



EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

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

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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 (Cl₂) and alkali, sodium hydroxide (NaOH) or potassium hydroxide (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 (NaCl) as feed or to a lesser extent using potassium chloride (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/m³ 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/m³ in the case of partial liquefaction and less than 3 mg/m³ 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:

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- 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 (ClO_3^-) and bromate (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 1.2 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.