Euro Chlor
representing the chlor-alkali industry

GUIDELINE FOR THE

MINIMISATION OF MERCURY EMISSIONS AND WASTES

FROM MERCURY CHLOR-ALKALI PLANTS

Env. Prot. 13

2nd Edition

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Euro Chlor

Euro Chlor is the European federation which represents the producers of chlorine and its primary derivatives.

Euro Chlor is working to:

- improve awareness and understanding of the contribution that chlorine chemistry has made to the thousands of products, which have improved our health, nutrition, standard of living and quality of life;
- maintain open and timely dialogue with regulators, politicians, scientists, the media and other interested stakeholders in the debate on chlorine;
- ensure our industry contributes actively to any public, regulatory or scientific debate and provides balanced and objective science-based information to help answer questions about chlorine and its derivatives;
- promote the best safety, health and environmental practices in the manufacture, handling and use of chlor-alkali products in order to assist our members in achieving continuous improvements (*Responsible Care)*.

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Prior to 1990, Euro Chlor's technical activities took place under the name BITC (Bureau International Technique du Chlore). References to BITC documents may be assumed to be to Euro Chlor documents.

RESPONSIBLE CARE IN ACTION

Chlorine is essential in the chemical industry and consequently there is a need for chlorine to be produced, stored, transported and used. The chlorine industry has co-operated over many years to ensure the well-being of its employees, local communities and the wider environment. This document is one in a series which the European producers, acting through Euro Chlor, have drawn up to promote continuous improvement in the general standards of health, safety and the environment associated with chlorine manufacture in the spirit of *Responsible Care.*

The voluntary recommendations, techniques and standards presented in these documents are based on the experiences and best practices adopted by member companies of Euro Chlor at their date of issue. They can be taken into account in full or partly, whenever companies decide it individually, in the operation of existing processes and in the design of new installations. They are in no way intended as a substitute for the relevant national or international regulations which should be fully complied with.

It has been assumed in the preparation of these publications that the users will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance they have been prepared. The contents are based on the most authoritative information available at the time of writing and on good engineering, medical or technical practice but it is essential to take account of appropriate subsequent developments or legislation. As a result, the text may be modified in the future to incorporate evolution of these and other factors.

This edition of the document has been drawn up by the Environmental Protection Working Group to whom all suggestions concerning possible revision should be addressed through the offices of Euro Chlor.

Summary of the Main Modifications in this version

Section	Nature
All	Merge with Env. Prot. 10 (will be deleted)
2.1.	Paragraph rewritten by INEOS
2.2.	Addition of other sulphur compounds for precipitation
3.1.	Addition of electrochemical and biochemical reduction techniques
3.5.	Addition of scrubbing with chlorinated brine for chlorine coming directly from the cells and sent to hypo production
3.5.	Mercury content in hypo corrected according to the study done for the hypo risk assessment

TABLE OF CONTENTS

TABLE OF FIGURES

INTERPRETATION OF THIS GUIDELINE

This document presents a statement of the Best Available Techniques for chlorine production plants using the amalgam chlor-alkali electrolysis process, in relation to mercury emissions to air, to water and in products. It includes also information on the handling of solid wastes coming from normal operation (but not mercury containing construction waste or rubber coatings), and has been based on the practices of existing plants whose current performance provides the best examples of mercury emission control. However it must be interpreted on the basis of several important principles contained within the IPPC Directive and the associated Reference Document.

1. The Directive recognises that consideration of Best Available Techniques must include not only technology, i.e. equipment and processes, but also the procedures for operation and maintenance of the plant. Both have been considered.

2. The Directive recognises that Best Available Techniques have to be established in the context of individual plants, since there will be variations in the technology used within an industry.

3. The Directive recognises the need for plants to comply with any Water Quality Objectives or other environmental quality standards, or with any emission standards set by local regulation.

This document has been written to provide guidelines for the performance that can be achieved in each emission category expressed primarily as grams of mercury per tonne of chlorine capacity. Whilst some flexibility may be needed within an individual category, the guidelines lead to a maximum level of total mercury emission from all categories that are applicable to all plants. The guidelines are intended to represent the emission performance that will be achieved over the course of the year. They are not intended to be an instantaneous standard of performance which will be achieved by employing a particular technique, because there will be some variation depending on, for example work load of the plant or weather conditions, equipment being under maintenance, etc. The quoted value is the maximum level of total mercury emission, achieved over the year if the techniques are applied as described.

All Euro Chlor members have accepted the standard defined by this maximum level of mercury emission and will work to achieve it, within the framework of their national and local regulations. In some cases this may require substantial investment and time before the improvements have been made in all plants; this is consistent with Article 5 of the IPPC Directive. Since the Directive recognises BAT as being plant-specific, there may be technical or economic constraints on the improvements possible at some individual plants, but the maximum level of total mercury emission is seen to be achievable on the stated time scale.

The Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry, adopted in December 2001 by the European Commission, provides further guidance on techniques and quotes guideline values for emissions on the basis that the best techniques can be applied in all circumstances.

Remark

Some other electrolysis processes use mercury (production of alkoxides, dithionites, sodium and potassium metals …) but, as they are not a lot of such units in Europe, this guideline is not intended to cover them. They have the same environmental objective to minimise the mercury emissions and apply, when possible, the here described methods, but they also use specific ones.

1. INTRODUCTION

In the electrolysis of brine for the production of chlorine, hydrogen and caustic soda (or caustic potash and some other specialty products like alkoxides …) by the mercury process, the mercury is in intimate contact with the raw materials and some of the final products. It is thus inevitable that the untreated process streams contain mercury. A key element, therefore, of operating this technology is to apply techniques that minimise any contamination in the final discharged streams and that, wherever possible, the mercury removed is recycled within the process. The purpose of this document is to describe these techniques.

2. GENERAL INFORMATION

Due to the process characteristics, mercury can be emitted from the process through air, water and in the products; solid waste sent to safe deposits can also contain some mercury.

2.1. Gaseous Streams

Hydrogen and process exhaust streams are generally cooled and then treated in operations involving absorption or reaction of the mercury (for example calomel formation in a washing column, fixation on copper or carbon impregnated with sulphur iodine or silver). For some of these operations the mercury emerges in a liquid stream, which may be recycled to the brine system or treated as in paragraph 2.2. For other operations the mercury emerges in a solids stream, which may be treated as in paragraph 2.3.

Chlorine emerging from the cells contains very little mercury; the normal processes of gas cooling and washing then remove the mercury down to insignificant concentrations. The mercury emerges from these operations in a liquid stream, which may be recycled to the brine system or treated as in paragraph 2.2.

2.2. Liquid Streams

Mercury in liquid effluent streams can be removed by the following processes:

- Precipitation of mercury sulphide which is then filtered; the precipitate can be dissolved (solution containing active chlorine) and recycled in the brine loop, or treated as solid waste. The use of thiourea or special mercury binders like trimercaptotriazine is also possible.
- Absorption on ion exchange resins; the regeneration of those resins gives a mercury concentrated liquid that can be recycled in the brine.
- Treatment by a reducing agent in order to precipitate metallic mercury that is filtered and recycled.

The caustic solution produced, is purified from mercury by passage on active carbon, giving rise to solid waste.

Sometimes, the treated liquid stream is further ‘polished’ by filters. This can give rise to additional solid waste.

2.3. Other Sources of Mercury Emissions

Mercury emissions in the air are influenced by the basic design of the cell room, the area of the cells, the leak tightness, the type of decomposers, the accessibility of the cells and the construction materials. These emissions are also influenced by the use of operating and maintenance techniques which minimise the possibility of mercury emission.

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, especially for older cell rooms.

Some accidental mercury spillage can occur during operations involving cells or decomposers, such as opening the cells for anode changing or cleaning, assembling or dismantling equipment, or replacing defective pipes, and cause supplementary emissions in the cell room.