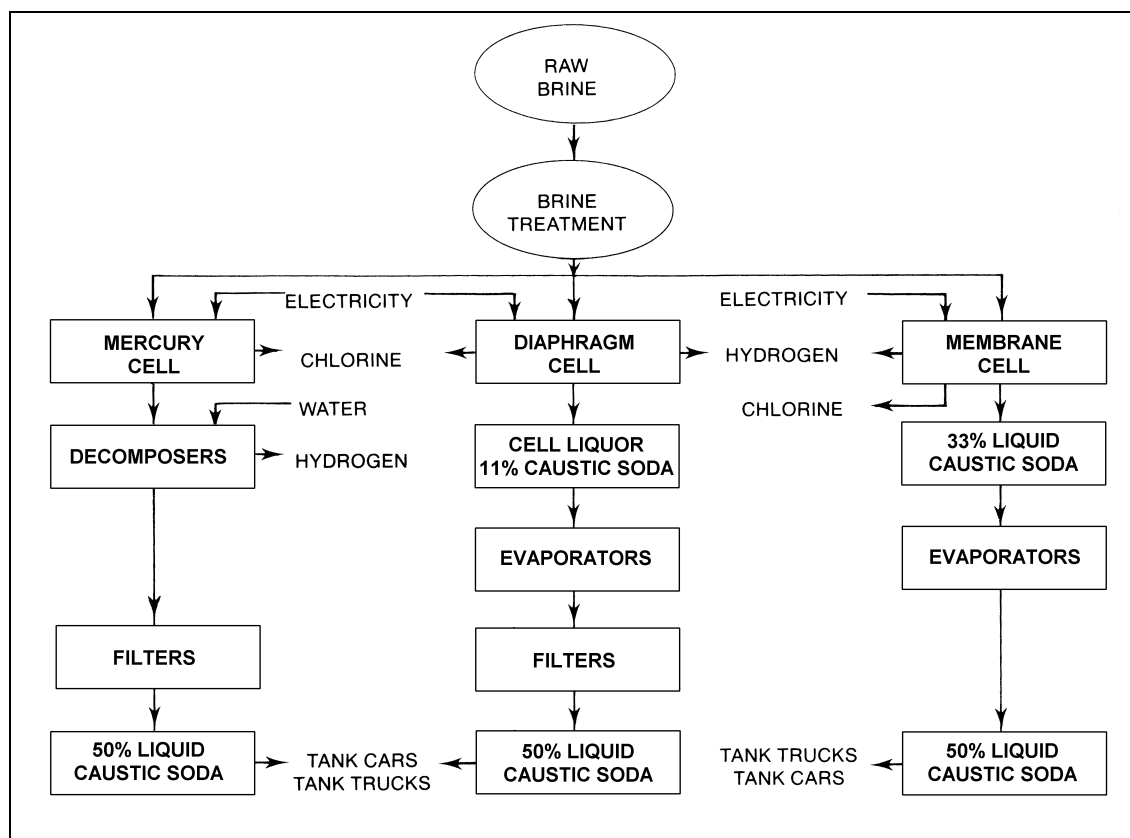


**Figure 2.15: View of caustic production and storage**  
[OxyChem, 1992]

The caustic soda solution from the three technologies is treated in slightly different ways due to the difference in composition and concentration.

In the mercury cell process, 50% caustic soda is obtained directly from the decomposers. The caustic soda is normally pumped through a cooler, then through a mercury removal system and then to the intermediate and final storage sections. In some cases the caustic is heated before filtration. The most common method for removal of mercury from caustic soda is a plate (or leaf) filter with carbon precoat. Under normal operating conditions, mercury-cell caustic soda (as 100% NaOH) contains 20-100 ppm of sodium chloride and 40-60  $\mu\text{g}$  Hg/kg NaOH.

In the case of diaphragm and membrane technologies the caustic soda is concentrated by evaporation before final storage.



**Figure 2.16: The flow to storage of caustic soda from the different technologies**

Based on [OxyChem, 1992]

Steam is used as the source of evaporative energy. The presence of salt in the diaphragm cell liquor requires that the evaporator is equipped with scraper blades or other devices to draw off the precipitated salt. This high quality sodium chloride can then be used to enrich depleted brine, sometimes it is used as a raw material for an amalgam or membrane process. The residual level of sodium chloride in sodium hydroxide from diaphragm cell is about 1% and sodium chlorate 0.1%. For this reason, it is unsuitable for certain end applications such as the manufacture of rayon.

Salt and sodium chlorate in the caustic soda from diaphragm cells can be reduced by ammonia extraction to increase marketability, but at increased cost.

The caustic soda from membrane cells is of high quality, although the caustic soda produced (usually around 33% NaOH) needs concentration to 50% NaOH for some applications. The salt content of the membrane-cell caustic soda lies between 20-100 ppm (in 100% NaOH), but is on average slightly higher than mercury cell caustic (see Table 2.1).

In some plants the caustic soda is further concentrated to a 73% solution and to 100% as solid caustic prills or flakes.

Some chlor-alkali production facilities can combine the caustic production process from mercury and membrane cells in order to minimise energy costs. It is possible to feed 33% caustic from the membrane cells to the decomposer to produce 50% caustic without the need for evaporation.



### Storage and handling

Because of its highly reactive and corrosive properties, caustic soda may corrode containers and handling equipment. Construction materials must be suited to the caustic soda handled and stored.

Sodium hydroxide solutions require steam or electrical heating where temperatures can fall below the upper freezing point. Frozen pipelines present both safety and environmental risks when attempts are made to unblock them. Safety measures are set out in Chapter 4.

Storage tanks may be lined in order to minimise iron contamination of the product or to avoid stress corrosion cracking the tank. Tanks are usually included in procedures to prevent overflow or spillage of caustic soda. Such procedures include containment and mitigation.

It should be noted that dissolved hydrogen gas can be released into the vapour space above the liquid in storage tanks. Tanks are normally vented from the highest point. Testing for an explosive mixture of hydrogen in air normally precedes any maintenance activity in the area.

### 2.4.5 Hydrogen production, storage and handling

Hydrogen is produced in a fixed ratio of 28 kg per tonne chlorine produced. Hydrogen leaving the cells is highly concentrated (>99.9% by volume) and normally cooled to remove water vapour, sodium hydroxide and salt. The solution of condensed salt water and sodium hydroxide is either recycled as brine make-up or treated with other waste water streams. In the mercury cell process, hydrogen has to be treated to remove mercury. Primary cooling at ambient temperature is carried out at the electrolyser, allowing mercury vapour to condense into the main mercury circuit. Further cooling takes place at a later stage using large heat exchangers and condensate is sent for mercury recovery.

Hydrogen may be distributed to users using booster fans or fed to the main compression plant. The main hydrogen compression plant usually comprises a number of compressors and a gas holder (surge chamber). The hydrogen gas holder is incorporated into the system to minimise fluctuations in the gas pressure from the primary stage. The hydrogen product gas stream is always kept pressurised to avoid ingress of air. All electrical equipment taken into the hydrogen compression plant area must be "intrinsically safe", i.e. the equipment will not produce a spark. A relief valve is normally provided within the system to relieve high pressure to atmosphere.

Hydrogen is normally analysed for oxygen content; the compression will shut down automatically in critical situations [Euro Chlor report, 1997].

The hydrogen is in general used for on-site energy production. It is burnt as a fuel, either by the company operating the chlorine plant or by another company to whom it has been sold as a fuel. Some or all of it can also be used on site in the case of integrated sites or sold to other companies as chemical feedstock (production of hydroxylamines, hydrochloric acid, hydrogen peroxide, sodium sulphite, for example).

### 3 PRESENT CONSUMPTION AND EMISSION LEVELS

In this chapter, the quantitative consumption and emission levels are given for the three chlor-alkali processes (amalgam, diaphragm, membrane). Some information on the inputs and pollutant outputs from the auxiliary processes such as brine purification, chlorine processing, caustic soda processing and hydrogen is also included. Reported emissions are taken from plants that operate with a number of process-integrated and end-of-pipe techniques to reduce emissions. The figures given are either directly from the plants or from the Member States. Mercury emissions at European level have been provided by Euro Chlor. Other figures are from OSPARCOM<sup>5</sup> reports or from the literature. Emissions resulting from impurities contained in the products are outside the scope of this document.

#### 3.1 Overall consumption and emission levels of all cell plants

Inputs and pollutant outputs of the chlor-alkali industry are quite specific to the cell technology used but also depend on the specifications of the products (O<sub>2</sub> or CO<sub>2</sub> content, for example), the purity of the incoming salt and the geographical location of the plant. The inputs are primarily salt and water as feedstock; acids and chemical precipitants used to remove impurities in the input brine or output chlorine/caustic soda; cooling agents (CFCs, HCFCs, HFCs, ammonia, etc.) for liquefying and purifying the chlorine gas produced. The chlor-alkali process needs huge amounts of electricity and electrical energy is a major input. The main pollutant outputs which are common to all three electrolytic processes are chlorine gas emissions, spent acids, cooling agents, impurities removed from the input salt or brine. The major pollutant in terms of environmental impact, originating from the amalgam technology, is mercury. Due to the process characteristics, mercury can be emitted from the process through air, water, wastes and in the products. The diaphragm cell and membrane techniques are more concerned with spent materials generation because of the replacement of the cell materials needed for the process. In the diaphragm process, deterioration of the asbestos-based diaphragms is the main reason for cell renewal. In view of the potential exposure of employees to asbestos and releases into the environment, special care must be taken. In addition, the improvement in cell component materials such as metal anodes and modified diaphragms, which are more stable, has helped to reduce the formation of undesirable and polluted by-products.

Mercury outputs have decreased in the last twenty years as amalgam cell plant operators have been more active in reducing mercury emissions, although the attention paid to this may vary from one country to another. According to Euro Chlor, mercury emissions to air and water per tonne chlorine capacity in western Europe were 27 g in 1977, 8 g in 1987 and around 2 g in 1997. Furthermore, the industry moved away in the 1990s from the mercury process to the more efficient (in terms of material and energy inputs and outputs) membrane cell process (first European membrane plant in 1983 at Akzo in Rotterdam).

Table 3.1 gives an overview of the inputs and outputs of the three chlor-alkali technologies, using a brine recirculation process. The information is collected from available sources and is not complete. Chlorine liquefaction is not included, nor are emissions from cooling systems.

---

<sup>5</sup> Commission for the Protection of the Marine Environment of the North-East Atlantic. Publications can be found at <http://www.ospar.org>

INPUTS, per tonne of chlorine produced				
	Membrane	Amalgam	Diaphragm	Comments
<b>Raw materials</b>				
salt (NaCl)	1750 kg			in theory 1660 kg (no losses)
water	1-2.8 m <sup>3</sup>			only process water
steam	180 kWh	-	610 kWh	AC, typical use for 50% caustic
electricity	2790 kWh	3560 kWh	2970 kWh	AC, typical use, depends on the current density
<b>Auxiliaries</b>				
mercury	-	2.6-10.9 g	-	
asbestos	-	-	0.1-0.3 kg	
<b>EMISSIONS, per tonne of chlorine produced</b>				
	Membrane	Amalgam	Diaphragm	Comments
<b>To air</b>				
hydrogen	100-1000 g			
chlorine	0-16 g			
CO <sub>2</sub>	1.2-5 kg			
mercury	-	0.2-2.1 g	-	western Europe 1998
asbestos	-	-	0.04 mg	
<b>To water</b>				
free oxidants	0.001-1.5 kg			higher figure if remains from bleach destruction are discharged
chlorate	0.14-4 kg			depends on whether a chlorate decomposer is installed or not; higher figure if thermal bleach destruction is applied
bromate	0.22-550 g			higher figure if thermal bleach destruction is applied
chloride	4-25 kg			
chlorinated hydrocarbons	0.03-1.16 g			
sulphate	0.3-0.7 kg (vacuum salt) 15 kg (rock salt)			depends on the purity of the salt
metals	Cr, Cu, Fe, Ni, Zn, etc			depends on the purity of the salt
mercury	-	0.01-0.65 g	-	western Europe 1998
asbestos	-	-	≤30 mg/l	no specific data available
<b>To waste</b>				
brine filtration sludges	120-775 g (vacuum salt) ~30 kg (rock salt)			
brine softening sludges	600 g	-	-	
mercury	-	0-84 g	-	western Europe 1998
asbestos	-	-	0.09-0.2 kg	depends on lifetime of diaphragms
<b>PRODUCTS, per tonne of chlorine produced</b>				
	Membrane	Amalgam	Diaphragm	Comments
sodium hydroxide	1128 kg			NaOH (100%); NaCl feedstock
potassium hydroxide	1577 kg			KOH (100%); KCl feedstock
hydrogen	28 kg			

These figures are from different available sources and refer to chlor-alkali plants in Europe using a brine recirculation process. The table does not claim to be complete. Chlorine liquefaction is not included, nor are emissions from cooling systems.

**Table 3.1: Overview of inputs and outputs of the chlor-alkali manufacturing processes**

### 3.1.1 Inputs in the production line

#### 3.1.1.1 Sodium chloride/potassium chloride

Different types of salt are used to produce the brine for electrolysis. These types are vacuum-crystallised salt from solution-mined brine, rock salt and solar salt. The stoichiometric salt consumption is 1.66 tonnes per tonne chlorine produced. In fact, 1.75 tonnes per tonne of chlorine produced is closer to reality because of impurities control of the brine by purge. Another particular case which can occur concerns diaphragm plants which prefer to sell the salt from caustic evaporators and buy new feedstock, for economic reasons.

In plants which operate with waste brine using a once-through brine process, the consumption of salt is about 3 times as much as in plants using a brine recirculation process, i.e. about 5 tonnes of salt per tonne of chlorine produced. Chlor-alkali plants using a waste brine process are located close to big underground salt deposits which can be found in Spain, Italy, Portugal and the United Kingdom.

In plants using KCl, the amount of salt needed is a bit more than for plants using NaCl feedstock, due to the higher molecular weight of KCl. Consumption in this case is about 2.1-2.2 tonnes of salt/tonne of chlorine produced. Plants using KCl do not use the waste brine process.

#### 3.1.1.2 Water

Water is used in the process for:

- purges
- preparation of the brine
- the caustic circuit: for maintaining the water balance in the reaction to form NaOH in the membrane and mercury cells
- the chlorine absorption unit: the quantity used will depend on the amount of chlorine released to absorption.

Water can also be used for cooling. However, cooling systems are not considered in this document. Apart from the water needed for cooling, generally 2-2.5 m<sup>3</sup> of water is consumed per tonne of chlorine produced for plants using a brine recirculation process. For waste brine processes, about 10 m<sup>3</sup> of water per tonne of chlorine produced is required.

#### 3.1.1.3 Energy

Energy is used both as electricity and as heat. About half of the energy expended is converted into the enthalpy of the products. The rest is converted into heat transferred to the air in the building and the products, which have to be cooled. The heat is partly recirculated through preheating of the brine. Surplus heat might also be used for heating surrounding buildings or for the concentration of caustic soda. Insulation of the cells and salt dissolvers reduces the need for ventilation of the cell room and increases the amount of heat transferable. The hydrogen produced in chlor-alkali plants can be used as a raw material in the synthesis of chemicals or as a fuel. [UN/ECE, 1985].

The operation of a chlor-alkali plant is dependent on the availability of huge quantities of direct-current (DC) electric power, which is usually obtained from a high voltage source of alternating current (AC). The lower voltage required for an electrolyser circuit is produced by a series of step-down transformers. Silicon diode rectifiers convert the alternative current electricity to direct current for electrolysis [Kirk-Othmer, 1991].

The voltage is increased with increasing distance between the anode and the cathode. On the other hand, a close distance means a higher frequency of short-circuiting in the amalgam cell. Thus, the distance between the electrodes ought to be monitored and often adjusted. This can easily be done by a computer which measures the voltage over each pair of electrodes and compares it to the desired value according to the actual production rate. The computer might also be used for control of the transformers to keep the reactive power low at varying production rates.

A comparison of typical energy use for the three technologies is given in Table 3.2.

	<b>Amalgam Technology</b>	<b>Asbestos Diaphragm Technology</b>	<b>Membrane Technology</b>
Theoretical voltage (V)	3.15	2.19	2.19
Current density (kA/ m <sup>2</sup> )	8 - 13	0.9 - 2.6	3 - 5 <sup>1</sup>
Cell voltage (V)	3.9 - 4.2	2.9 - 3.5	3 - 3.6
Caustic strength (% by weight)	50	12	33
Electrical energy use (alternating current) (ACkWh/t Cl <sub>2</sub> )	3360 at 10 kA/m <sup>2</sup>	2720 at 1.7 kA/m <sup>2</sup>	2650 <sup>2</sup> at 5 kA/m <sup>2</sup>
Electrical energy use by other electrical equipment (pumps, compressors, etc) (ACkWh/t Cl <sub>2</sub> )	200	250	140
<b>Total energy use (ACkWh/t Cl<sub>2</sub>)</b>	<b>3560</b>	<b>2970</b>	<b>2790</b>
Energy use by steam to concentrate caustic to 50% (ACkWh/t Cl <sub>2</sub> ) <sup>3</sup>	0	610	180
<b>Adjusted total energy use (ACkWh/t Cl<sub>2</sub>)</b>	<b>3560</b>	<b>3580</b>	<b>2970</b>

- 1) There is a tendency towards membrane cells operating at a higher current density, allowing higher production per m<sup>2</sup> but causing a higher electrical energy use per tonne Cl<sub>2</sub>. A higher current density causes more resistance heat which results in less steam being required for brine preheating.
- 2) According to the main suppliers the best values at 5 kA/m<sup>2</sup> are 2575 ACkWh/tonne Cl<sub>2</sub> at start up and 2650 ACkWh/tonne Cl<sub>2</sub> after two years in production.
- 3) 1 tonne steam = 250 kWh at 19 bar (figure based on the electricity that would be generated by passing 1 tonne of steam through a condensing steam turbine. Provided by EdF, French energy supplier).

**Table 3.2: Comparison of typical energy use by the mercury, diaphragm and membrane cell chlor-alkali technologies, assuming production of 50% caustic soda and before liquefaction of chlorine**  
[Dutch Report, 1998], [Euro Chlor report, 1997], [Lindley, 1997]

The energy required to liquefy chlorine is not included in the table above. It should be noted, however, that chlorine from membrane cells might need to be liquefied and evaporated to remove oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). The energy required to liquefy and evaporate 1 tonne of chlorine is about 200 kWh (AC).

Electrical energy use is lower in the membrane technology. The power costs are lower, even allowing for the steam requirements and brine purification.

Increased current density reduces the capital costs of an installation because the production per unit cell capacity is higher. However, there is a trade-off in that higher current densities mean higher power consumption, and the unit cost of electricity can be a factor when determining the appropriate trade-off between capital cost and power consumption. [Lindley, 1997].

### 3.1.1.4 Ancillary materials

Ancillary materials are used in various steps of the processes:

- the main products used to remove impurities from the brine are:  
sodium carbonate, barium salts, calcium chloride and sodium hydroxide
- hydrochloric acid is used to adjust the pH of cells and reduce undesirable products in chlorine
- sulphuric acid is used for chlorine drying
- inhibitors can be added to cooling water systems
- sodium carbonate can be used in mercury retorting to react with sulphur compounds as well as sodium hydrosulphide
- reducing agents (hydrazine or sulphides) are used to remove mercury in waste water, flocculants such as ferric chloride and polyaluminium chloride are used for water purification in the waste water treatment process

Substance	Use	Consumption kg/tonne chlorine produced
Sodium(bi)carbonate $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$	precipitation of calcium ions as calcium carbonate ( $\text{CaCO}_3$ ) - essential if vacuum salt is not used	3-20 This range can vary and reach 60 if the brine contains a lot of impurities (mainly rock salt).
Barium salts ( $\text{BaCl}_2$ , $\text{BaCO}_3$ )	precipitation of sulphate in case of high level content in brine	~3.5 - not always used (high price and toxicity) - purging is an alternative
Calcium chloride ( $\text{CaCl}_2$ )	precipitation and elimination of sulphate - formation of $\text{CaSO}_4$ in case of high levels in brine	0.6-35 The value is higher for plants using membrane technology which requires more sophisticated brine purification. $\text{CaCl}_2$ can be used in place of barium salts or direct purge
Hydrochloric acid ( $\text{HCl}$ )	-used for pH adjustment of cells. -used for dechlorination of brine in the membrane process and on occasion in the mercury process if there is no hypochlorite production unit. - used for regeneration of ion-exchange resins	20-30
Sodium bisulphite ( $\text{Na}_2\text{SO}_3$ )	- used for dechlorination of brine, final stage to eliminate chlorine, in the membrane process	(no data about consumption) This final chlorine elimination can also be done with other reducing agents, or by passing the brine through an activated carbon bed
Sodium hydroxide ( $\text{NaOH}$ )	- removal of magnesium and heavy metals (iron mainly if an anticaking agent is used for salt transportation) - used for pH control in brine circuit - regeneration of ion exchange resins	} 3-5 (mercury cells) 40 (membrane cells) 2
Sulphuric acid ( $\text{H}_2\text{SO}_4$ , 92-98%)	Chlorine drying processes	15-20 if not recycled

**Table 3.3: Consumption and use of chemical auxiliaries in chlor-alkali plants using a brine recirculation process.**

### 3.1.2 Outputs in the production line

#### Main products

The products are obtained more or less in a fixed ratio, independent of the technology used:

Per 1000 kg of chlorine produced,

- 1128 kg of NaOH (100 %) is produced if NaCl is used as a raw material
- 1577 kg of KOH (100%) is produced if KCl is used as a raw material (the molecular weight of KOH is higher than that of NaOH)
- 28 kg of hydrogen is produced

#### Chlorine emissions

Because chlorine is a hazardous gas, leakage from electrolytic cells is avoided. However, small amounts of chlorine might be emitted through leakage and handling of the cell covers. Several chlorine detectors are normally placed in the electrolysis hall, giving immediate indication of any significant leakage. Chlorine concentration in the electrolysis hall can be below odour detection level if the cells are operated in a slight vacuum. Estimated emissions vary from close to zero to 16 g chlorine per tonne of chlorine produced.

#### 3.1.2.1 Emissions from the mercury cell process

At present some 12000 tonnes of mercury are contained in mercury cells used for chlorine production in the EU. This is based on an average of 1.8 kg of mercury per tonne of annual chlorine capacity and an EU mercury cell chlorine capacity of 6.9 millions tonnes of chlorine per year [Lindley, 1997]. This mercury is contained and recycled within the chemical process. Nevertheless, due to the process characteristics, mercury emissions into air, water and also in wastes are generated. Products, mainly caustic soda, and to a lesser extent hydrogen, contain certain amounts of mercury. As regards the mercury level in chlorine, it is virtually zero and no mercury removal processes are used for this product. Any attempt to draw a balance generally results in a difference between inputs and outputs of mercury, either positive or negative. This item is specifically addressed in Section 3.1.2.1.5.

##### 3.1.2.1.1 Air emissions

Air emissions consist of mercury and, in small quantities, chlorine gas from the cells (see Section 3.1.2). Other fugitive emissions are described in the paragraphs concerning outputs from the auxiliary processes.

Releases of mercury are specific to the amalgam technology. Air emissions consist of mercury vapour coming from:

- cell-room ventilation
- process exhausts
- brine purification
- stack of caustic evaporators
- hydrogen burnt or vented to atmosphere
- mercury retorting
- maintenance outside cell room



### *Cell-room ventilation*

Ventilation air from the cell room is one of the main sources of mercury emissions to air. Compared to process exhaust, it can be more than ten times as much. The cell room with the hot mercury cells (approx. 80 °C) is usually ventilated by means of natural ventilation. The heat produced during electrolysis requires the air to be changed 10-25 times per hour, depending on the type of building [Ullmann's, 1996]. Ventilation air flows in the range of 20000-120000 Nm<sup>3</sup>/tonne chlorine capacity were found. This correspond to total ventilation air flows between 300000-2000000 Nm<sup>3</sup>/h, depending on weather conditions, season, design and size of the plant. With good mercury housekeeping the ventilation air contain mercury levels of 2-20 µg/Nm<sup>3</sup>. [Dutch report, 1998]

Some 2-8 µg/Nm<sup>3</sup> of mercury were reported, with an air flow of 300000-600000 Nm<sup>3</sup>/h. This plant (chlorine capacity of 120000 tonnes/year) was commissioned in the late 1960s and has developed a very efficient mercury housekeeping since 1978. In 1997, the mercury emitted to air from the cell room was estimated at 19.6 kg, corresponding to 0.17-0.21 g/tonne chlorine capacity.

Mercury losses are influenced by the basic design of the cell room, the area of the cells, the leak tightness, the type of decomposers (see Figure 2.4 and Figure 2.5), the accessibility of the cells and the construction materials. Mercury emissions are also influenced by the use of operating and maintenance techniques which minimise the possibility of mercury emission. Mercury spillage can occur during essential operations involving cells or decomposers, such as opening the cells for anode changing or cleaning, assembling or dismantling equipment, or replacing defective pipes. Optimisation by keeping the cells closed as far as possible reduces the emissions due to maintenance operations. The existence of a maintenance plan has been shown to increase the lifetime of cells six-fold and reduce the frequency of opening to only once every two or three years (see Chapter 4). The frequency of cell opening can be higher for potassium chloride electrolysis, depending on the purity of the available salt.

Mercury emissions are also significantly reduced by good housekeeping practices which are backed up by people with the motivation to work in such a way. The lowest values of mercury emissions have been observed in companies which have a specific and stringent cleaning and housekeeping programme.

Another source of emissions into air is the evaporation of mercury deposited in the equipment and in the building, for instance in cracks in the floor and in porous concrete and bricks.

In 1997, mercury emissions from western European cell rooms were in the range of 0.17-1.93 g/t chlorine production capacity, as reported by Euro Chlor.

### *Process exhaust*

Process exhaust refers to all gaseous streams by which mercury can be emitted to atmosphere apart from cell-room ventilation air and product hydrogen. One of the most significant sources of mercury emission is the purge of inlet and outlet boxes ("end boxes"). Today, they are usually connected to a separate ventilation system. The vacuum cleaning equipment is also a significant mercury source and it is normally also connected to a ventilation system.

Mercury is removed by:

- scrubbing with hypochlorite, chlorinated brine or using a calomel reaction, or
- using a sulphurised charcoal system.



Emissions of mercury from process exhaust can be reduced to very low levels in existing plants, depending on the removal technology used.

In 1997, mercury emissions from process exhaust were in the range of 0.01-1.0 g/tonne chlorine production capacity, as reported by Euro Chlor.

#### *The brine circuit*

Mercury may be released in vapours from brine systems if presence of oxidising species is not maintained. Depleted brine from the mercury cells normally contains up to 25 ppm of ionic mercury. It is maintained in this form by control of dechlorination to leave a residual oxidising environment which prevents metallic mercury from being formed and emitted to atmosphere from salt dissolvers, brine resaturators or brine filters and treatment vessels.

#### *Caustic soda after the decomposer*

The mercury contained in the caustic soda after the decomposer (in the range of 2.5 to 25 mg/l) can be emitted from the vents from pumping tanks or from the vents from caustic filters, depending on the type of denuder (vertical ones have a very low flow) and temperature. Releases of mercury from this source are included in the figures given for the mercury content in the process exhausts.

Normally, the caustic soda is filtered with activated carbon to remove mercury before handling. The predominant technique, which achieves low levels, is the plate filter with carbon precoat [Euro Chlor report, 1997]. The 50 % caustic produced is usually directly marketable after filtration. Any remaining mercury is in the range of 0.009 to 0.05 g per tonne chlorine capacity after filtration. When concentrated caustic soda (100 %) is required, the 50 % solution has to be concentrated in a caustic evaporator after mercury filtration. The mercury then evaporates from the caustic as a result of the heat treatment in the caustic evaporator.

#### *Hydrogen produced in the decomposer*

Hydrogen is formed from the exothermic reaction of sodium amalgam with water. It is referred to as “strong hydrogen”, indicating its high concentration. The hydrogen gas stream is nearly saturated with mercury when it leaves the decomposer at a temperature of 90-130 °C. Mercury vapour is entrained in the process stream and passes through a heat exchanger to decrease temperature to ambient. After cooling, mercury vapour condenses and is collected. The mercury is recovered directly as a metal inside the decomposer and can be recycled. Hydrogen may be compressed and cooled, to reduce the mercury content further.

A two-stage method (cooling followed by chemical or catalytic treatment) for the removal of mercury from hydrogen appears to be particularly effective. The hydrogen gas is usually cooled to 20 °C with a heat exchanger and cooled with a second heat exchanger to 5 °C (two-stage cooling). The quantity of mercury released will depend on whether the cooling step is followed by a chemical reaction (for instance, with CuO) or with a catalyst reaction (e.g. sulphurised carbon). The range can then vary. For a plant which reports a total mercury emission in air of 19.9 kg in 1997 (capacity of 120000 tonnes of chlorine), 0.23 kg of mercury was emitted from hydrogen production after cooling and treatment with sulphurised carbon, i.e. 1% of total emissions. Mercury releases from hydrogen can be considered a potentially important emission source of mercury, when the hydrogen gas is not properly purified.

A further hydrogen stream is produced from mercury cells during the wash operations performed on the mercury, on its entrance to, and exit from, the cell. It is called “weak hydrogen”. The quantities of hydrogen are much smaller, and are diluted with air to maintain the concentrations below explosive limits. This hydrogen stream also contains mercury, which may be treated by addition of chlorine or hypochlorite. The chlorine reacts with mercury to form  $\text{Hg}_2\text{Cl}_2$  which deposits as a solid. Alternatively, the mercury can be adsorbed on activated carbon. The cleaned gas is vented to atmosphere. The mercuric chloride residue is washed with brine, which reacts to form  $\text{HgCl}_4^{2-}$  and is recycled to the electrolysis plant. During electrolysis, the  $\text{HgCl}_4^{2-}$  complex produces mercury metal and chlorine [UK Guidance note, 1993].

Any remaining mercury is emitted if hydrogen is burnt as fuel. In the event of irregular operation, hydrogen is blown off or flared, usually after (at least partial) mercury removal. Hydrogen blow-off before mercury removal is rare and only occurs in emergencies. It has been estimated at 0.005 g of mercury released per tonne of chlorine produced by BASF in Antwerp (Belgium). This figure is of course only representative of one company and may vary. This source of emission should nevertheless not be omitted.

#### *Other fugitive mercury releases from the amalgam process*

##### Mercury from storage

Storage and handling of mercury-contaminated material may lead to diffuse emissions of mercury from the store houses. Emissions depend mainly on the type of storage (open/closed), the storage temperature and the amount of mercury-contaminated material in storage. Reported emissions from one plant are around 0.1 g Hg/tonne chlorine capacity. [Dutch report, 1998]

If mercury is stored, the emission will also depend on the type of containers (big containers of 600 kg avoid mercury handling and reduce emissions compared to bottles). Reported emissions from BASF in Antwerp (Belgium) are in the range of 0.004-0.005 mg/Nm<sup>3</sup> (period of measurement: January 1997 to April 1998, the storage contains bottles of 35 kg of mercury and the consumption of mercury is 2.636 g/tonne chlorine produced).

Generally, storage of contaminated materials should be separate from storage of mercury, and there should be no emission from the latter [Euro Chlor].

##### Mercury from the recovery retort

In the mercury recovery retort, mercury-containing waste is distilled in order to reduce the mercury content of the waste. The flue gas leaving the retort contains a small amount of mercury. In some cases these gases are passed through a mercury filter before they are emitted; in others, the flue gases are directly emitted to the atmosphere. Emissions from the mercury recovery retorts should be controlled to ensure that they are insignificant.

#### **3.1.2.1.2 Water emissions**

Waste water emissions consist of mercury and other substances in waste water streams, which are described in the paragraphs concerning outputs from the auxiliary processes.

The releases of mercury are specific to the amalgam technology. Mercury emitted from mercury cell facilities mainly arises from:

- the process: bleed from brine purification, condensate from hydrogen drying, condensate from caustic soda concentration units, brine leakage, ion-exchange eluate from process-water treatment

- the wash water from the cell cleaning operations: inlet and outlet boxes
- the rinsing water from the electrolysis hall: cleaning of the floors, tanks, pipes and dismantled apparatus
- the rinsing water from maintenance areas outside the electrolysis hall, if they are cleaned with water

*Brine purge, filter washings and waste liquor from the brine purification plant*

The depleted brine from the cells contains some dissolved mercury. The largest part of this mercury is recirculated into the cells. Part of the mercury is discharged through the purge of the brine circuit. This waste water is normally treated to remove mercury before discharge into the environment.

The mercury-contaminated filter-cakes are normally pumped with mercury-containing waste-waters to the purification stage and the sludge therefrom is either distilled at the plant, stored or sent to a deposit.

*Mercury-contaminated wash water from the inlet and outlet boxes and from the electrolysis hall*

The wash water from the inlet boxes flushes entrained caustic from the recycled mercury. This water contains mercury, but can be used as feed water to the decomposer. Wash water from the outlet boxes flushes entrained brine from the amalgam. This water also contains mercury, but can also be reused as feed water to the electrolytic cells.

*Condensate from hydrogen drying*

Mercury can be released during hydrogen drying. The hydrogen which is formed in the decomposer contains significant amounts of water and mercury. A large part of this water is condensed by cooling the hydrogen. The condensate contains mercury, but can be used as feed water to the decomposer.

*Filtered caustic liquor*

Filtered 50% (by weight) caustic liquor contains some mercury. Akzo Nobel in Bohus (Sweden) reported an average mercury content of 8 µg/l NaOH and 33 µg/l KOH for 1998. Small quantities of mercury thus appear in the effluents of user plants.

*Mercury contamination of rainwater effluents from mercury process plants*

There can be considerable emissions of mercury with run-off water. The soil at many sites is contaminated with mercury due to deposition of diffuse emissions and/or historical disposal of mercury contaminated wastes. The mercury leaks from the soil and ends up in the run-off water.

Rainwater is normally collected and treated with the other water streams of the plant. In some plants the rainwater is collected in sewer systems.

### **Mercury in waste water streams**

Mercury-contaminated waste water streams are collected from all sources and generally treated in a waste-water treatment plant. The amount of waste water can be reduced by filtration and washing of the sludges to remove mercury before feeding the condensate back into the brine. A waste-water rate of 0.3 to 1 m<sup>3</sup> per tonne of chlorine is achievable [Ullmann's, 1996]. The liquid effluent for processes operating once-through brine systems is, however, much greater than for recycled brine systems since it includes the total plant depleted brine flow.

Several processes are in use which are capable of purifying both depleted brine as it leaves the plant and all other mercury-containing waste-water streams. At one waste-brine mercury plant the mercury in the depleted brine is removed by precipitation as sulphide and recycled in the brine.

Mercury releases to water, plant-by-plant, were in the range of 0.01-0.65 g/tonne chlorine capacity in 1998, as reported by Euro Chlor.

The three waste-brine mercury plants operating in western Europe reported total aqueous (aqueous streams and depleted brine) mercury emissions between 0.01-0.28 g/t chlorine capacity in 1998, as reported by Euro Chlor.

#### **3.1.2.1.3 Generation of wastes**

Solid wastes can arise at several points in the process as shown in Figure 3.1, note that wastes from waste-water treatments are not shown in the figure. Wastes containing mercury include: sludges from waste water treatment, solids generated during brine purification (filter residue), spent graphite from decomposer cells, sludges from caustic filters (spent caustic filters from the filtration of caustic solution such as graphite candles), etc.

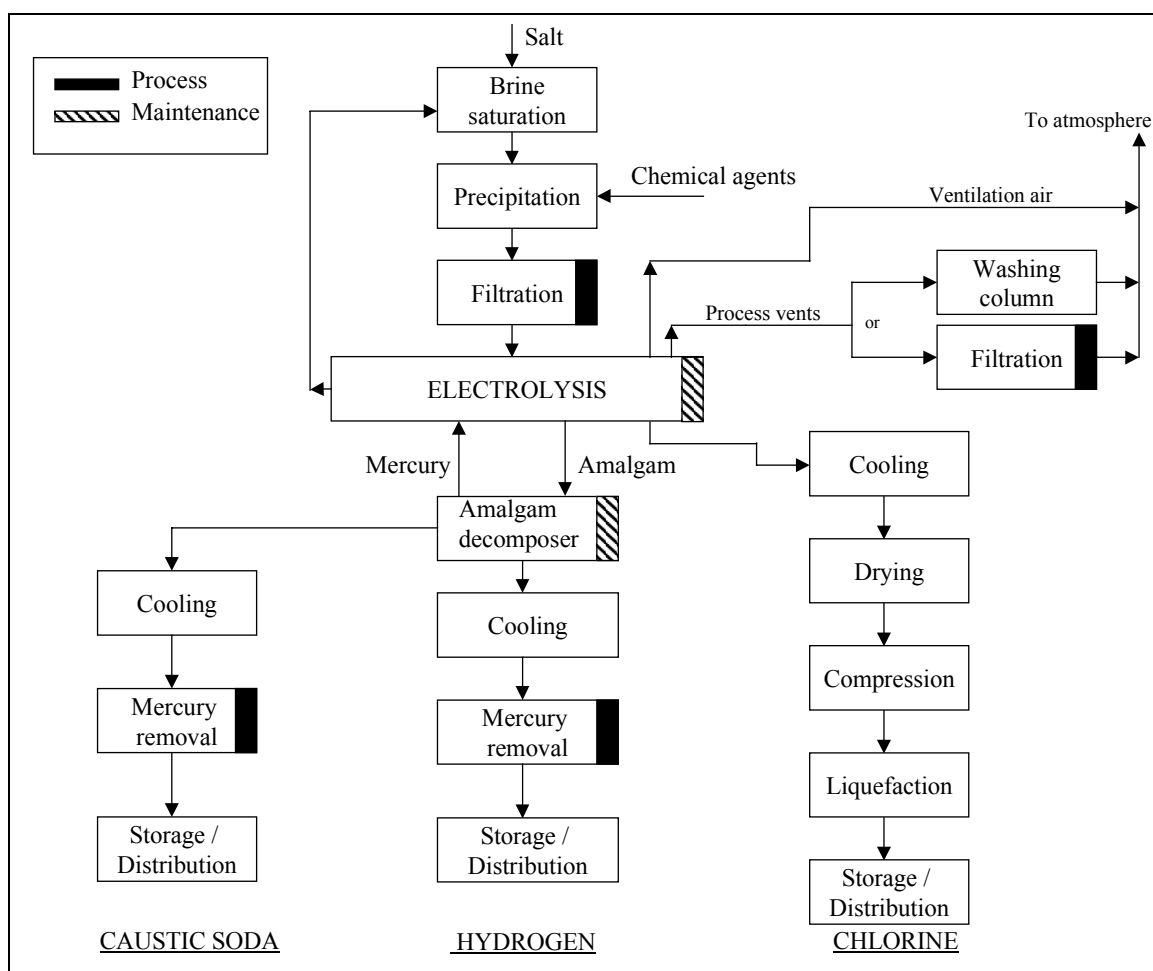
#### **Solids from brine purification**

(See Section 2.4.2.1). The quantities of precipitated solids depend on the purity of the salt used to make the brine. It should be noted that in the once-through brine process, purification and filtration is carried out prior to the cell and there is no contact of the purification sludges with mercury.

The quantity of mercury contained in sludges from brine filters is variable: A plant using vacuum salt reported a mercury amount of 1.8 kg in 21.3 tonnes of sludges produced from the brine filters for 1997 and 1.8 kg in 18 tonnes of sludges for 1998 (chlorine production capacity is about 120000 tonnes). Another plant, also using vacuum salt, reports figures of 12 tonnes of sludges from brine filtration, but an amount of mercury of 60 kg a year (chlorine production capacity of 110000 tonnes).

**Solids from caustic filtration:** (See Section 4.2.1.3)

**Graphite and activated carbon from treatment of gaseous streams:** (See Section 4.2.1.1)



**Figure 3.1: Solid waste sources in the mercury process**

[Euro Chlor]

### Graphite from decomposer packing

The packing within the decomposers (the reactors where the mercury/sodium amalgam is converted to caustic soda and hydrogen) is usually composed of graphite balls or granules. In normal use there is an attrition of the graphite and approximately every 10 years decomposers will need repacking. The graphite, typically containing 1-10% mercury, can be retorted. The quantity of graphite is approximately 1-2 tonnes for each 100 000 tonnes of  $\text{Cl}_2$  capacity.

### Residues from retorts

The retorting or distillation process can be applied to most materials containing metallic mercury, such as caustic filter media and decomposer graphite, stock tank sludges, etc. The distilled mercury is recovered. The final solids typically contain from less than 10 up to 200 mg mercury/kg. In some cases, particularly materials having very fine pore sizes, this may increase to about 1000 mg mercury/kg. Under normal circumstances, the quantity of retort residues will be determined by the volume of caustic filtration solids, say 5 tonnes per 100 000 tonnes of  $\text{Cl}_2$  capacity. However, retorts are frequently worked in campaigns and the quantity may be highly augmented by special activities such as stock tank recoveries or sump cleaning.

### Wastes from maintenance, renewal and demolition

By their nature, both the quantity and character of these wastes is highly variable. Materials can range from protective gloves to thousands of tonnes of bricks from demolished cellrooms.

### Reported waste generation

To give an idea of what types and amounts of waste that are generated, Table 3.4 and Table 3.5 presents the yearly waste generation and treatment for Akzo Nobel in Bohus and Hydro Polymers AB in Stenungsund (both plants in Sweden). The production is based on vacuum salt at both sites. The amount of waste varies between years depending on the type of maintenance work that is done and other factors.

Mercury in solids disposal plant-by-plant were in the range of 0-84 g/t chlorine capacity in 1998, as reported by Euro Chlor (see Annex C). OSPARCOM reported 31 tonnes of mercury in solid wastes not recycled for 1997.

Waste type	[tonnes/year]	Hg content before treatment	Treatment	Final mercury content [mg/kg]
Brine sludge	12-20	50-150 mg/kg	Landfilled after stabilisation	
Waste water treatment sludge	30-40	15-30 g/kg	Distilled Landfilled after stabilisation	<10
Carbon sludge	2	150-300 g/kg	Distilled Landfilled after stabilisation	20-200
Decomposer carbon	2	15-30 g/kg	Distilled Landfilled after stabilisation	20-200
Rubberlining	0,5		Acid bath Incineration	300
Steel/iron construction parts	Varies		Acid bath Sold as scrap	<5
Concrete and other construction waste	Varies 5 in 1998		Landfilled as hazardous waste or as other waste depending on content	>5 <5

**Table 3.4: Waste generation and final treatment at Akzo Nobel Bohus in 1998/99**

Annual plant capacity: 100000 tonnes of chlorine. Production based on vacuum salt.

Waste type	[tonnes/year]	Hg content before treatment	Treatment	Final mercury content [mg/kg]
Brine sludge	20-25	50-100 mg/kg	Landfilled	
Waste water treatment sludge	5-15	5-10 g/kg	Distilled Landfilled after stabilisation	<10
Carbon sludge	2-3,5	150-450 g/kg	Distilled Landfilled after stabilisation	20-200
Decomposer carbon	0,5-1	150-300 g/kg	Distilled Landfilled after stabilisation	20-200
Rubberlining	0,5		Acid bath Incineration	300
Steel/iron construction parts	10-15		Acid bath Sold as scrap	<15
Concrete and other construction waste	1-3	10-400 mg/kg	Landfilled after stabilisation	

**Table 3.5: Yearly waste generation and final treatment at Hydro Polymers AB**

Annual plant capacity: 120000 tonnes of chlorine. Production based on vacuum salt.

#### 3.1.2.1.4 Mercury contained in products

Hydrogen and caustic soda from amalgam chlor-alkali plants contain a certain amount of mercury. The mercury level in chlorine is negligible, i.e. less than 0.001 g/tonne. No mercury removal processes are used for this product. Traces of mercury in chlorine may be due to the presence of mercury in the sulphuric acid used to dry chlorine. As regards sodium and potassium hydroxides and hydrogen, purification techniques are needed before the products are sold. Mercury content in sodium and potassium hydroxides remains the most important compared to other products.

Mercury losses to products in 1996, as reported by OSPARCOM, varied from 0.01 to 0.93 g per tonne chlorine capacity, corresponding to 612 kg emitted. These figures correspond to the sum of mercury in chlorine gas, in alkalis and in hydrogen which is sold for further processing or use, but which is not sold as a fuel.

#### 3.1.2.1.5 Mass balance calculation

##### Reported figures

As regards mercury outputs, figures are expressed and reported by the industry in terms of chlorine capacity rather than real production. This is quite specific to the mercury chlor-alkali sector. Because of the electrolytic process in itself, emissions are not linked to production in a linear way. The majority of the emissions are from the cell room where the absolute amount is far more related to the equipment, plant design, maintenance requirements, pressure and temperature of cell and denuder. However, it could be assumed that if half of the cells are switched off this reasoning may be wrong. The industry gives two main reasons for reporting mercury emissions in terms of chlorine capacity. The first one is economic and the second technical. For economic reasons, a plant will always prefer to run all its cells because it is the cheapest way of operating and minimising costs. This is particularly true in countries like Spain or the United Kingdom where electricity tariffs can vary a lot during the year or even the day. Running at lower current densities is cheaper than switching off the cells. The second reason given is the design of the electric circuit. The rectifier is specified for a certain voltage and the electrical equipment may not support a voltage drop, especially for processes using a combination of diaphragm and amalgam technologies or amalgam and membrane. In Europe, however, the figures reported refer to 90% running capacity.

The industry also reports that production figures on a plant by plant basis are confidential data for “competitive reasons”.

##### Mass balance calculation

When making a balance between mercury inputs and outputs, the balance is frequently positive or, from time to time, negative. In 1998, the mercury difference to balance were, plant by plant, in the range of -35 - +36 g Hg/tonne chlorine capacity (see Annex C). Mercury is recycled within the process to a large extent but some of the mercury is accumulated in equipment and some is lost to air, water, wastes and products. A methodology for making a mercury balance in a chlor-alkali plant is laid out in [Euro Chlor Env. Prot. 12, 1998]. These guidelines are adopted by OSPARCOM for the annual reporting of mercury losses, and companies have to state where they have departed from them.

An accurate balance depends on the ability to measure the mercury inventory in the cells. The mercury cell inventory can be measured to 0.5% accuracy when using a radioactive tracer. With



an average cell inventory of 1.8 kg Hg/tonne chlorine capacity, this correspond to 9 g Hg/tonne chlorine capacity.

The mercury difference to balance is also due to the fact that mercury accumulates inside pipes, tanks, traps, sewers and in sludges, until some form of equilibrium is reached. Euro Chlor recommends purging this type of equipment, where possible, just prior to making the balance. Some 10 tonnes of mercury was said to be found by a company in a cooling water tower used for hydrogen (diameter 3.6 m). Mercury is often recovered when mercury cell rooms are decommissioned.

Because of the difficulty in recording an accurate follow-up of the mercury outputs, some proposals, in order to avoid discussion as to the credibility of the balance, could be to:

- operate rigorous and precise control of emissions, periodically, by third parties,
- optimise the recycling of mercury at each step of the process; in particular, extensive recycling of mercury in solid wastes should be possible,
- adoption of a recognised standard methodology to do the mercury balance.

### **3.1.2.2 Emissions from the diaphragm cell process**

Over the past twenty years all diaphragm cell facilities in western European countries have switched from the use of lead and graphite anodes with asbestos diaphragms to metal anodes and treated diaphragms, which resist corrosion and degradation. The diaphragms used to become clogged with graphite particles and had to be renewed after a few weeks. The use of lead and graphite anodes and asbestos diaphragms generated lead, asbestos, and chlorinated hydrocarbons in the caustic soda and chlorine processing waste. Lead salts and chlorinated hydrocarbons were generated from corrosion of the anodes and asbestos particles formed by the degradation of the diaphragm with use [USEPA, 1995]. Nowadays, Modified Diaphragms are made of a mixture of chrysotile asbestos and PTFE fibres. They are fabricated at an average rate of approximately 150 g asbestos per tonne of chlorine capacity.

EC Directive 87/217 concerning the prevention and reduction of pollution of the environment by asbestos has the aim of defining steps and complementing measures already in existence to reduce and prevent pollution by asbestos, and to protect human health and the environment. The Directive applies to discharges from all plants where more than 100 kg a year of raw asbestos is used, which is the case in chlor-alkali plants using diaphragm technology. The provisions came into effect on 31 December 1988 for all new plants and from 30 June 1991 for existing plants. Limits have been set to ensure that the concentration of asbestos discharged into the air does not exceed the limit of 0.1 mg/m<sup>3</sup> of released air. As far as the aquatic environment is concerned, there is a general requirement to ensure that discharges of asbestos are, as far as reasonably practicable, reduced at source and prevented. No specific provisions linked to the chlor-alkali sector are given.

#### **3.1.2.2.1 Air emissions**

Air emissions consist of asbestos and fugitive emissions of chlorine from the cells and in the process tail gases. Other emissions coming from auxiliaries are described in the relevant paragraphs.

#### **Asbestos**

Air emissions can appear during production of the diaphragms and, excluding potential accidental releases during transportation, unloading and storage, the major potential sources of air emission are during bag handling and opening and the disposal of spent asbestos.



Three sources of asbestos emission can be identified in the cell room maintenance area:

- from the off-gas compressor,
- from the off-gas drying oven,
- from the off-gas asbestos weighing room.

The fibre concentration in the cell room maintenance area is estimated by the industry to be less than 100000 fibres/m<sup>3</sup>.

Asbestos emissions from the baking furnace were calculated as being about 5 g per year, corresponding to an emission of 0.036 mg of asbestos per tonne of chlorine capacity in a plant of 140000 tonnes annual chlorine capacity [Dutch report, 1998].

Dry asbestos fibres can cause serious health problems if not properly used and handled in the diaphragm process. Asbestos fibres are thin and sharp crystals, which can be split into even thinner crystals. Due to its physical properties, asbestos is considered to be carcinogenic. The fibres are insoluble in body fluids and easily penetrate cell membranes. They can enter the human body by either inhalation or ingestion.

#### **3.1.2.2.2 Water emissions**

Waste water streams from the diaphragm cell process mainly originate from the condenser during caustic soda evaporation, chlorine drying, and brine purification of salt recovered from the evaporators. These waste water streams are described in the relevant paragraphs about auxiliary processes.

At the end of the lifetime of an asbestos diaphragm, the asbestos is removed from the cathode can by means of high pressure water-jet cleaning. Asbestos is collected with the rinsing water and can be discharged. A filter press can be installed to remove asbestos from the rinsing water. Reported emissions give values of under or equal to 30 mg/l.

#### **3.1.2.2.3 Generation of wastes**

Solid wastes in the diaphragm process consist of wastes generated during brine purification and scrapped cell parts, including cell covers, piping and used diaphragms.

#### **Bagged asbestos from scrap diaphragms**

The asbestos diaphragms in modern diaphragm chlor-alkali plants have a lifetime of approximately one year. After this year the cell is taken out of operation and the old asbestos is removed from the cathode can. Reported figures are in the range of 0.09 kg solid residues per tonne of chlorine capacity (~13.5 tonnes of asbestos per year, with a chlorine capacity of 150000 tonnes) to 0.2 kg per tonne of chlorine capacity (~30 tonnes of asbestos per year, considering a chlorine capacity of 150000 tonnes). 0.1 kg per tonne chlorine capacity is the medium average reported by the industry.

Discarded cell parts are either landfilled on-site or sent off-site for disposal, depending on the legislation of the country.

### **3.1.2.3 Emissions from the membrane cell process**

Emissions from chlor-alkali plants using the membrane technology are, apart from chlorine, linked to the brine purification needed to avoid undesirable impurities in the membrane cell and solid wastes generated by the used membranes. Emissions coming from auxiliaries are described in the relevant paragraphs.

#### **3.1.2.3.1 Water emissions**

Waste water from the membrane cell process originates from caustic evaporation, chlorine drying and wash water from the ion exchange resin used to purify the brine. Membrane plants usually use a bleed from the brine circuit in order to prevent accumulation of contaminants. All these emissions are described in the Section about auxiliary processes.

#### **3.1.2.3.2 Generation of wastes**

Wastes are generated during the secondary brine purification and consist of used materials such as precoat and body feed material made of cellulose. The precoat filter sludge from the brine softener consists mainly of alpha-cellulose, contaminated with iron hydroxide and silica. Membrane plants report a figure of 600 g/t for sludges from brine softening. Ion exchange resins for secondary brine purification are very rarely changed. Resins are regenerated about 30 times per year.

Spent membranes and gaskets from membrane cells become waste after their service life. The membranes have a lifetime of between 2 and 4 years. The waste from cell gaskets and membranes has been estimated at about 60 g per tonne of chlorine produced (data from one membrane plant). In [Dutch report, 1998] other values are given: 3.3 g/t for gaskets and spent membranes respectively.

### **3.1.2.4 Emissions from auxiliary processes**

#### **3.1.2.4.1 Emissions from salt unloading and storage**

The salt is normally stored in sealed areas, sometimes equipped with a roof, to prevent it from blowing off site. Protective systems are installed to prevent contamination of the brine, in particular in case of rain or if the storage is located near to surface waters or ground waters.

#### **3.1.2.4.2 Emissions from the brine circuit**

Table 3.3, page 38, shows the different chemical agents which are employed to purify the brine before electrolysis. The consumption of chemicals varies from plant to plant depending on the impurities of the brine and the type and sensitivity of the local environment into which the purge is discharged.

As explained in Chapter 2, brine purification by pH adjustment, precipitation, flocculation and filtration is required, on a full flow or sidestream basis, to keep impurities at acceptable levels. Membrane and mercury cells may use recycled brine requiring dechlorination. Specifically for membrane technology, brine purification is of critical importance to long membrane life and high efficiency. Thus, impurities need to be removed by ion exchange resin units which then require regeneration with caustic soda and acid washing. Some plants use vacuum crystallised salt, which is the most pure salt form (but also the most expensive) and for this reason have a simplified brine purification step.

Releases depend on the purity of the incoming salt used, the technology used (amalgam, diaphragm or membrane), the purification trade-off (use of chemical agents or direct purge in the media) and whether the brine is recirculated or wasted. Brine sludges are one of the largest waste streams of the chlor-alkali industry.

#### 3.1.2.4.2.1 Air emissions

The fugitive emission of carbon dioxide is possible from all three chlor-alkali technologies. Carbon dioxide is emitted from the brine acidification tanks due to the decomposition of carbonate and bicarbonate ions into water and carbon dioxide. The carbonate and bicarbonate ions are from the auxiliary chemicals used in the purification step. The carbon dioxide either escapes from the brine and is emitted to the atmosphere or is led to the chlorine destruction unit, depending on the presence of chlorine in the brine. The concentration of (bi)carbonate is expected to be lower when the depleted brine is recirculated and resaturated with solid salts (membrane and mercury cells). CO<sub>2</sub> emission due to brine acidification is about 1.2 kg per tonne of chlorine produced.

When the amalgam technology is used, mercury emissions may occur from brine resaturators and salt dissolvers, if there is no oxidising species.

#### 3.1.2.4.2.2 Water emissions

Table 3.6 summarises the main releases from the brine circuit using a recirculation process (except mercury which is described in Section 3.1.2.1.2, water emissions from the mercury cell process). Each release is described in more detail below.

Substance	Emission in kg/tonne chlorine capacity	
Sulphate	0.3-0.7 (Vacuum salt) 15 (rock salt)	Strictly depends on the purity of the incoming salt
Chloride	4–25	
Free oxidants	0.001–1.5 <sup>(1)</sup>	Generally treated before discharging
Chlorate	0.14-4 <sup>(2)</sup>	
Metals	Depends on the purity of the incoming salt	
Chlorinated hydrocarbons (measured as EOX)	0.03-1.16 <sup>(3)</sup> g/tonne Cl <sub>2</sub> capacity	

- 1) Higher figure from a plant that destroy the produced bleach in a chlorine destruction unit and releases the remaining liquid. In this case, a value of 1.5 kg/tonne chlorine capacity is reported.
- 2) Values will depend on the presence or not of a chlorate decomposer.
- 3) Higher figure from a plant that destroy the produced bleach in a chlorine destruction unit and releases the remaining liquid. In this case, a value of 1.16 g/tonne chlorine capacity is reported.

**Table 3.6: Releases into water from the brine circuit using a recirculation process**

#### Sulphate

Brine is generally purged from cells to reduce the levels of sodium sulphate and/or sodium chlorate in the cells. The source of sulphate in brine is the salt used. Sulphate has a negative effect on the electrolysis process (damages the anode coating) and its level is carefully controlled. This is normally done by a bleed from the brine treatment system for amalgam and membrane processes and by purge in the caustic evaporator from diaphragm cell chlor-alkali plants. The figures reported show that independently of the capacity of the plant, releases of sulphate are in the range of 0.3-0.7 kg per tonne chlorine produced if vacuum salt is used

(corresponding to about 34 tonnes a year for production of 100 kt) and around 15 kg per tonne chlorine produced if rock salt is used. This discharge may be considered problematic depending on where the releases occur.

### **Chloride**

During purification of the brine about 3-4% is purged to avoid build-up of undesired components. This purge can have a high concentration of chloride. Generally, after treatment to remove free oxidants, the purge is discharged into the ambient water. Emissions reported are in the range of 4-20 kg/tonne chlorine produced. This variation can be explained by the trade-off used for the purification to remove chloride and salt quality. This discharge may have some impact in the recipient where it is released.

In the case of the process using waste brine, 50-70 % of the brine is purged and releases are around 2000 kg/tonne chlorine produced.

### **Free oxidants**

Free oxidants include halogenated components with a high reactivity:  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{OCl}^-$ ,  $\text{OBr}^-$  and  $\text{NH}_x\text{Br}_y$ . Free oxidants are toxic to aquatic biota and are found in water streams which have been in direct contact with chlorine and bromine. The purge from the brine purification is normally treated before discharging into the environment. A concentration of 10 mg/l is generally observed. The release of free oxidants is higher for plants that destroy the produced bleach in the chlorine destruction unit and discharge the remaining liquid, which may contain significant amounts of free oxidants [Dutch report, 1998].

### **Chlorate and bromate**

The main sources of chlorate and bromate are the purge from brine purification and sometimes also water streams that have been treated to decompose free oxidants into the less reactive chlorate and bromate. Chlorate ( $\text{ClO}_3^-$ ) and (to a much lesser extent) bromate ( $\text{BrO}_3^-$ ) are formed as by-products during electrolysis. Chlorine may react with hydroxyl anions ( $\text{OH}^-$ ) to produce chlorate while bromine may react with hydroxyl anions ( $\text{OH}^-$ ) to produce bromate. Due to the recycling of the brine, these components build up. Chlorate and bromate are unwanted compounds in the process as their presence will reduce the solubility of incoming salt. Measures are usually taken to keep the level of chlorate low (usually below 10 g/l in the feed brine). To maintain this level, there is a need to operate under acid conditions (approx. pH 2) in the anolyte. If this is not the option chosen for the process (higher pH), a chlorate decomposer may be necessary to remove chlorate before purging. The reported concentration is between 5 to 10 g/l if no chlorate decomposer is installed and around 1 to 2 g/l after decomposition [Bayer Uerdingen, 1998]. Specific emissions are between 0.14 and 1 kg per tonne of chlorine produced. Chlorate is less reactive than chlorine and has a lower toxicity for aquatic biota. Bromate, on the contrary, is a reactive compound. Nevertheless, it is present in small quantities, as bromine is only present as a contaminant of the salt. Bromate releases are typically 10-100 times lower than the chlorate figures.

Especially relevant with regard to chlorate and bromate are plants that do not use the bleach produced from the chlorine containing waste gases and destroy the bleach by means of heating to 70 °C and acidifying to pH 6 or 7. In this case the free oxidants are decomposed into the less reactive chlorate. A value of 4 kg chlorate per tonne of chlorine produced is reported for a plant applying thermal bleach destruction, while bromate was in the range of 0.22-550 g per tonne of chlorine produced [Dutch report, 1998].

## Metals

Brine contains a certain amount of dissolved metals: nickel, zinc, iron, copper, depending on the salt used. In some cases the addition of an anti-caking agent (ferrocyanides) to the solid salt for transport, loading and unloading purposes provides an extra source of iron. Part of this iron is removed by the bleed from brine treatment, although the larger part is precipitated as iron hydroxide ( $\text{Fe}(\text{OH})_3$ ) and removed during brine filtration. Reported values of iron releases are about 100 ppb from amalgam plants using vacuum salt. A decomposition unit to prevent iron complexes may be necessary for membrane plants. After decomposition, releases of iron are about 30 to 40 ppb.

A mercury plant, which measures the releases of some metals, reports a value for zinc of 0.6 mg/tonne, which is near or below the detection limit. Metals are to be avoided in the mercury cells as even trace amounts can cause the release of dangerous amounts of hydrogen.

The second brine purification step, which is needed in membrane technology, requires the use of ion exchange brine softeners. During regeneration small amounts of metals are released with the waste water. A membrane chlor-alkali plant reported metal emissions from brine softener regeneration. The highest values concerned nickel (150 mg/tonne chlorine capacity, corresponding to a release of 40 kg/y), copper and zinc (55 mg/tonne chlorine capacity for each metal, corresponding to a release of 15 kg/y) and chromium (37 mg/t, 10 kg/y) [Dutch report, 1998].

## Chlorinated hydrocarbons

Chlorinated hydrocarbons ( $\text{C}_x\text{Cl}_y\text{H}_z$ ) are formed in a reaction between organic contaminants in the electrolyser and free oxidants. One or more of the C-H bonds are attacked by the chlorine and a C-Cl bond is formed. Examples of chlorinated hydrocarbons which can be found in the effluent of chlor-alkali plants are chloroform ( $\text{CCl}_3\text{H}$ ), dichloromethane ( $\text{CCl}_2\text{H}_2$ ), carbon tetrachloride ( $\text{CCl}_4$ ), tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ), but other chlorinated and also brominated compounds may be found. [Dutch report, 1998]

The emissions of chlorinated hydrocarbons from chlor-alkali plants have decreased significantly after the switch from graphite to metal anodes. The releases of chlorinated hydrocarbons is normally low but can be higher for plants that destroy the produced bleach in the chlorine destruction unit and discharge the remaining liquid. Discharges to water of the sum of these components (measured as EOX, extractable organic halogens) were found in the range of 0.03-1.16 g/tonne chlorine capacity, where the higher figure is reported from a plant with bleach destruction. [Dutch report, 1998]

### 3.1.2.4.2.3 Generation of wastes

#### Brine filtration sludges

The quantity of brine filtration sludges mainly depends on the incoming salt. The precipitated salts used for the purification of the brine are removed from the brine in a filter unit or a clarifier. The sludge is usually removed discontinuously by flushing with a weak hydrochloric acid solution. The acid causes the precipitate to dissolve and the relatively harmless solution can be discharged with liquid effluent. The remaining solid cake consists mainly of calcium carbonate and magnesium hydroxide, in some cases barium sulphate and, if the amalgam process is used, mercury.

For plants using vacuum salt, reported figures for brine purification sludges are in the range of 120-775 g per tonne of chlorine produced (i.e. 12-77 tonnes of sludges per year for an annual chlorine production of 100000 tonnes).

For plants using rock salt, about 30 kg, on average, of brine sludges are generated for every tonne of chlorine produced (i.e. 3000 tonnes of sludges per year for an annual chlorine production of 100000 tonnes).

In the mercury process, brine filtration sludges contain mercury (see Sections 3.1.2.1.3 and 4.2.1.4). As regards the membrane process, the technology requires more rigorous purification of the brine, and sludge disposal from the filters is thus more significant.

#### **3.1.2.4.3 Emissions from chlorine gas production, cooling, drying, liquefaction and storage**

Air emissions consist of fugitive emissions of carbon dioxide and chlorine from the process, the chlorine destruction unit and the handling/storage of chlorine. The process of purifying and liquefying impure chlorine gas involve carbon tetrachloride at a few installations in Europe, which is recovered to a large extent or incinerated.

The condensed water formed after cooling is usually recycled as brine make-up although some facilities combine this waste stream with other waste water streams prior to treatment. The remaining water vapour is removed by scrubbing the chlorine gas with concentrated sulphuric acid. The spent sulphuric acid waste is either sent back to the vendor, recycled or released.

##### **3.1.2.4.3.1 Air emissions**

#### **Carbon dioxide**

Small amounts of carbon dioxide are released from the anode compartment and are collected and treated together with the chlorine. During chlorine liquefaction, carbon dioxide (and N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>) remain in the gas phase and are finally purged from the system, together with a small amount of chlorine. This waste stream is usually processed in the chlorine destruction unit. The part of the carbon dioxide that is not absorbed by the chlorine destruction unit is emitted into the atmosphere.

#### **Chlorine**

Because chlorine is a hazardous gas, extreme precaution is taken to avoid emissions of chlorine from the process and from handling and storage. Therefore, emissions of chlorine gas into the atmosphere are generally low and the sources of significant potential emission are normally connected with the chlorine destruction unit.

##### *Emissions from non-condensable gases remaining from liquefaction*

Chlorine is liquefied in several steps of cooling and compressing. Gases (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>) in the process stream tend to concentrate in the gas phase. Therefore, chlorine gas liquefaction has an outlet for non-condensable gases. The chlorine content of these non-condensable gases ranges from 1-8% of the raw chlorine gas produced. The non-condensable gases are directed to a system which is able to handle chlorine such as a chlorine absorption/destruction unit or the manufacture of HCl, FeCl<sub>3</sub> or ethylene dichloride, thus avoiding emissions into the atmosphere.



### *Emissions during the cooling of gaseous chlorine*

During condensation of the water in the raw chlorine gas, the condensate gets saturated with gaseous chlorine. The condensate is usually led through a packed tower, where the chlorine is stripped from the liquid by means of steam and/or air. To enhance the stripper efficiency, hydrochloric acid is often added. The chlorine-containing vapour is subsequently fed back into the raw chlorine collecting main or directed to the chlorine destruction unit. As a rule, emissions into the atmosphere are avoided.

### *Emissions from the chlorine destruction unit*

Most chlor-alkali plants have a chlorine destruction unit to destroy the chlorine present in waste gases. The most common types of chlorine destruction are the bleach production unit and the hydrochloric acid production unit. The specific emissions lie in the range of 0.5-2 g Cl<sub>2</sub> per tonne of chlorine production capacity [Dutch report, 1998].

During normal operation of the chlor-alkali plant, the bleach produced can be sold. When the bleach production unit must handle a large amount of chlorine in a short period of time (in the event of release of chlorine due to a malfunctioning of equipment), the bleach produced does not usually comply with the product specifications. In that case the “off-spec” bleach is either destroyed on site and discharged with the waste water, or removed and processed elsewhere.

### *Emissions from storage and loading*

Emissions from storage and handling of chlorine are due to ventilation air during loading and unloading of tanks, vessels, containers and during emergency venting. In normal situations emissions are around 5 ppm. Generally speaking, the vented chlorine-containing gases are collected and directed to the chlorine destruction unit.

## **Carbon tetrachloride**

When emitted, carbon tetrachloride has the potential to destroy ozone in the stratosphere and therefore poses a threat to the global environment. The ozone depleting potential (ODP) is 1.1. The ODP is calculated by comparing the ozone depleting potential of the substance to the ozone depleting potential of CFC-11 (CFCl<sub>3</sub>). The use and production of carbon tetrachloride in the EU has, in principle, been prohibited since 31 December 1994. Only under strict conditions can annual exceptions be made for so-called “essential” applications.

Country	Number of chlor-alkali plants using CCl <sub>4</sub>	Application: Destruction of NCl <sub>3</sub>	Application: Chlorine liquefaction
France*	4	3	2
Netherlands**	2	2	2
Portugal	1	1	-
USA	9	7	2

\* One plant uses CCl<sub>4</sub> for both NCl<sub>3</sub>-destruction and liquefaction purposes.

\*\* Two plants use CCl<sub>4</sub> for both NCl<sub>3</sub>-destruction and liquefaction purposes.

**Table 3.7: Application of carbon tetrachloride in the chlor-alkali industry in western Europe**  
[EC, 1998], [Euro Chlor]

The Montreal Protocol allows the use of carbon tetrachloride as a process agent for liquefaction and purification of chlorine gas.  $\text{CCl}_4$  is only allowed in new installations if it is “essential”. Otherwise its use is forbidden. For existing plants, limit values will be set for process agents.

It should be noted that only 7 chlor-alkali plants in the EU use carbon tetrachloride for liquefaction and purification of chlorine gas (see Table 3.7). The other 86 European chlor-alkali plants have a different lay-out for chlorine liquefaction and purification, which allows operation without carbon tetrachloride (see Section 4.1.6).

The carbon tetrachloride for purification (absorption of tail gas, in particular to absorb  $\text{NCl}_3$ ) and/or liquefaction of chlorine is circulated in a closed loop. Thus, in principle no process emissions of  $\text{CCl}_4$  occur. However, small amounts are emitted by leakage. The gas tightness of the system is of paramount importance to achieve low emission values from the system. [Dutch report, 1998] Reported emissions from some companies are from less than 0.5 g  $\text{CCl}_4$ /tonne  $\text{Cl}_2$  capacity to up to 4 g per tonne. Some plants in Europe report emissions of about 6 tonnes a year.

#### **3.1.2.4.3.2 Water emissions**

##### **Sulphates**

Sulphuric acid mists coming from the drying towers are captured on candle filters and may be released as sulphates when the filters are washed for maintenance.

#### **3.1.2.4.3.3 Generation of wastes**

##### **Spent sulphuric acid from chlorine drying**

Highly concentrated sulphuric acid (92-98%) is used to dry chlorine. Up to 20 kg of sulphuric acid is consumed per tonne of chlorine produced. The spent acid usually becomes a waste product or one that requires reprocessing. Often the spent sulphuric acid is returned to the supplier for refortification. The spent acid can also be used to control pH in process and waste water streams or to destroy surplus hypochlorite, or it can be sold to an user who can accept this quality of acid.

Where it is possible to reconcentrate it in a closed loop, consumption is very low, close to 0.1 kg sulphuric acid per tonne of chlorine produced. Acid consumption can also be reduced by optimising the time contact between chlorine and acid, keeping the fresh acid concentration as high and the spent acid concentration as low as possible.

##### **Carbon tetrachloride**

When carbon tetrachloride is used to absorb  $\text{NCl}_3$  from the liquid chlorine, the carbon tetrachloride needs to be replaced periodically because of the build-up of pollutants (bromine,  $\text{FeCl}_3$ , chlorinated hydrocarbons, for example). The removed carbon tetrachloride is either incinerated or sent as hazardous waste. It must, however, be destroyed according to approved destruction processes, as mentioned in Annex VI of the report of the fourth meeting of the parties to the Montreal Protocol. A plant with a capacity of 300000 tonnes chlorine per year uses carbon tetrachloride for  $\text{NCl}_3$  destruction and consumes approximately 12 tonnes of  $\text{CCl}_4$  per year, corresponding to 40 g  $\text{CCl}_4$ /tonne of chlorine capacity (this figure includes fugitive emissions from the  $\text{CCl}_4$  system of 0-4 g  $\text{CCl}_4$ /tonne of chlorine capacity) [Dutch report, 1998].

#### 3.1.2.4.4 Emissions from sodium and potassium hydroxide processing

Caustic soda solution from the diaphragm process have a concentration of 10-12% NaOH with 15-17% NaCl when leaving the electrolytic cell and the caustic concentration from membrane cells is 30-33% NaOH with little NaCl. Generally speaking, the caustic needs to be concentrated to at least 50% and impurities need to be removed.

In the diaphragm process, about 5 tonnes of water must be evaporated per tonne of 50 percent caustic soda solution produced [USEPA, 1995]. If sodium sulphate is not removed during the brine purification process, salt recovered from the evaporators is often recrystallized to avoid sulphate build-up in the brine. If the salt is recrystallized, the waste water will also contain sodium sulphates. Significant levels of copper may also be present in the waste water due to corrosion of pipes and other equipment, along with iron and nickel which can dissolve to a certain extent from the stainless steel equipment. In addition, the presence of nickel may be related to the use of activated cathodes in the electrolytic cells. These metals are removed from the caustic by means of filtration and/or electrochemical reduction. The regeneration of the filters or the reduction cathodes generates an acid waste water flow which may contain iron and nickel at levels which ought to be taken care of.

Waste water from the caustic evaporators in the membrane process contains caustic soda solution and virtually no salt or sodium sulphates. It is usually recycled.

In the mercury process, caustic soda leaving the decomposer is directly concentrated to 50%. It contains practically no salt impurities, but it does contain mercury. The mercury (ranging from 2.5 to 25 mg/l) can be released from the pumping tank vents or from the vents from caustic filters, depending on the type of denuder and temperature. Normally, the caustic soda is filtered with activated carbon to remove mercury before handling. Charcoal from the filtration contains around 150-500 g of mercury/kg carbon.

In mercury cell chlor-alkali plants, the filter sludge is dewatered and in some cases led to a mercury recovery retort and subsequently disposed of. In cases where no mercury retort is present, the sludge has to be disposed of without mercury recovery. In membrane and diaphragm cell plants, the filters can be flushed with a weak acid solution, causing the iron hydroxide and metals to dissolve. The effluent is usually discharged, as most chlor-alkali plants have a physical-chemical waste water treatment unit which partially removes suspended solids and free oxidants. 3 tonnes of sludge from caustic filtration out of a total of 38 tonnes of sludges (the other sources being the brine treatment sludge and the waste water treatment sludges) produced per year has been reported for one amalgam chlor-alkali plant (chlorine production capacity of 115000 tonnes).

#### 3.1.2.4.5 Hydrogen processing

The hydrogen produced in all of the electrolytic processes contains small amounts of water vapour, sodium hydroxide and salt, which is removed through cooling and recycled or treated with other waste water streams. However, in the amalgam cells the hydrogen leaving the decomposer is nearly saturated with mercury, which must be recovered prior to compression. Some facilities further purify the hydrogen of mercury using sulphurised carbon which may be treated to recover mercury or disposed of in an approved landfill.

### 3.2 Historical contamination of chlor-alkali plant sites

Many old chlor-alkali plant sites are contaminated with PCDD/PCDF compounds (mercury and diaphragm cell plants) and mercury (mercury cell plants). The soil contamination is due to

fallout of mercury and historical disposal of graphite sludges, from the use of graphite anodes, and other wastes on and around the plant sites.

Graphite anodes were used almost exclusively for chlorine production before being replaced in the 1970s by metal anodes. The graphite anode was composed of various types of particulate coke mixed with a pitch binder. Some oxygen was liberated at the anodes with the chlorine, and this oxygen attacked the graphite forming carbon monoxide and carbon dioxide. This electrode wear was the cause of a graphite consumption of about 2 kg per tonne of chlorine produced from sodium chloride and 3-4 kg per tonne of chlorine from potassium chloride. The graphite residue produced was contaminated with PCDD/PCDF compounds, mainly from the reaction between chlorine and the pitch binder containing polycyclic aromatic hydrocarbons (PAH). [Müllmagazin, 1991], [Ullmann's, 1996]

The “dioxin” pattern (mixture of PCDD/PCDF compounds) is specific for the chlor-alkali industry, compared to other “dioxin” sources. At PCDD/Fs contaminated sites, high levels of mercury in soil does not necessarily correspond with high levels of PCDD/Fs, and vice versa. This means that the mercury level is not an indicator of the PCDD/Fs level. [Stenhammar]

Cases of land and sediment contamination by mercury in the sea or lakes are reported for some sites in Sweden. In one case, a decision has been taken to build a barrier and dredge the sediment from the bottom of the harbour area and place it behind the barrier. The volume of sediment is 500000 m<sup>3</sup> and the amount of mercury is 4000 kg. The content of mercury varies between 1 and 110 mg/kg dry substance, with an average of 24 mg/kg.

The Akzo Nobel site at Bohus, Sweden, has a permit from the licensing authority to build a treatment plant for 15000 tonnes/year of soil contaminated with mercury and PCDD/PCDF compounds. The treatment plant will cost approximately 6 million euros (50 million SEK, exchange rate 1998) to build (treatment cost not included).

A technique from Canada is currently being tested in Sweden for mercury contamination. It has been used to clean up a highly contaminated chlor-alkali site in Canada. The technology is called the KMS Separator and separates metallic mercury from contaminated soil. [Stenhammar]

### **3.3 Safety aspects of chlor-alkali plants**

Safety aspects are of much concern in the chlor-alkali industry. Production, loading, storage and transportation of chlorine require compliance with certain provisions designed to minimise the possibility of incidents giving rise to danger to operators, the public or the plant. A general policy for the prevention of and response to industrial accidents is usually based on the prevention principle (e.g. Annex IV to IPPC Directive), i.e. the plant is constructed and operated in such a way as to prevent any uncontrolled development and to reduce the consequences of accidents.

In the European Union, Member States agreed in 1982 on a Directive, the SEVESO Directive (82/501/EEC), as a means of controlling major industrial hazards connected with process and storage facilities where dangerous substances are present. The principles of the Directive set out:

- general requirements for industries which use dangerous substances to take all preventive measures to reduce the risks and to inform neighbouring populations of such hazards;
- requirements for authorities to control the activities and prepare appropriate emergency planning in the event of major accidents.

Since then, advancing knowledge and experience have provided new insights. The “SEVESO II” Directive (96/82/EC) represents a fundamental revision of the Directive. By 1999, Member States must implement the Directive through their laws, regulations and administrative practices. Storage and processes using chlorine are part of the scope of the Directive starting from 10 tonnes, along with hydrogen starting from 5 tonnes, while the alkali solutions are not covered.

Among the new provisions is one which requires operators of certain establishments holding substantial quantities of hazardous substances to produce a safety report which is accessible to the public and contains the information listed in Annex II of the Directive. The safety report appears to be one of the most important tools used to improve safety. It must provide a detailed description of the installation, presenting the main activities and products of the parts of the establishment which are important from the safety point of view (not only chlorine, but also, for example, flammable liquid or ammonia, if present), sources of major-accident risks and conditions under which such a major accident could happen, together with a description of proposed preventive measures. A lot of methodologies, such as HAZOP (Hazard and Operability Study), HAZAN (Hazard analysis numerical methods), QRA (Quantified Risk Assessment), generic fault trees, etc., are used for that purpose. The safety report should also describe the measures to be taken, if a major accident occurs, to: issue an alert; protect the people affected and intervene to limit the consequences. Its requirements are specified in the Directive for upper quantities: 25 tonnes for chlorine, 50 tonnes for hydrogen.

Based on lessons learnt from accidents, namely, that the contribution to risk from people failures is of equal importance, whether they be simple human errors or more complex procedural or organisational dysfunction, the Directive also asks operators to satisfy basic principles for management systems. The major-accident prevention policy includes:

- the training needs of personnel and the provision of the training so identified,
- management procedures for critical situations such as start-ups and shut-downs, disturbances or emergencies,
- an assessment of the effectiveness and suitability of the safety management system through an internal audit and review.

Besides the implementation of safety measures by the operators, the Directive includes provisions concerning controls on land use planning when new installations are authorised and when urban development takes place around existing installations. A lot of initiatives already exist in the Member States. In some countries, land use planning is based on a case-by-case study, taking into account the scenarios of possible major accidents as described in the safety report when deciding whether or not to allow new constructions around a hazardous plant. In other countries, land use planning is based on fixed external safety criteria which in some countries, like the Netherlands, require the agreement of Parliament. Safety zones are determined to permit different types of construction, depending on population density, to keep a suitable distance between such areas and hazardous establishments.

Another safety measure consists of establishing external and internal emergency plans and creating systems to ensure those plans are tested and revised. Data and information to be included in the emergency plans are specified in Article 11 of the “SEVESO II” Directive. The main objective is to contain and control incidents so as to minimise the effects and to limit damage to man, the environment and property.

The application of safety measures is part of best available techniques for chlor-alkali plants. Examples of preventive and corrective safety measures are given, in Chapter 4 of the document, on plant operation, storage and loading of products. Transport of chlorine, which also requires certain precautions, is not covered.

## 4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BEST AVAILABLE TECHNIQUES

In this chapter, relevant techniques available for prevention and/or reduction of emissions, wastes and energy use are given both for new and existing plants. This list of techniques, based on the information supplied by the members of the technical working group, should not be considered as exhaustive; it may be added to when this document is reviewed. Process-integrated techniques, end-of-pipe techniques and changes of production process are presented as techniques to consider to achieve integrated pollution prevention and control.

Safety measures are described, as safety is an issue of top priority for chlor-alkali plants due to the potentially serious hazards that are connected with the synthesis, storage and use of chlorine, sodium/potassium hydroxide and hydrogen.

The structure is the same for all presentations of suggested techniques to consider in the determination of BAT; a description of the applied technique including information on operation and applicability to new and existing plants, the achieved emission levels/main achievements, cross-media effects, reference plants, costs of application and references. When possible, the driving force for the implementation of the technique (environmental regulation, economics, subsidies) has been mentioned.

Some techniques listed are applicable to all three cell technologies. Others are specific to a particular technology.

### 4.1 All cell plants

#### 4.1.1 Safety measures

##### **Description**

In hazard and risk assessment studies, the design of chlor-alkali installations and equipment and the operating and maintenance routines are examined in detail to reduce the risks for people and the environment at source as much as possible. The most important substance to consider is chlorine. Preventative measures are the most important, although corrective and emergency measures are also of importance. The design principles of the plant, scheduled maintenance and inspection, procedures and instrumentation (control systems) for operating the unit are covered, as well as hardware. An overview is given, below, of measures that can be applied to reduce the risks in operating a chlor-alkali plant, including storage and loading of products. The measures presented are an indication of possible measures that can be taken. The local situation will determine the final package of measures that is required.

##### *General measures*

General measures related to safety are mainly linked to reliable and efficient safety management systems based on:

##### Training of personnel including:

- basic knowledge of chlorine properties
- correct operating practice
- emergency procedures
- frequent refresher training
- making sure that contractors' personnel on the site are familiar with the safety regulations and procedures for the site



Identification and evaluation of major hazards

- written information for personnel about safety measures in normal and abnormal conditions

Instructions for safe operation including:

- permanent monitoring of the installations under the responsibility of a designated person specially trained for chlorine hazards
- good compliance with safety parameters defined in the safety report, including periodic inspection and control of materials specified according to safety hazards
- maintenance programmes for the installations: for example, storage, maintenance of pipework, pumps, compressors, monitoring of moisture concentrations, impurities in liquid chlorine

Planning for emergencies and recording of accidents and near-misses

- preparation, test and review of emergency plans

The safety management systems should be completed with appropriate technical measures, such as:

- high quality preventive and protective systems, in particular in the loading area
- enhanced leak detection and leak isolation
- good protection of employees and temporary workers on the site with appropriate and well maintained equipment

*In the chlor-alkali plant*

In the chlor-alkali plant, safety measures refer in particular to the prevention of liquid chlorine spillage, using means such as:

- overfilling protection systems
- correct choice of construction material and regular inspection of vessels
- bunding for vessels containing hazardous material

and also:

- Preventing impurities to avoid any explosive mixture. Measuring and control of hydrogen concentration in the chlorine gas from the cell room and after each liquefaction step, and measuring and prevention of possible  $\text{NCl}_3$  accumulation.
- Prevention of failure of the electrical supply. Emergency generators for supply of power to vital equipment when/if grid power fails and also the prevention of failure of the instrument air supply.
- Prevention of chlorine releases by a collection of chlorine releases during maintenance operation to the absorption unit, a correct warning for process deviations and irregularities.

In a more general way, a good layout of the installation and provision for instant shut-down of some compartments help to prevent domino-effects. Manual emergency push buttons which can be used by any of the site personnel on discovery of a chlorine leak should be present around the plant.

*In the loading area*

In any liquid chlorine loading (or unloading) system, the weakest link is the connection between the static plant and the mobile tank. The use of pneumatic valves with automatic shut down in case of failure of the link, at both ends of the link, is essential to limit the leak.

Only a risk assessment study, proper to each installation, can give the most likely modes of failure during loading and the associated safety measures to avoid them. Examples of some standard measures are:

- Improved chlorine detection and location and rapid isolation of sources feeding a leak
- Connection of loading area to a chlorine absorption system
- PTFE hoses should not be used (based on information reported to accident databases)
- Articulated arms or correctly specified flexible hoses and coils for chlorine transfers

Loading area hazards	Examples of preventative measures	Examples of corrective or emergency measures
- Tank overfill	- Overfilling protection of the transport vehicle: a double weighing installation (two weighbridges operated by two different workers) should be installed	- Warning for loading deviations and irregularities - Automatic pump shutdown - Chlorine detectors connected to alarms in the control room - Remotely controlled shutdown valves - Emergency procedures
- Tank over-pressurisation during filling	- Venting procedure to remove inert gases	- Supply pump can be tripped manually or from control room
- Corrosion due to chlorine/water reaction	- Check tare weight of tank - Moisture control system and avoidance of possible back-flow	- Moisture analysis in chlorine gas and padding gas, with alarm - Response by process operators to evidence of ferric chloride in valves - Suction failure alarm in vent gas scrubbing system
- Fire due to chlorine/iron reaction	- Use of appropriate materials - Avoidance of “hot work” areas - No flammable liquids or materials in the surroundings of loading areas	
- Fire due to contaminants (oil, organics)	- Prohibition of use of hydrocarbon oils, greases and solvents - Use of oil-free compressors in padding gas systems	
- Internal corrosion	- Moisture control system in chlorine and avoidance of possible back-flow - Monitoring procedures for wet ferric chloride in valves	
- Collision with other rail/road tanks	- Braking the transport vehicle and blocking the road or railway track during loading - Prevention of runaway rail wagons or tankers getting into filling area - Alarms linked to rail retarders	- Emergency shut off valves on tank and supply initiated by push buttons
- Rupture of the filling pipe	- Containment of the loading installation - Use of articulated arms or correctly specified flexible hoses and coils for chlorine transfer - Maintenance and inspection procedures	- Emergency shut-off valves - Connection of dissipated chlorine gas from the transport vehicle to the chlorine destruction unit
Other causes: - Liquid chlorine in vent - Back-flow of chlorine into padding gas system - Valve leaks	- Control procedures on gas supplies system to avoid over-pressurisation due to warming - Avoidance of possibility of inversion on the connection between liquid and gaseous phases	- Liquid chlorine in vent detector (alarm/trip) to alert operator - Increasing venting rate and draining liquid to vented tanks - High and low pressure alarms on padding gas system - Padding gas chlorine detector and differential pressure control

**Table 4.1: List of some preventative and corrective or emergency measures to avoid accidents at loading areas of a chlor-alkali plant**

#### *In the storage area*

Some standard safety measures to achieve optimum risk reduction in the storage area are:

- Chlorine detection and location and rapid isolation of sources feeding a leak
- Availability of at least one empty tank of sufficient capacity as an emergency spare

- Good pipework design to minimise the length of pipeline containing liquid chlorine
- Limitation of the overall liquid chlorine inventory to what is really needed. A simplified layout and a reduction in the number of valves, pipes and connections reduce the risk of leakage
- For large storage capacities, low-temperature storage at -34 °C is recommended

Storage tank hazards	Examples of preventative measures	Examples of corrective or emergency measures
- Vessel failure due to over pressurisation (vapour padding/ inert, liquid overfill)	<ul style="list-style-type: none"> <li>- Physical tank protection against over-pressurisation or hydraulic overfill</li> <li>- Maintain stock tank pressure below the maximum allowable pressure</li> <li>- Pump maximum discharge pressure less than maximum allowable system pressure</li> <li>- Design standards of pump, pipework and vessels</li> </ul>	<ul style="list-style-type: none"> <li>- High-pressure alarms on stock tanks</li> <li>- Two independent level/weight alarms on receiving tank</li> <li>- Relief valves at appropriate settings and capacities. It includes, in series: a bursting disk protecting the valve from corrosion; a detection device giving an alarm in case of failure of the disk; a protection against corrosion due to back-flow of moisture from the absorption unit. A protective membrane may be used, or a continuous flow of inert dry gas may be added after the valve.</li> <li>- Pump trips at high level and/or pressure</li> <li>- Pump can be tripped remotely</li> </ul>
- Internal explosion due to build up of $\text{NCl}_3$	- Never allow liquid chlorine to evaporate completely to dryness; no branches or wells at bottom of small tanks; brine quality control	
- Internal explosion due to hydrogen	- No direct connection between a chlorine storage tank and a chlorine gas stream containing hydrogen	
- Contamination with organics	- Prohibition of use of solvents or organic drying agents	
- Contamination with oil	- Prohibition of use of oil or hydrocarbon greases, use of oil-free compressors in padding gas system	
- Fire due to chlorine/iron reaction	<ul style="list-style-type: none"> <li>- Use of appropriate materials</li> <li>- Avoidance of “hot work” areas</li> <li>- No flammable liquids or materials in the surroundings of loading areas</li> </ul>	
- Corrosion due to chlorine/water reaction; internal corrosion	<ul style="list-style-type: none"> <li>- Check tare weight of tank</li> <li>- Moisture control system and avoidance of possible back-flow</li> </ul>	<ul style="list-style-type: none"> <li>- Alarm on padding gas moisture indicator</li> <li>- Response by process operators to evidence of ferric chloride</li> <li>- Chlorine monitors on cooling waterside of heat exchangers</li> </ul>
- External corrosion	- All stock tanks operated at temperatures below zero insulated; fully watertight lagging where freeze/thaw conditions exist	- Pressure vessel inspections include selective removal of insulation to permit inspection of external surfaces
- Low temperature thermal stress	<ul style="list-style-type: none"> <li>- Tanks have to be stress-relieved to prevent failure from high induced stress</li> <li>- Prohibit excessive physical force on valves</li> <li>- Use of steel resilient at low temperature (-40 °C)</li> </ul>	
- Pump failure	<ul style="list-style-type: none"> <li>- The pump shall be equipped with high temperature alarm</li> <li>- Pump should be banded</li> <li>- Pump design specifications respected</li> </ul>	- Chlorine detectors close to the pump

**Table 4.2: List of some preventative and corrective or emergency measures to avoid accidents associated with storage of liquid chlorine**

### Main achieved risk levels

This level should tend to zero. Methodologies such as HAZOP (Hazard and Operability Study), HAZAN and QRA are designed to ensure that the operation of a chlorine installation poses a negligible risk to employees, the neighbouring public and the natural environment. The use of checklists is also a useful methodology to reduce the risk; an example is [Gest 92/175, 1993].

### Cross-media effects

Note that storage at low temperature requires deep cooling with CO<sub>2</sub>, HCFCs/HFCs or ammonia. Thus, fugitive emissions of the employed cooling agent may occur. Furthermore, low-temperature storage requires more energy than ambient storage.

### Reference plants

Safety measures are well implemented in all chlorine producing plants in Europe. The options chosen by the operator will differ, depending on the plant location (proximity of residential areas for example), stored quantities on site and/or chlorine directly consumed in situ.

### Economics

Examples are given for some applied safety measures. The choices made are of course dependent on the specific activity:

1. General Electric Plastics in Bergen op Zoom (Netherlands) where chlorine is used for the synthesis of phosgene. Cryogenic storage of chlorine includes:  
1 tank of 58 tonnes currently in use, 1 full tank of 58 tonnes and 1 emergency tank. All tanks are kept at -34 °C and atmospheric pressure. The whole storage is contained inside a building of 8000 m<sup>3</sup>. The chlorine absorption unit is 11 m high and 1.8 m in diameter. A fan allows a continuous venting of 5000 m<sup>3</sup>/h. The cost of the storage built in Bergen op Zoom in 1988 is estimated at about 4.3 million euros (10 million NLG, exchange rate 1998) and the maintenance cost at about 2% of the building cost.
2. ICI in Wilhelmshaven (Germany), a large quantity chlorine storage:  
2 tanks of 1600 tonnes each and 1 emergency tank. Chlorine is stored in steel tanks enclosed within a shell constructed of a steel/polyurethane/aluminium sandwich material. This storage was built in the 1970s and cost about 7.7 million euros (about 15 million DEM). This storage was the solution at that time to a specific situation; today it might not have been built for such large quantities.
3. ATOCHEM in Jarrie (Isère, France), loading area:  
Containment of a separated loading area (2 x 58 tonnes railway tanks), chlorine destruction unit and water spray equipment. The cost was approximately 1.5 million euros (September 1998). The cost can vary, depending on adaptations needed to existing installations.

### References

[Gest 87/130, 1996], [Gest 92/175, 1993], [J. Loss Prev. Proc. Ind., March/94], [Mason, 1995]

### 4.1.2 The chlorine absorption unit

#### Description

The purpose of the chlorine destruction unit is to avoid large emissions of chlorine gas to the environment during irregular plant operation and/or emergencies, and to take care of all chlorine-containing waste gases during normal operation. The most common way to destroy the chlorine is to absorb it in weak caustic soda to produce sodium hypochlorite. The absorption system can make use of packed towers or venturi ejectors. However, packed columns, even though more complex, are better in case of emergency if electricity supply fails. They can continue to absorb chlorine from a pressure relief system using caustic soda stored in a gravity-fed head tank. The concentration of caustic soda should not exceed 22% NaOH because of the risk of salt deposition, causing blockages in the absorption plant, and freezing.

The design of an absorption system requires clear specifications of:

- the maximum quantity of chlorine
- the composition of the gas stream
- the maximum instantaneous flow

It is very important to ensure that in case of a major accident, a massive release of chlorine could be absorbed. The size of the unit is of great importance and should be calculated to cope with emergency conditions. Caustic soda supply and the storage capacity for caustic soda and hypochlorite solution should be correctly sized as well. It is essential that faults are detected quickly and adequate instrumentation with alarms should be applied at the vent absorption plant to ensure that warning is given if equipment fails. In particular, temperature control of the absorption solution is essential, as is measurement to prevent over-chlorination. The emergency power supply should be tested periodically.

If the sodium hypochlorite cannot be sold, it has to be treated before it is discharged. Several technologies are available to destroy sodium hypochlorite without generating significant cross-media effects, in particular catalytic processes.

#### Main achieved emission levels

Absorption units are generally designed to limit the chlorine content to below 5-10 mg/m<sup>3</sup> in the emitted gas in the worst case scenario. Under normal operation the concentration of chlorine is less than 1-3 mg/m<sup>3</sup> in the case of partial liquefaction and less than 3-6 mg/m<sup>3</sup> in the case of total liquefaction.

#### Cross-media effects

When the sodium hypochlorite (bleach) produced can be sold, no cross-media effects occur, although it should be noted that the consumer might discharge free oxidants from the bleach. When there is no demand for bleach, the bleach has to be destroyed before it can be discharged. The effluent from the bleach destruction may have an adverse effect on the recipient water, depending on the technology used (see Section 4.1.5).

**Reference plants:** All existing plants are equipped with emergency absorption systems.

## **References**

[Dutch report, 1998], [Gest 76/52, 1986], [Gest 87/130, 1996], [Gest 92/169, 1994], [Le Chlore, 1996], [Schubert], [Wunderlich]

### **4.1.3 Metal anodes**

#### **Description**

In 1965, H. B. Beer presented a metal oxide coated titanium electrode which was a big improvement over earlier graphite anodes. The coated titanium anodes allow high current density at a low voltage, are dimensionally stable and have long life. All coatings that are used on an industrial scale are composed of an oxide of a platinum group metal (usually ruthenium) and an oxide of a nonplatinum metal group (usually titanium, tin or zirconium). Coating failure may occur, depending on the type of cell in which the anode is operated. Lifetime of metal anodes in diaphragm cells is more than 12 years and in membrane and mercury cells 4-8 years. In the amalgam process the unavoidable occurrence of minor short circuits, through contact with the mercury cathode, causes gradual physical wear of the anode coating. Impurity levels in brine have to be controlled; compounds that negatively affect the metal anodes are for example organic acids, fluoride and manganese. Operation in strongly alkaline brine (pH >11) may rapidly destroy the coating, and operation with NaCl concentration so low that oxygen is evolved with the chlorine must also be avoided.

Metal anodes are used by all chlor-alkali plants in Western Europe.

#### **Main performance characteristics**

- Long lifetime
- Low operating voltage
- High energy efficiency
- Improved process control
- Reduced need for maintenance and inspection
- Reduced amounts of waste and pollution

**References:** [Dutch report, 1998], [Kirk-Othmer, 1991], [Ullmann's, 1996]

### **4.1.4 On-site reconcentration of spent sulphuric acid**

#### **Description**

Concentrated sulphuric acid (92-98%) is used to dry chlorine. Up to 20 kg of acid is consumed per tonne chlorine produced. The spent acid usually becomes a waste product or one that requires reprocessing. The spent acid can be used to control pH in process and waste water streams or to destroy surplus hypochlorite. It can be returned to an acid producer for reconcentration or sold to any user who can accept this quality of acid.

Sulphuric acid can also be reconcentrated on-site in closed loop evaporators which reduces the consumption to 0.1 kg of acid per tonne of chlorine produced. The spent sulphuric acid is concentrated to 92-98% by indirect heating with steam. Materials used must be highly corrosion-resistant to avoid corrosion problems, in particular if the feed acid is polluted.



On-site reconcentration in closed loop evaporators can be applied at new and existing plants. The required installation area depends on the capacity of the plant. If the acid is concentrated only to 92%, investment cost as well as utility consumption may be reduced, as it may be possible to concentrate in a single stage.

**Main achievements:** Significant reduction in sulphuric acid consumption.

#### **Cross-media effects**

The concentration of sulphuric acid requires energy. Depending on the energy source used, several types of air emission may be generated ( $\text{CO}_2$  and  $\text{NO}_x$  among others). Water is evaporated during the concentration. A small bleed of the acid will probably be necessary to avoid build-up of contaminants in the concentrated acid.

#### **Reference plants**

More than 50 plants worldwide have been supplied with recycling units for spent sulphuric acid by one supplier.

#### **Economics**

One supplier gives a price of around 360000 euros (700000 DEM, January 1999) for a new installation designed for 1000 kg/h sulphuric acid. The price depends on the customer's requirements. The operating costs mainly depend on the energy costs.

**References:** Information mainly communicated by QVF Engineering GmbH.

### **4.1.5 Treatment of waste water containing free oxidants, including bleach destruction**

#### **Description**

The chlor-alkali industry potentially discharges waste water containing free oxidants. Free oxidants are defined according to water analysis methods as the sum of the following compounds:  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{OCl}^-$ ,  $\text{OBr}^-$  and  $\text{NH}_x\text{Br}_y$ . This does not necessarily imply that all of the mentioned compounds are actually present in waste water from chlor-alkali plants.

All water streams that have been in contact with chlorine and or bromine may contain free oxidants. In the chlor-alkali plants these streams are:

- the bleed from the brine circuit
- the condensate from the chlorine gas cooling
- the bleach (sodium hypochlorite) produced by the chlorine absorption unit

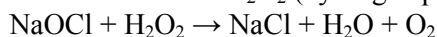
The free oxidants can be destroyed by chemical reduction, by catalytic reduction or by thermal decomposition. All these methods can be applied at existing and new chlor-alkali plants.

The formation of chlorates by destruction of bleach depends on the methodology used. It is also possible to recover the chlorine by acidification of the waste hypochlorite stream. This would seem especially attractive to large chlorine plants when considerable amounts of spent acid are available (spent sulphuric acid from chlorine drying).

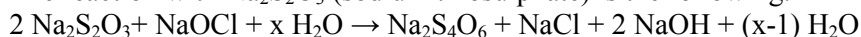
*Chemical reduction*

Chemical reduction agents such as sulphur dioxide (SO<sub>2</sub>), sodium sulphide (Na<sub>2</sub>S), sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) or sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) are used to destroy the free oxidants. The chlorine or hypochlorite is reduced to chloride (Cl<sup>-</sup>). The choice of the chemical reducing agent is influenced by cost, availability and ease of handling. The added chemicals in turn form a range of sulphur oxy anions, predominantly sulphates (SO<sub>4</sub><sup>2-</sup>). In some cases, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is used to destroy the free oxidants if chlorine concentrations are very low. A final treatment with H<sub>2</sub>O<sub>2</sub> can reduce the free chlorine concentration from 300 ppm to 1 ppm of free chlorine [Le Chlore, 1996].

The reaction with H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) is the following:



The reaction with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (sodium thiosulphate) is the following:

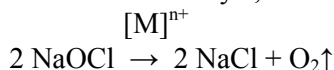


Since the chemicals are added on a stoichiometric basis, the chemical costs can be considerable when decomposing concentrated solutions of hypochlorite. In addition, to facilitate the reaction, sufficient residence time is required and excess chemical is used to ensure full reaction. Disposal of waste water streams with excess reducing agent can be a problem because of the high load of COD (chemical oxygen demand) [Kelly, 1998].

In order to control the heat of the exothermic reaction, highly diluted solutions are used to limit the temperature to about 50 °C. For 1 kg of chlorine absorbed, 4.45 kg of reactive agent Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or 89 kg of diluted 5% solution is required [Le Chlore, 1996].

*Catalytic reduction*

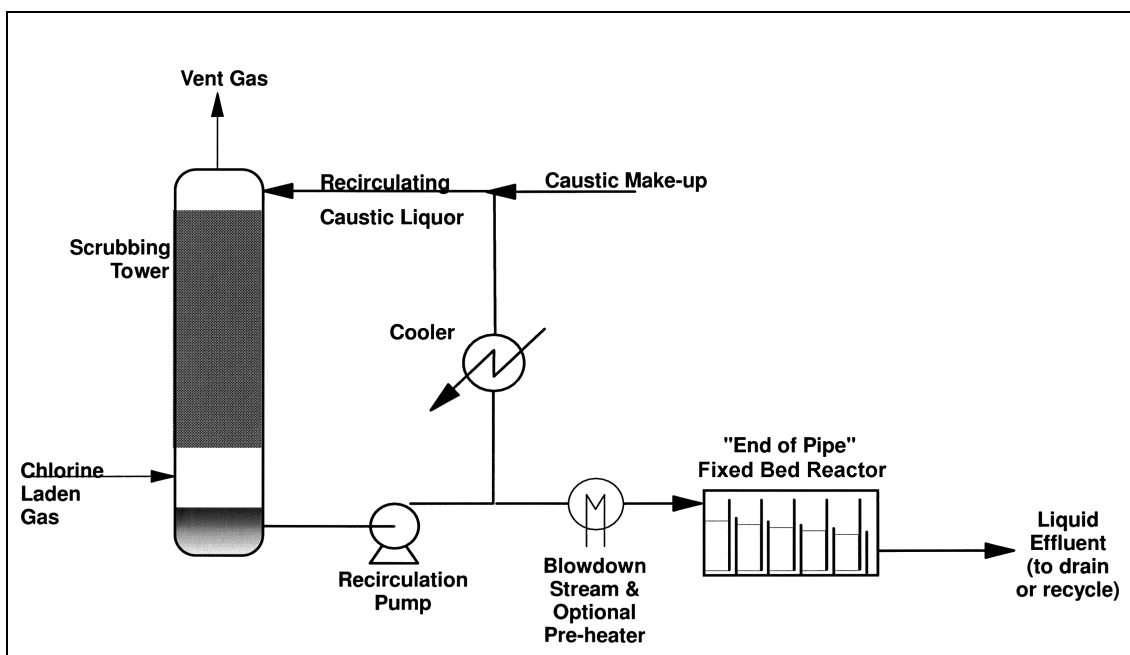
The decomposition of free oxidants to chloride and oxygen can be catalysed by a nickel, iron or cobalt based catalyst, according to the following overall reaction:



Some systems operate with a catalyst slurry, which is blended with the waste water stream to promote the reaction, in a batch process. To avoid emissions of metals, the catalyst must be allowed to settle before the supernatant water can be discharged. The catalyst activity decreases from batch to batch, although it is unclear whether this is due to deactivation of the catalyst or loss of metal.

Other systems operate with the catalyst on a fixed bed reactor, see Figure 4.1, reducing the loss of metals and increasing the capacity (no settling required) compared to slurry type catalytic systems. Also, the necessary concentration of catalyst is low (20 ppm), [Le Chlore, 1996].

In some cases, it is possible to recycle the effluent from the reactor back to the electrochemical cell. It is then necessary to control the concentration of chlorate and other impurities, in particular for membrane processes. Chlorate ion formation depends on the hypochlorite ion concentration in the caustic scrubber recirculation liquor and the temperature in the scrubber itself.



**Figure 4.1: Schematic diagram of a catalytic reduction fixed bed reactor process**

Based on figure from [Denye et al., 1995]

### *Thermal decomposition*

Decomposition of free oxidants (especially hypochlorite ( $\text{OCl}^-$ )) can be achieved by acidifying the waste water to pH 6-7 and heating to approximately 70 °C. By this means, present hypochlorite is reacted to chlorate ( $\text{ClO}_3^-$ ) and hydrochloric acid (HCl), according to the overall reaction:  $2 \text{HOCl} + \text{OCl}^- \rightarrow \text{ClO}_3^- + 2 \text{HCl}$

### *Recycling of hypochlorite*

If the quantities are low, the hypochlorite produced can be recycled in the cell brine at low pH. This seems easier for diaphragm electrolysis (open circuit) and membrane electrolysis but more difficult for mercury technology plants, where recycling of brine is in closed systems and for which the water balance may not permit this addition.

### **Main achieved emission levels**

- **Chemical reduction:** the efficiency of the reaction depends on the amount and type of chemical used. The bleed from the brine circuit at a membrane cell plant contains 10-30 mg/l free oxidants and 1000-3500 mg/l chlorate after treatment with sodium sulphite in the brine treatment. A reduction efficiency of more than 95% can be achieved, but depends mainly on the amount of chemicals added. Akzo Nobel in Bohus (Sweden) reports the use of hydrogen peroxide and a treatment efficiency of 95%, the consumption of  $\text{H}_2\text{O}_2$  being approximately 30 m<sup>3</sup> per year (100000 tonnes of  $\text{Cl}_2$  capacity/year).
- **Catalytic reduction:** a hypochlorite solution of 15% by weight can be treated in a single pass to free oxidants levels of less than 10 mg/l at ambient pressure and temperature with a catalytic reduction fixed bed process. Since the reactor has a fixed bed configuration, no emissions of metals occur, contrary to classic catalytic reduction. Note that this process does not reduce the levels of bromine, hypobromite, chlorate or bromate. [Denye et al., 1995]

- **Thermal decomposition:** the destruction efficiency of hypochlorite in a Dutch chlor-alkali plant is 95%. Residual concentration in the effluent is nevertheless high and most samples are in the range 500-2000 mg/l free oxidants [Dutch report, 1998].

### Cross-media effects

- Chemical reduction leads to the formation of chloride and oxy sulphur compounds (for example  $\text{SO}_4^{2-}$ ). The amount formed depends on the amount of free oxidants to be reduced. Because of the large number of chemical agents that may be used, this technique may increase the COD of the waste water.
- A potential emission of metals occurs in systems using a catalyst slurry. In systems with a fixed bed configuration, no emissions of metals occur, as the catalyst is fixed in the bed. Nevertheless, the used catalyst cannot be regenerated and needs to be handled as hazardous waste. Research is being carried out in this field.
- Thermal decomposition produces chlorate and hydrochloric acid. Depending on the amount of bromine compounds in the treated water, bromate may also be formed.

### Reference plants

- **Chemical reduction:**  
Many plants use classic chemical reduction to remove free oxidants from the waste water streams. However, chemical costs and the production of oxy sulphur compounds may become a problem, especially in cases where large amounts of off-spec hypochlorite (bleach) have to be destroyed.
- **Catalytic fixed bed reduction:**  
Shin Etsu Chemicals, Japan, November 1993  
Polifin, South Africa, June 1994  
Mitsui Toatsu Company, Japan, December 1996  
Solvay in Jemeppe, Belgium, June 1997

Besides the above-mentioned chlor-alkali plants, the catalytic fixed bed reduction process is used at more than 10 other industrial sites where there is a need for bleach destruction.

- **Thermal decomposition:**  
Thermal destruction of hypochlorite is applied at Akzo Nobel Chemicals Delfzijl plant.

### Economics

The cost of traditional chemical destruction of free oxidants is mainly the cost of chemicals. When the amount of free oxidants to be destroyed is low, chemical destruction might be the cheapest option.

Whenever large amounts of free oxidants have to be destroyed (for example, in bleach destruction), catalytic or thermal destruction may be more economical.

The costs of a catalytic reduction fixed bed system will mainly depend on the quantity of product to be treated. Operating costs include electricity for pumps and steam for heating the effluent to 30-38 °C. One company reports a total investment of 250000 euros in 1997

(currency rate November 1998) for a catalytic reduction fixed bed system. The average amount of bleach to be treated is 24 m<sup>3</sup>/day.

As an illustration, the costs of a catalytic reduction fixed bed system are given [Denye et al., 1995], according to the following conditions:

Amount of bleach to be destroyed: 50 m<sup>3</sup>/day (average); 100 m<sup>3</sup>/day (maximum)  
 Bleach concentration: 100 g NaOCl/litre  
 Required outlet: <0.1 g NaOCl/litre (99.9% efficiency)  
 Temperature of bleach: 40 °C

Process package:	11000	euros
Hardware:	36500	euros; when using GRP
	51000	euros; when using titanium
Catalyst:	105000	euros; assuming up-front payment; 3-years lifetime
Licence fee:	36500-73000	euros per annum

Figures are calculated from British pounds (assuming 1 £ = 1.46 euros in 1997). It should be noted that no extra investments are required for pumps and utilities, because this system is gravity-fed. Engineering costs (the “installation factor”) are estimated to be 2 times the capital expenditure. This is relatively low because no moving parts are included.

**References:** [Denye et al., 1995], [Dutch report, 1998], [Kelly, 1998], [Le Chlore, 1996]

#### 4.1.6 Carbon tetrachloride-free chlorine liquefaction and purification

##### Description

Carbon tetrachloride is still used at some locations for removal of nitrogen trichloride (NCl<sub>3</sub>) and for absorption of tail gas. However, other alternatives which do not use CCl<sub>4</sub> are available and applicable to existing plants.

First of all, if chlorine can be used directly without liquefaction it may not be necessary to remove the NCl<sub>3</sub>. A preventative measure to avoid the accumulation of NCl<sub>3</sub> is to specify low ammonium ion concentration in purchased salt (for example vacuum salt without addition of ferrocyanides to avoid caking), another is to purify the brine to remove ammonium ions (for example by chlorination at a pH higher than 8.5 or hypochlorite treatment of the brine).

Available techniques for NCl<sub>3</sub> destruction, not using CCl<sub>4</sub>, include:

- Adsorption with activated carbon filters. This technique also removes other impurities, such as organic compounds. NCl<sub>3</sub> is decomposed into nitrogen and chlorine.
- Ultra-violet light, and
- High metal temperatures, particularly of copper base alloys at temperatures of 80-100 °C, to decompose NCl<sub>3</sub>.
- Elimination of NCl<sub>3</sub> by reaction in a number of chemical processes, for example absorption of chlorine containing NCl<sub>3</sub> in caustic soda.

Several methods are available for handling the residual gas (non-condensables such as CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> saturated with chlorine) leaving the liquefaction unit. The most common is absorption in caustic soda to produce sodium hypochlorite. The product, depending on the market, is often saleable. If not, it is destroyed using the techniques described in Section 4.1.5. Other methods include the manufacture of HCl, FeCl<sub>3</sub> or ethylene dichloride.

Techniques not using carbon tetrachloride can be applied to new and existing plants. Hydro Polymers in Stenungsund (Sweden) stopped using  $\text{CCl}_4$  for purification purposes some years ago. They now use a static mixer to cool the gaseous chlorine as much as possible without getting any liquefaction, and then send the gaseous chlorine to the VCM-plant where  $\text{NCl}_3$  is decomposed at an elevated temperature. This method is a standard technique for plants with integrated VCM production.

### **Main achievements**

Avoid the use of carbon tetrachloride which is considered as harmful under the provisions of the Montreal Protocol.

### **Reference plants**

Carbon tetrachloride-free chlorine liquefaction and purification processes are applied in nearly all chlor-alkali plants in Europe.

### **Driving force**

Emissions from leakage of  $\text{CCl}_4$  are avoided. Carbon tetrachloride-free chlorine liquefaction and purification processes do not generate discarded carbon tetrachloride which has to be destroyed according to approved destruction processes.

### **Economics**

To stop using  $\text{CCl}_4$  may involve a change of compressor type, depending on the chlorine temperature.

**References:** [Debelle], [Gest 76/55, 1990], [Jorlöv]

## **4.2 Mercury cell plants**

### **4.2.1 Overview of mercury emission abatement**

This Section presents an overview of abatement of mercury emissions. Sections 4.2.1.1, 4.2.1.2, 4.2.1.3 and 4.2.1.4 address in more detail the reduction of mercury emissions to air and water, the removal of mercury from products and the treatment of mercury-containing wastes respectively.

### **Description**

There are currently approximately 12000 tonnes of mercury contained in mercury cells used for chlorine production in the EU. This is based on an average of 1.8 kg of mercury per tonne annual chlorine capacity and an EU mercury cell chlorine capacity of 6.7 million tonnes chlorine per year. During the operation of mercury cells, mercury losses occur to air, water, products and wastes. Although emissions have been greatly reduced, it is understood from comparing performances of applied abatement techniques that improvements are still possible.



Good housekeeping based on motivated staff is of great importance for the reduction of air emissions.

<b>Monitoring of possible leakages and recovery of mercury</b>	Aim: React as quickly as possible to avoid mercury evaporation
<ul style="list-style-type: none"> <li>• Continuous monitoring of mercury concentration in cell room</li> <li>• Removal of mercury spillage <ul style="list-style-type: none"> <li>– Daily housekeeping</li> <li>– Vacuum cleaners for mercury recovery</li> <li>– Immediate intervention at leakage (aided by appropriate housekeeping and continuous monitoring) and immediate isolation of Hg in closed vessels</li> </ul> </li> <li>• Use water for cleaning: avoid too high pressure which may generate micro droplets difficult to detect, in particular when cleaning upper floors of the cell room</li> </ul>	
<b>Good Housekeeping</b>	Aim: Avoid as much as possible any accumulation of mercury
<ul style="list-style-type: none"> <li>• Design of the cell room <ul style="list-style-type: none"> <li>– Smooth floor without cracks and regularly cleaned</li> <li>– No obstacles (avoid all types of storage)</li> <li>– Cell room concrete coated with a material resistant to absorption of mercury (e.g. epoxy/acrylate resin) and coloured to see droplets</li> <li>– No wood in the cell room</li> <li>– Avoid hidden mercury traps on pipe supports and cable trails (e.g. hang cable trays vertically)</li> <li>– Powerful lighting system (mercury shines)</li> </ul> </li> </ul>	
<b>Influence of human factors</b>	Aim: Motivation, education and training of staff for overall reduction of emissions
<ul style="list-style-type: none"> <li>• Development of housekeeping methodologies</li> <li>• Personal hygiene</li> <li>• Daily cleaning of clothes of personnel</li> <li>• Detailed routines for service jobs and hygiene in cell rooms</li> </ul>	
<b>End-of-pipe measures</b>	Aim: Recover mercury emitted during process or maintenance operations
<ul style="list-style-type: none"> <li>• Hg removal from hydrogen gas</li> <li>• Hg removal from caustic soda</li> <li>• Evacuation and treatment of mercury-containing process gases from: <ul style="list-style-type: none"> <li>– Closed end boxes and separate end box ventilation</li> <li>– Vacuum cleaners</li> <li>– Mercury pump seals</li> <li>– Brine circuit and salt dissolver</li> <li>– Off-gas from mercury recovery retort</li> </ul> </li> <li>• Mercury removal from waste water</li> <li>• Closed storage of mercury-contaminated wastes and parts</li> </ul>	

Process-integrated measures	
<ul style="list-style-type: none"> <li>• During normal operation               <ul style="list-style-type: none"> <li>– Use of salt with low impurity content</li> <li>– Verify and clean the inter-cell buss for good current distribution</li> <li>– Monitoring of mercury pressure</li> <li>– Mercury flow meter</li> <li>– Optimum quantity of mercury in cells</li> <li>– Adjustable anodes over different segments of the cell</li> <li>– Computerised control of electrode gap, current and voltage</li> <li>– Consider graphite reactivation without opening decomposer (for example: sodium molybdate treatment, ferric sulphate treatment, cobalt treatment)</li> <li>– Computer data base system for tracking life of cell components</li> </ul> </li> </ul>	<p>Aim: Avoid opening of cells</p> <p>More constant operation of cells and less waste produced            More constant operation of cells and less waste produced            Lower frequency of opening of cells for removal of Hg butter            Less heat development, lower Hg emissions            Increase carbon life in the decomposer</p> <p>Coordinate changes and repair with the opening of the cell</p>
<ul style="list-style-type: none"> <li>• During operations that require opening of the cells               <ul style="list-style-type: none"> <li>– Detailed routines and planning for dismantling of cells</li> <li>– Cells cooled prior to and during opening</li> <li>– Reduce duration of cell opening:                   <ul style="list-style-type: none"> <li>* Replacement parts available</li> <li>* Manpower available</li> <li>* If practical, spare decomposer completely assembled with carbon</li> </ul> </li> <li>– Cell bottom cleaned and covered during repair</li> <li>– Dedicated areas for maintenance and repair or mobile screening with suction ducts led to Hg removal</li> <li>– Avoid the use of rubber hoses to transfer mercury because of difficulty of decontamination</li> <li>– Stepping into the cell bottom should be minimised since decontamination of boots is difficult</li> <li>– In case of interruption of operation, all parts that might evaporate mercury should be covered</li> </ul> </li> </ul>	<p>Aim: Reduce Hg evaporation and get better control of Hg emitted</p>

The overall loss of mercury from a plant depends on the combined effectiveness of all the measures taken. Apart from the above-mentioned measures, other parameters also influence mercury losses:

- number and size of cells
- design of cells
- lay out of cell room (number of floors for example)
- current density and distribution
- electricity prices and associated (daily) modifications in production rate
- brine quality
- anode lifetime.

### Achieved emission levels

The mercury losses to air, to water and with products achieved by applying the presented reduction measures, reported in more detail in Sections 4.2.1.1, 4.2.1.2, and 4.2.1.3, are in the best cases:

	g Hg/tonne chlorine capacity (yearly average)
Air: cell room	0.2-0.3
process exhausts, including Hg distillation unit	0.0003-0.01
untreated cooling air from Hg distillation unit	0.006-0.1
hydrogen gas	<0.003
Water, process emissions	0.004-0.055
Caustic soda	0.01-0.05
<b>Total</b>	<b>0.2-0.5</b>

Old cell-room buildings might be, so to say, “saturated” with mercury and measures to reduce the mercury emissions from the cell room might only be noticeable after several years, when a new equilibrium is reached.

Apart from the process emissions reported above, there can also be considerable emissions of mercury with run-off water. The soil at many sites is contaminated with mercury due to deposition of diffuse emissions and/or historical disposal of mercury-contaminated wastes. The mercury leaches from the soil and ends up in the run-off water.

The majority of the mercury losses occur, however, in the various process wastes. It is therefore important that the wastes are handled and treated so as to minimise current and future emissions of mercury to the environment.

When completing the annual mercury balance for a site, there is frequently a difference to balance between ‘IN’ and ‘OUT’. This is because mercury accumulates in plant equipment and structures during the life of the plant. Nevertheless, efforts should be made to keep the ‘Difference to Balance’ as low as possible to avoid suspicions of unknown mercury emissions. Some guidance on how to make a mercury balance is given in [Euro Chlor Env. Prot. 12, 1998]. Some main points to reduce the ‘Difference to Balance’ are:

- adoption of a recognised standard methodology to calculate the mercury balance
- accurate inventory of mercury in cells and in store
- all equipment where mercury is able to accumulate should, if possible, be purged shortly before making the balance
- application of high-performance monitoring systems to minimise differences in the balance calculation due to inaccuracies of mercury emission measurements

### Cross-media effects

Cross-media effects occur when measures are applied to remove mercury from contaminated gas flows, water streams and products. The resulting wastes and sludges have to be appropriately treated.

It should be noted that some methods to treat process exhausts, waste waters and wastes generate less waste, or waste that can be directly recycled into the process (for example, mercury removal with chlorine containing brine or with the calomel process) but do not achieve the lowest emission of mercury.

### Reference plants

The success of the measures depends on a number of factors, which are described above. It appears that plants built in the 1970s took the abatement of mercury emissions into consideration from the beginning. Two plants that reported very low emissions of mercury in 1997 are (See Table 4.3 and Table 4.4):

- Akzo Nobel in Bohus (Sweden), two cell rooms commissioned in 1960 and 1969
- Hydro Polymers in Stenungsund (Sweden), commissioned in 1969

These low emissions are achieved by implementing a large number of measures and by having worked continuously to lower the emissions during the last 20 years.

### Driving force

The driving force can be either a requirement by the authorities to reduce mercury emissions or the operator's own initiative.

### Economics

It is very difficult to make an assessment of the costs associated with minimising mercury losses. However, it appears that companies still seem to prefer investing in measures to reduce mercury emissions to changing to mercury-free technology. Efforts are today concentrated on reducing emissions to air.

### References

[Akzo Nobel, 1998], [Blomgren], [Debelle], [Dutch report, 1998], [Euro Chlor Env. Prot. 11, 1998], [Euro Chlor Env. Prot. 12, 1998], [Euro Chlor report, 1997], [Gest 93/187, 1993], [Grunden], [Hydro Polymers, 1998], [UBA (D), 1997], [USEPA, 1998]

Mercury source	Measures	Hg-level after measures	Flow	Emission (g/tonne Cl <sub>2</sub> -capacity)	Compartment
General	Education and training Mercury monitoring (continuous) Detailed routines for service	-		-	
Process optimisation	Dimensionally Stable Anodes Computerised control of current and voltage Mercury flow meter Use of vacuum crystallised salt	-		-	
Cell room	Improved sealing of equipment Closing and suction of end boxes Acrylate resin floor Immediate removal of spillage Cell cooling during maintenance	2-8 µg/m <sup>3</sup> in cell room	300000 - 600000 Nm <sup>3</sup> /hr or 22500 - 45000 Nm <sup>3</sup> /t Cl <sub>2</sub>	0.17-0.21	Air
NaOH-treatment	Filtration with activated carbon	5-10 µg/l 50% NaOH	1.128 tonne 100% NaOH/t Cl <sub>2</sub>	0.01 – 0.02	Product
H <sub>2</sub> -treatment	Activated carbon filtration	< 0.01 mg/Nm <sup>3</sup> H <sub>2</sub>	311 Nm <sup>3</sup> H <sub>2</sub> /t Cl <sub>2</sub>	0.002	Product/Air
Process gas treatment, including: • Vacuum cleaner • Depleted precoat drying	Activated carbon filtration. Note that end boxes are connected to chlorine and hydrogen treatment.	< 1 µg/Nm <sup>3</sup> air	20 Nm <sup>3</sup> /minute when using the vacuum cleaner.	0.000	Air
Waste water treatment	Treatment with hydrazine followed by sedimentation, sand filtration and activated carbon filtration	< 20 µg/l water 0.5 kg Hg per year	<30000 m <sup>3</sup> /year	0.004	Water
Waste treatment (regular)	No treatment on site. The caustic filter residue and the waste water sludge are stored for treatment in a distillation unit off site. The amount of recovered Hg is unknown. Brine filtration sludge is landfilled.		Brine filtration sludge: 21.3 tonnes, with 1.8 kg Hg Caustic filter residue: 3 tonnes with appr. 800 kg Hg Waste water sludge: 4 tonnes with appr. 200 kg Hg	?	Waste
Off-gas from mercury waste storage	Untreated	n/a	n/a	n/a	Air
Irregular waste	Untreated	n/a	n/a	n/a	Waste
Total emissions				0.2 – 0.25	

Hydro Polymers, Stenungsund, Sweden: Capacity 114000 tonne Cl<sub>2</sub> per year; 64 electrolyzers of Uhde design (15 m<sup>2</sup>); commissioned 1969. The electrolyzers are all situated on the second floor. The first floor is coated with an acrylate resin.

**Table 4.3: Overview of measures, corresponding mercury levels and emissions from the Hydro Polymers (Stenungsund, Sweden) mercury cell chlor-alkali plant in 1997.**

Table based on table 29 in [Dutch report, 1998] and information from: [Hydro Polymers, 1998], [Stenhammar]

Mercury source	Measures	Hg-level after measures	Flow	Emission (g/tonne Cl <sub>2</sub> -capacity)	Compartment
General	Education and training Mercury monitoring (continuous) Detailed routines for service	-		-	
Process optimisation	Dimensionally Stable Anodes Computerised control of current and voltage Mercury flow meter Use of vacuum crystallised salt	-		-	
Cell room	Improved sealing of equipment Closing and suction of end boxes Cells are connected to vacuum system Acrylate and epoxy resin floor Immediate removal of spillage Cell cooling during maintenance	5-10 µg/m <sup>3</sup> in cell room	400000 – 600000 Nm <sup>3</sup> /hr or 35000 - 50000 Nm <sup>3</sup> /t Cl <sub>2</sub>	0.3-0.4*	Air
NaOH-treatment	Filtration with activated carbon	5-10 µg/l 50% NaOH	1.128 tonne 100% NaOH/t Cl <sub>2</sub>	0.01 – 0.02	Product
H <sub>2</sub> -treatment	Scrubbing with chlorinated brine Filtration with activated carbon	0.01 mg/Nm <sup>3</sup> H <sub>2</sub>	311 Nm <sup>3</sup> H <sub>2</sub> /t Cl <sub>2</sub>	0.003	Product/Air
Process gas treatment, including: • End box ventilation • Vacuum cleaner • Mercury pump seals and • Storage of untreated waste	Filtration with activated carbon, in three different systems. The mercury pumps have been replaced by mechanical sealed pumps, which allows the use of the carbon filter for common purposes.	µg/Nm <sup>3</sup> air 4 1 0.5 (pump seals and storage)	Nm <sup>3</sup> /hr 2500 500 950 (pump seals and storage)	0.0003	Air
Waste water treatment	Treatment with hydrazine, sedimentation, sand filtration, carbon filter and ion exchange Run-off water not treated	5-8 µg/l water	7 m <sup>3</sup> /hr	0.005 0.04	Water
Waste treatment (regular)	Stored in drums and removed	<< 500 mg/kg waste	Brine sludge: 1600 kg/month Caustic sludge: 200 kg/month WWT sludge: 1500 kg/month	?	Waste
Irregular waste	n/a	n/a	n/a	n/a	Waste
Total emissions				0.36 – 0.47	

Akzo Nobel, Bohus, Sweden: Capacity 100000 tonne Cl<sub>2</sub> per year; 54+12 electrolyzers of Uhde in EKA design; commissioned 1960 and 1969. The electrolyzers are situated in two cell rooms (only one cell room since 27 August 1999).

\* 30 kg Hg according to periodical measurements (4 samplings per year). 40 kg Hg according to the continuous monitoring programme.

**Table 4.4: Overview of measures, corresponding mercury levels and emissions from the Akzo Nobel (Bohus, Sweden) mercury cell chlor-alkali plant in 1997.**

Table based on table 30 in [Dutch report, 1998] and information from: [Akzo Nobel, 1998], [Stenhammar]



#### 4.2.1.1 Reduction of mercury emissions to air, including hydrogen gas

The best environmentally performing plants have put a lot of effort into reducing mercury emissions to air and the lowest achieved emission levels result from the application of both organisational and technical measures.

##### Minimising mercury emissions from the cell room

Nowadays, the cell room is the biggest source of mercury emissions to air. These emissions are mainly due to leakage of mercury from the cells and evaporation of mercury during maintenance and repair. Only continued and dedicated efforts based on motivated staff, with target levels and follow-ups of the emissions, will result in systematic low losses of mercury from the cell room. The most important measures to reduce emissions from the cell room are summarised in Section 4.2.1 and mainly concern:

- housekeeping of the cell room including daily cleaning of staff clothes
- good practices during maintenance and repair. A maintenance plan has a direct effect on the lifetime and opening frequency of the cells
- improvements of the cells: inlet/outlet end boxes of closed type, cell bottom wiper to enable periodical mechanical cleaning of the cell bottom without opening the cells, new technologies cell covers, etc
- accessibility of the equipment to be cleaned inside the cell room: vertical alignment of cables instead of horizontal for example

As the factors influencing the mercury concentration in cell rooms are directly linked to the age and design of the cell room, it appears that the same emission levels cannot be achieved by all plants. Very low losses of mercury to air are achieved by two plants located in Sweden:

- 0.17-0.21 g/tonne  $\text{Cl}_2$  capacity at Hydro Polymers in Stenungsund (see Table 4.3)
- 0.3 g/tonne  $\text{Cl}_2$  capacity at Akzo Nobel in Bohus (See Table 4.4)

The Swedish plants were built in the early 1970s and have only one floor with electrolyzers. Furthermore, the companies have a long history of mercury emission abatement.

From the visits made, it has been noticed that emissions reported from cell rooms using cells with KCl as feedstock are generally higher than from cells using NaCl. The lifetime of equipment seems to be shorter when KCl is used; this may be because the driving force K-Hg of the amalgam is weaker than Na-Hg. Also, the cell rooms are often old buildings.

It is recognised that monitoring and calculation of mercury losses from the cell room is difficult. Calculation of the ventilation flow in the cell room is especially difficult, because of the large volumes involved and because the air is ventilated by natural draft through louvres in the roof and/or the walls (the roof design is important). As a result of this, the accuracy with which the mercury loss from the cell room can be assessed varies from 20-50%, depending on the configuration of the plant and the equipment used. Some guidance on how to perform the measurements is given in [Euro Chlor Env. Prot. 5, 1999].

##### *Influence of the “mercury memory” of the cell room*

It is a fact that one source of emissions is the evaporation of mercury deposited in the building (in cracks in the floor for example), in particular in buildings built before the 1970s when prevention of mercury losses was not a matter of priority. In practice, this could imply that a building is “saturated” with mercury and that measures to reduce the mercury emissions from the cell room are only noticeable after several years, when a new equilibrium is reached.

### *Influence of season and climate on cell room emissions*

This is a much discussed topic. From discussions during a visit to plants in Sweden, the following picture was given and is also supported in [Dutch report, 1998]:

- The emissions from the cell room are mainly caused directly and indirectly by leakage from the equipment.
- Spilled mercury may be deposited in the building (in concrete, steel, wood etc.) and may evaporate a long time after the actual spilling has taken place (“mercury memory”).
- There are no reasons to assume that leakage from the equipment is dependent on the ambient temperature. The operational temperature of the equipment itself and the state of the art of the equipment are much more important in this respect.
- When the ambient temperature is high (mainly in summer), the ventilation flow is higher in order to maintain an acceptable temperature in the cell room (max. 40 °C). At high ventilation flow rates, the evaporation of spilled mercury is more rapid and thus there is less time to remove spillage.

Thus, it can be concluded that a seasonal and climatic effect does exist, but applies only to mercury that is released into the cell room, either directly by spillage or indirectly from the “mercury memory” of the cell room. This means that the seasonal and climatic effect becomes less important when the amount of leakage is reduced and when the historical mercury level in the building is low.

### **Removal of mercury from the process exhausts**

Process exhausts refer to all gaseous streams by which mercury can be emitted to the atmosphere apart from the cell room ventilation air and the hydrogen gas. The waste gases can be collected and treated together. The main sources are end boxes and mercury pump seal vents. Vacuum cleaners are usually connected to a separate ventilation system.

### *Adsorption on impregnated activated carbon*

Description: Mercury contained in the waste gas is removed by adsorption on activated carbon impregnated with sulphur or iodine.

Achieved levels: A lot of examples are available and indicate a specific emission of mercury close to zero. Solvay in Roermond (Netherlands) was achieving a concentration level of less than 0.003 mg Hg/m<sup>3</sup> air, corresponding to less than 0.001g Hg/tonne chlorine capacity (the plant was shut down in the end of 1999). Akzo Nobel in Bohus (Sweden) reported an emission of 0.03 kg Hg with process exhausts for 1997, corresponding to 0.0003 g Hg/tonne chlorine capacity (no mercury recovery retort). Solvay in Martorell (Spain) reports an emission level of 0,01 g Hg/tonne chlorine capacity. Note that a contaminated waste is generated.

### *Calomel reaction*

Description: Mercury contained in the waste gas is converted to Hg<sub>2</sub>Cl<sub>2</sub> (calomel) by adding chlorine. Hg<sub>2</sub>Cl<sub>2</sub> is then absorbed in a packed column. The tower packing can be regenerated using chlorine-containing brine, which is recycled to the mercury cell brine cycle.

Achieved level: The residual mercury concentration is reported to be 0.05-0.1 mg/m<sup>3</sup>, which corresponds to an emission of 0.006-0.01 g Hg/tonne chlorine capacity [UBA (D), 1997]. However, it has been reported by ICI that the removal of the calomel from the exhaust gas

stream is not always satisfactory when using a simple fluidised scrubber system and could lead to harmful emissions of mercury to air.

Cost: The cost has been estimated to 1.3 euros (2.58 DEM) per tonne chlorine capacity for a plant with a capacity of 100000 tonnes chlorine per year and a waste gas volume of 2000 m<sup>3</sup>/h [UBA (D), 1997].

#### *Scrubbing with chlorinated brine or hypochlorite*

Description: Generally, such processes involve packed columns with a countercurrent flow of hypochlorite or chlorinated brine. By scrubbing with chlorine-containing brine HgCl<sub>2</sub> is produced forming a mercury-chlorine complex in the brine. The chlorine has to be removed and the brine can be recirculated. By scrubbing with alkaline hypochlorite solution, the mercury contained in the process exhausts is oxidised as well but no subsequent chlorine removal is necessary. The cleaned gas needs to pass through a separator to remove entrained liquid droplets. The mercury is recirculated via the brine.

Achieved level by BASF in Antwerp (Belgium): mercury concentration in the process gas was 50 ppb in 1997 (top of the absorption tower) corresponding to an emission of 0.023 g Hg per tonne chlorine capacity, and 20 ppb in 1998 (monthly averages). All gases are treated in an absorption tower. The first Section is used to neutralise the chlorine in the gas by transforming it into hypochlorite. The mercury in the waste gas is partly absorbed by the hypochlorite in the first Section of the tower; no absorption takes place in the upper Section of the tower because it does not contain hypochlorite. The technique consists of adding hypochlorite to NaOH in the upper Section. The higher efficiency of the absorption in 1998 was due to an increase of hypochlorite in the tower.

Cost: The cost has been estimated at approximately 0.9 euros (1.74-1.77 DEM) per tonne chlorine capacity for a plant with a capacity of 100000 tonnes chlorine per year and a waste gas volume of 2000 m<sup>3</sup>/h, using a scrubbing process with chlorine-containing brine or alkaline hypochlorite solution to achieve a residual mercury concentration of 0.05-0.1 mg/m<sup>3</sup>, which corresponds to an emission of 0.006-0.01 g Hg/tonne chlorine capacity [UBA (D), 1997].

#### **Removal of mercury from the hydrogen gas**

The equilibrium mercury concentration in hydrogen gas is a function of temperature and pressure. The hydrogen gas stream leaving the denuder is at a temperature of 90-130 °C and nearly saturated with mercury vapour (up to 400 mg/m<sup>3</sup>). Most of the mercury is condensed out and collected by cooling the gas stream down in one or more stages. The cooling step is normally followed by adsorption on activated carbon impregnated with sulphur or iodine, but other techniques are also reported.

#### *Scrubbing with chlorinated brine or hypochlorite*

Description: As above in the section about removal of mercury from the process exhausts. At Akzo Nobel in Bohus (Sweden) the hydrogen gas is scrubbed with chlorinated brine before the adsorption on activated carbon.

Achievable level: No information.

Cost: No information.

*Adsorption on impregnated active carbon*

Description: Mercury contained in hydrogen is removed by adsorption on activated carbon impregnated with sulphur or iodine, leaving a mercury concentration in hydrogen gas of 0.002-0.015 mg/m<sup>3</sup> [Ullmann's, 1996]. Note that a contaminated waste is generated.

Achievable level: A lot of examples are available in Europe and this technique is increasingly applied because mercury from hydrogen is an important source of emission. Solvay in Antwerp (Belgium) reports a concentration of around 0.01 mg Hg/m<sup>3</sup> hydrogen gas for a maximum flow of 8000 m<sup>3</sup>/h, corresponding to a maximum residual emission of 0.003 g Hg/tonne Chlorine capacity. Suppliers guarantee a concentration of 0.005 mg Hg/m<sup>3</sup>.

Cost: Atochem in Lavera (France) installed a sulphurised active carbon system in 1997 to remove mercury from hydrogen gas. The plant has a mercury process chlorine capacity of 166000 tonnes. The total cost reported is in the range of 0.45-0.5 million euros, including the heat exchanger necessary to increase the temperature after the cooling step to 20-25 °C, the equipped tower and the necessary filters. The sulphurised active carbon needs to be changed every 2-3 years. Its lifetime can be longer, depending on the efficiency of the cooling step, which influences the mercury concentration in the hydrogen gas.

*Chemical reaction with cupric oxide*

BASF in Antwerp (Belgium) reports the use of a chemical reaction with CuO after the cooling step in order to absorb mercury. The average concentration achieved with the technique is 10 ppb after treatment, corresponding to an emission level of 0.003 g Hg/tonne chlorine capacity.

*Adsorption on copper/aluminium or silver/zinc oxides*

By adsorption on copper/aluminium oxide or silver/zinc oxide a mercury concentration of less than 0.001 mg Hg/m<sup>3</sup> hydrogen gas could be achieved [Ullmann's, 1996].

**4.2.1.2 Reduction of mercury emissions to water**

Mercury-containing waste water streams in the chlorine plant mainly arise from:

Process: bleed from brine purification; condensate and wash liquor from treatment of chlorine; hydrogen drying; filtered caustic liquor; brine leakages and ion-exchange eluate from process water treatment

Wash water from cell cleaning operations: inlet and outlet boxes

Rinsing water from the cell room: cleaning of the floors, tanks, pipes and dismantled apparatus

Most of these streams can be recycled into the process, but the bleed from brine purification and the rinsing water do generally need to be treated and discharged. The waste water contains metallic mercury and mercury compounds such as mercury chloride as well as magnesium hydroxide, ferric hydroxide and calcium carbonate.

There can also be considerable emissions of mercury with run-off water. The soil at many sites is contaminated with mercury due to deposition of diffuse emissions and/or historical disposal of mercury contaminated wastes. The mercury leaches from the soil and ends up in the run-off water.

At an integrated site, different values can be reported from the chlorine plant unit and from the central waste water treatment plant. It is recommended that the mercury level in the waste water be continuously monitored.

## Description

The first step to reduce the mercury emissions to water is to reduce the amount of waste water to be treated. A waste water rate of 0.3-1.0 m<sup>3</sup>/tonne of chlorine is reported to be achievable in [Ullmann's, 1996]. The discharge of process water at Solvay in Roermond (Netherlands) was 0.18 m<sup>3</sup>/tonne chlorine capacity in 1996, a specific volume reduction of more than 90% compared to the 1970s [Dutch report, 1998].

The mercury level in waste water is usually reduced in several steps by a combination of techniques. Several examples of waste water treatments are given in the achievable level section below.

## Achievable level

At Hydro Polymers in Stenungsund (Sweden) the waste water mercury removal system consists of treatment with hydrazine, sedimentation, sand filters and activated carbon filters. The resultant mercury concentration in the waste water was less than 20 µg/l in 1997, corresponding to an emission of 0.004 g Hg/tonne chlorine capacity.

At Akzo Nobel in Bohus (Sweden) the waste water mercury removal system consists of a mixing unit where hydrazine is added to the waste water, two sedimentation tanks, sand filters, activated carbon filters and ion exchange filters. The treated waste water flow was 7 m<sup>3</sup>/h with a mercury content of 3000-5000 µg/l in 1997 and the resultant mercury concentration in the waste water was 5-8 µg/l, corresponding to an emission of 0.005 g Hg/tonne chlorine capacity. The total mercury emission to water from the site is approximately 0.045 g Hg/tonne chlorine capacity, which means that about 10% of the mercury emissions are process emissions and the other 90% are emissions from deposited/disposed mercury ending up in the run-off water.

At Solvay in Roermond (Netherlands) the waste water mercury removal system consisted of sedimentation of solid mercury and chemical precipitation with sulphide (NaHS). The treated waste water flow was around 3 m<sup>3</sup>/h and the resultant mercury concentration in the waste water was about 30 µg/l, corresponding to an emission of 0.005 g Hg/tonne chlorine capacity. The total mercury emission to water from the site was approximately 0.1 g Hg/tonne chlorine capacity, which means that about 5% of the mercury emissions were process emissions and the other 95% were emissions from deposited/disposed mercury ending up in the run-off water. (The plant was shut down in the end of 1999)

At ICI in Wilhelmshaven (Germany) the waste water mercury removal system consists of chemical precipitation of mercuric sulphide followed by filtration. The treated waste water flow is around 15 m<sup>3</sup>/h (reported levels of AOX: 0.5-3 mg/l and COD: 50 mg/l), and the resultant mercury concentration in the waste water is about 4 µg/l, corresponding to an emission of 0.006-0.008 g Hg/tonne chlorine capacity.

At Tessenderlo Chemie in Tessenderlo (Belgium) the waste water mercury removal system consists of chemical precipitation with sulphide (NaHS) followed by filtration with a precoated filter. The resultant mercury (HgS) concentration in the waste water is 10-15 ppb and the total emission to water from the site is 0.01-0.02 g Hg/tonne chlorine capacity.

At Akzo in Hengelo (Netherlands) the waste water mercury removal system consists of sedimentation of solid mercury and ion exchange filters. The treated waste water flow was around 8 m<sup>3</sup>/h in 1997 and the resultant mercury concentration in the waste water was about 50 µg/l, corresponding to an emission of 0.05 g Hg/tonne chlorine capacity. The total mercury emission to water from the site was 0.11 g Hg/tonne chlorine capacity, which means that about 50% of the mercury emissions are process emissions and the other 50% are emissions from deposited/disposed mercury ending up in the run-off water.

At BASF in Antwerp (Belgium) the waste water mercury removal system consists of a reducing step with hydroxylamine, followed by filtration and activated carbon filters. The mercury emission from waste water is 0.055 g Hg/tonne chlorine capacity.

A mercury removal system proposed by suppliers, De Nora for example, consists of oxidation with chlorine to mercurous chloride (Hg<sub>2</sub>Cl<sub>2</sub>), followed by adsorption on an ion exchange medium. Elutriation is done with hydrochloric acid (HCl), which is then used to acidify the brine. All waste water is collected and treated with hypochlorite solution (OCI<sup>-</sup>) to oxidise the metallic mercury. The pH value is adjusted with HCl and the waste water is treated with a small excess of sodium sulphite, in order to eliminate the chlorine introduced. Activated carbon is necessary inside the dechlorination tower to eliminate the remaining traces of chlorine, which are harmful to the mercury adsorbing resin. The acidic chlorine-free waste water enters the ion exchangers placed in series, filled with thylic resin, reducing the mercury content of the water to below 5 µg Hg/l. The resin must be regenerated every now and then with concentrated HCl acid. The mercury-containing eluate is recovered in the brine system and used in the dechlorination/acidification of the circulating brine.

#### 4.2.1.3 Removal of mercury from caustic soda

The (approximately 50%) caustic soda leaving the mercury cells usually contains metallic mercury in the range of 2.5 to 25 mg/l, depending on the type of denuders and temperature. For some applications very pure sodium and potassium hydroxide are needed.

Description: The predominant technique to reduce mercury levels in caustic soda is by activated carbon filtration in precoated candle or plate filters. On a special carbon precoat, the mercury is absorbed and is discharged from the filter as a dry cake. This technique guarantees a maximum of mercury content in 50% caustic of 0.05 ppm if the content before filtration is in the range of 5-20 ppm of mercury. It has been installed in many chlor-alkali plants. It is reported in [Dutch report, 1998] that the caustic filtration unit is sensitive to flow rate changes and that low mercury levels are only achieved during undisturbed operational conditions. Note that the activated carbon filtration generates mercury-contaminated waste. The discharged filter cakes can be subjected to distillation to recover the mercury.

Achievable level: Hydro Polymers in Stenungsund and Akzo Nobel in Bohus (Sweden) both report for 1997 a residual mercury concentration in caustic of 5-10 µg/l 50% NaOH, corresponding to a mercury loss of 0.01-0.02 g Hg/tonne chlorine capacity. Akzo in Hengelo (Netherlands) reports for 1997 a residual mercury concentration in caustic of 40-60 µg/kg 100% NaOH, corresponding to a mercury loss of 0.03-0.05 g Hg/tonne chlorine capacity.

Cost: The price of one 15 m<sup>2</sup> filter is about 0.125 million euros and its installation, including all operating instruments is around 0.25 million euros (source: FUNDA<sup>R</sup> filter). It should be noted that the reported mercury concentrations in caustic above at Hydro Polymers in Stenungsund and Akzo Nobel in Bohus (Sweden) are achieved with filter areas of 100-150 m<sup>2</sup> (100000-120000 tonnes of chlorine/year).



#### 4.2.1.4 Treatment of mercury-containing wastes, including recovery of mercury

The various processes already described for the treatment of mercury-contaminated gaseous, liquid and product streams give rise to mercury-contaminated solid wastes. Additionally, there are maintenance, construction and demolition solid wastes which also may contain mercury.

Prior to treatment of the wastes, it is essential to characterise each waste by type, chemical state and mercury concentration. Preferably, the characterisation should be done by assay; however, by their nature, solid wastes are non-homogeneous, making sampling difficult. This may result in estimates having to be made. The materials range from semi-solid sludges from water, brine and caustic treatment, graphite and active carbon from gas treatment, residues from retorting and mercury in tanks/sumps to miscellaneous contaminated metallic equipment, sometimes lined with organic materials such as rubber. The mercury may be present both as metallic mercury and as inorganic compounds. Table 4.5 shows available treatment possibilities for mercury-containing wastes.

	Recycle or recovery techniques				Disposal techniques
	Physical/mechanical treatment *	Washing	Chemical treatment	Distillation	Landfill or underground storage
Maintenance materials					
Solids from water & brine treatment					
Solids from caustic treatment					
Solids from gas treatment; graphite from decomposers					
Solids from retorts					
Notes	Metallic mercury recovered directly from treatment			For distillation residues, see "Solids from retorts"	

\* includes cryogenic and thermal options

**Table 4.5: Treatment possibilities for mercury-containing wastes**

[Euro Chlor]

A waste management plan should be drawn up at each plant after consultation with the appropriate authorities. It should include:

- the routines and records necessary to follow the recommended procedures
- a description of the different types of wastes that are generated and ways to minimise waste generation
- methods for quantification of the types of waste
- storage procedures for different types of waste
- treatment procedures including stabilisation and final destination of wastes. Any waste treatment and disposal off-site should be described
- methods and frequencies for sampling and analysis before and after waste treatment.



The choice of equipment, materials and processes and methods of operation should aim at waste reduction and mercury should be recycled wherever possible within the process.

Table 4.6 shows some available techniques for treatment of mercury-containing wastes, described in more detail below, with typical performances and with references given to other sections of this document where waste generation and treatments are described.

Waste type (References)	Characteristics/ Typical Amounts	Hg content before treatment	Treatment	Final mercury content (mg/kg)
Brine sludge (3.1.2.2.2, 3.1.2.5.2.3)	Inorganic waste Up to 20 000 g/t Cl <sub>2</sub> depending on salt quality	<150 mg/kg	Landfilled after stabilisation	
Waste water treatment sludge (3.1.2.2.2, 4.2.1.2)	Activated carbon 50-400 g/t Cl <sub>2</sub>	10-50 g/kg	Distillation Landfilled after stabilisation	Hg recovered <10 in residue
Carbon sludge from caustic filtration (3.1.2.5.4, 4.2.1.3)	Activated carbon 20-50 g/t Cl <sub>2</sub>	150-500 g/kg	Distillation Landfilled after stabilisation	Hg recovered 20-200 in residue
Decomposer carbon	Activated carbon 10-20 g/t Cl <sub>2</sub>	10-100 g/kg	Distillation Landfilled after stabilisation	Hg recovered 20-200 in residue
Filters from gaseous exhausts (3.1.2.5.5, 4.2.1.1)	Activated carbon 10-20 g/t Cl <sub>2</sub>	100-200 g/kg	Chemical treatment Landfilled after stabilisation	Hg recovered 20-200 in residue
Sludges from storage tanks, sumps etc	Can contain considerable amounts	Often high mercury content	Distillation	Hg recovered
Rubberlining	Variable	Variable	Acid bath, cryogenic and/or washing Incineration	300
Coated metallic materials	Contamination of surface	Usually <0.1%	Thermal, cut and washed, or cryogenic	
Steel/iron construction parts	Amounts vary	Non-homogeneous Usually <1%	Acid bath Sold as scrap	<5-10
Concrete and other construction waste	Amounts vary	Non-homogeneous Usually <0.1%	Landfilled as hazardous waste or as other waste depending on content	>10  < 10

**Table 4.6: Some available techniques with typical performances for treatment of mercury containing wastes**

[Euro Chlor], [Stenhammar]

The legislation with regard to mercury-containing waste differs from country to country. Some countries do not have mercury recovering retorts and store all the waste either in underground deposits such as mines or in secure landfills. This also influences the way the mercury-containing waste is treated, handled, counted and reported.

## Brine sludge

If a residual quantity of chlorine is left in the brine when it leaves the cell, the mercury will remain in a soluble ionic form. Thus, when the brine is filtered to remove the precipitated impurities, the only mercury contamination is from the soluble mercury in the mother liquor trapped within the filter cake. This can be removed by washing the cake prior to discharge. There would therefore be very little mercury in the final solids which can be disposed of to normal landfill. In certain cases, because of the materials the plant is made of, it is not possible to maintain a chlorine excess in the brine circuit. In such circumstances it may be possible to wash the filter cake with hypochlorite, thus resolubilising the mercury, which may be recovered to the brine system. This may however cause problems with the water balance. The alternative is retorting or landfilling the filter cake, depending on the mercury content. The use of vacuum salt in such circumstances would minimise the quantities to be retorted or landfilled.

Sludges can be distilled in a recovery retort or be stored on site, generally after treatment with sodium sulphide to convert the mercury into an insoluble sulphide. Sludges are also stored in old salt mines that are no longer in use, in safe barrels (as is the case in some plants in Germany) without being pretreated.

## Solid wastes

### *Mechanical/physical treatment (including cryogenic and thermal treatment)*

Mechanical treatment can be used if significant quantities of metallic mercury are present. Techniques include brushing, ultrasonic vibration, vacuum cleaning and/or nitrogen freezing (for rubber coated steel). Thermal treatment, for instance warm sandblasting in a fluidised bed or pyrolysis in a furnace, is an alternative for coated metallic materials. As for every type of treatment, special attention should be given to minimising mercury emissions to air and to avoiding cross-media effects. [Euro Chlor report, 1997], [Euro Chlor Env. Prot.3, 1999]

### *Water treatment*

Water treatment in closed washing machines with high pressure jets can remove attached mercury. [Euro Chlor report, 1997]

### *Chemical treatment*

Chemical treatment can be made with hypochlorite, chlorinated brine, hydrochloric acid or solutions of hydrogen peroxide. Dissolved mercury can be recirculated in the brine stream or recovered in the water treatment system. [Euro Chlor report, 1997]

### *Distillation*

Distillation of mercury from solid waste can be carried out in special distillation units. To be distilled, mercury has to be in elemental form. This means that some solid waste (for example, when the mercury is present as a salt) cannot be distilled. Special attention should be given to treatment of the exhaust gases from these installations. Filtration with activated carbon may provide a good solution (see section about removal of mercury from the process exhausts in 4.2.1.1). [Euro Chlor report, 1997]

The retorting process (distillation) removes mercury to a large extent. The residual mercury content is reported to be less than 50 mg/kg waste [Dutch report, 1998], possibly after repeated treatments. The mercury is recovered as metallic mercury and can be stored for future make-up to the cells.

After treatment, the waste may be cooled by ventilation air. This ventilation air contains a small amount of mercury. Akzo in Hengelo (Netherlands) reported a mercury emission of 0.006 g Hg/tonne chlorine capacity with the cooling air from the mercury recovery unit in 1997. Solvay in Roermond (Netherlands) reported a mercury emission of 0.1 g Hg/tonne chlorine capacity with the cooling air from the mercury recovery unit in 1996. [Dutch report, 1998].

The solid residue is landfilled or stored underground.

### **Recuperation of mercury**

After treatment, mercury can be recovered and reused. Recuperation of mercury is possible from:

- caustic treatment sludges
- hydrogen and waste gas treatment when using chemical processes
- water treatment sludges
- the mercury distillation unit
- area for handling mercury-contaminated parts (for example, when changing the decomposer graphite).

### **Final disposal**

In most cases, the mercury-containing solid residues that result from treatment need stabilisation before being disposed of. Stabilisation serves to transform metallic mercury to a less soluble, more stable chemical state in order to reduce the risk of leaching from the final disposal site in the short and long term. In many cases, mercury is treated with sulphur or sulphur compounds to transform it to mercury sulphide or with selenium to mercury selenide. This can also be combined with physical stabilisation, for example in cement-based materials.

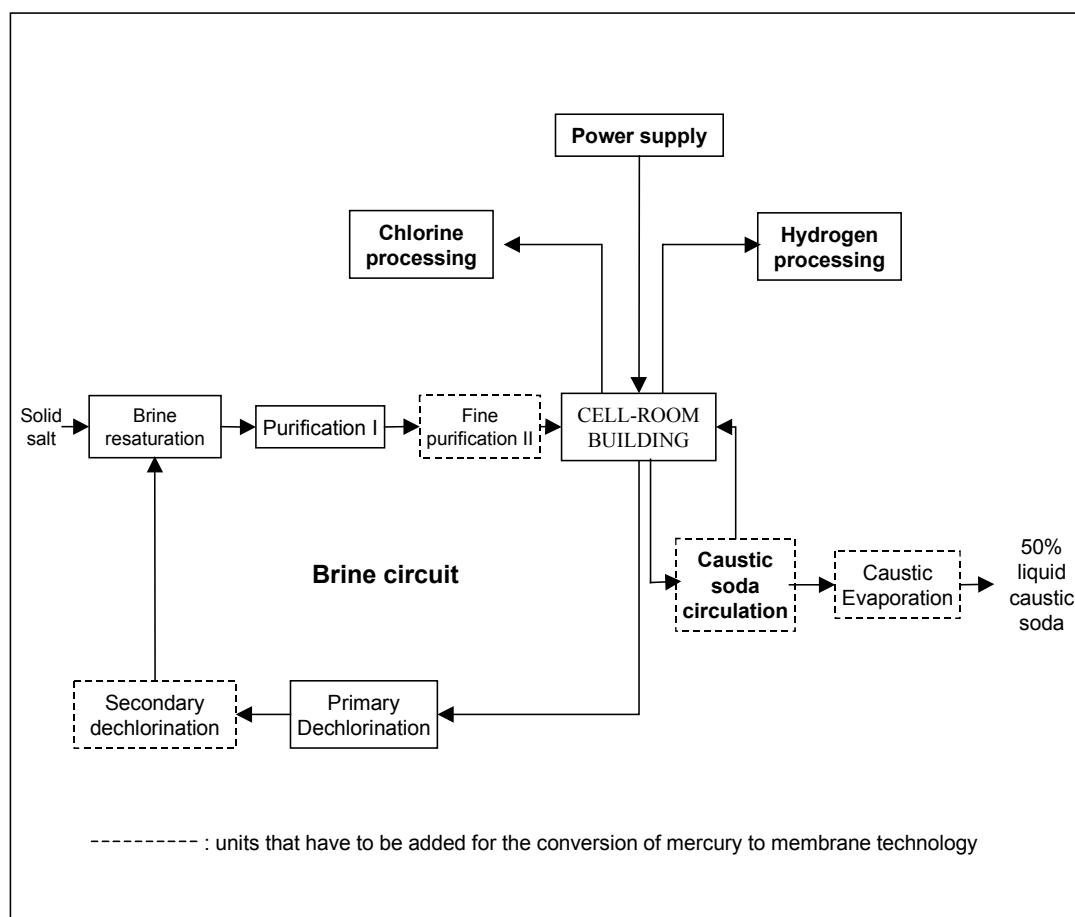
For final disposal, the residues can be sent to a waste landfill (hazardous or non-hazardous, depending on mercury content), to deep rock storage (now in the planning stage in Sweden) or to salt mines.

## **4.2.2 Conversion of mercury cell plants to membrane technology**

### **Description**

The conversion of mercury cell plants to membrane technology has the advantage of avoiding any future losses of mercury to the environment and reduces the energy consumption. To realise the conversion, technical changes are required, depending on the existing situation. Most membrane cell operators have either built a new “green field” plant or expanded production capacity with a new plant alongside their mercury facilities. Some have completely converted their existing plant, but there are also examples of partial conversion. Figure 4.2 below shows the main changes that need to be carried out to an existing plant when converting from mercury cell to membrane technology.

Conversion is technically applicable at all existing mercury cell chlor-alkali plants. Economic feasibility may vary from site to site (see Table 4.8, page 94).



**Figure 4.2: Mercury plant conversion to membrane technology**

Based on [Dibble-White, 1988]

The main changes to an existing plant when converting from mercury to membrane technology include:

### 1. The brine system

The main concern is the purity of the brine feed to the existing cell room system. As mentioned in Chapter 2, membrane electrolyzers need purer brine than do mercury cells. Practical experiences have shown that the mercury brine system can be reused after demercuration and a careful clean-out of the whole system. The brine has to be drained out and the whole system has to be cleaned to remove impurities deposits and solubilise mercury to recover it. For good performance of the membrane cells a secondary brine purification step must also be added, usually using ion exchange units. Some material, such as rubber linings, plastics and gasket materials containing calcium and magnesium, may need to be changed to avoid contamination of the ion exchange unit.

A new high-performance brine dechlorination facility is required to reduce the residual chlorine to levels below those which could deactivate the ion exchange resins of the secondary brine purification step. Generally, either chemical reduction using sodium sulphite (for example Solvay in Jemeppe, Belgium), catalytic reduction or activated carbon adsorption are used, depending on the type of salt and the overall economics.

There is a difference in the water balance between membrane and mercury circuits. There is also a difference in mass flow rates, the brine recirculation being higher in mercury cell plants

than in membrane cell plants at comparable capacities. Both the water balance and the mass flow rates need to be taken into account in any conversion.

Very pure hydrochloric acid (HCl) is needed for brine acidification and a HCl burner might need to be installed.

### 2. The cell-room building

It is reported that existing cell room buildings can be reused to accommodate membrane electrolyzers. The saving of space makes it theoretically possible to install up to 400% more capacity with membrane technology in an existing building. However, a clean space is needed for the membrane cells. The decision to reuse an existing building will depend on:

- the condition of the existing building
- whether space for a new cell room is available
- extent of savings from reduced loss of production

Some old cell room buildings may be in a poor condition and thus may justify total replacement. Environmental concerns may also lead to consideration of building replacement. This particularly applies to mercury contamination of existing concrete structures, where some emission will continue even after replacement of the mercury cells. In the conversion of the mercury cell plant of Associated Octel in Ellesmere Port (UK), the existing cell room has been kept, but mercury decontamination of the site and hygiene for the workforce were reported to be of paramount importance [Lott, 1995].

Some chlor-alkali plants have space available close to existing cell rooms. This allows the erection of a new cell room building whilst reusing other plant systems in situ. Some companies, because they have plenty of space, succeed in having the two technologies in the same cell-room, mercury and membrane, without any problem of contamination of membranes or products [Bayer Uerdingen, 1998]. The construction of the building should also be able to support the normally higher weight density of membrane electrolyzers.

The major advantage of a new building is the ability to minimise production losses during conversion, since it can be erected and the electrolyser system installed while production continues in the old building. In 1997, Borregaard in Norway converted its Sarpsborg mercury cell chlor-alkali plant to a membrane cell plant, building a completely new cell room. The total production stoppage reported was 7 weeks. [Dibble-White, 1988] reports a case where the building was reused and production could be maintained during the conversion by operation of other cell rooms elsewhere on the site. The penalty of production loss in this case was not significant, which is not the case if there is only a single cell room.

### 3. The electrolyzers

The design and operation of the electrolyzers are essentially different and no old parts can be reused.

### 4. The power supply

Reuse of the rectifiers depends on the type of membrane cell configuration and power requirements. The decision to renew the power supply or not will depend, among other things, on the balance between investment and operating costs. A monopolar conversion should be possible using existing rectifiers and transformers, as, with few exceptions, existing plants are monopolar. Bipolar conversions can also be carried out keeping the existing power supply, one

example being the conversion of Donau Chemie in Brückl, Austria, in 1999 [Schindler]. A careful review of voltage is required to ensure that adequate control is achievable for the membrane system.

### 5. Gas treatment facilities

Chlorine and hydrogen collection and treatment are not essentially different in membrane cell plants compared to the mercury process. Process steps to remove mercury are no longer needed. The main concern for the new cell room is the method of pressure control of the gases. Membrane technology requires a steady differential pressure of hydrogen over chlorine. This means that a differential pressure controller must be added to the existing control system.

The chlorine and hydrogen gases leave the cell at higher temperatures than with mercury technology. The gases will be saturated with water vapour and so the loading on gas coolers will be higher, as will the volume of resulting condensate. New cooling equipment may be needed.

Chlorine from membrane cells contains more oxygen, which for some applications needs to be removed prior to downstream use of the chlorine. For this purpose, total liquefaction followed by subsequent evaporation of liquid chlorine is necessary. Larger liquefaction units than those normally in operation are required.

### 6. Caustic treatment

Mercury cell technology produces 50% caustic soda. Membrane cells require a recirculating system with associated heat exchange and dilution and produce 33% caustic soda. If more concentrated caustic soda is needed, an evaporator system is also necessary.

### 7. Process piping

The reuse of existing process piping is not appropriate when converting to a membrane process, as the physical location is often very different from that required by membrane electrolyzers. The existing piping may also be made of material unsuitable for use with membrane electrolyzers.

## **Main achievements**

Conversion to membrane technology avoids future emissions of mercury to the environment and reduces the energy use. How big the reduction of total energy use will be depends on the operating characteristics before and after the conversion. At the Borregaard plant in Sarpsborg (Norway) recently installed membrane cells have resulted in electrical energy savings of 30% per tonne of 100% NaOH compared to the mercury process which was used before (See Table 4.7). According to Euro Chlor an estimated typical electrical energy saving after conversion is 15% and the total energy saving about 10%.

## **Cross-media effects**

No direct cross-media effects occur. Future mercury emissions are avoided and lower energy use is achieved. During conversion a temporary increase in losses of mercury to the

environment can be expected, due to the demolition of the old cells. Also, substantial amounts of mercury-contaminated waste are generated in the decommissioning process.

Note that, as a result of conversion, a large amount of mercury becomes available (on average 1.8 kg/tonne annual  $\text{Cl}_2$  capacity). This mercury has the potential to be released into the global environment. Currently, no legislation exists which regulates the handling of this mercury from chlor-alkali plants, with the exception of Sweden, which has banned exports of mercury.

### **Driving force**

The driving force for a conversion can be either an authority's requirement for mercury-free production or an operator initiative for site-specific economic reasons such as an increase in caustic, hydrochloric acid or chlorine demand and/or because significant changes are needed because of obsolete equipment.

### **Reference plants**

Many plants around the world have been converted from mercury cell technology to membrane cell technology. The increases in capacity that took place in Europe at the end of the 1980s and beginning of the 1990s all involved the installation of membrane technology. A well documented conversion is the chlor-alkali plant of Associated Octel in Ellesmere Port (UK) which took place in 1992 [Lott, 1995].

Table 4.7 below presents data from the conversion of the Borregaard chlor-alkali plant in Sarpsborg (Norway) to membrane technology in 1997.

### **Economics – capital costs of conversion**

There have been numerous estimates of the capital cost of cellroom conversion and inevitably these vary from plant to plant, even on a capacity-normalised basis. Even bigger variations in published estimates arise from the classic 'boundary problem' – what is included and what is not. The capital cost of conversion for a typical mercury cellroom should include not only the cost of the electrolyzers but also, as a minimum base case, the inextricably linked capital costs associated with caustic recycle, caustic evaporation and brine secondary purification and dechlorination. In many cases additional capital will be required for additional gas cooling, new rectifiers (and possibly new electrical supply and switchgear), changes to the supply of utilities and gaseous  $\text{HCl}$ , new building structures, decommissioning and site remediation. Reported capital costs range from 194 up to 700 euros per tonne of chlorine capacity.

The calculation is further complicated since trade-offs exist between capital and operating costs. Designing for high current density operation can decrease the initial capital cost but this increases operating costs and energy consumption. The development of lower voltage membranes is tending to shift the balance somewhat towards higher current densities – but regulatory pressure on energy consumption may reverse this trend and increase capital costs.

A conversion from mercury cells to membrane technology is presented in Table 4.7 and a comparison of reported conversion costs is presented in Table 4.8.



**Context of the old production units**

- Cell room built in 1949: 3 floors, 122 cells
- mercury air emissions: 1.4 g/tonne chlorine capacity
- mercury water emissions (water ion exchange process): 0.25 g/tonne chlorine capacity

**Driving force for conversion**

- Demand from the Norwegian authorities to switch to a mercury-free process
- Demand for higher production of sodium hydroxide and wish to lower operating costs.

**The conversion**

- Decision made to convert: autumn 1995
- Conversion carried out: autumn 1997
- Shutdown time: 7 weeks

**Characteristics of new plant**

- 40000 tonnes  $\text{Cl}_2$  capacity/year at 4.35 kA/m<sup>2</sup>
- Supplier: Asahi Glass Co. Ltd. Japan
- Engineering: Krebs-Swiss
- Electrolyser: AZEC-B1 bipolar, 4 electrolyzers, each 75 cells.
- Membrane area: 2.88 m<sup>2</sup> per cell
- Membrane: Flemion 893

**Reused equipment:**

- Rectifiers
- Hydrogen treatment and HCl production units
- Chlorine liquefaction section and compression

**New equipment**

- Cell room for electrolyzers: The existing building was considered old and mercury-contaminated
- Electrolysis section
- Brine circuit: brine filtration unit, ion exchange unit, brine dechlorination unit
- Sodium hydroxide concentration unit and evaporation system
- Chlorine gas drying unit and chlorine gas absorption unit
- Power supply and wiring (excluding rectifiers)
- Pumps, instruments and piping

**Cost of conversion**

- Total cost of conversion was about 210 million NOK (26.6 million euros October 1997) corresponding to about 665 euros/tonne chlorine capacity. This figure includes 2.4 million euros for the clean-up of the old plant and the storage of mercury-contaminated waste but excludes the clean-up of soil pollution.

**Economic benefits**

- Electricity: 30% reduced per tonne 100% NaOH
- Personnel: 25% reduced
- Some mercury sold for batteries, instruments and to mercury chlor-alkali plants
- Return on investment: 5 years (depending on the caustic market)

**Decommissioning**

- No cleaning-up of mercury-contaminated soil
- Monitoring of mercury emission to air from old cell room
- Construction of a sealed disposal facility for mercury-contaminated wastes: 1800m<sup>3</sup>, 3 special membranes with sand filter seals between. The bunker is ventilated and the vented air led through a carbon filter. The majority of the wastes (about 55%) was mercury contaminated process equipment (steel and rubberlined steel).
- 95 tonnes of mercury drained from the cells

**Table 4.7: Data from the conversion of the Borregaard chlor-alkali plant to membrane technology**  
[de Flon, 1998]

Source Plant/base (year of conversion)	Annual plant capacity [tonne Cl <sub>2</sub> ]	Investment in original currency	Investment in euros (currency date)	euros/tonne Cl <sub>2</sub>	Comments
[Lindley, 1997] European union, OSPARCOM impact	Calculation for 1 tonne of Chlorine	EURO 560–610	560–610	560-610	worst case assumptions; non-conversion costs included
[Lindley, 1997] European union, OSPARCOM impact	Calculation for 1 tonne of Chlorine	EURO 360	360	360	“ideal case”: no changes in power supply and buildings
[SRI Consulting, 1997] average Western European chlorine plant	157000	USD 111 M	92.5 M (April 1997)	590	worst case assumptions; non-conversion costs (chlorine drying, liquefaction, bleach unit etc.) and disposal costs included
[Schindler], [UBA (A), 1998]  Donau Chemie, Brückl, Austria (1999)	60000	ATS 200 M	14.5 M (fixed EMU conversion rate)	242	power supply and cell-room building reused; non-conversion costs included such as downstream modifications and increased capacity of HCl and bleach; site clean-up not included
		ATS 160 M	11.6 M (fixed EMU conversion rate)	194	pure conversion cost; estimated waste disposal costs included
[Schubert], [Chemie Prod., Mai 2000]  Bayer, Dormagen, Germany (1999)	300000	DEM 240 M	122.7 M (fixed EMU conversion rate)	409	total cost including engineering and construction (new equipment: DEM 170 M); cell-room building, brine filtration, H <sub>2</sub> and Cl <sub>2</sub> gas treatment facilities and compressors reused; dismantling of most Hg-cells not included;
[de Flon, 1998]  Borregaard, Sarpsborg, Norway (1997)	40000	NOK 210 M	26.6 M (October 1997)	665	rectifiers reused; new cell room; new brine circuit; construction and building of a landfill; non-conversion costs included
[Lott, 1995]  Associated Octel, Ellesmere Port, UK (1992)	40000	GBP 11.6 M	14.5 M (January 1995)	362.5	"old" costs (no previous practical experience); includes the clean-up and disposal of the contaminated parts of the plant (excluding soil)
[García Ara]  Aragonesas, Vilaseca, Spain, (new capacity together with a mercury plant 1992/1998)	40000	ESP 4660 M	28 M (fixed EMU conversion rate)	700	cell equipment (approx. 150-170 euros/t Cl <sub>2</sub> ), brine supply (rock salt), rectifiers, new building, training and start-up included; not included are caustic soda conc., liquefaction and evaporation unit for oxygen elimination
Akzo Nobel, Skoghall, Sweden, 2000  Akzo Nobel, Skoghall, Sweden (conversion of one membrane cell design to another 1999)	75000	SEK 250 M	29 M (December 1999)	387	new cell room, rectifiers, cells and caustic evaporation included
OxyTech Systems, Inc. 1998  adapted calculation of an actual conversion project	122500	USD 56.2 M	51 M (April 1998)	416	net cost: no changes in power supply and no reconstruction, some overhauling of existing equipment included
[SEPA, 1997]  Akzo Nobel, Bohus, Sweden (estimated 1997)	100000	SEK 250 M	29 M (October 1997)	290	rectifiers, site clean-up and waste disposal costs not included
UHDE GmbH, 1998 average conversion costs	Calculation for 1 tonne of Chlorine	DEM 500	255 (December 1998)	255	average conversion costs excluding disposal
Asahi glass Co., 1998 average conversion costs	166000	JPY 5000 M	35.4 M (December 1998)	213	average conversion: including rectifiers, excluding disposal

**Table 4.8: Comparison of reported conversion costs**

Based on [UBA (A), 1998] and personal communication with plants and suppliers

Generally, conversion costs of more than 600 euros/tonne  $\text{Cl}_2$  include costs not directly related to the conversion such as landfill construction, site clean-up, training of personnel, capacity increase, start-up, etc. Costs between 400-600 euros generally include new cell room, power supply, waste disposal, down stream modifications, etc. Reported minimum conversion costs range from below 200 to 400 euros per tonne of chlorine capacity and generally include some costs for waste disposal and/or clean-up of contaminated parts.

A typical conversion cost according to Euro Chlor is around 530 euros per tonne chlorine capacity. This cost would include engineering, equipment and construction as well as dismantling and cleaning of the old mercury cells and piping. It would not include new buildings, additional services or site remediation.

The cost of loss of production may play a significant part in conversion economics. There are techniques, such as prefabrication, to minimise shutdown time. The Brückl plant (Austria) converted in summer 1999 and the mercury cells were running at 80% production rate while the membrane cells were installed. During the change of cells and system components the plant was shutdown from Monday night to Friday (4 days). In the future, we can assume that plant shutdowns could be minimised so that costs will be reduced compared to early conversions. [Schindler], [UBA (A), 1998]

A gradual conversion has been carried out at the Bayer site in Uerdingen taking advantage of an increased demand for chlorine. The same building could be used and no concentration plant or gas treatment facilities were needed. Membrane production has been increased progressively, switching off mercury cells and balancing the demand between the two technologies when it was possible. However, industry reports that generally a step by step conversion is not economically attractive compared to a complete conversion, mainly because of cross-contamination of mercury into new equipment and of the possible need for adaptations to the power supply.

There are also economic benefits resulting from the conversion of mercury cells to membrane cells. Some economic benefits are [de Flon, 1998], [Lott, 1995]:

- reduced energy use
- reduced need for maintenance, reduced workforce
- sale of mercury
- cost savings from mercury emission abatement and mercury medicals for the workforce.

According to Euro Chlor, conversions are only sufficiently profitable in special circumstances such as the need for increased capacity, high energy costs or high maintenance costs when the plant is reaching the end of its natural life.

Operating and maintenance conditions can influence the lifetime of equipment and environmental performance and so make the operator decide to convert to membrane technology. Most of the mercury cells in the EU were installed up to the mid-1970s and economic plant lifetimes can be in the range of 40-60 years [Lindley, 1997].

### *Effects on competitiveness*

SRI Consulting, who made a study of the competitiveness of the western European chlor-alkali industry, reports that production costs for chlorine production by mercury technology are mainly linked to fixed costs in which plant size plays an important role. Most mercury technology plants in western Europe have capacities between 50 and 200 kt/y with an average of about 157 kt/y of chlorine capacity. The situation is quite different in the U.S. Gulf where the average plant size is significantly larger, with an average of 678 kt/y and structural economic advantages linked to lower costs for main raw materials: salt and electricity higher in

western Europe (2.0 US cents/kg versus 3.6 in western Europe for salt and 2.8 US cents/kWh versus 4.3 for electricity). The SRI study concludes that the industry's view of a forced phase-out of mercury technology by 2010 is that conversion would be uneconomic for about 33% (2.2 million tonnes) of present mercury cell capacity, and that these plants would be closed. [SRI Consulting, 1997]

In western Europe, the cost of electrical energy is very dependent on the basic source of energy and the type of contracts negotiated with suppliers, but the relative differences between countries and regions remain. The special circumstances making a mercury plant economic can change if the price of electrical energy increase sharply; in that case a conversion to membrane technology can become more attractive economically.

#### *Effect on downstream production*

According to a chlorine flow study undertaken by Euro Chlor, sales of virgin chlorine account for only a few percent of the trade balance. That means that most of the chlorine produced is used as a chemical intermediate either internally or by other companies. A key consideration, therefore, is the down-time associated with the conversion and the impact on the production of downstream products such as PVC. Caustic users will also be affected by restrictions in chlor-alkali production.

#### **References**

[de Flon, 1998], [Dibble-White, 1988], [Euro Chlor paper, 1998], [Lindley, 1997], [Lott, 1995], [SRI Consulting, 1997], [UBA (A), 1998]

### **4.2.3 Decommissioning**

#### **Description**

The decommissioning of a mercury technology chlor-alkali plant should include all provisions and measures which have to be taken into account to prevent environmental impact during and after the shut-down process as well as safeguarding of human health. The operation should include plant shutdown, dismantling/demolition of equipment and circuits, handling of dismantled materials and the restoration and clean-up of the site so that the land can be reused (depending on the local authorities' decision on land use planning).

In many cases the clean-up of the site has to be done in a step by step procedure. At the beginning it is not known how contaminated the site is or what types of contaminants are present. If graphite anodes have been used the site can be contaminated with PCDD/PCDF compounds as well as mercury. Experience has shown that there is no direct correlation between PCDD/PCDF and mercury levels on old chlor-alkali sites. One study that covers a large area might have to be followed by more detailed studies on particular areas where contamination is found. Sometimes this means that the project quite a long time.

When cell rooms are closed and decommissioned, there will be some loss of mercury to the environment, and this has to be considered when planning the operation. Loss of mercury to the atmosphere during decommissioning and demolition may be difficult to avoid completely and could to some extent be influenced by cell room design and geographic location. However, once the cells are shut down, the cell room temperature will decrease, and the evaporation rate of any exposed mercury is reduced [Lindley, 1997].

The closure of a cell room does not remove the operation from regulation. Much of the legislation applicable to operational plants also applies whilst dismantling a mercury cell room, for example:

- Protection of the health and safety of workers
- Protection of the environment (air and water emissions, soil contamination)
- Handling, transport, treatment and disposal of wastes

Before proceeding with closure it is strongly recommended that a small task force be set up to prepare the overall planning of the project. The role of the team is to prepare a well documented plan of action for discussion with the appropriate authorities before obtaining formal approval for it. It is vital that this team contains personnel from the chlor-alkali management of the site. Contractors, if used, should be involved in this procedure as soon as appointed. [Euro Chlor Env. Prot.3, 1999]

The organisation of project groups is also recommended, each responsible for a special issue during the decommission operation. Examples of project group issues are:

- Clean-up and demolition of buildings
- Recovery of mercury; treatment and disposal of material derived from general clean-up; plant demolition; demolition of buildings, pipes, etc
- Planning for transport and demolition activities
- Health and safety monitoring: monitoring of mercury emissions to air and water and also health checks for personnel involved
- Follow-up after plant is stopped: survey on possible contamination of the whole site and surroundings, including soil, old waste dumps and sediments in nearby waterways. In addition to mercury the soil/sediment samples should be analysed for PCDD/Fs if graphite anodes have been used on the site.

Guidelines for the shut-down and decommissioning of mercury cell plants are presented in [Euro Chlor Env. Prot.3, 1999] and [Italian report, 1997].

### **Cross-media effects**

A large amount of mercury will become available (1.8 kg/tonne  $\text{Cl}_2$  capacity per year). This mercury has the potential to be released into the global environment. Currently, no legislation exists which regulates the fate of mercury from chlor-alkali plants, with the exception of Sweden which has banned exports of mercury. According to [SRI Consulting, 1997], the decommissioning of all mercury cells in the EU may lead to over 12000 tonnes of available mercury.

### **Reference plants**

#### *Example of decommissioning carried out at the Borregaard plant (Norway)*

Project groups were organised for the different operations involved in the conversion and decommissioning. The task of the demolition group was to work out methods, procedures, budget and schedule for demolition and handling of mercury-contaminated waste. The group was made up of representatives from local production and maintenance staff, local safety/health/environment people and representatives from the Health Department.

A large number of samples was taken to determine the quantity of wastes. The total quantity of contaminated waste material was estimated at 1750 m<sup>3</sup>, of which 50% was contaminated process equipment such as steel and rubberlined steel. Before the plant was stopped, all

equipment which was going to be dismantled was marked with different colours, indicating the destination of the wastes and method of treatment.

The authorities asked for special precautions concerning the landfill deposit:

- No emission to water, air or ground from the deposit
- Possibility to open the landfill and take out the contaminated waste for other treatment if new technologies should be available in the future to completely detoxify the residues
- Deposit to be built for long-term deposition as long as geological conditions are unchanged
- Transportation to the landfill with minimised risk of mercury loss
- Measures to monitor possible leaks
- Marked with appropriate signs describing the content
- Designed to blend into its surroundings
- Secure against trespassers
- Programme of monitoring and maintenance routines

Costs for cleaning the old plant and depositing of contaminated waste:

	million NOK 1997	million euros*
Cell room (removing and bottling of mercury, dismantling equipment, sand washing of walls, floor, ceiling)	3.6	0.5
Dismantling of pipelines and other equipment in cell room	1.9	0.2
Treatment of mercury-contaminated waste (washing, solidification, etc)	1.5	0.2
Construction and building of landfill	9.0	1.1
Transport and filling into landfill	2.1	0.3
Extra analyses, measurements and safety equipment	0.5	0.06
<b>Total</b>	<b>18.6</b>	<b>2.36</b>

\* exchange rate of October 1997

## References

[de Flon, 1998], [Euro Chlor Env. Prot.3, 1999], [Italian report, 1997], [Lindley, 1997]

## 4.3 Diaphragm cell plants

### 4.3.1 Abatement of asbestos emissions and discharges

#### Description

In its various formulations, the polymer modified asbestos (PMA) diaphragm is the most common diaphragm in use today. The modified diaphragm still contains a minimum of 75% of chrysotile asbestos mixed with PTFE fibres. The major potential sources of air emissions are during diaphragm deposition, treatment of operating cells with asbestos slurry and the disposal of spent asbestos. Contaminated water also needs to be collected and recycled as far as possible.

It is recommended that personnel exposed to asbestos be provided with individual protective equipment and a personal health check programme.



### 1. To avoid as much as possible the deterioration of the diaphragms

Since diaphragm deposition and disposal of spent asbestos are sources of asbestos emissions, deterioration of diaphragms should be avoided as much as possible to reduce the need for replacement, by:

- avoiding high concentrations of brine impurities: high brine impurities cause plugging of the diaphragm with insoluble hydroxides, which reduce the diaphragm's separation ability
- avoiding irregular operation, such as electrical load changes, cell liquor strength changes, changes in brine concentration or pH, gas-pressure fluctuations, shutdowns, changes in pH of the various regions of the diaphragm, thus accelerating chemical attack on the asbestos.

### 2. To avoid air emissions

Emissions of dry asbestos can be restricted by several actions:

- Avoid air emissions during delivery, unloading and handling of dry asbestos. Asbestos is usually delivered to the chlor-alkali producer dry and packed in bags. The bags are best palletised and covered with shrink-wrapped, sheet-wrapped or other non-porous material to minimise the likelihood of torn bags or loose material. Asbestos should be stored and handled in an isolated and enclosed area (for example a dedicated storage room) with restricted access and marked with specified warning signs. Wooden pallets should not be allowed to accumulate in the storage area. Automated systems as well as systems using robots for the handling of dry asbestos are used by some companies. With such technology, totally encapsulated rooms for unloading, bag-opening and preparation of asbestos slurry prevents asbestos emissions. The rooms contain lock chamber systems under reduced pressure. No personnel have to enter the rooms for normal operation because no handling of dry asbestos by personnel is necessary.
- Avoid air emissions during the diaphragm preparation and deposition. Asbestos bag cutting and emptying is best performed within an enclosed system. The bags should be fully cut and carefully emptied with minimal disturbance of the contents. Bags should never be shaken. Empty bags should be folded over the cut and deposited in a closed labelled container within the enclosed area. Workers involved in the physical handling of asbestos bag transfer and slitting, sorting, weighing and slurry preparation should wear approved respirators and protective clothing if the tasks are not carried out inside sealed glove boxes. There should be no visible asbestos on floor and equipment. Neither compressed air blowing, nor dry broom sweeping should be used to clean up loose asbestos. Fugitive asbestos fibres should be removed with a HEPA filter-equipped vacuum cleaner or by wet cleaning. Prior to installation in a cell, completed diaphragms should be managed in a manner to prevent asbestos from entering the atmosphere. Covering of stored diaphragms may be appropriate.
- Avoid air emissions from spent asbestos. After a certain operating time, asbestos diaphragms are replaced. The spent asbestos is removed from the cathode body by hydroblasting. The area for hydroblasting should be enclosed, for example a separate room or an enclosure with shielding and with smooth surfaces, to prevent asbestos from adhering and drying.
- Avoid air emissions from the cathode baking furnace. Emissions of asbestos occur from the furnace where the green diaphragm cathodes are baked. A filter may be necessary to reduce emissions from this furnace.

### 3. To avoid wet asbestos drying out and becoming airborne

In the handling room, asbestos is handled under wet conditions. Asbestos that is suspended in water will not directly have the potential to be emitted to the atmosphere. However, when spillage or changes of the level of the suspension occur, the asbestos may dry out and become airborne. This also applies to depleted asbestos material which is hydroblasted from the cathode



can. When the asbestos-containing water is discharged, the asbestos has the potential to become airborne if it is transported to areas where it may dry out. Therefore, within the plant, all spillage should be removed immediately and all places where asbestos may have the potential to dry out should be flushed regularly.

### 4. Contaminated water

Contaminated water has to be collected in an appropriate building. A filter press permits the removal of asbestos from the waste water. Separation of spent asbestos from the hydroblasting water wash is typically accomplished by pond settling, separation tanks or filtering, for example plate and/or frame filters. Residual levels of 0.1 g/tonne annual chlorine capacity are possible.

### 5. Waste Treatments

Thermal or chemical treatments can be applied to denature asbestos inside wastes. The vitrification process is one of them. During this process the dangerous fibre structure is destroyed and converted to 'sand type' silicate structures through thermal treatment. In order to achieve this, all spent asbestos is dewatered in a centrifuge and chemicals are added to generate a mixture with a significantly reduced melting point. This mixture is then pelletised and the pellets are fed to a rotary kiln for the vitrification process. The resulting slag no longer contains asbestos fibres. Note that energy is used in the vitrification process.

Asbestos-containing wastes may be landfilled, providing it is done in a way which is consistent with national asbestos regulation.

### *Monitoring*

Asbestos fibres in suspension in air can be collected on a filter using a sampling system with a small portable pump. Fibres are generally counted using an electron microscope. Fibre in this context is defined as an object of length greater than 5µm, breadth less than 3 µm and having a length/breadth ratio greater than 3. Results are expressed in number of fibres/m<sup>3</sup> of air. Only competent and trained people are able to do such measurements.

Directive 87/217/EEC contains an annex which provides a methodology for analysis and sampling of asbestos in aqueous effluents and air (gravimetric methodology or counting fibres).

Instructions on reporting and monitoring as well as records and notifications relating to incidents should be specified by the operator. Practically, all release points associated with asbestos should be fitted with continuous particulate monitors which can be alarmed to detect abnormal emissions.

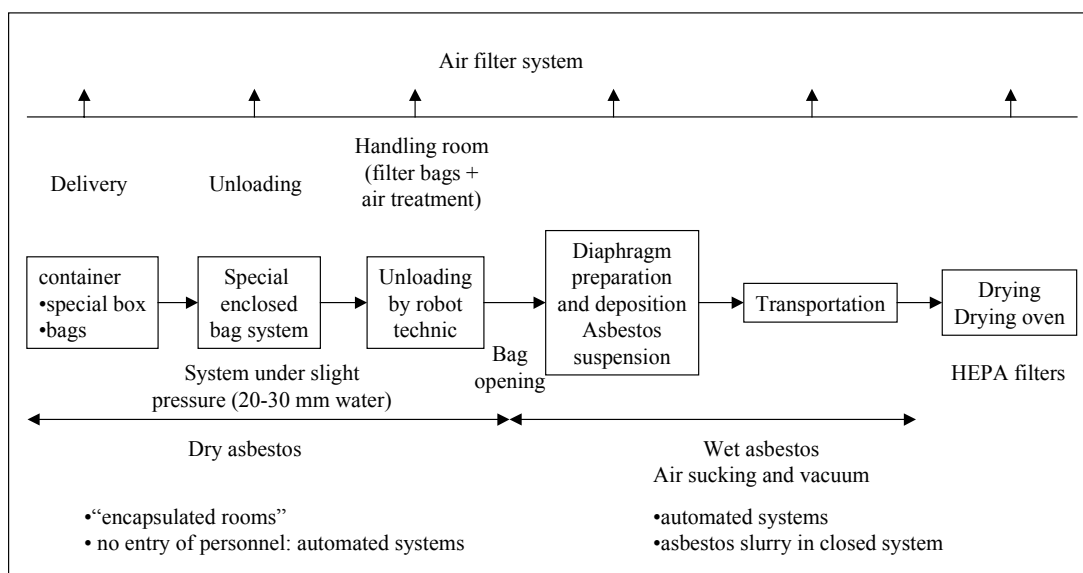
### **Main achieved emission levels**

Automated systems, asbestos fixed and enclosed in cell body, modern monitoring and control systems, high industrial hygiene standards and high operating discipline achieve a fibre concentration in the workplace and in the outlet to atmosphere of less than 1000 fibres/m<sup>3</sup>. This emission level is achieved by Dow in Stade (Germany).

## Cross-media effects

Measures to avoid asbestos becoming airborne generate an asbestos-containing waste or sludge. This waste is generally landfilled. If the waste is landfilled, precautions must be taken to prevent it drying out and becoming a fresh source of emissions to air.

**Reference plants:** Figure 4.3 shows the handling of asbestos at Dow in Stade (Germany).



**Figure 4.3: Example of handling of asbestos from Dow in Stade (Germany).**

## Economics

Depending on the equipment installed, costs may vary a lot. The “encapsulated” rooms for unloading and handling asbestos may be expensive because automated systems are generally involved.

**References:** [Dutch report, 1998], [Euro Chlor report, 1997], [Hollmann]

### 4.3.2 Application of non-asbestos diaphragm material

#### Description

Laboratory tests using non-asbestos diaphragms began in the mid-1980s, following the increasing pressure to reduce the use and emissions of asbestos. Suitable alternatives have been developed at industrial scale with the objective of bringing the new asbestos-free diaphragm technology to the same commercial level as the polymer modified asbestos (PMA) diaphragms. Some requirements on the asbestos-free diaphragms are:

- same deposition procedures as those used for making asbestos diaphragms
- suitable permeability (prevent reaction of chlorine with  $\text{OH}^-$ , isolate chlorine from hydrogen for safety reasons)
- chemical stability (inert to oxidation by chlorine, hypochlorite and chlorate and/or to acids and strong base conditions)
- mechanically strong
- provide a high current efficiency under a wide range of current density/brine flow conditions

Research on asbestos-free diaphragms is also carried out with the objectives of:

- achieving an extended service life
- obtaining a power consumption advantage
- meeting safety and environmental needs

There are today two patents that are applied on a commercial scale: OxyTech's Polyramix (PMX) diaphragm and PPG's Tephram diaphragm.

In addition, ChlorAlp's patented microporous Asbestos Free Diaphragm is being installed in the company's industrial cell room at Pont de Claix, France. The plant will be fully converted by 2001.

### *Composition of non-asbestos diaphragms*

OxyTech's PMX diaphragms are composed of (1) fibres with a PTFE polymer backbone with zirconia ( $\text{ZrO}_2$ ) particles embedded in and on the PTFE and (2) free zirconia particles. This mixture is deposited from a slurry bath and then fused in an oven. Together with the replacement of the existing diaphragm cell cathodes (at a minimum, the inner assembly portion of the cathode), the PMX diaphragms can directly replace other diaphragms in Hooker or Diamond type cells. [Florkiewicz, 1997], [Florkiewicz-Curlin, 1991]

The PPG's Tephram diaphragms are composed of a base diaphragm and a topcoat. The base diaphragm is made of PTFE fluoropolymer, PTFE microfibrils and a perfluorinated ion exchange resin. The topcoat, composed of inorganic particulate materials (metal oxides such as zirconium oxide or titanium dioxide) is incorporated into, and becomes an integral part of, the base diaphragm. The purpose of the topcoat is to adjust permeability and uniformity. The Tephram diaphragms can in some cases directly replace other diaphragms in chlor-alkali cells. [Dilmore-DuBois, 1995]

The differences between the patents lie in the way the hydrophobe PTFE fibres are treated and deposited in order to form a permeable and hydrophilic diaphragm and in the mineral fillers used.

### *Operation and applicability of non-asbestos diaphragms*

Non-asbestos diaphragms can be applied at new and existing diaphragm chlor-alkali plants. However, some operators still have doubts concerning the economics and safety of the asbestos-free diaphragms.

The Dow diaphragm cell is optimised for low current density ( $\sim 0.5 \text{ kA/m}^2$ ) and requires a large active area ( $\sim 100 \text{ m}^2$  for one single bipolar element) [Kirk-Othmer, 1991]. The flow rate is lower compared to other industrial cells and the company reports that there is a danger of chlorine and hydrogen getting mixed, because of the specificity of their cells, which could lead to an explosion.

On the other hand, for non-asbestos diaphragms the separator is no longer the most short-lived component of the diaphragm cell. As the non-asbestos diaphragm is expected to last several years, the highest cause of failure of the diaphragm cell is the gaskets (base covers and perimeter gaskets). It is these gaskets which now pose the biggest challenge to overcome if a 3-5 year cell life is to be achieved.

Long life for PMX diaphragms has been commercially demonstrated. The Vulcan-Geismar plant in Louisiana (USA), fully converted since 1993, is achieving average diaphragm lives of

greater than 1000 days, while operating at an average current density of 2.55-2.65 kA/m<sup>2</sup>. Demonstration blocks of 10 to 20 PMX diaphragm cells in Europe have lasted over 5 years and the oldest PMX diaphragm cell at the Occidental Chemical Deer Park plant in Texas (USA) has been operating for over 8 years. [Florkiewicz, 1997]

Particular attention must be paid to the brine system, since poor brine will cause a fibre diaphragm to plug at least as quickly as an asbestos diaphragm. The cathode must be protected from corrosion during shutdowns, since an accumulation of corrosion products over several years may result in high levels of hydrogen in chlorine before the end of the useful diaphragm life. Patented procedures to overcome the plugging of a diaphragm with brine impurities are available (for example from OxyTech). A plugged diaphragm is frequently the cause of low cell efficiency. Removing iron from the diaphragm is also important, as iron also can be a source of elevated hydrogen levels in chlorine. However, the preferred method of operation is to avoid these problems by using pure brine. General Electric in Mount Vernon (USA), was fully converted to PMX diaphragms at one time but problems with iron in the brine forced GE to switch back to PMA diaphragms.

### Main achievements

Avoids consumption and emission of asbestos. Reduced energy use is also reported, depending on operating conditions.

Non-asbestos diaphragms have demonstrated a number of advantages over asbestos diaphragms in chlor-alkali cell operation:

- long lifetimes; at least 3 years can be considered as an average for an industrial cell room
- extreme stability concerning load variations and outages

PMX diaphragm cells with three years on line show no increase in energy use, even after repeated shutdowns at 95 °C. The operation of non-asbestos diaphragms may actually result in net energy savings. Additional savings in material handling and waste disposal might be realised, compared to asbestos diaphragms.

### Cross-media effects

Polyramix diaphragms require the use of biocides in the suspension to avoid fermentation of the biogum used to suspend the dense fibres in the depositing slurry bath. The waste water is fairly alkaline and contains organics from the suspension thickener. The effluent system therefore needs to be able to handle a COD load.

The Tephram diaphragms require “doping” during operation to maintain the required wettability and permeability.

### Reference plants

#### OxyTech’s Polyramix (PMX) Diaphragm

**Vulcan Chemicals, Geismar, Louisiana, USA**, has been fully converted to PMX diaphragms since 1993. This plant uses OxyTech MDC-55 cells at 150 kA. All of the 152 cells are equipped with PMX diaphragms. The Vulcan Chemicals plant personnel conducted a “make good” analysis after the complete conversion of their plant. They achieved the power cost savings as expected in their appropriation and reduced the chlorate content of their caustic product and the hydrogen content in the chlorine gas. Today Vulcan Chemicals maintains

performance by using appropriate procedures on individual cells to reduce anolyte levels as necessary. They maintain the chlorate in caustic with occasional acid brine flushes of the complete circuit to remove accumulated brine impurities. The diaphragms achieve a life of more than three years and a cell liquor strength of 145 g/l. [Curlin]

**Hüls, Rheinfelden, Germany**, operated for several years fully converted with PMX diaphragms before the plant was closed. [Dutch report, 1998]

**Elf Atochem in Fos sur Mer and in Lavera, both in France**, are proceeding to full conversions of both sites. The conversions should be complete by 2002. The plant located in Fos sur Mer is equipped with OxyTech MDC-55 cells (chlorine capacity: 160 kt/y). The plant located in Lavera is equipped with OxyTech HC-4B (42 m<sup>2</sup> area) cells (chlorine capacity: 160 kt/y).

Many other plants, mainly in USA, have tested PMX diaphragms in one or more of their cells and some of these cells are still operating, due to the long lifetime of the PMX diaphragm.

### PPG's Tephram Diaphragm

**PPG Natrium, West Virginia, USA**: full-scale demonstration of Columbia N6 and OxyTech MDC-55 electrolyzers.

**PPG Lake Charles, Louisiana, USA**: full-scale demonstration of PPG's GlanorV-1244 electrolyzers.

On a trial basis, six plants outside of PPG are currently operating cells equipped with Tephram Diaphragms.

### Rhone Poulenc Chimie's Asbestos Free Diaphragm

**ChlorAlp, Le Pont de Claix, Isère, France** (chlorine capacity: 240 kt/y) is converting to asbestos-free diaphragms. In 1998 10% of the Hooker S3B cells in the industrial cell room were converted with this material; in 1999 30% were to have been converted; at the end of 2000 60% of the S3B and H4 cells were to have been converted and in 2001 the site will be fully equipped with Asbestos Free Diaphragms. [Perineau]

## **Driving force**

Environmental occupational health regulations (asbestos ban, tighter asbestos regulations) are the key driving forces leading to the following benefits:

- no emissions of asbestos
- less generation of wastes because the renewal of the diaphragm is less frequent
- generated waste is non-hazardous

## **Economics**

Economic benefits of using non-asbestos diaphragms come from reduced operating costs due to lower cell voltage, the reduction of cell renewal labour costs due to the long lifetime of the diaphragms and the reduction of the waste handling and disposal costs due to asbestos-free materials. However, this needs to be offset against the substantially higher purchase costs (up to 20 times the cost of a PMA diaphragm) and the costs due to the need for closer control and

monitoring. According to [Florkiewicz, 1997] a 3 year life of the PMX diaphragm is the minimum required to achieve breakeven.

On-site capital requirements for a conversion remain highly site-specific and the configuration of the cells (cells with large active area, linked to the chlorine production per m<sup>2</sup> of diaphragm) may greatly influence the cost of a conversion.

The total cost (everything included) for converting a diaphragm plant with an annual capacity of 160 kt Cl<sub>2</sub> to PMX diaphragms is reported to be 1.4-2 million euros. A new diaphragm preparation plant will be built to supply two sites with PMX diaphragms in France.

ChlorAlp in Pont de Claix (France) has estimated the costs for the modification of existing equipment at 0.4-0.8 million euros (costs of raw materials not included).

**References:** [Curlin], [Dilmore-DuBois, 1995], [Dutch report, 1998], [Florkiewicz, 1997], [Florkiewicz-Curlin, 1991], [Foller et al, 1997], [Kuntzburger et al, 1995], [Perineau]

### 4.3.3 Conversion of asbestos diaphragm cell plants to membrane technology or to asbestos-free diaphragms

#### Description

##### *Converting to membranes*

The important changes to an existing plant when converting from diaphragm cells to membrane technology are:

- Additional brine purification, including hardness removal ion exchange techniques. Modifications to brine treatment to control other impurities, such as sulphate, may also be required.
- Additional brine dechlorination to protect the ion exchange resin. It is necessary to complete the brine recirculation loop by adding primary and secondary dechlorination and possibly resaturation.
- Inclusion of a cell room caustic soda recirculation system. If 50% product is required, the existing diaphragm cell caustic soda evaporator must be modified and simplified to accept high-strength, salt-free caustic soda.
- Change of electrolyzers and details of the cell room system.

##### *Converting to asbestos-free diaphragms*

In some cases the Tephram diaphragms can directly replace the old diaphragms and the Polyramix diaphragms can replace the old diaphragms if the cathodes are also replaced. How much change other designs of asbestos-free diaphragms require is not known to the author at the time of writing.

##### *Comparison between converting to membranes or to asbestos-free diaphragms*

Conversion of a diaphragm plant to membrane technology can be an attractive choice because of the high energy efficiency and the pure 33% caustic produced directly from the cells. This is especially the case when there is a need for high purity 50% caustic, due to the reduced costs of evaporation and the higher caustic quality of the membrane technology.

A conversion to asbestos-free diaphragms requires substantially less change in the existing cell room than a conversion to membranes, and thus a lower capital investment. A comparison of the manufacturing costs is dependent on steam costs and the required caustic quality.

The final decision of the diaphragm cell producer between membranes and asbestos-free diaphragms will depend on the situation at the individual site.

### **Main achievements**

Avoids emission of asbestos and, in the case of membranes, significantly reduces the energy use. Another advantage with membranes is the increased tolerance of power fluctuations, which is especially attractive in regions with fluctuating energy prices.

### **Reference plants and economics**

Any specific examples of conversions of diaphragm plants to membranes are not known to the author at the time of writing. However, [Dibble-White, 1988] reports involvements in the design and implementation of conversion of diaphragm cell plants to membrane technology.

Examples of conversions of diaphragm plants to asbestos-free diaphragms, including some economic data, are presented in the previous section, 4.3.2 Application of non-asbestos diaphragm material.

### **Driving force**

#### For membranes and asbestos-free diaphragms

Environmental regulation: no emissions of asbestos

#### For membranes

End-use market : need for high purity caustic without salt

Economic: high energy efficiency and less need for caustic evaporation

#### For asbestos-free diaphragms, “the long-life diaphragm cell”

Economic: reduced operating cost and reduced amounts of solid wastes

### **References**

[Dibble-White, 1988], [Dutch report, 1998], [Florkiewicz, 1997], [Florkiewicz-Curlin, 1991]

## **4.4 Membrane cell plants**

### **4.4.1 High performance membranes**

#### **Description**

The membrane is the most critical component of this cell technology. Current density and cell voltage, and hence energy use, are greatly dependent on its quality. New high-performance membranes are now commercially available to equip electrolyzers. There are high-performance membranes for use in narrow and zero gap electrolyzers (low cell voltage, reduced energy use) for the production of chlorine and 30-35% caustic soda. They are all reinforced composite



membranes, having sulphonate and carboxylate polymer layers. They are specifically designed for optimum gas/liquid circulation between the anode and the membrane's anode surface. They are reinforced for safe operation and modified on both the anode and cathode surface to enhance gas release. [DuPont]

In the design of a membrane electrolyser using standard membranes, minimising the voltage drop through the electrolyte gap is accomplished by reducing the gap. When the gap is very small, however, an increase in voltage may result from the entrapment of hydrogen gas bubbles between the cathode and the hydrophobic membrane. In developed membranes the bubble effect problem has been solved by coating the cathodic surface with a thin layer of a porous inorganic material to improve the membrane's hydrophilicity. These surface-modified membranes have allowed the development of modern electrolyzers with very small (narrow) or no (zero) gap between the electrodes.

### **Achievements**

Cell voltage is reported for new perfluorinated Nafion<sup>®</sup> membranes to be 2.88 V at a current efficiency of >95% (conditions: 0 mm gap, DSA anode, activated cathode, 32% NaOH, 200 g/l anolyte, 90 °C, 3.0 kA/m<sup>2</sup>). The lifetime of the membranes ranges between 3 and 5 years. [DuPont]

Energy saving by developing a membrane having low ohmic drop has also been realised with Flemion membranes. They show a small increase in cell voltage while current density is reported up to 6 kA/m<sup>2</sup>. [Asahi Glass]

**Driving force:** Cost reduction by reducing energy use.

### **Economics**

No specific economic information for the high-performance type membranes is known to the author at the time of writing.

**References:** [Asahi Glass], [DuPont]

## 5 BEST AVAILABLE TECHNIQUES

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface to this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector; for the manufacture of chlor-alkali these are potential hazards concerning chlorine, hydrogen gas and alkalis, energy use, mercury releases from mercury cell plants and asbestos releases from asbestos diaphragm cell plants;
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of this techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication of the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this

document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

### **Process technology selection**

The selected process technology has a major impact on the energy use and emissions from the manufacture of chlor-alkali.

- Best available techniques for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT.

The total energy use associated with BAT for producing chlorine gas and 50% caustic soda is less than 3000 kWh (AC) per tonne of chlorine when chlorine liquefaction is excluded and less than 3200 kWh (AC) per tonne of chlorine when chlorine liquefaction and evaporation are included.

### **All cell plants**

Best available techniques for the manufacture of chlor-alkali include the following measures:

- Use of management systems to reduce the environmental, health and safety risks of operating a chlor-alkali plant. The risk level should tend to zero. The management systems will include (see Section 4.1.1 for more details):
  - training of personnel
  - identification and evaluation of major hazards
  - instructions for safe operation
  - planning for emergencies and recording of accidents and near-misses
  - continuous improvement including feedback and learning from experience.
- A chlorine destruction unit designed to be able to absorb the full cell-room production in the event of a process upset until the plant can be shut down. The chlorine absorption unit prevents emissions of chlorine gas in the event of emergencies and/or irregular plant operation (see Section 4.1.2 for more details).

The absorption unit should be designed to lower the chlorine content in the emitted gas to less than 5 mg/m<sup>3</sup> in the worst case scenario.

All chlorine-containing waste gas streams should be directed to the chlorine absorption unit. The chlorine emission level to air associated with BAT during normal operation is less than 1 mg/m<sup>3</sup> in the case of partial liquefaction and less than 3 mg/m<sup>3</sup> in the case of total liquefaction.

No systematic discharge of hypochlorite to water should take place from the chlorine destruction unit.

- Minimising consumption/avoiding discharge of sulphuric acid by means of one or more of the following options or equivalent systems (see Section 4.1.4 for more details):
  - on-site reconcentration in closed loop evaporators
  - using the spent acid to control pH in process and waste water streams
  - selling the spent acid to a user that accepts this quality of acid
  - returning the spent acid to a sulphuric acid manufacturer for reconcentration.

If the sulphuric acid is reconcentrated on-site in closed loop evaporators, the consumption can be reduced to 0.1 kg of acid per tonne of chlorine produced.

- Minimising the discharge of free oxidants to water by applying (see Section 4.1.5 for more details):
  - fixed bed catalytic reduction
  - chemical reduction
  - any other method with equally efficient performance.

The emission level of free oxidants to water associated with BAT is less than 10 mg/l. The overall environmental impact should be considered when the destruction method is chosen.

- Use of carbon tetrachloride-free chlorine liquefaction and purification processes (see Section 4.1.6 for more details).
- Hydrogen should be used as a chemical or as fuel in order to conserve resources.

### **Membrane cell plants**

Best available techniques specific to membrane cell plants include the following measures:

- Minimising the discharge of chlorate and bromate to water by applying:
  - acid conditions in the anolyte (pH 1-2) to minimise the formation of chlorate (ClO<sub>3</sub><sup>-</sup>) and bromate (BrO<sub>3</sub><sup>-</sup>)
  - chlorate destruction in the brine circuit to remove chlorate before purging.

The acidity of the anolyte is a design parameter of membrane cell plants and cannot be adjusted without affecting the operation of the membrane cell. If this is not the chosen, option a chlorate decomposer may be necessary to remove chlorate before purging. The chlorate level associated with BAT in the brine circuit is 1-5 g/l and the associated bromate level is 2-10 mg/l (note that the bromate level depends on the bromide level in the salt).

- Appropriate handling of spent membranes and gaskets.

## Mercury cell plants

Best available techniques specific to mercury cell plants include the following measures (see Section 4.2.2 for more details):

- Conversion to membrane cell technology.

During the remaining life of mercury cell plants, all possible measures should be taken to protect the environment as a whole including:

- Minimising mercury losses to air, water and with products by:
  - use of equipment and materials and, when possible, a lay-out of the plant (for example, dedicated areas for certain activities) that minimise losses of mercury due to evaporation and/or spillage (see Sections 4.2.1 and 4.2.1.1 for more details)
  - good housekeeping practices and motivation of personnel to work in such a way (see Sections 4.2.1 and 4.2.1.1 for more details)
  - good maintenance routines including planning of periodical maintenance and repair works (see Sections 4.2.1 and 4.2.1.1 for more details)
  - collection and treatment of mercury-containing gas streams from all possible sources, including hydrogen gas (see Sections 4.2.1 and 4.2.1.1 for more details)
  - minimising the amount of waste water and treatment of all mercury-containing waste water streams (see Sections 4.2.1 and 4.2.1.2 for more details)
  - reduction of mercury levels in caustic soda (see Sections 4.2.1 and 4.2.1.3 for more details).

The best performing mercury cell plants are achieving total mercury losses to air, water and with products in the range of 0.2-0.5 g Hg per tonne of chlorine capacity as a yearly average, as shown in the table below:

	g Hg/tonne chlorine capacity
Air: cell room	0.2-0.3
process exhausts, including Hg distillation unit	0.0003-0.01
untreated cooling air from Hg distillation unit	0.006-0.1
hydrogen gas	<0.003
Water, process emissions	0.004-0.055
Caustic soda	0.01-0.05
<b>Total</b>	<b>0.2-0.5</b>

Apart from the process emissions reported above, there can also be considerable emissions of mercury with run-off water. The soil at many sites is contaminated with mercury due to deposition of diffuse emissions and/or historical disposal of mercury-contaminated wastes. The mercury leaches from the soil and ends up in the run-off water.

The majority of mercury losses are in the various wastes from the process.

- Minimising current and future mercury emissions from handling, storage, treatment and disposal of mercury-contaminated wastes by (see Section 4.2.1.4 for more details):
  - implementation of a waste management plan drawn up after consultation with the appropriate authorities
  - minimising the amount of mercury-containing wastes
  - recycling the mercury contained in wastes when possible
  - treatment of mercury-contaminated wastes to reduce the mercury content in the wastes
  - stabilisation of residual mercury-contaminated wastes before final disposal.

- Decommissioning carried out in a way that prevents environmental impact during and after the shutdown process as well as safeguarding human health (see Section 4.2.3 for more details).

Before proceeding with closure it is strongly recommended that a small task force be set up to prepare the overall planning of the project. The role of the team is to prepare a well documented plan of action for discussion with the appropriate authorities before obtaining formal approval for it.

The organisation of project groups is also recommended, each responsible for a special issue during the decommission operation. Examples of project group issues are:

- clean-up and demolition of buildings
- recovery of mercury; treatment and disposal of material derived from general clean-up; plant demolitions; demolition of buildings, pipes, etc
- planning for transport and demolition activities
- health and safety monitoring: monitoring of mercury emissions to air and water and also health checks for personnel involved
- follow-up after plant is stopped: survey on possible contamination of the whole site and surroundings, including soil, old waste dumps and sediments in nearby waterways; in addition to mercury, the soil/sediment samples should be analysed for PCDD/Fs if graphite anodes have been used on the site.

### **Diaphragm cell plants**

Best available techniques specific to diaphragm cell plants include the following measures (see Sections 4.3.3 and 4.3.2 for more details):

- Conversion to membrane cell technology
- Use of non-asbestos diaphragms.

During the remaining life of asbestos diaphragm cell plants, all possible measures should be taken to protect the environment as a whole including (see Section 4.3.1 for more details):

- Extending the diaphragm lifetime by using improved diaphragms and pure brine and by operating in a way that does not accelerate the chemical attack on the asbestos. Diaphragm lifetime of 1 year (5 years being achieved by one company) has been achieved. Asbestos consumption (and waste generation) can be reduced to around 0.1 kg per tonne of chlorine capacity as a yearly average.
- Minimising asbestos emissions to air by applying: automated systems; asbestos fixed and enclosed in cell body; modern monitoring and control system to react in case of incidents; efficient air filter system; high industrial hygiene standards and high operating discipline. One plant is reported to achieve a fibre concentration in the workplace and in the outlet to atmosphere of less than 1000 fibres/m<sup>3</sup>.
- Minimising asbestos emissions to water by applying a filter press to remove asbestos from the waste water. A residual level of 0.1 g asbestos per tonne of chlorine capacity, as a yearly average, has been achieved.
- Treatment of asbestos-contaminated wastes by thermal or chemical methods to denature asbestos inside wastes. Normally, the resulting slag no longer contain asbestos fibres.

## 6 EMERGING TECHNIQUES

A number of new promising techniques are being developed with energy savings as the main driving force. Some of these new techniques for the membrane and diaphragm processes are described below. Fundamental research programmes related to mercury technology are not being developed since it is very unlikely that any new mercury plants will be built. The only recent improvements in mercury cells concern the anode geometry with the aim of improving gas release in order to decrease electrical energy usage and increase anode coating life.

In diaphragm technology, with the exception of non-asbestos technology referred to in section 4.3.2, improvements are minor and related to reducing power consumption in the cell. An interesting example is a specific development of activated cathode technology, the pre-cathode concept, which is presented in section 0.

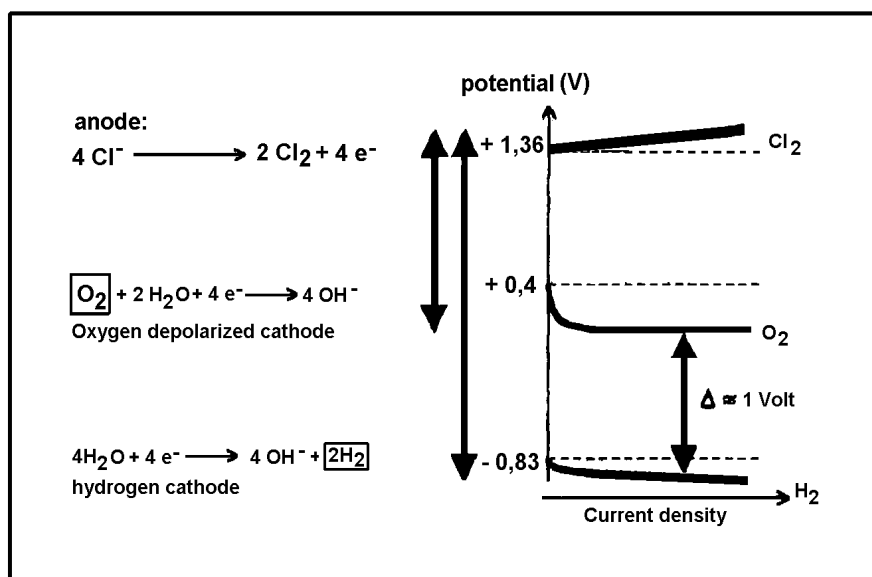
Oxygen depolarised cathodes in membrane cells have the potential to save around 500-600 kWh/tonne of chlorine produced and are now being tested at the industrial scale.

At least one supplier is developing a membrane that can produce high concentration (50%) caustic soda and believes that it could be available at an acceptable cost within a few years.

### 6.1 Oxygen depolarised cathodes in modified membrane cells

#### Description

The utilisation of oxygen depolarised cathodes (ODC) in the chlor-alkali electrolysis is an integration of the fuel cell process into the membrane electrolysis cell: the cathode half cell reduces oxygen instead of producing hydrogen. This lowers the cell voltage by about 1 volt and means a substantial energy saving, as predicted from the theory and taking into account the typical electrode overpotentials. Figure 6.1 shows the expected potential differences for the two cathode types.

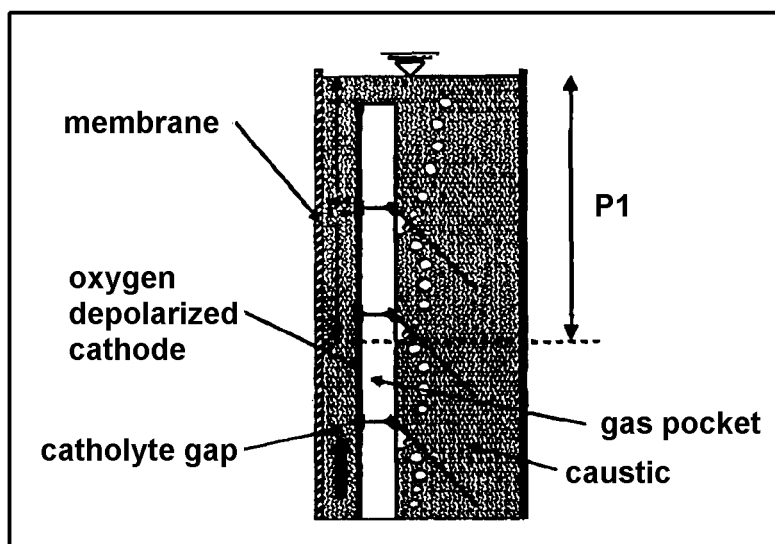


**Figure 6.1:** The influence of oxygen depolarised cathodes on the electrode potentials, NaCl [Gestermann, 1998]



The ODC is a gas diffusion electrode which separates caustic from the oxygen side, from where the gas diffuses into the porous electrode structure to the catalyst centres and reacts with the cathodic water to produce  $\text{OH}^-$  ions. All other functions are the same as in the normal membrane electrolysis.

Due to its porous structure the ODC can only withstand limited differential pressure between caustic and oxygen, which normally limits the active height to some 20-30 cm. This problem has been solved in a joint collaboration between DeNora and Bayer with the development of a pressure compensation system which supplies the oxygen to the ODC via gas pockets. The principle is shown in Figure 6.2.



**Figure 6.2: Principle of the Gas Pocket Electrode for pressure compensation**  
[Gestermann, 1998]

### Main achievements

In laboratory experiments at Bayer with oxygen depleted cathodes supplied by the DeNora group it was shown that under normal conditions, i.e. 32% caustic, 90 °C, the operation voltage could be reduced by about 1 volt. An energy gain of about 500-600 kWh/t chlorine produced was achieved.

A four element bipolar pilot electrolyser incorporating the pressure compensation design was constructed by DeNora and was tested at the Bayer endurance test facility. It had an element size of 0.3 m<sup>2</sup> with a full industrial-size height of 1.3 m. The experimental results demonstrated that at 3 kA/m<sup>2</sup> an operation around 2 volts was possible as well as a continuous operation with 6 kA/m<sup>2</sup> slightly above 2.4 volts.

In December 1998 a test with 16 cells, each with 2.5 m<sup>2</sup> active area, was put into operation at the Bayer test-site in Leverkusen with good results. The results were comparable to the pilot plant operating experience; the standardised power consumption at 3 kA/m<sup>2</sup> was <1400 kWh/t NaOH (<1250 kWh/t Cl<sub>2</sub>). The trials resulted in a design review to simplify the manufacturing techniques. Currently (mid-2000) a full-scale industrial electrolyser with more than 70 elements is under preparation for installation in the Bayer Dormagen plant.

### Availability and applicability

The oxygen depolarised cathode technology is reported by Bayer to be expected to be available for licensing for industrial application by 2002 [Wienkenhöver, 2000].

The technique described is for an oxygen depolarised cathode which implies a source of pure oxygen. Other technology suppliers have experimented with air cathodes which do not require an air separation unit. According to [Kirk-Othmer, 1991] the essential features of an air cathode cell are identical to those of the oxygen cathode cell. The first is the inclusion of an air chamber behind the electrode to provide oxygen for the cathodic reaction. Second, because no hydrogen is produced, there is no need for hydrogen collection equipment. Third, and most important, is that the air cathode cell operates at approximately 1 V lower than a conventional hydrogen evolving chlorine cell.

The air cathode technology has been demonstrated in commercial sized equipment at Occidental Chemical's Muscle Shoals, Alabama plant but is not presently being practised because of being too expensive to commercialise at the currently low (US) power costs [Kirk-Othmer, 1991].

The plant incorporating the air cathode electrolyser must include a high performance air scrubbing system to eliminate carbon dioxide from the air. Also, if there are downstream chemical uses for the hydrogen, or if the hydrogen gas is used for energy production, it might off-set the energy reduction gained by introducing air or oxygen depolarised cathodes.

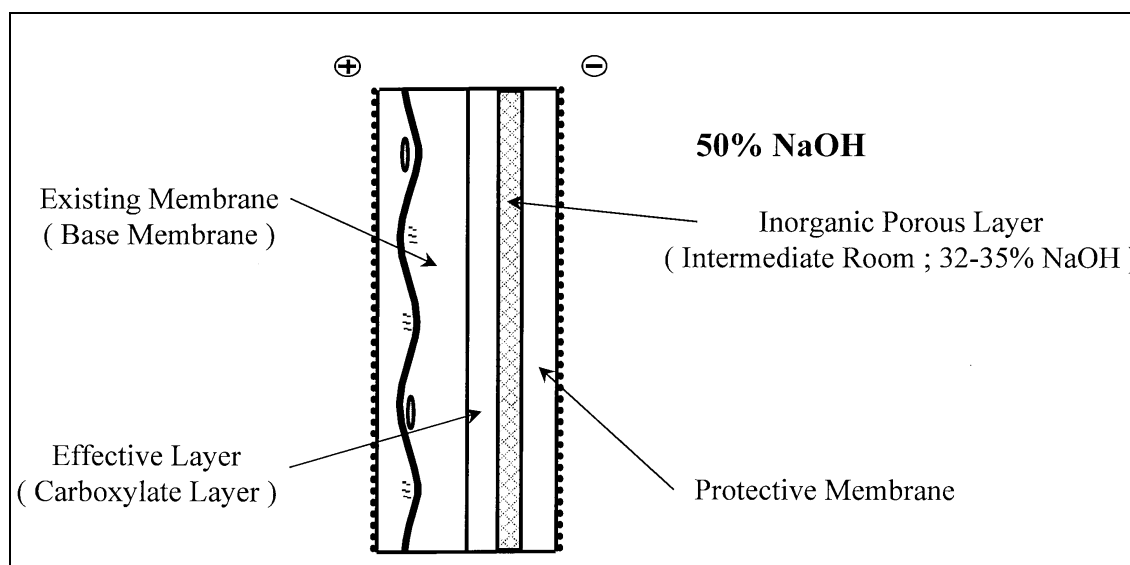
It is not possible to retrofit air and oxygen depolarised cathodes into existing membrane cells.

**References:** [Gestermann-Ottaviani, 2000], [Wienkenhöver, 2000], [Gestermann, 1998], [Kirk-Othmer, 1991]

## 6.2 Membrane for direct production of 50% caustic soda

### Description

Standard chlor-alkali membranes produce caustic soda with a concentration of approximately 30-35% which then might have to be evaporated to the normal 50% strength. Both sulphonic and carboxylic membranes show a reduction in current efficiency and destabilisation of the membrane when caustic strength is increased to more than 35%. One company is developing a new membrane for direct production of 50% caustic soda which has an additional protective layer on the cathode side of the traditional bi-functional membrane forming an intermediate 'room' between the carboxylic and the protective layers (See Figure 6.3). Owing to the difference of transport number between the two layers, the caustic concentration of the intermediate 'room' can be maintained in the range of 32-35% while the external catholyte concentration is raised to 50%.



**Figure 6.3: Structure of Fx-50 membrane producing 50% caustic soda**

[Asahi Glass]

### Main achievements

A prototype membrane, Fx-50B, has been evaluated in an Asahi Glass AZEC F-2 electrolyser. The membrane showed stable performance (200 kA, 3 kA/m<sup>2</sup>, 80-85 °C) with a power consumption of less than 2400 DC kWh/tonne caustic (<2850 AC kWh/tonne Cl<sub>2</sub>). After about 3 years on line the membrane was dismantled and checked. No unusual damage or impurity accumulation was found.

### Economics and availability

There is an increased voltage penalty due to both the lower conductivity of the 50% caustic and the resistance of the protective layer. This may be off-set by a reduced or zero steam demand for evaporation. According to the manufacture, the Fx-50 membrane for direct production of 50% caustic soda is deemed to be economically feasible if the steam cost is, comparatively, high and the electricity cost is, comparatively, low. These are conditions that currently do not exist in the main markets and thus the new membrane has not yet been commercialised.

Reference: [Asahi Glass]

### 6.3 Built-in precathode diaphragm

#### Description

The term “built-in precathode diaphragm” is used to describe a composite assembly comprising

- the standard mild steel cathode screen
- the precathode itself
- the microporous asbestos or asbestos-free diaphragm.

The latter two are consecutively vacuum deposited onto the normal diaphragm cell cathode box in the same manner and with the same equipment as asbestos diaphragms.

The precathode technology is based on the incorporation of a volumetric cathode area in the first section of the diaphragm itself: it includes conducting fibres, electrocatalytic material, pore forming agents and a fluoro-containing polymer binder.

The role of the pore-forming agent is to regulate the porosity of the separator which influences the flow of liquid and the discharge of the gases. It is a solid inorganic compound (type of silica) which is subsequently removed by leaching or thermal or chemical decomposition.

The electrocatalytic agent is incorporated into the precathode in the form of a powder and chosen from among the metals of the platinum group such as Raney alloys, Raney metals and especially Raney Nickel.

Figure 6.4 shows the built-in precathode diaphragm operating principle. The steel screen structure of the cathode box acts as a support and ensures distribution of the current to the conductive fibres. These in turn conduct the current to the electrocatalytic particles homogeneously dispersed in the volumetric electrode. The electrochemical reduction of water takes place directly on the large active surface area of the electrocatalyst which has a lower overpotential than the standard cathode thus reducing the cell voltage.

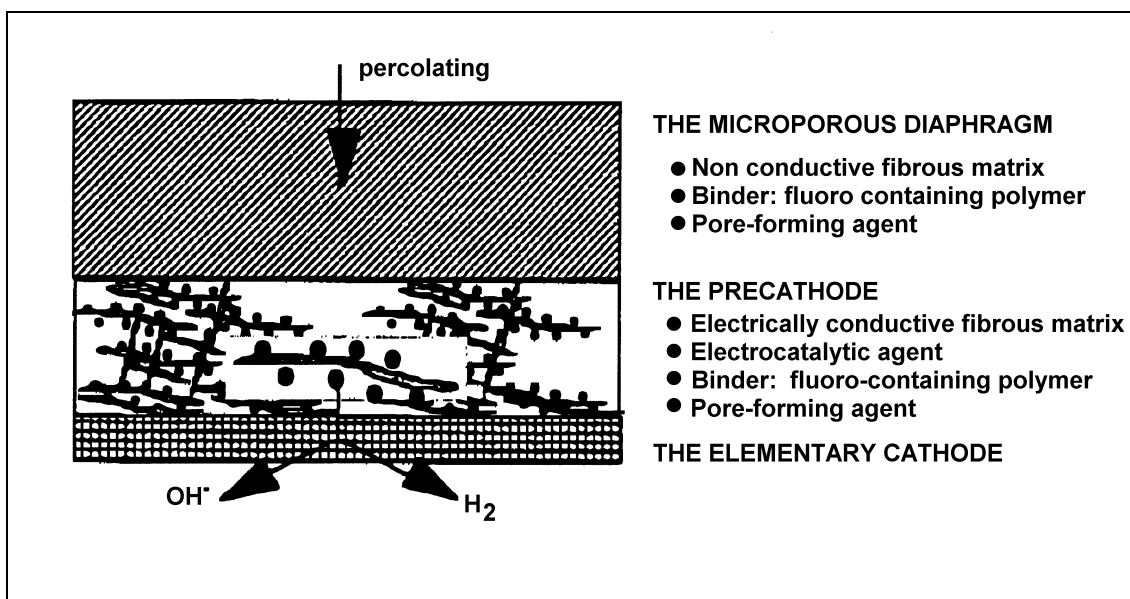


Figure 6.4: The built in precathode diaphragm operating principle  
[Kuntzburger et al, 1997]

It is claimed that the built-in precathode can be applied at all existing and new plants using diaphragm technology (asbestos or non-asbestos). The manufacture of the built-in precathode diaphragm requires no equipment changes as it is vacuum-deposited on the cathode from a water-based slurry in the same manner as modified diaphragms and heated in the same oven.

### **Main achievements**

According to the industrial experience in CHLORALP and test results in Heraeus Elektrochemie the advantages of the precathode have been found to be:

- reduction of cell voltage by 100-150 mV, with respect to current density from 1.7-2.6 kA/m<sup>2</sup>, and thereby energy savings
- reduction of oxygen content in chlorine and increase of current efficiency by 0.7-3.0% due to the improvement of the diaphragm homogeneity and additional resistance by the precathode layer to back-migration of hydroxyl ions from catholyte to anolyte
- improvements of the cell performance in the field of:
  - safe operation: safety is improved particularly during start up and shut down and the hydrogen content in chlorine is lowered below 0.1% during standard operation
  - electrocatalytic reduction of chlorate: chlorate content is reduced by 30-50% in caustic soda due to strong (chemical) reduction of ClO<sub>3</sub><sup>-</sup> on the precathode
- extended diaphragm life (lifetime between 2 and 3 years instead of one year). This can be explained by the improved chemical stability of the materials and the substantially smaller swelling of the diaphragm during use
- permeability of the diaphragm is improved, making high current density under constant anolyte level possible.

### **Cross media effects**

After being used, the precathode and the diaphragm are eliminated by hydroblasting. Sludges (mix of asbestos fibres, PTFE, carbon, nickel particles) are considered as hazardous waste.

### **Reference plants**

Heraeus Elektrochemie (now DeNora): has installed the precathode technology within its own test facilities in MDC-55 cells (current density 2.64 kA/m<sup>2</sup>) and has found a test average energy saving of 200 kWh per tonne of chlorine produced. The cell voltage was found to be reduced by 140 mV (from 3.73 V to 3.59 V) and current efficiency increased by 3% (from 95% to 98%). Chlorate decreased from 0.25 g/l to <0.01 g/l in 130 g/l caustic soda. The oxygen in chlorine decreased from 1.8% to 0.95% and hydrogen in chlorine decreased from 0.2% to <0.1%.

CHLORALP, Le Pont de Claix, Isère (France): Built-in precathode diaphragm was first installed at the Le Pont de Claix plant in 1986. The plant was fully converted in 1987. The plant capacity is 240 ktonne of chlorine per year using only diaphragm cells (Hooker-S3B and Hooker-H4). Cells are equipped with modified diaphragms and metal anodes. The brine supply is alkaline and not saturated. Table 6.1 presents average performance data before and after the conversion to precathode technology. The average energy saving is estimated to be 175 kWh per tonne of chlorine (about 5% of total energy consumption).

		With Precathode (average)	Without Precathode (average)
Current density	kA/m <sup>2</sup>	1.7-1.9	1.7-1.9
Catholyte temperature	°C	75-80	75-80
NaOH concentration	g/l	130	130
Cell Voltage (without connection)	V	3.10-3.20	3.25-3.35
Chlorate in caustic soda	g/l	0.2-0.3	0.5-0.6
Current efficiency	%	94-95	91.5-93.5
O <sub>2</sub> in chlorine	%	1.5-2.0	1.5-2.5
H <sub>2</sub> in chlorine	%	< 0.1	< 0.5
Power consumption	kWh/tCl <sub>2</sub>	2465-2570	2625-2765
Average Energy saving	kWh/tCl <sub>2</sub>	175	

**Table 6.1: Precathode technology at CHLORALP (Le Pont de Claix-France)**

### Economics

Economics of built-in precathode diaphragm technology depend on the individual plant situation. The economics depend on site-specific factors such as the brine quality and the cell specific performance characteristics. However, energy savings are possible due to the lowered cell voltage and the increased current efficiency which both effect lower power consumption. Also, the lifetime of the diaphragm has been found to be improved by introduction of the precathode and maintenance costs, therefore, are reduced.

Chloralp has come to an agreement with Heraeus Electrochemie and DeNora s.p.a. for the world wide licensing of the precathode technology.

**Reference literature:** [Kuntzburger et al, 1997], [Kuntzburger et al, 1995]

## 7 CONCLUDING REMARKS

The experts nominated to the technical working group (TWG) by Member States, the European Environmental Bureau and European industry (Euro Chlor) have all taken part in this exchange of information. Some very useful reports have been provided by, for example, the Netherlands [Dutch report, 1998] and Euro Chlor [Euro Chlor report, 1997]. A lot of information has also been collected during plant visits.

The work of writing this BREF document started with a TWG kick-off meeting on 4-5 December 1997. A first draft of Chapters 1, 2 and 3 was sent out for consultation in August 1998 and a second draft covering Chapters 1-6 was sent to the TWG in February 1999. There was then a break of more than six months in the writing because of a change of BREF author. A third draft was sent to the TWG for consultation in January 2000 and the work concluded with a second TWG meeting on 29-31 March 2000. After the second TWG meeting the final redrafting took place.

The TWG reached a very high degree of consensus on the BREF document and on the conclusions on best available techniques (BAT).

At present some 12000 tonnes of mercury are contained in mercury cells used for chlorine production in the EU. When the plants are converted or shut down, this mercury has the potential to be released into the global environment. Currently, there is no European Union policy or legislation on how to deal with this huge amount of pure mercury.

A lot of the work on this BREF document has focused on the mercury cell technology, although it is not BAT. This is because mercury emissions will continue from existing mercury cell plants during their remaining life. Consequently, the membrane cell process has not been scrutinised to the same extent. When this document is updated, consideration could be given to having a more in-depth look at possibilities to reduce emissions from membrane cell plants, especially of chlorinated substances and free oxidants to water.

It was proposed, at the second TWG meeting, that cost information about conversions that are carried out could be given to the European IPPC Bureau so that the most recent conversion cost information will be put into the update of the BREF document.

Missing in this document are the time averages for the emission levels associated with BAT. The issue has as yet not been considered by the TWG and it is recommended to address the time averages when this BREF document is reviewed.

It is recommended that consideration be given to an update of this BAT reference document around year 2005, in particular to follow-up the phase-out of mercury cell capacity. Another issue to follow-up is the development of non-asbestos diaphragms.



## ANNEX A: CHLOR-ALKALI PLANT CAPACITIES IN WESTERN EUROPE (JUNE 2000)

COUNTRY	PLANT	COMPANY	SITE	PROCESS	CAPACITY kt Cl <sub>2</sub> /year	TOTAL Hg	TOTAL DIA	TOTAL MEM	TOTAL OTHER	TOTAL CAPACITY kt Cl <sub>2</sub> /year
<b>AUSTRIA</b>	1	Donau Chemie	Brückl	M	55			55		55
<b>BELGIUM</b>	2	BASF	Antwerp	Hg	100					
	3	Bayer	Antwerp	HCl	50					
	4	Solvay	Antwerp	Hg	230					
	5	Solvay	Jemeppe	Hg	82					
	6	Solvay	Jemeppe	M	120					
	7	Tessenderlo Chemie	Tessenderlo	Hg (NaOH)	205					
	8	Tessenderlo Chemie	Tessenderlo	Hg(NaOH/KOH)	45					
						662		120	50	832
<b>FINLAND</b>	9	Akzo Nobel	Oulu	Hg	40					
	10	Finnish Chemicals	Joutseno	M	75					
						40		75		115
<b>FRANCE</b>	11	Albemarle	Thann	Hg	72					
	12	ChlorAlp	Pont de Claix	D	240					
	13	Elf Atochem	Fos	D	160					
	14	Elf Atochem	Fos	M	110					
	15	Elf Atochem	Jarrie	Hg	170					
	16	Elf Atochem	Lavera	D	160					
	17	Elf Atochem	Lavera	Hg	166					
	18	Elf Atochem	Saint Auban	Hg	184					
	19	Métaux Spéciaux	Pomblières	Na	20					
	20	Prod Chem d'Harbonnières	Harbonnières	Hg	23					
	21	Solvay	Tavaux	Hg	241					
	22	Solvay	Tavaux	M	122					
	23	Tessenderlo Chemie	Loos	Hg	18					
						874	560	232	20	1686

COUNTRY		COMPANY	SITE	PROCESS	CAPACITY kt Cl <sub>2</sub> /year	TOTAL Hg	TOTAL DIA	TOTAL MEM	TOTAL OTHER	TOTAL CAPACITY kt Cl <sub>2</sub> /year
GERMANY	24	BASF	Ludwigshafen	D	210					
	25	BASF	Ludwigshafen	Hg	150					
	26	Bayer	Brunsbüttel	HCl	120					
	27	Bayer	Dormagen	HCl	80					
	28	Bayer	Dormagen	M	300					
	29	Bayer	Leverkusen	HCl	30					
	30	Bayer	Leverkusen	Hg	300					
	31	Bayer	Uerdingen	Hg	130					
	32	Bayer	Uerdingen	M	90					
	33	Dow	Schkopau	M	220					
	34	Celanese	Knapsack	Hg	150					
	35	Clariant	Gersthofen	Hg	60					
	36	Dow	Stade	D	1036					
	37	Dow	Stade	M	234					
	38	Chlor IV Elektrolyse	Bitterfeld	Hg	65					
	39	ECI	Ibbenbüren	Hg	120					
	41	Hüls	Lülsdorf	Hg	98					
	42	ICI	Wilhemshafen	Hg	130					
	43	LII	Hoechst-Frankfurt	Hg	150					
	44	Solvay	Rheinberg	D	200					
	45	Vestolit	Marl	Hg	180					
	46	Vinnolit	Gendorf	Hg	72					
	47	Wacker	Burghausen	Hg	157					
						1762	1446	844	230	4282

COUNTRY		COMPANY	SITE	PROCESS	CAPACITY kt Cl <sub>2</sub> /year	TOTAL Hg	TOTAL DIA	TOTAL MEM	TOTAL OTHER	TOTAL CAPACITY kt Cl <sub>2</sub> /year
GREECE	48	Hellenic Petroleum SA	Thessaloniki	Hg	37					
						37				37
IRELAND	49	MicroBio	Fermoy	M	6					
								6		6
ITALY	50	Altair Chimica	Volterra	Hg	27					
	51	Ausimont/Montedison	Bussi	Hg	70					
	52	Caffaro	Torviscosa	Hg	69					
	53	Enichem	Assemini/Cagliari	M	170					
	54	Enichem	Porto Marghera	Hg	200					
	55	Enichem	Porto Torres	Hg	90					
	56	Enichem	Priolo	Hg	190					
	57	Eredi Zarelli	Picinisco	Hg	6					
	58	Solvay	Rosignano	Hg	120					
	59	Tessengerlo	Pieve Vergonte	Hg	40					
						812		170		982
NETHERLANDS	60	Akzo Nobel	Botlek	M	350					
	61	Akzo Nobel	Delfzijl	D	140					
	62	Akzo Nobel	Hengelo	Hg	70					
	63	GEP	Bergen-op-Zoom	M	64					
						70	140	414		624
NORWAY	64	Borregaard	Sarpsborg	M	40					
	65	Elkem	Bremanger	M	10					
	66	Norsk Hydro	Rafnes	D	130					
							130	50		180
PORTUGAL	67	Solvay	Pova	M	28					
	68	Uniteca	Estarreja	Hg	43					
	69	Uniteca	Estarreja	M	18					
						43		46		89

COUNTRY		COMPANY	SITE	PROCESS	CAPACITY kt Cl <sub>2</sub> /year	TOTAL Hg	TOTAL DIA	TOTAL MEM	TOTAL OTHER	TOTAL CAPACITY kt Cl <sub>2</sub> /year
SPAIN	70	EIASA (Aragonesas)	Huelva	Hg	101					
	71	EIASA (Aragonesas)	Sabinanigo	Hg	25					
	72	EIASA (Aragonesas)	Villaseca	Hg	135					
	73	EIASA (Aragonesas)	Villaseca	M	40					
	74	Electroq. de Hernani	Hernani	Hg	15					
	75	Elnosa	Lourizan	Hg	33.5					
	76	Erkimia	Flix	Hg	150					
	77	Quimica del Cinca	Monzon	Hg	30					
	78	Solvay	Martorell	Hg	209					
	79	Solvay	Torrelavega	Hg	63					
						761.5		40		801.5
SWEDEN	80	Akzo Nobel	Bohus	Hg	100					
	81	Akzo Nobel	Skoghall	M	90					
	82	Hydro Polymers	Stenungsund	Hg	120					
						220		90		310
SWITZERLAND	83	Novartis	Monthey	Hg	22					
	84	Säurefabrik Schweizerhall	Pratteln	Hg	26.5					
	85	Solvay	Zurzach	Hg	55					
						103.5				103.5
UK	86	Associated Octel	Ellesmere Port	M	40					
	87	Hays	Sandbach	Hg	89					
	88	ICI	Lostock	D	50					
	89	ICI	Lostock	M	20					
	90	ICI	Runcorn	Hg	738					
	91	ICI	Runcorn	M (KOH)	25					
	92	ICI	Wilton	D	170					
	93	Rhodia	Staveley	Hg	29					
	94	Roche	Dalry	M	20					
						856	220	105		1181
<b>TOTAL</b>						<b>6241</b>	<b>2496</b>	<b>2247</b>	<b>300</b>	<b>11284</b>

## ANNEX B: MONITORING OF MERCURY

This annex intends to give general information on the monitoring of mercury emissions from mercury cell chlor-alkali plants. No attention is paid to the other chlor-alkali production processes (membrane cell and diaphragm cell processes).

The focus on mercury emissions in this annex should not be understood as a qualification of relative importance, but is based on the fact that the monitoring of mercury emissions is difficult. This is especially valid with respect to the monitoring of mercury emissions from the cell room.

It is well known that monitoring of chlorine is of utmost importance with respect to safety, but chlorine monitoring presents little practical problems and is common practice in the chlor-alkali industry. Therefore, chlorine monitoring is not included here. The same applies to other components that may arise from chlor-alkali plant operation (see Chapter 3). These are generally emitted through point sources and are relatively easy to monitor.

### Relevant items with regard to mercury monitoring

There are many potential mercury sources in the mercury cell chlor-alkali plant. A full description of the sources can be found in Chapter 3. In this annex, only a summary table is presented which gives the potential emission sources, but also other items that are relevant with respect to the mercury monitoring. These are for example the losses of mercury to product and the assessment of the so called ‘difference to balance’.

Monitoring of emissions is ultimately applied to check if the requirements are complied with. Meanwhile, it enables plant operators to monitor their own performance and take corrective measures if necessary. The mode and the frequency of monitoring should be related to the extent of emissions to be verified and to the control technology that is being used.

The table on the next page presents relevant mercury monitoring items and their characteristics in mercury cell chlor-alkali plants.

Medium	Relevant monitoring items*	Characteristics
Air	Cell room	Continuous fugitive emission, low concentration, large flow, untreated.
	Process air vents: <ul style="list-style-type: none"> <li>• End-box ventilation</li> <li>• Brine and salt dissolver</li> <li>• Mercury vacuum cleaner</li> <li>• Et cetera</li> </ul>	Continuous point source emission, normally treated.
	Hydrogen combustion	Continuous point source emission. Hydrogen used as fuel is normally treated.
	Stack of the caustic evaporator	Continuous point source emission. Off gases normally untreated, but only treated caustic is used in the evaporator.
	Mercury recovery retort	Discontinuous point source emission. Normally treated.
	Storage of mercury containing parts	Continuous point source emission in case of active ventilation in building. Continuous fugitive emission in case of open air storage or natural ventilation in building. Normally untreated.
Water	Process water: <ul style="list-style-type: none"> <li>• Bleed from brine purification</li> <li>• Rinsing water</li> <li>• Et cetera</li> </ul>	Continuous point source emission, normally treated.
	Storm water	Discontinuous emission. Point source in case of connection to sewer system. Fugitive source in case of no connection to sewer system. Normally untreated.
Waste**	Caustic filter residue	Discontinuous. Usually carbon based.
	Hydrogen filter residue	Discontinuous. Usually carbon based.
	Process air filter residue	Discontinuous. Usually carbon based.
	Brine sludge	(Dis)continuous. Precipitated salts.
	Waste water treatment sludge	(Dis)continuous. Precipitated salts.
	Spent decomposer graphite	Discontinuous. Carbon based.
	Spent rubber lining of cells	Discontinuous. Rubber based.
	Steel/iron construction parts	Discontinuous. Steel/iron based.
	Other construction waste	Discontinuous. Different materials.
Product	Hydrogen	Continuous. Treated to remove Hg.
	Caustic soda/potash	Continuous. Treated to remove Hg.
Difference to balance	Cell inventory	Assessed once a year.
	Other mercury inventory	Assessed once a year.
	Mercury purchase/sale	Assessed once a year.

\* The mentioned items are not necessarily found or relevant at all mercury cell chlor-alkali plants. Individual differences between plants may result in deviations from this list.

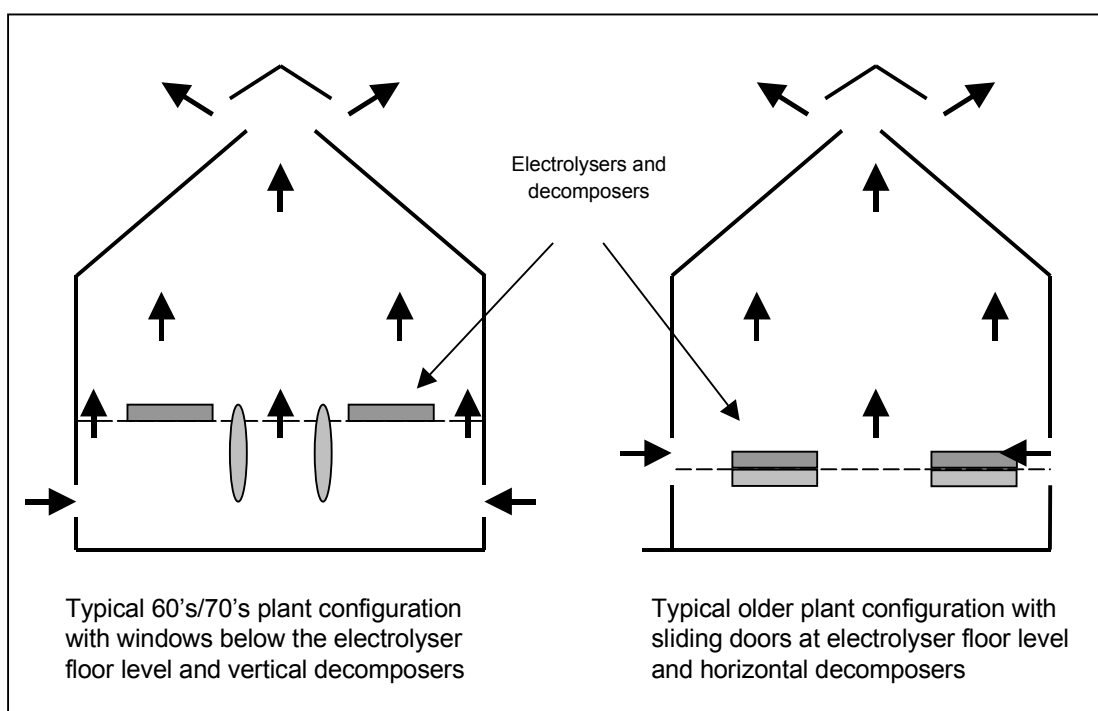
\*\* Homogeneous waste (sludge, activated carbon) and smaller parts of construction material are sometimes (pre)treated on-site for Hg-recovery and subsequently removed. In other cases they are offered without on-site treatment to specialised companies for treatment and/or secured landfill.

## Mercury monitoring of air

### Cell room

The most critical part of the emission monitoring from chlor-alkali plants is the monitoring of mercury emissions from the cell room. This is mainly caused by the difficulty to assess the quantity of ventilation air from the cell room.

Most mercury cell rooms around the world are ventilated by means of natural draught. In many plants from the 1960s and 1970s, the ventilation air comes in through ‘windows’ in the wall underneath the cells and flows out through the open roof of the cell room. In many plants of older design, the ventilation air may enter the cell room through windows or sliding doors at the cell level (see Figure 1). In addition, some plants only have a roof and some are placed in the open air (not depicted).

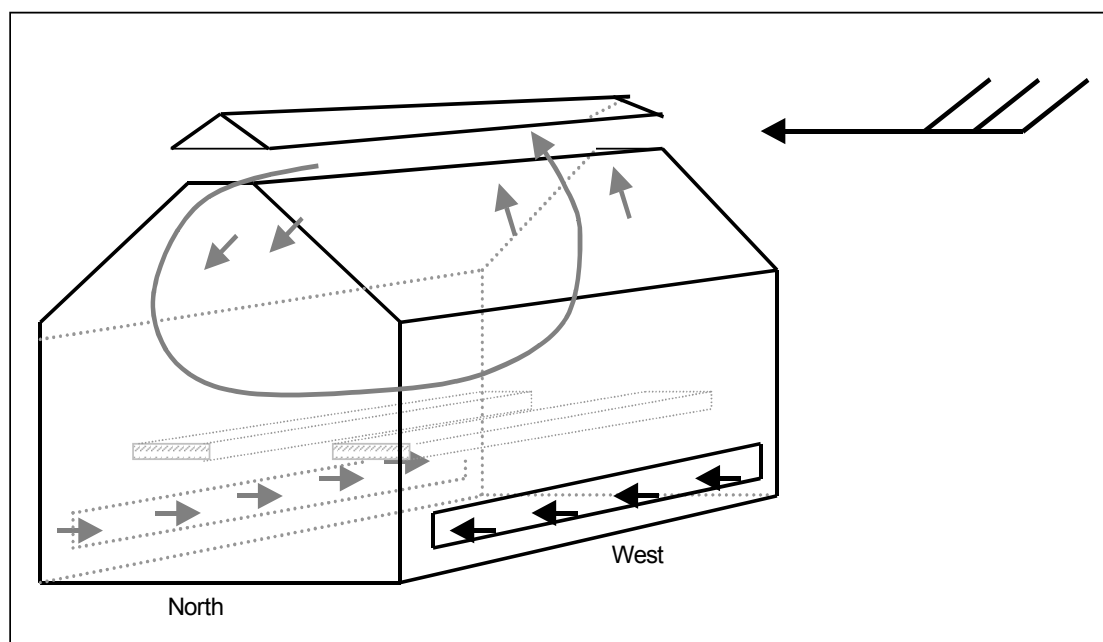


**Figure 1: Simplified scheme of ‘ideal’ air flow in two typical mercury cell chlor-alkali plant configurations. Note that the air flow direction is influenced not only by the heat generated from the cells, but also by wind speed and direction. Note that also open air cell rooms and cell rooms without walls exist.**

The main driving force of the air flow is the heat from the electrolyzers and decomposers. In the ‘ideal’ situation, the air flows in through the windows or doors at the lowest floor and rises past the electrolyzers and out through the roof opening. Thus, the construction serves as a passive air cooling system.

However, it should be noted that wind speed and direction may create local disturbances of the rising air flow in the cell room. This is especially relevant for plants with windows or sliding walls at the cell level, as horizontal air movements may carry mercury emissions through the wall openings instead of through the roof opening. Another possible effect is local downward movement of air in the roof opening as a result of strong winds from certain direction (see Figure 2).





**Figure 2: Example of possible distortion of the rising air flow pattern in a mercury cell chlor-alkali plant as a result of strong winds from a certain direction. Less prominent distortions occur also at lower wind speeds.**

In theory, all mercury emitted from the cells is carried by the ventilation air through the open roof. Therefore, many companies focus on the measurement of the air flow and the mercury concentration in the ventilation air in order to determine the loss of mercury from the cell room.

Several methods are available to measure/determine the air flow. Euro Chlor [Euro Chlor Env. Prot. 5, 1999] mentions the following:

- Hot wire anemometer
- Vane anemometer
- Pilot-tubes, nozzles, orifice plates
- Smoke method
- Sulphur hexafluoride tracer method
- Heat balance method

Euro Chlor does not recommend a specific method, but from the point of accuracy, ease of operation and possibility to use for continuous monitoring, the anemometers are probably preferable. The disadvantage of the hot-wire anemometer is that the air flow direction can not be determined. So the hot-wire anemometer is preferably used in combination with equipment that indicates the flow direction. The disadvantage of the vane anemometer is its lower accuracy at lower flow rates, which may make it less preferable for accurate measurements.

The most important task in the determination of the ventilation rate is the selection of the right sampling points. The points should be selected so as to obtain a representative picture of the ventilation flow pattern. In plants with windows beneath the electrolyzers, it will normally be sufficient to have a number of sampling points evenly distributed over the length of the roof opening. In plants with doors or windows at the electrolyser level, provisions are needed to assess the potential horizontal air flow. Continuous monitoring of ventilation air flow is more difficult here, due to the changing pattern of open doors/windows, depending on the cooling requirements and the wind direction.

Determination of ventilation rate in open air cell rooms is even more difficult. Euro Chlor [Euro Chlor Env. Prot. 5, 1999] gives some guidance on the assessment in open air cell rooms.

The mercury concentration in the ventilation air can be determined by several methods. Euro Chlor [Euro Chlor Env. Prot. 5, 1999] mentions four analytical methods and two physical detection methods.

Analytical:

1. Absorption in acidified potassium permanganate ( $\text{KMnO}_4$ ).
2. Adsorption on cellulose powder and activated carbon, subsequent burning in an oxy-hydrogen flame followed by flameless atomic absorption spectrophotometry (AAS).
3. Adsorption of Hg on manganese dioxide ( $\text{MnO}_2$ ) and dissolution of the sample in aqua regia ( $\text{HCl}/\text{HNO}_3$ ).
4. Adsorption of mercury on gold wool.

Euro Chlor [Euro Chlor Anal.3-7, 1998 and Env. Prot. 5, 1999] does not recommend any specific method, but methods 2 and 3 are well validated and in addition to mercury vapour also allow determination of mercury aerosols. Analytical methods can be used for compliance measurements and for monitoring purposes.

Physical:

1. Portable UV mercury analyser
2. Portable Gold-film mercury analyser

The portable analysers can be used for quick indicative measurements. Especially tracing of mercury leaks and control of tightness of equipment can be very effectively done with portable analysers. Due to the lower accuracy and reproducibility, they are less fit for compliance measurements.

## Mercury monitoring of water

Monitoring will be made easier if all liquid effluent streams containing mercury are combined in such a way that, after mercury removal, a single sampling point can be used to analyse the entire output from the mercury treatment plant.

Automatic flow proportional sampling together with flow recording is preferred. Automatic sampling and analysing equipment must be frequently checked by approved laboratory methods. Analytical techniques have been developed by Euro Chlor [Euro Chlor Anal 3-7, 1998].

If sludge (for example, brine purification sludge) is contained in the liquid effluent, special sampling techniques must be applied since automatic analysers may not work properly.

## Mercury monitoring of products

### Chlorine

Chlorine, which has been cooled, dried and filtered, contains very little mercury (approximately 1 mg/tonne  $\text{Cl}_2$ ). It is sufficient to check a few samples per year.

Most of the mercury entrained by the chlorine from the cells is trapped in the condensates from cooling and in the sulphuric acid from the drying towers. If these liquids are not discharged into the plant effluent system, a sampling and analysis scheme is required.

Moist chlorine (cell gas and waste gases not sent to a drying unit) contains mercury and will contaminate the liquor of caustic absorption towers and/or other products manufactured. In this

case, sampling and analysing of the moist chlorine or the reaction products at reasonable intervals may be necessary. However, since flow metering of moist chlorine is not easy, analyses and measurements of the reaction products are often more accurate.

### **Sodium and potassium hydroxide**

Caustic and potassium hydroxide solutions leaving the cells are saturated with mercury. They have to be filtered and cooled. After filtration, the liquors contain only small amounts of mercury (10-100 mg/tonne caustic). Sampling and analysis are not a particular problem and sampling and analysis frequencies are generally high in order to meet customers specifications.

### **Hydrogen**

Hydrogen sampling after a mercury removal unit poses few problems; if there are aerosols from a washing step, isokinetic sampling is recommended.

Since the concentration of mercury after removal unit is very low, the analysis frequency is normally not relevant to measuring emissions but is necessary for control of the removal process performance.

However, the mercury concentration in pre-treatment hydrogen streams can be high. Any emergency venting of cell hydrogen or by-passing of the treatment plant for, say, maintenance purposes should be recorded as even a few hours operation without treatment may result in emissions equal to several weeks normal operation.

## **Mercury accumulation in equipment and wastes**

Although it would appear to be simple to balance mercury purchases against mercury emissions, in practice this is almost impossible since accumulation of mercury in process equipment, in residues awaiting treatment and in non-recovered deposited solid wastes are significantly larger than the emissions themselves.

These accumulations provide a large proportion of what is known as Difference to Balance (DB). [Euro Chlor Env. Prot. 12, 1998] describes the components of DB in detail.

Regular monitoring and analysis of the accumulations and wastes are nearly impossible. Techniques which may assist include drainage and cleaning prior to any balance, sampling and development of 'standard' concentrations combined with weighings.

The analytical techniques developed by Euro Chlor [Euro Chlor Anal 3-7, 1998] can be used for all waste streams.

### **Mercury in equipment other than cells**

Some equipment can be drained periodically (e.g. tanks, catch-pots, traps). Equipment of this type should be purged just prior to making the balance and the recovered mercury weighed and returned to stock.

Sewers, traps and mercury sumps should be cleaned and the mercury recovered shortly before making any balance.

There are other pieces of equipment (headers, - mainly wash water, hydrogen, brine, caustic -, stock tanks, etc.) which can only be drained during plant stoppages. For this type of equipment, experiments have shown that very significant quantities of mercury can accumulate. The equilibrium level of mercury in a header is sometimes reached only after several years of operation.

### **Mercury in sludges and wastes temporarily stored on site**

Dispersed mercury in sludges tends to agglomerate and settle. It is therefore very difficult to obtain representative samples from sludges such as caustic filtration filtercake, thick mercury and cell room dirt.

The best solution to this problem is to treat, as far as possible, all sludges for mercury recovery before making the balance.

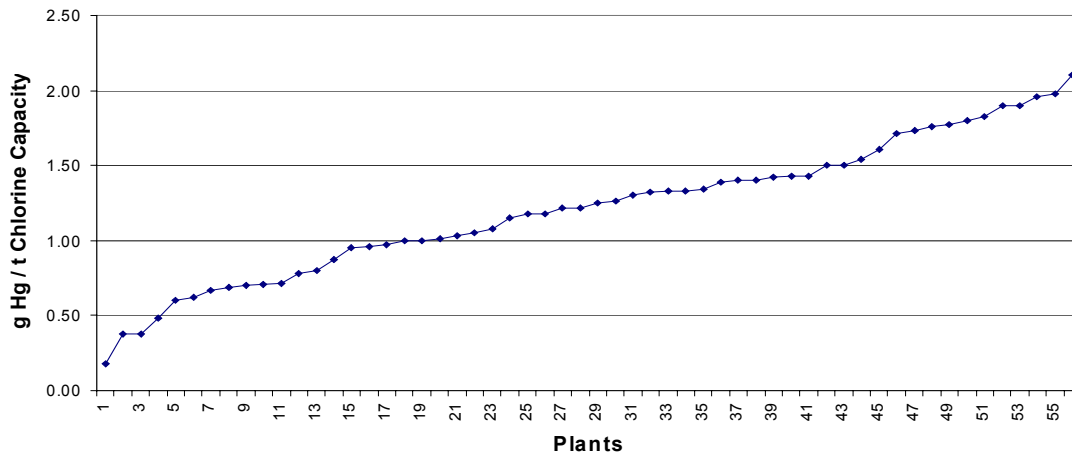
For those sludges for which recovery is not possible and for which a full analysis of the mercury content is not practical, it is suggested that detailed analyses are done on samples of each type of waste to establish a plant standard and that these are then used in combination with weighing of each quantity stored to obtain the mercury content.

### **Mercury-containing wastes removed to safe authorised disposal sites**

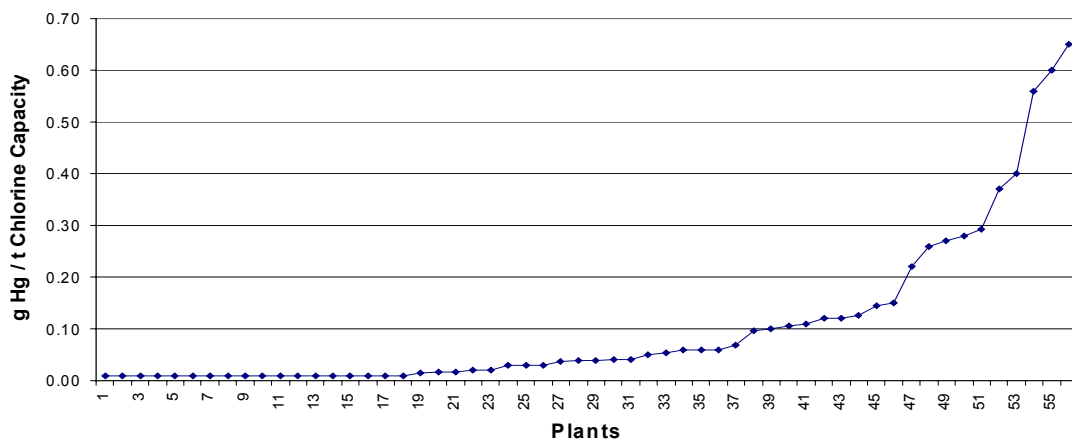
Sampling of the mercury content of some of these components may be difficult. Guidance can be found in Euro Chlor documents [Euro Chlor Env. Prot. 3, 1999]. It is suggested that a detailed analysis is done on a sample of each type of waste to establish a plant standard and that this is then used in combination with weighing of each load leaving the site to obtain the mercury content.

## ANNEX C: MERCURY LOSSES PLANT BY PLANT 1998 AND THE TREND 1977-1998

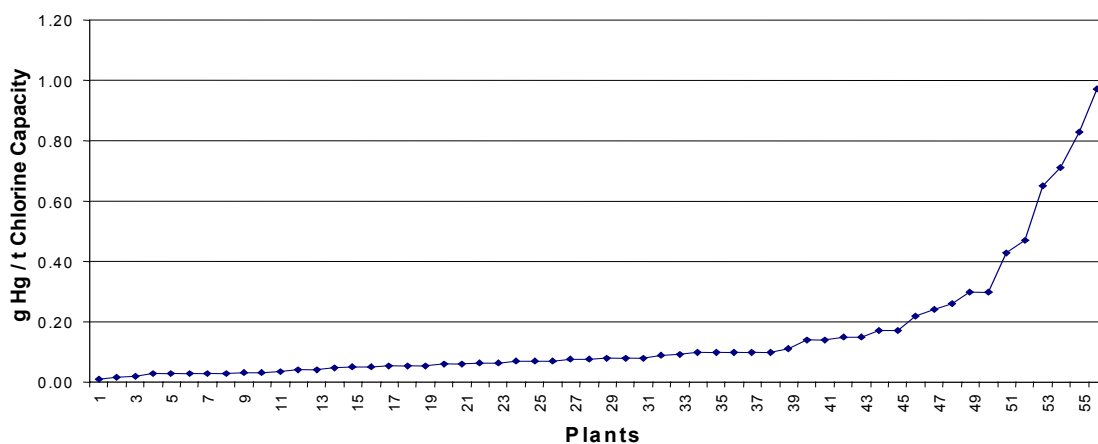
**MERCURY EMISSIONS TO AIR  
WESTERN EUROPE 1998**



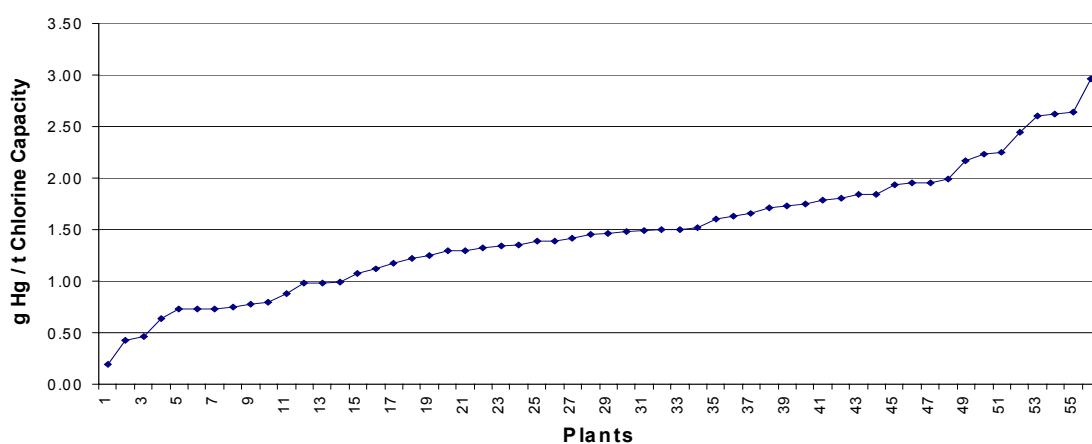
**MERCURY EMISSIONS TO WATER  
WESTERN EUROPE 1998**



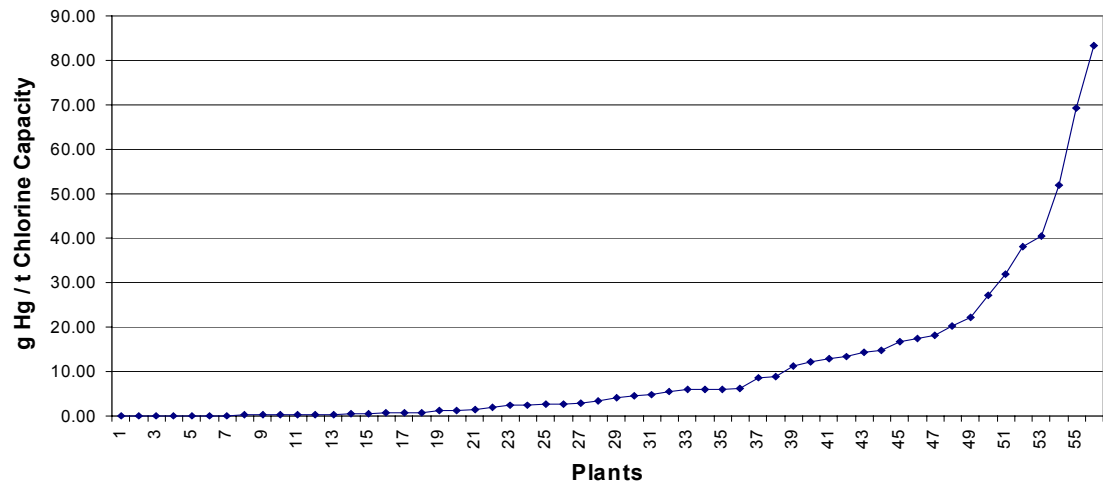
### MERCURY IN PRODUCTS WESTERN EUROPE 1998



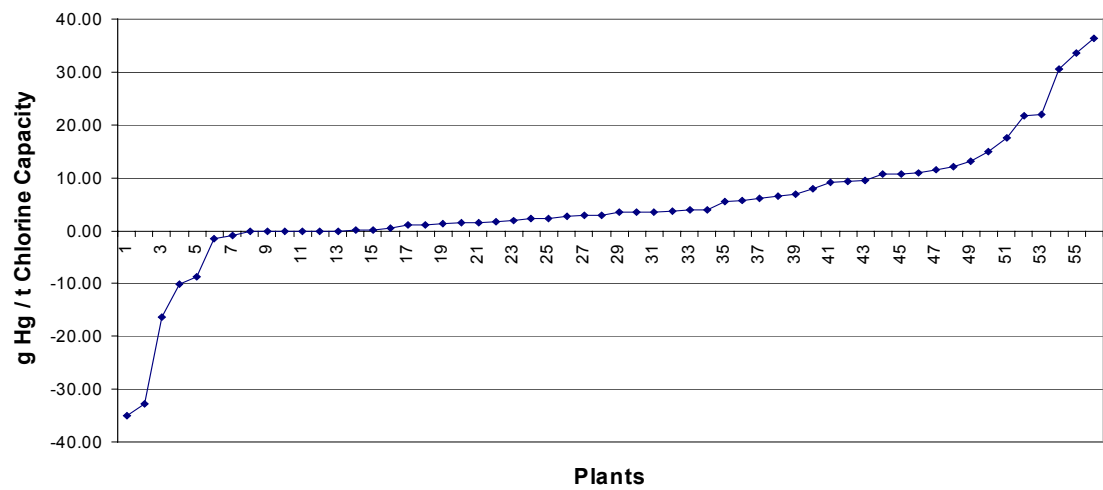
### MERCURY EMISSIONS TO AIR, WATER & IN PRODUCTS WESTERN EUROPE 1998



**MERCURY IN SOLIDS DISPOSAL  
WESTERN EUROPE 1998**

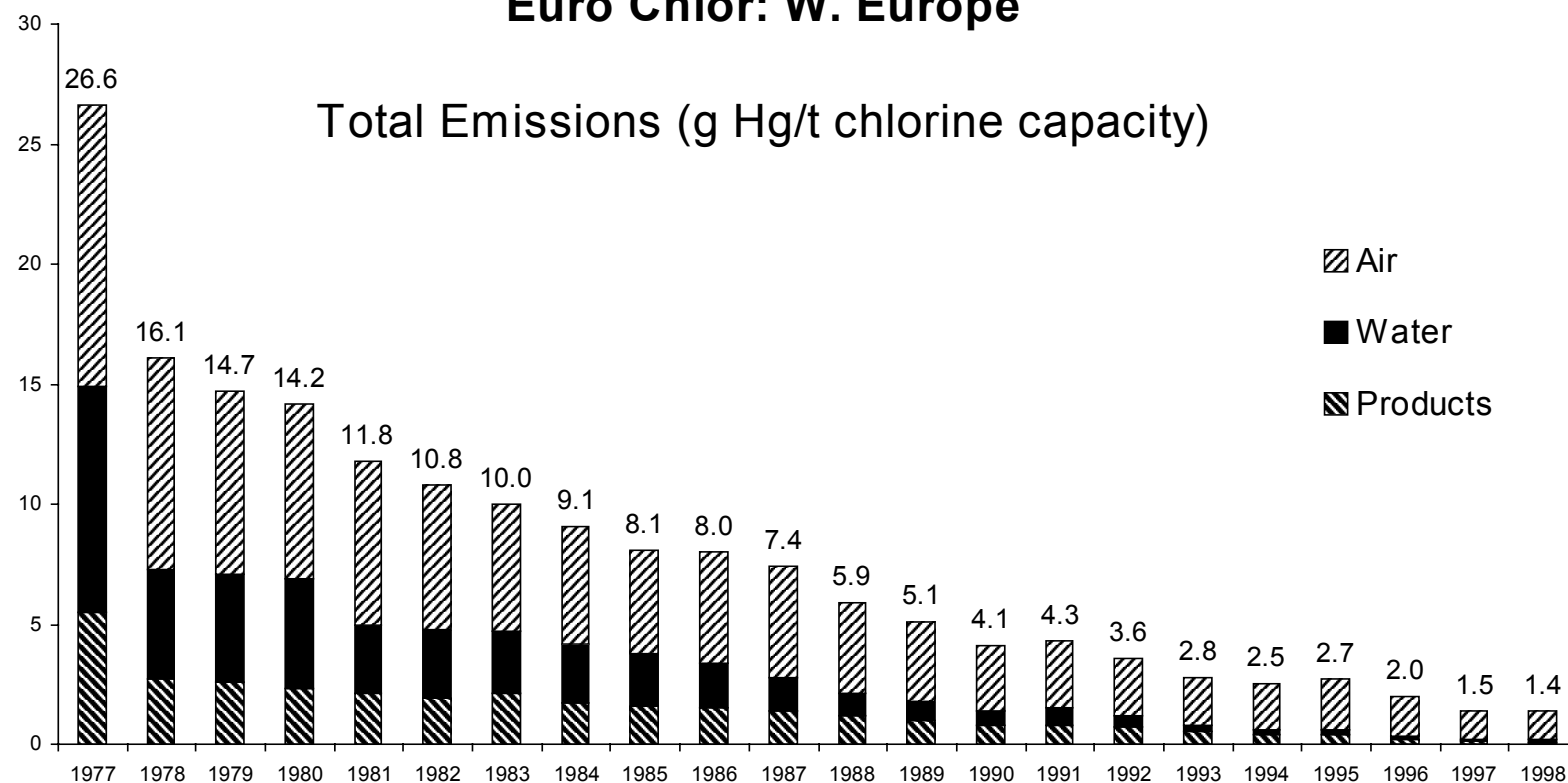


**MERCURY DIFFERENCE TO BALANCE  
WESTERN EUROPE 1998**





## Mercury Emissions 1977-1998 Euro Chlor: W. Europe



## ANNEX D: NATIONAL AND INTERNATIONAL LEGISLATION

### Flemish legislation concerning the Chlor-alkali industry

The environmental permit of a company in Flanders is written in accordance with the Flemish environmental legislation, called “Vlarem”. The Chlor-Alkali industry is part of the Chemical Industry and has to follow the same general legislation. Chapter 5.7 in part 5 of VLAREM 2 states the specific sectoral environmental conditions for the Chlor-Alkali Industry.

#### Section 5.7.5. Production of chlorine

##### Art. 5.7.5.1.

§1. The regulations of this section are applicable to the businesses mentioned in subdivision 7.5 of the list of classification (Vlarem 1).

§2. In contravention to and as a supplement to the regulations of section 4.4.3 the following emission limit values apply for:

1. chlorine:
  - a. installations for the production of chlorine with complete liquefaction: 6 mg/Nm<sup>3</sup>
  - b. in other cases: 1 mg/Nm<sup>3</sup>
2. mercury and its compounds:
  - a. at a mass flow of 1 g/u or more: 0.2 mg/Nm<sup>3</sup>
  - b. with chlor-alkali electrolysis according to the amalgam process the emissions of mercury in the exhaust air from the cell room may not exceed, a yearly average of:
    - i. 1.5 g per tonne chlorine production, for new installations;
    - ii. 2 g per tonne chlorine production, for existing installations;
    - iii. the mercury in the hydrogen emitted in the atmosphere or burned, is included in this limit value.

§3. The construction of new installations for the production of chlorine according to the mercury process will not be permitted any more. The mercury process can not be used after the year 2010.

### Summary of current German legislation relevant for the sector of Chlor - alkali industry

#### Introduction

Important regulations relevant for industrial installations in Germany are laid down in the Federal Immission Control Act [Bundesimmissionsschutzgesetz - BImSchG], the Federal Water Act [Wasserhaushaltsgesetz - WHG] and the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG]. Germany uses a segregated media permitting system for different environmental media, but the final decision on an application is reached by the assessment of environmental impacts on all media by the local authorities. Also noise requirements are considered in the licensing procedure, whereby Germany aims at favouring pollution prevention. The “precautionary principle” has a legal status which permits the settings of standards. Legal standards are not subject to any negotiation in the licensing process in Germany.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may implement the administrative procedure differently. For new plants, that are regarded as

relevant with respect to emissions and releases into the environment, also an environmental impact assessment is required during the licensing procedure (cf. Gesetz über die Umweltverträglichkeitsprüfung [UVPG]).

Table 1 gives an overview of the German legal basis and regulations for environmental protection in Germany alongside the process chain. In the following, the most important acts and regulations are presented. At the moment, some of these acts and regulations are revised in order to comply with the IPPC Directive.

**Table 1: Legal basis and regulations alongside the process chain**

Area	Legal basis	Regulations and ordinances
Transport	Verkehrsrecht	- Gefahrgutverordnung Straße - Gefahrgutverordnung Schiene - Gefahrgutverordnung Binnenschifffahrt
Health and safety at work	Chemikaliengesetz (ChemG)	- Chemikalienverbotsordnung - Gefahrstoffverordnung
	Gewerbeordnung	- TA Lärm - Arbeitsstättenverordnung und -richtlinien
Emissions	Bundes-Immissionsschutzgesetz (BImSchG)	- Bundes-Immissionsschutzverordnungen - Bundes-Immissionsschutzverwaltungs-vorschriften - TA Luft - TA Lärm
	Wasserhaushaltsgesetz (WHG) Abwasserabgabengesetz (AbwAG)	- Abwasserverordnung (AbwV) - Abwassergesetze der Länder or Indirekteinleiterverordnungen - Anlagenverordnungen der Länder - Katalog wassergefährdender Stoffe - Klärschlammverordnung
Treatment	Abfallgesetz (AbfG)	- Abfall- und Reststoffüberwachungsverordnung - Abfallbestimmungsverordnung - Reststoffbestimmungsverordnung - TA Abfall - TA Siedlungsabfall
	Kreislaufwirtschafts- und Abfallgesetz (KrW.-/AbfG)	

### German regulations concerning the air quality

The basic law for air pollution control is the Federal Immission Control Act [Bundes-Immissionsschutzgesetz BImSchG]. The BImSchG is specified by 21 ordinances and the Technical Instructions on Air Quality [TA Luft].

### Technical Instructions on Air Quality (TA Luft)

The Technical Instructions on Air Quality (TA Luft) have been set up as general administrative regulations in connection with the §48 BImSchG. The TA Luft further specifies the requirements to be met by installations subject to licensing. Therefore, it prescribes limit values for virtually all air pollutants as well as structural and operational requirements designed to limit diffuse emissions. Table 2 shows the limits for general emission control requirements of the TA Luft.

The emission limit values contained in the TA Luft represent the state of the art for technical measures for reducing emissions (dating from 1986). These values were developed referring to scientific findings and research taking into account toxicological, bioaccumulative and epidemiological aspects. The required concentration limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 1013 mbar) after subtraction of the water vapour content.

**Table 2: Emission control requirements laid down in the TA Luft**

Emitted substance (TA Luft section)	Class	Substances		Mass flow threshold [g/h]	Concentration limit [mg/m <sup>3</sup> ]
Total dust	-			≤ 500	150
				> 500	50
Inorganic dust	I	(Hg, Cd, Tl)	sum of substances	≥ 1	0.2
particles	II	(As, Co, Ni, Te, Se)	- " -	≥ 5	1
(3.1.4)	III	(e.g. Sb, Pb, Cr, CN, F, Cu, Mn, Pt, Pd, Rn, V, Sn, substances which are strongly suspected to cause cancer)	- " -	≥ 25	5
	I+II		- " -		1
	I+III, II+III		- " -		5
Vaporous or	I	(e.g. AsH <sub>3</sub> )	per substances	≥ 10	1
gaseous inorganic	II	(e.g. HF, Cl <sub>2</sub> , H <sub>2</sub> S)	- " -	≥ 50	5
substances	III	(e.g. Cl-compounds as HCl)	- " -	≥ 300	30
(3.1.6)	IV	(e.g. SO <sub>2</sub> + SO <sub>3</sub> as SO <sub>2</sub> , NO + NO <sub>2</sub> as NO <sub>2</sub> )	- " -	≥ 5 000	500
Organic substances	I	(e.g. chloromethane)	Classification	≥ 100	20
(3.1.7)	II	(e.g. chlorobenzene)	according to	≥ 2 000	100
	III	(e.g. alkylalcohols)	Annex E of TA Luft	≥ 3 000	150
Vaporous or gaseous emissions during treatment and refilling of organic substances (3.1.8)	Requirements for the minimisation of diffuse organic emission by the installation of technical equipment, e.g. pumping units, compressors, flanged joints, stop valves and in sampling stations				
Carcinogens	I	(e.g. Cd <sup>1)</sup> , As <sup>1)</sup> , asbestos, benzo(a)pyren)		≥ 0.5	0.1
(2.3)		- sum of substances -			
	II	(e.g. Ni, chromium VI) - " -		≥ 5	1
	III	(e.g. Acrylonitrile, benzene)		≥ 25	5

<sup>1)</sup> Based on the decision adopted by the Conference of the Federal Government/Federal States Ministers for the Environment on 21/22. November 1991, an emission concentration value of 0.1 mg/m<sup>3</sup> has been stipulated for Cd and its compounds, given as Cd, as well as for As and its compounds, given as As.

In case of high emission mass flows, emissions have to be monitored continuously.

All daily mean values of the respective emitted substances shall not exceed the established emission limits, 97 % of all half-hourly means shall not exceed six fifths of the established emission limits, and all half-hourly means shall not exceed the established emission limits by more than twice.

For the **Chlor-alkali industry** more specific requirements for the sector are laid down in a specific chapter 3.3.4.1.d of the TA Luft, which include the following requirements:

Concentration of chlorine(daily mean value): 1 mg/m<sup>3</sup>;  
in the case of full chlorine liquefaction: 6 mg/m<sup>3</sup>,  
In the case of chlorine production with mercury:  
 Annual average emission value of mercury in waste gas from the cellroom shall not exceed  
 1,5 g/ t chlorine capacity  
 (2 g/ t in the case of plants permitted before 1972)

Since the TA Luft stems from 1986, the local authorities sometimes demand stricter emission limit values than laid down in the TA Luft. At present, the TA Luft is revised in order to comply with the development of the state-of-the-art and the BREFs.

### German regulations concerning requirements of waste water discharges into waters

The legal framework for water management is the Federal Water Act [Wasserhaushaltsgesetz - WHG]. The WHG applies to waste water generated by various industrial processes. The use of surface, coastal, and ground waters and the discharge of waste waters requires the approval of the competent authority. **Discharges into water** are regulated in the Waste Water Ordinance including its Annexes [Abwasserverordnung, AbwV] which is mainly based on art. 7(a) of the Federal Water Act. This Ordinance specifies the minimum requirements to be stipulated when granting a permit to discharge waste water from the source categories listed in the Appendices into waterbodies.

Issued by the Federal Government in consent with the Federal States (Länder), these minimum requirements are binding for the authorities responsible for licensing and governmental control of the discharges. Depending on the local conditions, even more stringent requirements can be established. The minimum requirements are based on the 'emission principle' and the precautionary principle, i.e. application of stringent, technically derived emission standards irrespective of the loading reserves of the receiving water bodies resources or the potential effects of the various substances discharged. Additionally, the Federal Ministry of Environment publishes explanations and comments on the Waste Water Ordinance.

Definition of terms and general requirements according to the Waste Water Ordinance are listed below:

#### Definition of terms

**Random sample** shall refer to a single sample taken from a waste water flow

**Composite sample** shall refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or discontinuously over a given period and blended

**Qualified random sample** shall refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, and blended

**Production-specific load level** shall refer to the load level (e.g. m<sup>3</sup>/t, g/t, kg/t) in relation to the production capacity on which the water discharge licence is based.

**Site of occurrence** shall refer to the place where the waste water has been treated prior to blending with other waste water; otherwise, the place where it is first collected

**Blending** shall refer to the merging of waste water flows from different origins

**Allegation** shall refer to the calculation of a permissible load or concentration derived from the requirements in this Ordinance concerning the individual waste water flows.

### General requirements

- (1) Unless otherwise stated in the Appendices, a permit to discharge waste water into waterbodies shall only be granted if the pollutant load at the site of occurrence, based on an examination of the conditions in each individual case, is kept as low as the use of water-saving procedures such as washing and cleaning operations, indirect cooling and the use of low-pollutant feedstocks and auxiliary materials permit.
- (2) The requirements of this Ordinance must not be met by means of procedures whereby environmental pollution is transferred to other environmental media such as air or soil, contrary to the state of the art.
- (3) Requirements specified in the form of concentration levels must not be achieved via dilution, contrary to the state of the art.
- (4) If requirements prior to blending are specified, then blending shall be permissible for the purpose of joint treatment, provided at least the same overall reduction of contaminant load per parameter is achieved as would be the case via separate compliance with the relevant requirements.
- (5) If requirements are specified for the site of occurrence of waste water, blending is only permissible provided these requirements are adhered to.
- (6) If waste water flows which are subject to differing requirements are discharged jointly, then the relevant decisive requirement for each parameter shall be determined by means of allegation. If requirements governing the site of occurrence of the waste water or prior to blending are imposed in the applicable Appendices, then paragraphs (4) and (5) shall remain unaffected.

### Reference point of the requirements

The requirements refer to the point at which the waste water is discharged into the waterbodies and also, where specified in the Appendices to this Ordinance, to the site of occurrence of the waste water or the site prior to blending thereof. The point of discharge is synonymous with the outlet from the waste water plant where the waste water was last treated. The site prior to blending is also the point of discharge into a public waste water plant.

### Compliance with the requirements

If a level specified by this Ordinance is not complied with based on the results of analysis within the context of government monitoring, it shall nevertheless be deemed to have been met, provided the results of this and the four preceding government analyses do not exceed the level in four cases and no result exceeds the level by more than 100 percent. Analyses which were conducted more than three years ago shall be disregarded.

The productions of the specific sectors are covered by Annexes of this regulation. The sector of Chlor - alkali manufacturing industry is dealt with in Annex 42, which is detailed listed below.

## Appendix 42

### Chloralkali electrolysis

#### A Scope of application

(1) This Appendix shall apply to waste water whose contaminant load originates primarily from chloralkali electrolysis.

(2) This Appendix shall not apply to waste water from cooling systems or process water treatment facilities, nor from fused-salt electrolysis of sodium chloride or chloralkali electrolysis for the production of alcoholates.

#### B General requirements

As far as technical factors allow, waste water from the chloralkali electrolysis unit shall be returned to the production process.

#### C Requirements for waste water at the point of discharge

The following requirements apply to waste water at the point of discharge into the waterbody:

	Qualified random sample or 2-hour composite sample	
Chemical oxygen demand (COD)	mg/l	50
Fish toxicity	T <sub>F</sub>	2

#### D Requirements for waste water prior to blending

No requirements are placed on waste water prior to blending with other waste water.

#### E Requirements for waste water at the site of occurrence

(1) The waste water must not contain any mercury or asbestos used as feedstocks or auxiliary materials in the production process. These requirements shall also be deemed to have been met, provided mercury and asbestos are not used as feedstocks or auxiliary materials in the production process in the “chloralkali electrolysis” unit.

(2) The waste water must not contain more than 2.5 mg/l AOX and 0.2 mg/l free chlorine in the random sample.

#### F Requirements for existing discharges

##### I. Existing discharges from plants based on the mercury-cell process

(1) In derogation of part C, the following requirements shall apply to waste water from plants based on the mercury-cell process at the point of discharge into the waterbody:



	Qualified random sample or 2-hour composite sample	
Chemical oxygen demand	mg/l	50
Total mercury	mg/l	0.05
	g/t	0.3
Sulphide	mg/l	1
Fish toxicity	T <sub>F</sub>	2

(2) In derogation of part D, the following requirements shall apply to waste water from the chloralkali electrolysis unit based on the mercury-cell process prior to blending with other waste water:

Total mercury	0.04 g/t	Qualified random sample or 2-hour composite sample
AOX	3.5 mg/l	Random sample

(3) The requirements for mercury given as production-specific load levels refer to the chlorine production capacity in 24 hours.

(4) Part E shall not apply.

## II. Existing discharges from plants based on the diaphragm cell process

(1) In derogation of part C, the following requirements shall apply to waste water from plants based on the diaphragm cell process at the point of discharge into the waterbody:

	Qualified random sample or 2-hour composite sample	
Chemical oxygen demand (COD)	mg/l	130
Fish toxicity	T <sub>F</sub>	2

(2) In derogation of part D, the following requirements shall apply to waste water from the chloralkali electrolysis unit based on the diaphragm cell process prior to blending with other waste water:

AOX	3 mg/l	(Random sample).
-----	--------	------------------

(3) Part E shall not apply.

The WHG is complemented by the discharge levy act [Abwasserabgabengesetz - AbwAG]. The tariffs are related to the mass and possible hazard of the discharged waste water.

## German regulations concerning the waste management and disposal of hazardous materials

Regulations concerning the waste management and disposal of hazardous materials are laid down in the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG] and the Federal Immission Control Act [BImSchG]. According to the BImSchG, an operator of a waste generating installation which is subject to licensing, is obliged to avoid waste production or to make sure that the waste is environmentally soundly recovered. If that is technically or economically not reasonable, the waste has to be disposed of

without any harmful effects. A federal States' working group on immission control (Länderausschuß für Immissionsschutz, LAI) has published exemplary administrative regulations for particular industrial sectors containing measures for avoidance and recovery of wastes which are considered as technically and economically reasonable.

The KrW/AbfG states that installations generating more than 2 tonnes of hazardous waste or more than 2000 tonnes of non-hazardous waste (per waste key), must produce a waste management concept and yearly waste balances.

A working group of the federal states on waste (Länderarbeitsgemeinschaft Abfall, LAGA) issued a categorisation of waste types, comprising 589 types of waste, of which 333 have priority for control (*LAGA-Abfallartenkatalog*). This catalogue was valid till 12/31/1998 and is now replaced by the European waste catalogue (EWC). To facilitate the change from the LAGA catalogue to the EWC, the working group worked out an interim catalogue (*LAGA-Umsteigekatalog*).

## References

Abwasserabgabengesetz -AbwAG: Gesetz über Abgaben für das Einleiten von Abwasser in Gewässer, 3.11.1994

Abwasserverordnung - AbwV: Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer und zur Anpassung der Anlage des Abwasserabgabengesetzes, 21.03.1997

Bundesimmissionsschutzgesetz (BImSchG): Gesetz zum Schutz vor schädlichen Umwelteinwirkungen durch Luftverunreinigungen, Geräusche, Erschütterungen und ähnliche Vorgänge, 14.05.1990, last amendment 19.07.1995

Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG: Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Beseitigung von Abfällen, 27.09.1994

TA Luft: 1. Allgemeine Verwaltungsvorschrift zum Bundesimmissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft - TA Luft, 27.2.1986

TA Lärm: 6. Allgemeine Verwaltungsvorschrift zum Bundesimmissionsschutzgesetz (Technische Anleitung zum Schutz gegen Lärm - TA Lärm), 26.08.1998

UVPG: Gesetz über die Umweltverträglichkeitsprüfung - UVPG, 12.2.1990, last amendment 23.11.1994

Wasserhaushaltsgesetz - WHG: Gesetz zur Ordnung des Wasserhaushalts - WHG, 12.11.1996

## Italian Regulations

4. Non municipal wastes defined in the list of the annex D (on the basis of annexes G, H, and I) are “Dangerous wastes”.

### LIST OF DANGEROUS WASTES

Code CER	Designation
06	Wastes from inorganic chemical processes
.....	.....
060404	Wastes containing mercury
060701	Wastes from electrolytic processes containing asbestos
060702	Active coal from chlorine production

Note: All the storage, transport and disposal operations must be authorised according to Directives 91/56/CEE and 91/689/CEE

## § 29 Chlorine Production Plants

### Chlorine

The emission value is 1 mg/m<sup>3</sup>; for the plants for total liquefaction of chlorine production the emission value is 6 mg/m<sup>3</sup>.

### Mercury

In the electrolysis of alkaline chloride, with amalgam process, the emission value (as annual average) is 1.5 - 2 g/t of production.

## 1.2 Waste waters

For the production cycles specified in table 3/A, the mass emission limits per product unit of raw material of the above mentioned table must be observed. For the same production cycles also the limits of concentration shown in table 3 must be observed at the final drainage.

Among the emission limits in terms of mass production per product unit, shown in table 3/A, and the ones established by the regions, in conformity with article 28, paragraph 2, in terms of mass over time, the more precautionary ones must be observed.

Table 3/A Emission limits per product unit referred to specific productive cycles

Productive sector

Mercury (productive sector of the electrolysis of the alkaline chloride)

Recycled brine – to be applied to the Hg present in the effluents coming from the chlorine production unit	g Hg/t of chlorine production capacity, installed	0.5
Recycled brine – to be applied to the total of Hg present in all waste waters containing Hg coming from the area of the industrial site	g Hg/t of chlorine production capacity, installed	1
Disposable brine – to be applied to the total of Hg present in all waste waters containing Hg coming from the area of the industrial site	g Hg/t of chlorine production capacity	5

## Dutch legislation

### Policy

The Dutch Environmental Policy is laid down in the National Environmental Policy Plan (NEPP) and the Memorandum on Water Management (MWM), which are updated regularly. The NEPP and the MWM set the environmental targets for the medium long term and outline the policy to achieve these targets.

### Framework legislation

The Netherlands has two main framework environmental acts, being the “Environmental Management Act” and the “Surface Water Pollution Act”. These acts together provide the framework for environmental permitting and allow for setting conditions to the permit. The acts comply with the requirements of the IPPC Directive and integrated permitting is guaranteed by a co-ordinated licensing procedure from the competent authorities. Both framework acts govern a number of Decrees and Regulations that provide requirements with regard to potentially polluting activities.

### Safety legislation

Safety is a very important issue for the Chlor-alkali Industry. The main legislation with regard to safety is the Seveso II Directive. The Council Directive 96/82/EC of 9 December 1996 on the control of major-accident hazards involving dangerous substances (the Seveso II Directive) is aimed at the prevention of major accidents which involve dangerous substances, and the limitation of their consequences for man and the environment, with a view to ensuring high levels of protection throughout the Community in a consistent and effective manner.

The directive is mainly implemented in the Netherlands by means of the “Besluit risico’s zware ongevallen 1999” (Brzo 1999 for short) of 27 May 1999. The Seveso-II directive obliges operators of fixed hazardous establishments to supply the competent authorities with information on internal and external safety matters. Topics like process safety management systems, land use planning, safety measures, safety assessment studies (Safety Report), domino effects and disaster planning are important information requirements. Furthermore the competent authorities have obligations towards the reviewing and handling of safety reports and physical inspection of hazardous installations.

The report on Information Requirements BRZO 1999 (CPR 20) is intended to explain the rules as laid down in the BRZO 1999 and in detailed rules, and to indicate how various aspects should be implemented. CPR 20 has been drawn up to assist companies in fulfilling the requirements laid down in the BRZO 1999. CPR 20 is intended both for companies and for the government authorities involved. It should be noted that for the government authorities, besides CPR 20, there is also an administrative guideline Seveso II (HUBO). HUBO relates specifically to the approach by government authorities.

The BRZO 1999 is based on various acts. With the single-contact principle the information concerning safe working practice (the Labour Safety Report or in Dutch ‘AVR’), external safety and environmental risks (the External Safety Report or in Dutch ‘EVR’) and/or the company fire brigade provision (report relating to the company fire brigade) have been integrated into a single reporting obligation, and submission of the information takes place via a single contact point.

## Decrees and regulations

### Air: Netherlands emission regulations (NeR)

The Netherlands emission regulations apply to process emissions to air and provide guidelines for the conditions in environmental permits for emissions to air. In the NeR, concentration standards for different substances are given, which constitute upper limits for distinct point sources, depending on mass flow. The "special regulations" comprise measures to limit emissions from incidental discharges or diffuse sources. Furthermore, in the "special regulations" rules departing from the "general emission standards" for certain industries or specific installations are given.

The emissions standards in the NeR are not legally binding and the NeR does not replace existing binding agreements. However, if the licensing authority wishes to depart from the NeR, the reasons for doing so must be stated explicitly in the preamble to the licence.

For the chlor-alkali industry, one 'Special Regulation' is made: "NeR 3.5/29.1 Production of chlorine". This regulation requires that new installations are not based on the mercury cell process and existing installations are to be converted to mercury free processes before 2010. In the mean while, the mercury emissions to air from plants built before 1972 must be < 2g/tonne Cl<sub>2</sub> capacity and from plants built after 1972 must be < 1,5 g/tonne. Where no special provisions are explicitly stated in a special regulation, the general rules of the NeR apply. The most relevant general rule is for the emission of Cl<sub>2</sub>, for which a standard of 5 mg/Nm<sup>3</sup> applies.

### Water

The focus in water emission regulation is on the precautionary principle and the polluter pays principle. A distinction is made between black list components (e.g. mercury, chlorinated hydrocarbons) and other pollutants. Permit conditions are set on an individual basis and take into account technical, economical, managerial and site-specific aspects.

### Waste

The Decree BAGA (besluit aanwijzing gevaarlijke afvalstoffen/Decree appointing hazardous waste) gives the levels of pollution that may not be exceeded in waste. If the levels are too high, the waste is 'hazardous waste' and should be processed by a specialised waste management company. If the levels are below the threshold (e.g. 50 mg/kg for mercury) the waste can be processed by a 'normal' waste management company.

## Voluntary agreements

Voluntary agreements or covenants (in Dutch: "Convenanten") are declarations of intent on the implementation of environmental policy for certain industrial sectors. The declarations of intent are agreements between the authorities and the industry. The participation in a covenant gives the advantage for both competent authorities and companies of a more transparent, coherent and predictable path of environmental improvement and investments. The covenants are nowadays applied in three fields:

- General environmental performance on 'traditional' pollutants.
- Energy efficiency
- CO<sub>2</sub> reduction

### General environmental performance on 'traditional' pollutants

In the declaration of intent of this voluntary agreement, the authorities have drawn up an Integral Environmental Target Plan (IETP), based on the National Environmental Policy Plan (NEPP), the Memorandum on Water Management, the North Sea Action Plan, The Rhine Action Programme, the Memorandum on Energy Conservation and other official plans at the time of signature.

The Integral Environmental Target Plan is concerned with environmental pollution of the 'traditional' pollutants (SO<sub>x</sub>, NO<sub>x</sub>, VOC, heavy metals, PAH, et cetera) caused by the relevant industrial sector. The IETP has been drawn up for the years 1994/1995, 2000 and 2010.

Apart from the reduction in emissions into the air, water and soil, the IETP also incorporates policy with regard to energy conservation, water conservation, soil clean up, hazard risk, odour nuisance, noise and internal management systems. However, especially for energy conservation and CO<sub>2</sub> reduction, two other covenants have been agreed upon.

For the "chemical industry" of which the chlor-alkali industry is a part, a declaration of intent was signed on 2nd April 1993. A significant factor is the understanding that in view of the wide range of disparate companies in the chemical industry, the contribution of each individual company to the implementation of the IETP in the industry may vary. The responsibility of individual companies to contribute to the implementation of the IETP in the industry requires that these companies take an active stance. The contribution of a company will be defined in Company Environmental Plans ("BMP's"), which are drawn up by each company. These BMP's are renewed every four years and must be agreed upon by the licensing authority.

### Energy efficiency: Long-Term Agreements on Energy Efficiency

In the Netherlands, "Long-Term Agreements on Energy Efficiency (MJA's)" have been made between the Ministry of Economic Affairs and representative organisations of many industrial sectors. The most important aspect of the MJA's is the target value for improvement of energy efficiency in the relevant industrial sector within a certain time frame. For the elaboration of the MJA's, bilateral agreements are made between the individual companies and the facilitating agency, which is NOVEM. For the chemical industry, of which the chlor-alkali industry is a part, an MJA was signed on 24 November 1993 and the agreed improvement of energy efficiency was 20% over the period 1989-2000. The target has been achieved by the sector and a second round of MJA's is now in preparation, although most of the LVOC companies will probably join the 'Benchmarking' covenant (see next item).

### CO<sub>2</sub> reduction: Benchmarking covenant

In the light of the Kyoto agreements, the Netherlands has to reduce the emission of CO<sub>2</sub>. Improvement of the energy efficiency is one of the most important measures to reduce the CO<sub>2</sub> emissions. The Benchmarking covenant is an agreement between the Dutch authorities and the Dutch energy intensive industry. The industry agrees to belong to the world top in energy efficiency and the authorities will then refrain from impairing additional CO<sub>2</sub> reduction measures. The agreement is open to all companies with an energy use of 0,5 PJ per year or more.

The principle agreement was signed on 6 July 1999 between the industrial organisations and the authorities. Now that the principle agreement has been signed, the agreement is open to individual companies to sign in on the covenant.

For those companies that do not want to join or that have an energy use of less than 0,5 PJ per year, the 'traditional' MJA route (see above) will be followed [43,44].

## **Austrian wastewater legislation**

AEV Chlor-Alkali-Elektrolyse says in paragraph 1 that ‘Wastewater from any activity specified in section 2 is not allowed to contain mercury or asbestos. This provision is met, if mercury and asbestos are not used as an auxiliary material in any activity listed in section 2.’ (Chlor-alkali is listed in section 2)

## **Regulations concerning the chlor-alkali industry in Finland**

In Finland we don't have any special regulations concerning the chlor-alkali industry. The authorities set their requirements to the industry in the permits. The procedure is regulated in the Environmental Protection Act. This act implements those requirements in the IPPC directive including the BAT.

## **British Legislation Concerning the Chlor-Alkali Industry**

### Integrated Pollution Control

Proposals for an integrated approach to pollution control in the U.K were first recommended in the Fifth Report of the Royal Commission on Environmental Pollution presented to the U.K government in 1976. It recommended that a new unified inspectorate should be set up to ensure an integrated approach to difficult industrial pollution problems at source whether these affect air, water or land. The inspectorate would expand the concept of “best practicable means” to ensure the adoption of the “best practicable environmental option.” This recommendation was included as Integrated Pollution Control (IPC) in the Environmental Protection Act (1990). Regulations stemming from this act are The Environmental Protection (Prescribed Processes and Substances) regulations 1991. These include the chlor-alkali industry as an IPC prescribed process coming under the definition “Any process for the manufacture of fluorine, chlorine, bromine or iodine etc”. These regulations require that the prescribed process must be operated with the objective, of ensuring that, in carrying on the process, the best available technique not entailing excessive cost (BATNEEC) will be used:

- a.) for preventing the release of substances prescribed for any environmental medium into that medium or, where that is not practicable by such means, for reducing the release of such substances to a minimum and for rendering harmless any such substances which are so released;
- b.) for rendering harmless any other substances which might cause harm if released into any environmental medium; and
- c.) For minimising the pollution which may be caused to the environment taken as a whole by the releases having regard to the best practicable environmental option (BPEO) available as respects the substances which may be released.

Guidance for inspectors in assessing an application for an IPC authorisation is contained in a series of Process Guidance Notes. These give guidance on what constitutes BAT for each process and also include “achievable release levels” for new plants using best available techniques. The chlor-alkali industry is described in S2 4.03, Inorganic Acids and Halogens, (ISBN 0-11-310141-4).

There have been many pieces of amending legislation since the Environment Protection Act (1990). The main amendment has been the Environment Act (1995) which allowed for the establishment of the Environment Agency (for England and Wales) and the Scottish Environment Protection Agency. These are the authorities, which regulate the major industrial processes including the chlor-alkali industry. More recently the Pollution Prevention and



Control Act (1999) has transposed the provisions of E.C Directive 96/61/EC into the U.K. legislation. Under the provision of the U.K Act implementation of the requirements in England and Wales will be by The Pollution Prevention and Control (England and Wales) Regulations (2000) (SI1973). These regulations describe activities, which require a permit from the appropriate authority. In the case of the chlor-alkali industry, this falls into the activity description in Schedule1, Section 4.2; Inorganic Chemicals, Part A (1)(a) Producing inorganic chemicals such as:- (vi) halogens, or interhalogen compounds etc. The regulatory authority for the four installations in England is the Environment Agency.

### Health and Safety

The requirements of the Seveso II Directive (96/82/EC) have been implemented by the Control of Major Accident and Hazards Regulations 1999 (COMAH Regulations) (SI743).

They apply in England, Scotland and Wales, to establishments which keep (or transport) listed dangerous substances about certain thresholds. In the case of chlorine, the threshold is 10 tonnes, which brings in the chlor-alkali processes. The general duty is that every operator shall take all measures necessary to prevent major accidents and limit their consequences to persons and the environment. The Regulations applying at the four chlor-alkali installations in England are enforced jointly by the Environment Agency and the Health and Safety Executive.

### Surface and Groundwater

Mercury and its compounds are identified under the List I of families and groups of substances in the EC Council Directive “on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community” (76/464/EEC) – the Dangerous Substances Directive. Substances are included on List I on the basis of their toxicity, persistence and bioaccumulation. The Directive requires that Member States take steps to eliminate pollution by List I substances. However substances do not come under List I methods of control until a daughter Directive, setting emission standards and environmental quality standards, is adopted. In the case of mercury and its compounds two daughter directives have been issued – 82/176/EEC (Mercury from the chlor-alkali electrolysis industry) and 84/156/EEC (Mercury – other sectors). The Dangerous Substances Directive (76/464/EEC) states that limit values shall apply except where a Member State can prove that quality objectives are being met and maintained. The UK Government has adopted the quality objective approach and established these in UK legislation for List I substances under 2 statutory instruments. The Surface Waters (Dangerous Substances) (Classification) Regulations 1989 (SI 2286) includes EQSs for mercury of 1 microgram per litre for inland waters and 0.3 micrograms per litre for coastal waters. Both apply as annual means. The coastal EQS relates to dissolved concentrations whereas the inland EQS relates to total.

The provisions of Directive 76/464/EEC relating to groundwater were superseded by the provisions of the Directive “on the protection of groundwater against pollution caused by certain dangerous substances” (80/68/EEC). Both require that Member states shall prevent the introduction of List I substances to groundwater. The requirements of 80/68/EEC are established in UK legislation through the Groundwater Regulations 1998 (SI 2746).

## Contaminated Land

Regulatory controls on industrially contaminated land follow one of two routes.

Where any land is proposed to be redeveloped, then the control is through the Local Authority planning development control process under the Town and Country Planning Act 1990. The prerequisite for development of land is a planning permission with conditions to seek appropriate site investigation for contamination, risk assessment and remediation to a standard to protect both the development and the environment. The Environment Agency is a non-statutory consultee on planning applications involving contaminated land. The Environment Agency advises on the pollution impact to controlled waters (groundwater and surface water) and the related remediation of the contamination.

The Contaminated Land (England) Regulations 2000 (Pt 2A) were commenced on 1 April 2000 and seek to control contaminated land which is not dealt with through other legislation. The statutory definition of contaminated land relates to actual harm to a wide range of receptors or pollution of controlled waters, with pollutant linkages (Source - Pathway - Receptor) needing to be established and risk assessed. The prime regulator for the majority of Pt 2A sites would be the Local Authority whom also has the responsibility to produce a Strategy document by July 2001. The Environment Agency would regulate those sites designated as Special Sites, which include certain land, use types and three specific categories of pollution to controlled waters. The chlor-alkali use of land as an IPC process, is a designated land use to form a Special Site. Also specifically in relation to mercury, land would be a Special Site if it was causing drinking water to be treated before consumption; or if it was entering certain groundwater geologies; or was causing the failure of an EQS in a watercourse.

## Reference

The National Society for Clean Air and Environment Protection produce an up to date useful guide to U.K and European pollution control legislation and related issues, its most recent publication; "Pollution Handbook 2000" (ISBN 0 903474 48 4) contains chapters on Air, Water, Waste and Noise Pollution.

## **European Legislation regarding Mercury containing Wastes**

### **1. CLASSIFICATION AS HAZARDOUS WASTE**

General Directive 91/689/EEC on hazardous wastes sets out criteria for wastes which should be classified as hazardous. In Annex II, wastes containing mercury and mercury compounds are listed provided they have one or more of the properties described in Annex III. The Annex III properties relevant to mercury are H6 (toxic or very toxic) and H14 (ecotoxic). These properties are defined in Directive 67/548/EEC and its subsequent adaptations which categorise mercury as toxic and ecotoxic.

Decision 94/904/EEC adopted under Article 1(4) of Directive 91/689/EEC provides for a list of hazardous wastes. These wastes are considered to display one or more of the properties of Annex III of Directive 91/689/EEC and as regards toxicity are considered to contain one or more of the substances classified as toxic at a total concentration of 3% or more. Therefore, as currently defined under EU-legislation, wastes containing mercury (code 060404 of the hazardous waste list) are classified as hazardous unless it is proven that the concentration of mercury in these wastes is less than 3% or that they do not contain one of the properties of Annex III.

Apart from the general requirement on all waste disposal to record and maintain records of production, transportation and disposal, classification as hazardous waste imposes several obligations or restrictions:

- waste must be properly packaged and labelled during collection, transportation and temporary storage
- mixing with non-hazardous wastes or other categories of hazardous wastes is prohibited except under derogations which may be granted in specific cases
- whenever hazardous wastes are mixed with non-hazardous wastes, separation must be effected wherever it is technically and economically feasible
- disposal must be implemented in an installation dedicated to hazardous wastes

## **2. TRANSFRONTIER MOVEMENT OF WASTES (COUNCIL REGULATION (EEC) 259/93)**

The European regulation on transfrontier movement of wastes divides wastes into three categorised lists: the green list, the amber list and the red list.

Wastes and residues containing mercury appear on the amber list.

The consequence of this classification is that for transfer of mercury and/or mercury-containing wastes between E.U. countries the following procedure must be followed, either for recovery (e.g. distillation) or disposal:

- a contract for disposal or recovery must be established with the consignee. This contract must be supplied to the Competent Authority on request.
- mandatory notification by consignment note of the transfer prior to execution must be passed to the relevant authorities of the countries of origin, transit and final destination;
- conditions may be imposed by the countries of origin or transit;
- the country of destination can object to the transfer for specified reasons;
- export can be prohibited by the country of production in order to encourage local solutions (self sufficiency principle) in case of disposal only.
- disposal/recovery operations must be recorded (follow-up document).
- a certificate of final disposal or recovery, as appropriate, must be supplied to all the Competent Authorities concerned as well as the originator.

Exports from the EU area to other OECD countries, for disposal or recovery, are possible provided that adequate procedures are followed.

Exports to countries outside the OECD area are prohibited under the Basel Convention and by Council Decision of 20/01/97.

## ANNEX E: RELEVANT ADDRESSES

### Industrial organisations:

*The Chlorine Institute, Inc.*  
2001 L Street, NW, Suite 506  
Washington D.C. 20036  
United States of America  
Tel: +1 202 775 27 90  
Fax: +1 202 223 7225  
Internet: <http://www.cl2.com>

*Euro Chlor*  
Av. E. Van Nieuwenhuyse 4, box 2  
B-1160 Brussels  
Belgium  
Tel: +32 2 676 72 11  
Fax: +32 2 676 72 41  
Internet: <http://www.cefic.be>

### Technology Suppliers for electrolysis chlorine/caustic:

#### Electrolysers

*Asahi Chemical Industry Co., Ltd.*  
IEM Sales & Technical Dept.,  
Ion Exchange membranes Div.  
3-2 Yako 1-chome,  
Kawasaki-ku, Kawasaki  
Japan  
Internet: <http://www.asahi-kasei.co.jp>

*De Nora S.p.A*  
Via Bistolfi 35  
20134 Milan  
Italy  
Tel. +39 02 21 291  
e-mail: [DENORAspa@mail.sko.it](mailto:DENORAspa@mail.sko.it)  
Internet: <http://www.denora.com>

*Asahi Glass Co. Ltd.*  
1-2, Marunouchi, 2-chome  
Chiyoda-ku, Tokyo 100  
Japan  
Internet: <http://www.agc.co.jp>

*ICI Chemicals and Polymers Ltd.*  
PO Box 14  
The Heath Runcorn  
Cheshire WA7 4Q8  
United Kingdom  
Internet: <http://www.ici.com>

*OxyTech Systems, Inc.*  
100 7<sup>th</sup> Avenue  
Chardon, OH 44024-1000  
USA  
Tel: +1 440 285 00 00  
Fax: +1 440 285 00 70

*UHDE GmbH*  
Electrolysen  
Friedrich-Uhde-Straße 15  
D-44141 Dortmund  
Germany  
Tel. +49 231 547 24 38  
<http://www.Krupp.com/kud/company/Intern>

#### Metallic Anodes

*Degussa AG*  
Weißfrauenstraße 9  
D-60311 Frankfurt am Main  
Germany  
Tel. +49 69 218 01  
Fax. +49 69 218 32 18  
Internet: <http://www.degussa.de>

*Heraeus W.C. GmbH*  
Postfach 1553  
D-63405 Hanau  
Germany  
Tel: +49 (6181) 35-1  
Fax: +49 (6181) 35-658  
Internet: <http://www.heraeus.de>

*ICI Chemicals and Polymers Ltd.*  
PO Box 14  
The Heath Runcorn  
UK-Cheshire WA7 4Q8  
United Kingdom  
Internet: <http://www.ici.com>

*De Nora S.p.A*  
Via Bistolfi 35  
I-20134 Milan  
Italy  
Tel. +39 02 21 291  
e-mail: [DENORAspa@mail.sko.it](mailto:DENORAspa@mail.sko.it)  
Internet: <http://www.denora.com>

*OxyTech Systems, Inc.*  
100 7<sup>th</sup> Avenue  
Chardon, OH 44024-1000  
USA  
Tel: +1 440 285 00 00  
Fax: +1 440 285 00 70

*Permascand AB*  
Box 42  
S-840 10 Ljungaverk  
Sweden  
Tel: +46 691 355 00  
Fax: +46 691 330 40

### **Membranes**

*Asahi Chemical Industry Co., Ltd.*  
IEM Sales & Technical Dept.,  
Ion Exchange membranes Div.  
3-2 Yako 1-chome,  
Kawasaki-ku, Kawasaki  
Japan  
Internet: <http://www.asahi-kasei.co.jp>

*Du Pont*  
Nafion Global  
Customer Services  
P O Drawer Z.  
Fayetteville  
USA - NC 23302  
Tel: +1 910 678 13 80

*Asahi Glass Co. Ltd.*  
1-2, Marunouchi, 2-chome  
Chiyoda-ku, Tokyo 100  
Japan  
Internet: <http://www.agc.co.jp>

*Chlorine Engineers Corp., Ltd.*  
First Sales Dept.  
Tomlokabashi Bldg.  
6-11, Fukagawa 2-chome,  
Koto-ku Tokyo 135  
Japan

## REFERENCES

[Akzo Nobel, 1998]

Akzo Nobel AB, S-445 80 Bohus, Sweden

Miljörapport 1998 (Annual Environmental Report 1998)

[Asahi Glass]

Asahi Glass Co. Ltd., Tokyo, Japan

Personal communication, Recent Progress of Flemion Membrane, 1998 and 1999

[Bayer Uerdingen, 1998]

Bayer, Uerdingen, Germany

Personal communication, plant visit 1998

[Beal, 1995]

M. G. Beal, Harriman Chemsult Ltd, London, UK

Chlor-alkali: the impact of Economic and Environmental Pressures on the Industry

Modern Chlor-alkali Technology vol. 6 -SCI, p. 1-12 (1995)

[Blomgren]

J. Blomgren, Akzo Nobel, S-445 80 Bohus, Sweden

Personal communication, plant visit 1998

[Brien-White, 1995]

F. O. Brien, I. F. White, Raytheon Engineers and Constructors, USA and UK

Process Engineering Aspects of Chlorine Cooling and Drying

Modern Chlor-Alkali Technology, Vol. 6-SCI, p. 70-81 (1995)

[Chemie Prod., May 2000]

Reportage: Eingriff am offenen Herzen (Open heart surgery)

Chemie Produktion, p. 120-121 (May 2000)

[Curlin]

C. Curlin, OxyTech Systems Inc., USA

Personal communication 1998

[Debelle]

J-P Debelle, Solvay SA, rue de Ransbeek 310, B-1120 Brussels, Belgium

Member of the Technical Working group

[de Flon, 1998]

R. de Flon, Borregaard Industries Ltd, P.O. Box 162, N-1701 Sarpsborg, Norway

Personal communication, plant visit 1998

[Denye et al., 1995]

M. Denye, F. E. Hancock, M. E. Fakley - ICI Katalco, UK

The Hydecatt Process-Fit and Forget Technology for Hypochlorite Destruction

Modern Chlor-Alkali Technology, Vol. 6-SCI, p. 251-257 (1995)

[Dibble-White, 1988]

G. J. Dibble, I. F. White – Badger Catalytic Ltd, UK

Practical Experience in Mercury and Diaphragm Cell Conversions to Membrane Technology

Paper presented at the 1988 London International Chlorine Symposium

Modern Chlor-Alkali Technology, Vol. 4, p. 291-305

[Dilmore-DuBois, 1995]

C. Dilmore, D. DuBois – PPG Industries, USA

PPG's Tephram<sup>TM</sup> Synthetic Diaphragm Circuit Conversion

Modern Chlor-Alkali Technology, Vol. 6-SCI, p. 133-139 (1995)

[Dutch report, 1998]

Ministry of Housing, Spatial Planning and the Environment, The Netherlands

Dutch Notes on BAT for the Chlor-alkali Industry, (Infomil, 1998)

[DuPont, 1998]

DuPont Nafion<sup>®</sup>, Global customer service, Fayetteville, USA

Fact sheets and personal communication, 1998

[EC, 1998]

EC, DG XI-D4

Process Agents – list updated 8 June 1998

[Euro Chlor]

Euro Chlor – The European Chlor-Alkali Industry Association

Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Tel: +32 2 676 7265, Fax: +32 2 676 7241, E-mail: eurochlor@cefic.be

[Euro Chlor Anal 3-7, 1998]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Précis of the Standardization of Methods for the Determination of Traces of Mercury

Anal 3-7, 2<sup>nd</sup> edition (1998)

[Euro Chlor Env. Prot. 3, 1999]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Decommissioning of Mercury Chlor-Alkali Plants

Env. Prot. 3, 2<sup>nd</sup> edition (February 1999)

[Euro Chlor Env. Prot. 5, 1999]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Measurement of Air Flow and Mercury in Cellroom Ventilation

Env. Prot. 5, 2<sup>nd</sup> edition (February 1999)

[Euro Chlor Env. Prot. 11, 1998]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Code of Practice - Mercury Housekeeping

Env. Prot. 11, 4<sup>th</sup> edition (September 1998)

[Euro Chlor Env. Prot. 12, 1998]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Guidelines for Making a Mercury Balance in a Chlorine Plant

Env. Prot. 12, 2<sup>nd</sup> edition (July 1998)

[Euro Chlor paper, 1998]

Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium

Conversion of Amalgam-Plants to Membrane Technology - Considerations for possible use of existing equipment

Paper written by Euro Chlor (February 1998)



[Euro Chlor report, 1997]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
Recommendations for a Best Available Techniques Reference Support Document. Chlorine Production by the Electrolysis of Brine (November 1997)  
A contribution from the European Chlorine Industry to assist the IPPC Process

[Florkiewicz, 1997]  
T. F. Florkiewicz, OxyTech Systems, USA  
Long Life Diaphragm Cell

[Florkiewicz-Curlin, 1991]  
T. F. Florkiewicz, L. C. Curlin - OxyTech Systems, USA  
Polyramix<sup>TM</sup> Diaphragm – A Commercial Reality  
Paper presented at London Symposium (June 1991)

[Foller et al, 1997]  
P.C. Foller, D. W. Dubois, J. Hutchins – PPG Industries Inc., USA  
PPG's Tephram<sup>®</sup> Diaphragm: The Adaptable Non-Asbestos Diaphragm  
Paper presented at the SCI 1997 London International Chlorine Symposium (June 1997)

[García Ara]  
L. García Ara, ANE, Paseo de Recoleta 27, E-28004 Madrid, Spain  
Member of the Technical Working group

[Gest 76/52, 1986]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
Equipment for the Treatment of Gaseous Effluents Containing Chlorine  
Gest 76/52, 9<sup>th</sup> edition (October 1986)

[Gest 76/55, 1990]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
Maximum Levels of Nitrogen Trichloride in Liquid Chlorine  
Gest 76/55, 9<sup>th</sup> edition (September 1990)

[Gest 87/130, 1996]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
Hazard Analysis for Chlorine Plants  
Gest 87/130, 7<sup>th</sup> edition (April 1996)

[Gest 92/169, 1994]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
Guidelines for the Safe Handling and Use of Chlorine  
Gest 92/169, 1<sup>st</sup> edition (October 1994)

[Gest 92/175, 1993]  
Euro Chlor, Avenue E. Van Nieuwenhuyse 4 Box 2, B-1160 Brussels, Belgium  
A Scheme for Safety Visits to Chlorine Customers' Plants  
Gest 92/175, 1<sup>st</sup> edition (May 1993)

[Gest 93/186, 1993]  
W. D. Müller, Bayer AG, Germany  
Chlorine, its Fabrication and Handling - General Technology Overview  
Gest 93/186, Third Euro Chlor Technical Seminar (December 1993)

[Gest 93/187, 1993]

S. Grunden, Euro Chlor Environmental Protection Group  
Good Mercury Housekeeping

Gest 93/187, Third Euro Chlor Technical Seminar (December 1993)

[Gestermann, 1998]

F. Gestermann, Bayer AG, Germany

Depolarized Cathodes in the Chlor-Alkali Electrolysis

Paper presented at the DeNora Symposium held in Venice, Italy, May 1998

[Gestermann-Ottaviani, 2000]

F. Gestermann, Bayer AG, Germany – A. Ottaviani, DeNora s.p.a. Italy

Chlorine Production with Oxygen Depolarized Cathodes in Industrial scale

Paper presented at the London International Chlorine Symposium in June 2000

[Grunden]

S. Grunden, Hydro Polymers AB, S-444 83 Stenungsund, Sweden

Personal communication, plant visit 1998

[Hollmann]

G. Hollmann, Dow Deutschland Inc., Stade (Germany)

Personal communication, fax dated 22 October 1998

[Hydro Polymers, 1998]

Hydro Polymers AB, S-444 83 Stenungsund, Sweden

Miljörapport 1998 (Annual Environmental Report 1998)

[Italian report, 1997]

Italian Notes on the BREF for the Chlor-Alkali Industry

Italian BAT reference document (February 1997)

[J. Loss Prev. Proc. Ind., March/94]

G. Purdy, M. Wasilewski – DNV Technica, UK

Risk Management Strategies for Chlorine Installations

Journal of Loss Prevention in the Process Industries, Vol. 7, No. 2, p. 147-156 (March 1994)

Special Issue: Problem Clouds II

[J. Ind. Ecology, 1997]

R. Ayres, INSEAD, Fontainebleau, France

The Life-Cycle of Chlorine, Part I - Chlorine Production and the Chlorine-Mercury Connection

Journal of Industrial Ecology, Vol. I, No. 1, p. 81-94 (1997)

Massachusetts Institute of Technology Press

[Jorlöv]

B-O Jorlöv, Hydro Polymers AB, S-444 83 Stenungsund, Sweden

Personal communication, 1998

[Kelly, 1998]

K. Kelly, ICI Katalco, UK

Personal communication, 1998

[Kirk-Othmer, 1991]

John Wiley & Sons, Inc.

Alkali and chlorine products, Chlorine and sodium hydroxide

Kirk-Othmer - Encyclopedia of Chemical Technology, 4th edition, Vol. 1, 938-1025 (1991)

[Kuntzburger et al, 1995]

F. Kuntzburger, D. Horbez, J. Bachot – Rhone Poluenc Recherches, Aubervilliers, France and J. M. Perineau - Rhone Poluenc Chimie, Le Pont de Claix, France  
New Developments in Microporous Diaphragm Built-in Precathode and Asbestos-Free Diaphragm  
Modern Chlor-Alkali Technology, Vol.6-SCI, p. 140-148 (1995)

[Kuntzburger et al, 1997]

F. Kuntzburger, D. Horbez, J. G. Le Helloco – Rhone Poluenc Recherches, Aubervilliers, France and J. M. Perineau - Rhone Poluenc Chimie, Le Pont de Claix, France  
New developments in built-in precathode diaphragm technology  
Paper presented at the London International Chlorine Symposium in June 1997

[Le Chlore, 1996]

Syndicat des Halogènes et Dérivés, 14 rue de la République, F-92909 Paris, France  
Le Chlore, 4<sup>th</sup> edition (October 1996)

[Lindley, 1997]

A. A. Lindley, ICI Chemicals & Polymers, UK  
An Economic and Environmental Analysis of the Chlor-Alkali Production Process  
Report prepared for the European Commission during a secondment to DG III C-4 (1997)

[Lott, 1995]

B. Lott, The Associated Octel company Ltd, UK  
Practical Experiences on the Conversion of Mercury Cells to membrane Technology  
Modern Chlor-Alkali Technology, Vol.6-SCI, p. 243-250 (1995)

[Mason, 1995]

J.W. Mason, Hays Chemical Distribution Ltd, UK  
Design aspects of loading and unloading systems which can mitigate or eliminate accidental chlorine release  
Modern Chlor-Alkali Technology, Vol. 6-SCI, p. 48-61 (1995)

[Müllmagazin, 1991]

G. Lutz, W. Otto, H. Schönberger  
Chlorproduktion in neuem Licht; Altlastenerfassung  
Müllmagazin, 4. Jhg, No. 3/1991, p. 55-60 (1991)

[OxyChem, 1992]

Occidental Chemical Corporation, USA  
Caustic Soda Handbook (1992)

[Perineau]

J. M. Perineau, Rhone Poluenc Chimie, France  
Personal communication, 1998

[Schindler]

I. Schindler, Umweltbundesamt, Federal Environment Agency (UBA), Austria  
Member of the Technical Working group

[Schubert]

H. Schubert, Bayer AG, Germany  
Member of the Technical Working group

[SEPA, 1997]

O. Alterå – Naturvårdsverket, Swedish Environmental Protection Agency

Ekonomisk konsekvensbeskrivning för övergång till kvicksilverfri klor-alkaliproduktion vid Eka Chemicals i Bohus. (Economic assessment of conversion to mercury free production of chlor-alkali at Eka Chemicals (today Akzo Nobel) in Bohus.)

Presented at the meeting of the National Licensing Board for Environment Protection (October 1997)

[SRI Consulting, 1997]

SRI Consulting

Competitive Situation of the Western European Chlor-Alkali Industry in a Global Context

An independent assessment prepared for Euro Chlor (April 1997)

[Stenhammar]

S. Stenhammar, Naturvårdsverket, Swedish Environmental Protection Agency

Member of the Technical Working group

[UBA (A), 1998]

Umweltbundesamt, Federal Environment Agency (UBA), Austria

BAT Reference Document Chlor-Alkali: Austrian Statement (December 1998)

[UBA (D), 1997]

D. Wunderlich, S. Richter – Umweltbundesamt, Federal Environment Agency (UBA) Germany

Chlorine production by chlor-alkali processes

BAT Background document (November 1997)

[UBA (D)-TNO report, 1997]

TNO Institute of Environmental Sciences, Energy Research and Process Innovation

The European Emission Inventory of Heavy Metals and Persistent Organic Pollutants for 1990

Sponsored by UBA (D) and TNO, UBA-FB UFOPLAN-Ref.No. 104.02 672/03 (1997)

[UK Guidance note, 1993]

HMIP, UK

Processes for the Manufacture of, or Which Use or Release Halogens, Mixed Halogen Compounds or Oxohalocompounds

Chief Inspector's Guidance to Inspectors, Process Guidance Note IPR 4/13 (1993)

[Ullmann's, 1996]

VCH Verlagsgesellschaft mbH, D-6940 Weinheim

Chlorine

Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 6, 399-481 (1996)

[UN/ECE 1985]

United Nations Economic Commission for Europe, Task Force

Guidelines for the control of emissions from the inorganic chemical industry (1985)

[USEPA, 1995]

United States Environmental Protection Agency

Profile of the Inorganic Chemical Industry

EPA 310-R-95-004 (September 1995)

[USEPA, 1998]

United States Environmental Protection Agency

Mercury Cell Emission Control Practices and Techniques Guidelines (May 1998)

[Wienkenhöver, 2000]

Dr. M. Wienkenhöver, Bayer AG, Germany

A letter written to the members of the Euro Chlor Management Committee regarding an update on the development of the oxygen depolarised cathode (16 June 2000)

[Wunderlich]

D. Wunderlich, Umweltbundesamt, Federal Environment Agency (UBA) Germany

Member of the Technical Working group

## GLOSSARY OF TERMS AND ABBREVIATIONS

### Abbreviations and units

AC	alternating current	ppb	parts per billion
ACkWh	kWh (alternating current)	ppm	parts per million
bar	bar (1 bar = 100 kPa, 1.013 bar = 1 atm)	ppmv	parts per million by volume
barg	bar gauge (bar + 1 atm)	PTFE	polytetrafluorethylene
billion	thousand million (10 <sup>9</sup> )	PVC	polyvinyl chloride
BOD	biochemical oxygen demand	Raney Nickel	surface activated form of nickel (alloys, metals) used as hydrogen donor
°C	degree Celsius	rectiformer	rectifier/transformer
CFC	chlorofluorocarbon	s	second
CHP	co-generation of heat and power	t	tonne (10 <sup>6</sup> gram)
COD	chemical oxygen demand	V	Volt
DC	direct current	VCM	vinyl chloride monomer
“dioxins”	PCDD/PCDF compounds	vol%	Percentage by volume
DSA	dimensionally stable anodes	W	Watt (1 W = 1 J/s)
EDC	ethylene dichloride	Ω	Ohm
EOCl	extractable chloroorganics		
EOP	end-of-pipe	<b>Substances</b>	
EOX	extractable organic halogens	Ba	Barium
g	gram	Br <sup>-</sup>	Bromide
HCFC	hydrochlorofluorocarbon	Br <sub>2</sub>	Bromine
h	hour	BrO <sub>3</sub> <sup>-</sup>	Bromate
I-TEQ	dioxin/furan toxicity equivalent	C	Carbon
J	Joule	Ca	Calcium
K	degree Kelvin (0 °C = 273.15 K)	CCl <sub>4</sub>	Carbon tetrachloride
kA	kilo Ampère	C <sub>2</sub> Cl <sub>4</sub>	Tetrachloroethylene
kg	kilogram	Cd	Cadmium
kPa	kilo Pascal	CH <sub>3</sub> Cl	Monochloromethane (Methyl chloride)
kWh	kilowatt-hour (1 kWh = 3.6 MJ)	CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane (Methylene chloride)
l	litre	CHCl <sub>3</sub>	Trichloromethane (Chloroform)
m	metre	C <sub>x</sub> H <sub>y</sub> X <sub>z</sub>	Halogenated hydrocarbons
mg	milligram	Cl <sup>-</sup>	Chloride
m <sup>2</sup>	square metre	Cl <sub>2</sub>	Chlorine
m <sup>3</sup>	cubic metre	ClO <sub>3</sub> <sup>-</sup>	Chlorate
mV	millivolts	CO <sub>2</sub>	Carbon dioxide
Nm <sup>3</sup>	Normalised m <sup>3</sup> (gas, 273 K, 101.3 kPa)	CO <sub>3</sub> <sup>2-</sup>	Carbonate
ODP	ozone depletion potential	Cr	Chromium
pa	per annum (per year)	Cu	Copper
PCDDs	polychlorinated dibenzodioxins	F	Fluorine
PCDFs	polychlorinated dibenzofurans	Fe	Iron
PI	process integrated	FeCl <sub>3</sub>	Ferric chloride
		H <sub>2</sub>	Hydrogen
		HCO <sub>3</sub> <sup>-</sup>	Bicarbonate
		HCl	Hydrochloric acid

---

## Substances, continued

Hg	Mercury
Hg <sub>2</sub> Cl <sub>2</sub>	Mercuric chloride (Calomel)
H <sub>2</sub> O	Water
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HS <sup>-</sup>	Bisulphide
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
K	Potassium
Mg	Magnesium
N <sub>2</sub>	Nitrogen
Na	Sodium
NCl <sub>3</sub>	Nitrogen trichloride
N <sub>2</sub> H <sub>2</sub>	Hydrazine
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium
NH <sub>x</sub> Br <sub>y</sub>	Brominated amines
Ni	Nickel
O <sub>2</sub>	Oxygen
OBr <sup>-</sup>	Hypobromite
OCl <sup>-</sup>	Hypochlorite
Pb	Lead
S <sub>2</sub> <sup>-</sup>	Sulphide
SiO <sub>2</sub>	Silicon dioxide
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Thiosulphate
SO <sub>2</sub>	Sulphur dioxide
SO <sub>3</sub> <sup>2-</sup>	Sulphite
SO <sub>4</sub> <sup>2-</sup>	Sulphate
Sr	Strontium
Ti	Titanium
V	Vanadium
W	Tungsten
Zn	Zinc

## Prefixes

p	pico	10 <sup>-12</sup>
n	nano	10 <sup>-9</sup>
μ	micro	10 <sup>-6</sup>
m	milli	10 <sup>-3</sup>
c	centi	10 <sup>-2</sup>
k	kilo	10 <sup>3</sup>
M	mega	10 <sup>6</sup>
G	giga	10 <sup>9</sup>
T	tera	10 <sup>12</sup>
P	peta	10 <sup>15</sup>