Euro Chlor
representing the chlor-alkali industry

Decommissioning of Mercury Chlor-Alkali Plants

Env Prot 3

4th Edition

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EURO CHLOR PUBLICATION

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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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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 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 should be taken into account 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
1	In the first paragraph a comment was added on the fate of the building
2	Regional aspects are taken into account
3.1	Rephrasing of the first sentence (information of authorities)
3.2	Rephrasing of the last sentence A new concrete floor-layer should be considered.
3.4	Reference to asbestos was deleted
3.6	Rephrasing of the last paragraph (competence of the landfill company)
3.7	The last dot was added (washing of mercury)
4	New section (Speciation of Mercury)
5	The first two sentences were added (materials from dismantling are the same as those treated during normal operation)
5	The second paragraph was moved from the section 5.1 (water)
5.2	This section (Available Techniques) was added
5.3.2.1	The third paragraph of this section was changed: treating with HCl/Cl_2 was replaced by HCl then hypo)
5.3.2.2	Reorganisation of the first dot
6	The last sentence dealing with cleaning of trucks was added
7	Second paragraph: landfill is possible only if leaching conditions are satisfied
8.7	Atomic fluorescence was a technique added for determination of mercury.
9	A comment was added: analysis of mercury should also be carried on locations where mercury contaminated materials are handled
Appendix 1	Modification of the title (clarification)
Appendix 3	This appendix was added: recovery of mercury: possible treatment

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Summary

Many chlor-alkali cell rooms using mercury cell technology will be shut down over the next few decades. This paper has been drawn up as a reference document for Euro Chlor members on the best tried techniques for health, safety and environment protection during all stages of plant shut down of from initial decontamination materials through to final disposal.

It is based on the experience of member companies in shutting down more than 40 cell rooms in the last 15 years.

1. INTRODUCTION

At the present time there are about 60 chlorine cell rooms using mercury cell technology in Europe. The majority of these will be shut down and the equipment demolished. According to the local situation the building itself should be demolished or reused. As a result, thousands of tons of mercury contaminated materials will have to be reworked or disposed of in an environmentally satisfactory way.

The European chlorine producers grouped within Euro Chlor who have already faced this problem and in the spirit of collaboration that characterises their organisation have pooled their experience in this regard.

This document contains guidelines for the shut down and decommissioning of mercury cells plants and has been drawn up on the basis of the operations that have proved to be of value over the last 15 years during which a number of cell rooms have been shut down. The list of these cell rooms is given in APPENDIX 1 - SITES WITH EXPERIENCE OF SHUTTING DOWN MERCURY CELL ROOMS.

2. LEGISLATION

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:

Examples are:

- 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.

At the European level, several Directives have already been approved or are in preparation.
It should be noted that European Directives do not directly apply at local level but contain provisions that must be transposed into national and regional legislation. It is perfectly possible for any Member State to enforce stricter obligations and it is therefore essential to have a full understanding of the relevant national/regional requirements. Nonetheless, examination of European Directives provides a view on the general framework and common provisions which currently or shortly will apply in each country or region.

In particular, in dealing with mercury-containing wastes, the following common features apply:

- Mercury-containing wastes above a threshold concentration (3% in EU; may be lower in individual countries) are classified "hazardous".

- Hazardous and non-hazardous waste should be separated as far as possible. In particular, hazardous and non-hazardous wastes should not be mixed.
- Limitations and obligations apply to transfrontier movements of wastes, especially of hazardous wastes.
- Wastes sent to disposal have to fulfil acceptance conditions (fixed at national/regional level).

3. PROJECT MANAGEMENT

Before proceeding with closure it is strongly recommended that a small task force is 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 authorities before obtaining formal approval for it. It is vital that this team contains personnel from the chlor-alkali management of the site. If used contractors should be involved in this procedure as soon as appointed.

Project planning should be framed around the following procedures:

3.1. Contact with Authorities

The authorities should be informed as soon as possible on environmental, safety and health aspects of the project after the decision to decommission. For certain wastes the authority may require standardised testing to justify any disposal option. It is recommended that all aspects of decommissioning are formalised prior to project approval. The main aspects are described in the following points.

3.2. Options for Re-use of Buildings

An early decision is required on the future use of the buildings, i.e. whether to demolish or reuse.

If the building is to be re-used, then it must be decontaminated so that there is no residual hygiene problem. Experience has shown that this can be achieved by cleaning the walls, then coating or painting to give an impermeable surface. A new concrete floor-layer should be considered.

3.3. Options of Re-use of Materials and Equipment

Equipment in good condition, such as anodes, cell components, covers, pumps, etc. can be stored and eventually re-used as spares in existing plants.
Other materials, for example steel structures, can be recycled as raw materials after any necessary decontamination.

3.4. Decontamination

All chemicals must be removed, with special attention paid to those which contain mercury. When this has been done all metallic mercury must be removed as far as practicable. Several possible techniques can be considered for decontamination: on site or external retorting, and water or chemical cleaning, for example. Frequently, a combination of these will be required. This topic is covered in detail in section 5.

3.5. Demolition

Before demolition starts, a survey of all plants, buildings and associated equipment to be demolished should be carried out. The purpose of the survey is to assess in advance the total volumes and weights of the various parts of the plant to be dismantled and their respective mercury contamination. This information is essential both for internal planning and for discussions with the authorities on the various methods of disposal and/or treatment.

Experience has shown that, if the concrete is in good condition, contamination is limited to the surface layer. However this should be confirmed by analysis.

3.6. Disposal

If landfill is to be used for disposal the overall mercury content must be reduced to a level compatible with local regulations. To achieve this, heavily contaminated materials must be removed first. In the case of a building, it should first be cleaned and decontaminated. It should then be possible to knock down the whole building and dispose of it without waste segregation.

Segregation of demolition rubble into different ranges of mercury contamination is, in most cases, unrealistic and should not be attempted.

Mercury contaminated materials are classed as controlled waste and a duty of care is imposed by law on all procedures for their disposal.

Some specially designed landfills may accept high mercury content wastes if the necessary permit can be obtained.

Any landfill company must be competent to handle mercury wastes and will have to demonstrate that they can comply with the relevant water pollution and soil protection legislation.

3.7. Other Considerations

The project management team should also consider issues such as:

- Waste water containment and treatment.
- Handling of large quantities of mercury arising from draining the cells and the provision of associated equipment to undertake this task (possibly crane, storage vessels, system to fill flasks).
- The provision of written procedures for all decontamination and demolition operations.
- Training and protection of personnel, particularly in health and hygiene standards for handling mercury. If the dismantling of the plant is to be handed over to a contractor, provisions for safety and health should be even more detailed and stringent.
- Tracing, emptying and sealing of drainage systems.
- Development of systems for tracking mercury recoveries.
- Washing of mercury from the cell loop to remove residual sodium (hydrogen risk).

4. SPECIATION OF MERCURY

4.1. Metallic Mercury

During dismantling most contaminated pieces are contaminated with metallic mercury. The big amounts should be recovered by decantation or vacuum cleaner with appropriate adsorption/condensation system.

In the case of mercury trapped in non easily accessible areas techniques such as retorting or chemical oxidation may be used.

Metallic mercury is essentially present in:

- All components of the cells
- The washing water system for headers and footers
- The degassing system for headers and footers
- The caustic soda system
- The hydrogen pipes and equipments
- The maintenance area of cells and auxiliary equipment
- The retorting area

4.2. Solid Mercury

The main compound is HgO which is essentially located in the demisters of chemical treatment columns. This red product has to be dissolved with an acidic reagent.

4.3. Dissolved Mercury

The dissolved mercury is essentially present in the brine as a complex: $[HgCl_4]^{2-}$. It is easily recoverable in a demercurisation unit for liquids by precipitation as HgS or Hg or by treatment in an ion exchange unit.

Dissolved mercury is essentially present in:

- The brine loop
- The washing water for headers and footers
- The condensed water from the collecting gaseous system for headers and footers
- The condensed water of the hydrogen net
- The condensed water of the retort.

5. DECONTAMINATION

Materials from dismantling are the same as those treated during normal operation of a running plant. The only differences are due to the fact that the amounts to be treated are bigger. During the decontamination and clean up phase it is highly recommended that some of the staff experienced in running the plant are retained. If other personal who are not experienced in mercury handling are to be used, a detailed training and supervision program will be necessary. Medical supervision must continue through all stages of the project.

Water used during the dismantling and decontamination procedures must be treated for mercury removal before being released. The treatment system should remain in operation until all work is finished and the mercury content in waste water complies with statutory requirements.

All decontamination methods should be tested for efficacy in each application before use.

It is usually possible to categorise materials according to the level of mercury content as indicated in APPENDIX 2 - TYPE OF MATERIAL.

The following actions are recommended:

5.1. Preliminary Measures

An analysis programme should be set up. Only experienced personnel should be used to undertake mercury analyses. The project team must identify all measures to minimise the exposure of personnel to mercury and to avoid increased mercury emissions to atmosphere.

A decontamination pad with effluent control and treatment as well as air monitoring should be made available.

Before dismantling, cells should be emptied and washed out with an alkali peroxide solution.
Due to the potential risk of mercury sweating out from certain materials such as steel, a special area should be allocated for their temporary storage during treatment in order to avoid soil contamination. Once some cells have been removed, the cell room floor can be used for this purpose since it should be impermeable and connected to mercury drains.

In order to reduce exposure of the demolition workers to mercury vapour, it is desirable to replace hot cutting by cold cutting techniques where practicable. If used, hot cutting must be confined to a clearly defined area fitted with suitable ventilation to reduce mercury exposure. The operators must wear appropriate protection.
Retorting of waste for mercury recovery is a well-established technique. Contractors with mobile retorts or fixed retorts on their own premises can be used where there is no on-site retort.

5.2. Available Techniques

See **APPENDIX 3 - RECOVERY OF MERCURY: Possible Treatment**

5.2.1. Mechanical and Physical Treatment

This kind of treatment is suitable if significant quantities of metallic mercury are present.

Such treatments are water washing, ultrasonic technique and vacuum cleaner with appropriate adsorption/condensation system.

Care must be taken not to release mercury to the atmosphere. The final solid residue is land-filled or stored underground (mines).

5.2.2. Treatment with Hydrogen Peroxide (H2O2)

In alkaline conditions H_2O_2 is a reducing reagent. In contact with fine particles it decomposes with a very positive mechanical effect due to the production of gaseous oxygen.

It is recommended to take care of the specific requirements linked to environmental protection and safety aspects regarding the use of such a peroxide product.

5.2.3. Treatment with Hypo

Hypo dissolves metallic mercury, but the reaction is slow due to the fact that the reaction is a superficial one. By dissolving mercury iron is also dissolved. Dissolved iron reduces the efficiency of an ion exchange unit.

5.2.4. Precipitation of HgS

By adding of sulphide, ionic mercury is precipitated as mercuric sulphide. The solid sulphide is filtered from the waste water in sand, candle, or plate filters and may be then

- Either discharged as stabilised mercury sulphide in a secure landfill
- or treated thermally with air for recovering Hg.

5.2.5. Distillation or Retorting

Distillation or retorting is carried out in specially designed units. The mercury is recovered as metallic mercury. Special attention should be given to the treatment of the exhaust gases from these units. They should be treated in a two steps process. The solid residue is land-filled or stored underground (mines).

5.2.6. Ion exchange to Remove Mercury from Solution

Depending on the type of resin used, regeneration with hydrochloric acid gives a mercury-containing liquor to treated.

5.3. Decontamination of Materials and Equipment

On dismantling the parts should be transferred in plastic bags for storage and handling on the decontamination pad.

5.3.1. Non-Mercury Contaminated Materials

Usually materials and equipment that have only been in contact with caustic soda (after demercurisation) and chlorine are mercury free. The same situation can apply to certain pieces of equipment from the brine circuit. Their disposal requires cleaning appropriate to the chemicals handled and should not be mixed with mercury-contaminated material.

5.3.2. Materials in Contact with Mercury or Mercury Containing Products

For the design of the decontamination techniques, it is essential to ascertain the location of the mercury, its chemical state and its concentration for each category of material.

5.3.2.1. Non Coated Metallic Materials

Mercury adsorbed on the surface of metallic materials is mainly in the metallic form. Repeated cleaning with a high pressure water (taking precautions against mercury dispersion) eliminates the adsorbed mercury, and enables these materials to be recycled.

In some cases steel can be highly contaminated with mercury. On storage, such mercury can sweat out of the steel, able to cause serious problems. The steel should be cleaned until the level of mercury does not exceed a value agreed by the Authorities, typically 25 mg/kg. No visible mercury should be present. This scrap is then usually acceptable as uncontaminated material for recycling by smelting.

Steel components can be retorted or decontaminated by treating the surface with HCl then hypo or $NaOH/H_2O_2$ solution. An efficient method to clean mild-steel and mild-steel rubber lined pipe-work is washing with water containing detergents or hydrochloric acid containing from 0.01 to 0.5% chlorine.

Copper is generally contaminated with Hg to only a very small extent. The copper surface gains, if not coated, a protective layer of copper-chloride caused by exposure to small amounts of chlorine in the cell-room atmosphere. As a consequence copper is slightly contaminated at the surface only so after washing it is acceptable to sell it to the copper refining industry.

This treatment is also applied to the connections or bus – bars, be they made of aluminium or copper. Nevertheless, for flexible connections made of several copper sheets, this treatment is not sufficient. These pieces need to be treated in a mercury distillation oven.

In all cases, mercury must be recovered from the treatment solutions.

5.3.2.2. Coated Metallic Materials

Generally these materials will contain mercury, especially if the coating is in bad condition e.g. cracks or bubbles. The coating has to be separated from these materials.
There are several techniques to remove the coatings:

- Softening and scraping, warm sand blasting in a fluidised bed or pyrolysis in a furnace.
- Cryogenic treatment, resulting in mechanical separation due to the thermal shock obtained by vaporisation of liquid nitrogen.
- Rubber-lined steel can be washed, then compressed in a steel-press and cut into small parts. Rubber and steel are separated in this way and the steel is subsequently collected by a magnetic crane. The steel needs then to be washed. All rubber must be removed. The rubber-material can be deposited as chemical waste.

The burning of ebonite/rubber lined components must be avoided to prevent air pollution.

5.3.2.3. Graphite and Carbon Powder

The graphite from decomposers together with the carbon powder used as pre-coat for demercurisation of caustic soda and treatment of gases are washed, the mercury immobilised if necessary and placed in landfills after verification of decontamination.

Alternative options are mercury distillation in a furnace with gas blanketing (except for iodine activated carbon) and chemical treatment with chlorinated brine.

5.3.2.4. Sludges and Wet Residues

Sludges from storage tanks and sumps are often rich in mercury and can be easily retorted. If the mercury content is low, an alternative is immobilisation followed by landfill.

5.3.2.5. Organic Materials

Plastic materials can be washed with water or, if necessary, with an oxidising solution and then disposed of by standard methods.

Plastics such as PVC, PP etc. and reinforced plastics can be washed with a high pressure water jet in locations such as a closed cabin where metallic mercury will not be dispersed.

The effectiveness of water washing in baths can be improved by the addition of detergents or hydrochloric acid containing chlorine.

5.3.2.6. Construction Materials

Decontamination of construction materials such as bricks, concrete, asphalt or subfloor materials can be done on water-washed vibrating screens or alternatively with ultrasonic cleaning.

5.3.2.7. Miscellaneous Materials

Retorting can produce mercury residues of less then 100 mg/kg. If local legislation allows, this may be disposed of to landfill.

Retorting of sulphur containing materials such as carbon and mercury sulphide sludges can be done effectively by adding quicklime (calcium oxide).

After all the equipment has been removed, the walls and ceilings of the building should be washed with water under pressure.

6. TRANSPORT AND STORAGE OF MATERIALS

Components should be removed from cells by defined procedures using suitable trays and watertight bags or sheets to contain mercury spillages and to minimise loss to the environment. Local storage areas are desirable which are suitably bunded and drained to allow recovery of mercury from the aqueous effluent. Dedicated containers such as leak-tight skips transportable by fork lift trucks can be employed for local storage, while for some materials strong plastic bags are useful and can be suitably colour-coded to indicate content or source of material. The legal requirements for labelling waste are defined by EU Directive 91/689.

Transport of the materials should be done in watertight bags and in leak-tight vehicles or trailers. In the case of cell-room demolition, it is often possible to adapt propriety vehicles for this purpose. Techniques for cutting up large items such as steel baseplates can be used to make transport easier. If earth moving trucks are used, they have to be frequently cleaned, including tires to avoid export of mercury pollution.

7. DISPOSAL

The quantities and types of all materials to be disposed of must be identified before the unit is shutdown. All mercury contaminated materials must be decontaminated as far as reasonably practicable. If the average mercury concentration in the decontaminated materials is less than 100 mg/kg it may be possible to send it to landfill depending on national and/or local regulations.

If the mercury content of the material exceeds 100 mg/kg, it may still be possible to landfill if leaching conditions are satisfied or if mercury is immobilised.

The base, walls and final cover of a sealed landfill site or containment site must be constructed of an impermeable material such as clay.

Anhydrite (anhydrous calcium sulphate), which is tipped as a dry powder and then reacts with water to produce a concrete-like form of gypsum or equivalent material, is suitable for immobilisation of mercury. Appropriate mercury monitoring should be carried out on landfill sites.

Deposition in an underground salt mine is a good environmental solution for asphalt, cell sealant (layer on concrete) and other similar solid materials which are highly contaminated.

8. ANALYSIS FOR MERCURY

8.1. Introduction

When mercury cell brine electrolysis plants are decommissioned and demolished there are many types of materials involved, the majority being inorganic in nature such as metal, brick and concrete, but also including some organic type materials such as plastic, rubber and wood. A large proportion of these materials will, to varying degrees, be contaminated with mercury from part per million and sub parts per million levels to, in a few instances, percentage levels. Before any of these materials can be disposed of, by landfill or incineration, the level of mercury content in each source of material has to be determined. Unfortunately, as well as the wide range of types of materials involved, the nature of the mercury contamination can also vary widely, from purely surface contamination to complete penetration of the mercury into the bulk of the material. From a true analytical standpoint therefore, the data generated is extremely sample dependent and these factors have to be taken into account both when the initial analytical requests are discussed and also in the interpretation of the final analytical data generated.

8.2. Sampling

A wide range of mercury concentrations will be encountered during any sampling exercises involving these types of material. In order to minimise cross-contamination of the samples, and thereby minimise errors, it is important that scrupulously clean sampling equipment and sample containers are used for each individual sample and sample storage.

8.3. Metals

All types of metals, (plates, girders or pipework), can be sampled either by cutting, sawing or drilling. Unfortunately all of these procedures generate high levels of heat during the sampling process which, if not controlled, can lead to loss of mercury from the sample due to volatilisation. Consequently, it is recommended that only the initial (large) sampling be carried out in situ or on site and the analytical sampling subsequently performed in the laboratory where the necessary cooling precautions, water cooling, freezing etc., can be taken.

Slow drilling of water-cooled samples is currently the best technique to obtain analytical samples. This operation be carried out very slowly, thereby generating little heat, and the analytical sample produced is in the form of easily dissolvable metal turnings.

If a profile of the mercury contamination through the thickness of the original metal is required, samples of the turnings can be taken at prescribed depths of the metal.

Portable XRF apparatus is a useful monitoring tool.

8.4. Bricks. Mortar and Concrete

Initial sampling of these types of materials can be performed simply with a hammer and chisel but a more controlled procedure is to use a drill, (preferably water cooled), to obtain core samples. After drying at ambient temperature portions of these samples can then be ground to a coarse powder, again being careful not to generate too much heat during the grinding. The analytical (test) samples can be obtained from these coarse powders by taking appropriately sized portions, usually about l g.

8.5. Plastic. Rubber & Wood

Initial sampling of these types of material can be carried out either by cutting, (knife, shears etc.) or sawing. Shavings or drillings of these initial samples can be used to obtain appropriate analytical (test) samples, again these operations are best carried out under laboratory conditions.

8.6. Sample Preparation

8.6.1. Metals

The sample preparation of metal samples will depend on the type of samples available for analysis, (flat pieces, drillings, pipe, etc.), and the information required, (surface or bulk analysis).

Where the sample consists of very small pieces or metal drillings an appropriate weight can be totally dissolved using either aqua regia, or potassium permanganate solution mixed with sulphuric acid or nitric acid..

General details of this type of sample dissolution are described in Reference 1 [1].

When the sample consists of larger pieces of metal or when only surface contamination is required and it is inappropriate to dissolve the whole of the sample, a regime must be employed which both removes (dissolves) the mercury contamination and also gives some idea of the amount of associated metal, e.g. measurement of the dissolved iron would give some indication of the amount of iron removed during the mercury dissolution. Accordingly, the metal should have several sequential short periods of time immersed in acid and each extract individually measured for both mercury and iron.

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[1] Analytical Chimica Acta, **72** (1974) 37-48
Standardisation of Methods for the Determination of Traces of Mercury.
Part 1 - Determination of Total Inorganic Mercury in Inorganic Samples.

8.6.2. Bricks, Mortar & Concrete

A suitable portion of the ground sample is digested in acid (aqua regia, or potassium permanganate solution mixed with sulphuric acid or nitric acid) and an aliquot of this solution used for the measurement of mercury

8.6.3. Plastic, Rubber & Wood

Samples of material types containing organic matter must be subjected to complete oxidative decomposition in order to enable the total mercury content to be determined. This can be achieved using the techniques [2] described which include wet oxidation under reflux with nitric and sulphuric acids and digestion with nitric acid in a PTFE lined pressure digestion bomb.

8.7. Analytical Measurement

After dissolution of the sample, the mercury concentration is measured by flameless atomic absorption spectrometry as described in References. 1 & 2. (See section 8.6.2 and 8.6.3).

(Where available, inductively coupled plasma - either optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) - may be used instead of flameless atomic absorption spectrometry.).

Atomic fluorescence may also be used for determination of mercury.

See Euro Chlor document ***Anal 3-7 - Standardization of Methods for the Determination of Mercury Traces***

9. HEALTH AND SAFETY

Where the work is to be carried out by contractors, training in mercury hygiene is essential. Responsibilities for disposal of contaminated materials and for meeting health, safety and environmental standards must also be defined when work is carried out by contractors.

No eating, drinking or smoking should be allowed inside the workplace except within designated areas. Smoking materials and food should not be carried in working clothes because of potential contamination. No working clothes or plant footwear should be worn in eating areas. Provision of clean/dirty facilities should be made.

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2. Analytical Chimica Acta, **84** (1976) 231-257
Standardisation of Methods of the Determination of Traces of Mercury.
Part 2 - Determination of Total Mercury in Materials Containing Organic Matter.

During the demolition programme the importance of hygiene must be continually emphasised to all the work force by the supervisors and managers involved. Regular analyses of Hg in the atmosphere of the cell-room and locations where mercury contaminated materials are handled should be carried out at all stages of the project. All personnel handling contaminated materials should have medical health surveillance (urine checks) through all stages of the project. A strict mask cleaning system needs to be established. Specific laundry standards should be set with particular care taken to avoid cross-contamination with non-mercury clothing. Laundry wash water should be treated as mercury-contaminated.

9.1. Medical Examination before Start-up of the Demolition

A medical examination should be performed prior to employment. Besides the usual examinations and tests applied in the general pre-employment medical examinations, special attention should be given to:

1. Analysis of urinary mercury.
2. Previous history or clinical signs of renal insufficiency, neurological or psychiatric disturbances, liver disease, alcohol or drug abuse.

Any current or previous serious disease, especially if relevant to the conditions listed under (2) should exclude an employee from employment where he or she could be exposed to mercury.

9.2. Periodic Biological Monitoring

The concentration of mercury in urine of personnel involved with demolition must be carefully monitored. The frequency should be higher than during production

Weekly measurements for personnel working in the cell-rooms or handling contaminated waste.
Monthly measurements for personnel working in other areas.

9.3. Action Levels

When an individual value is below 50 µg/g creatinine there is no suggested action unless there has been a rapid increase in the value.
When an individual value is between 51 - 100 µg/g creatinine, there should be a review of individual employee work practices and use of personal protective equipment should be instituted.
When an individual value exceeds 100 µg/g creatinine the employee should be removed from exposure to mercury until tests for mercury urine are below 75 µg/g creatinine confirmed by a second sample taken during the next work period.
The Medical Advisor may recommend the removal of a worker from further exposure to mercury, on medical grounds, independent of mercury in urine levels.

9.4. Final Medical Examinations

These should be carried out at the end of demolition work for any individual, whose urinal concentration of mercury within the periodical biological monitoring programme exceeded the warning level of 75 µg/g creatinine.

10. REFERENCES

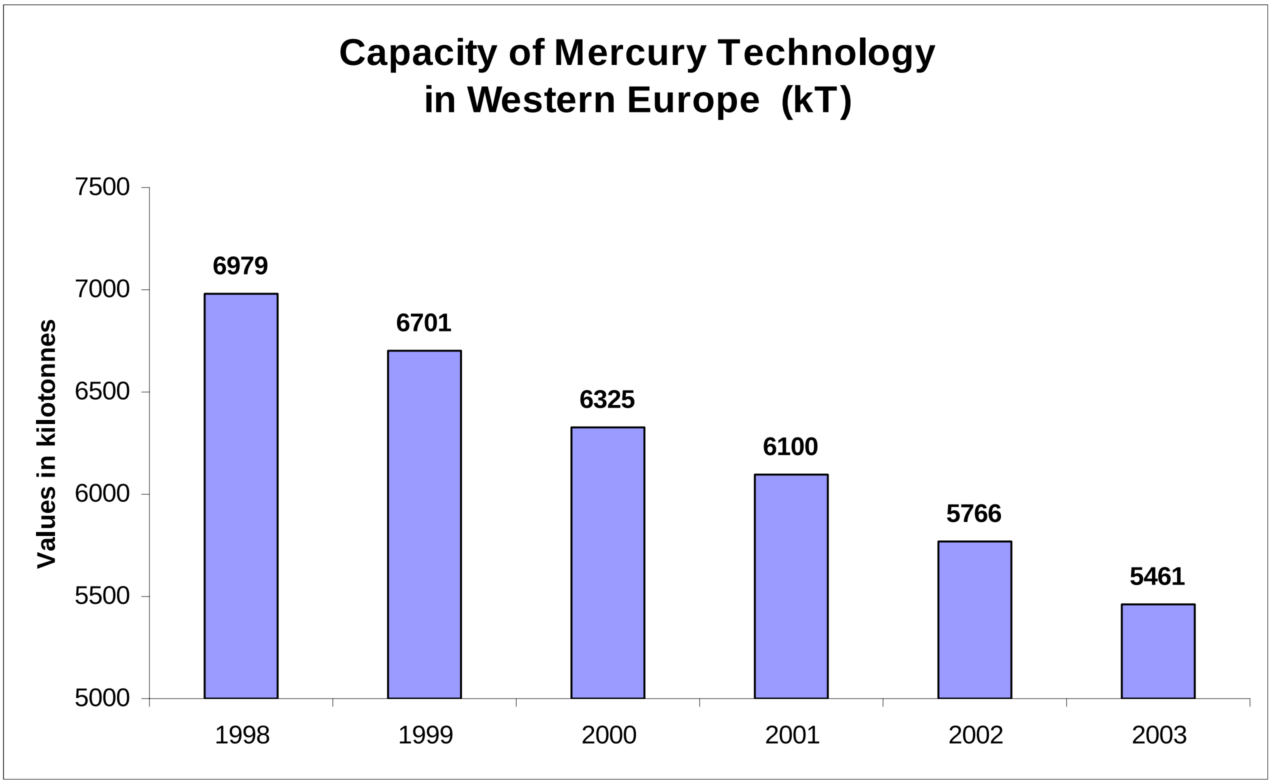
HEALTH 2 - Code of Practice: Control of Worker Exposure to Mercury in the Chlor-Alkali Industry

APPENDIX 1 - SITES WITH EXPERIENCE OF SHUTTING DOWN MERCURY CELL ROOMS

Country	Site	Company
AUSTRIA	Hallein	Solvay
BELGIUM	Jemeppe	Solvay
DENMARK	Copenhagen	DS Industries
FINLAND	Äetsä	Finnish Chemicals
FRANCE	Jarrie	Elf-Atochem
	Tavaux	Solvay
GERMANY	Frankfur	Hoechst
	Ludwigshafen	BASF
	Dormagen	Bayer
	Leverkusen	Bayer
	Uerdingen	Bayer
	Gerstofen	Clariant
	Marl	Hüls
	Rheinfelden	Hüls
	Schkopau	Nord BSL
	Bitterfeld	BVV Chemie
	Burghausen	Wacker Chemie
ITALY	Brescia	Caffaro
	Mantova	Enichem
	Gela	Enichem
	Tavazzano	Solvay
	Porto Torres	EniChem
NORWAY	Heroya	Norsk Hydro
	Opsund	Borregaard
PORTUGAL	Povoa	Solvay
	Estarreja	Uniteca
SPAIN	Torrelavega	Solvay
	Hernani	Electroquimica de Hernani
SWEDEN	Korsnäs	Diacell
	Skutskär	Stora
	Timra	SCA
	Domsjö	SCA-MoDo
	Skoghall	Billerud
THE NETHERLANDS	Delfzijl	Akzo Nobel
	Rotterdam	Akzo Nobel
	Linne Herten	Solvay
UK	Wilton	ICI
	Billingham	ICI
	Runcorn	ICI
	Hillhouse	ICI
	Baglan Bay	BP Chemicals
	Ellesmere Port	Associated Octel

*On some sites mercury capacities are still running

The decreasing of capacities of mercury technology in Western Europe since 1998 is shown in the following chart:



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APPENDIX 2 - TYPE OF MATERIAL

Material	Typical Mercury Content % w/w	Physical state
Sludges from storage tanks and sumps	10 - 30	wet solid
Sludges from settling catch pits, drains etc.	2 - 80	wet solid
Sulphurised or iodised charcoal from hydrogen purification	10 - 20	dry solid
Carbon from caustic filters	up to 40	dry solid
Graphite from decomposers	2	porous solid
Rubber/packing	variable	variable
Brick work/concrete	0,01-0,1	variable
Retort residues	< 0,1 - 0,1	dry porous solid
Ebonite-lined cell components : ➢ anode covers ➢ end boxes ➢ side walls ➢ pipe work	variable	non-homogeneous contamination
Steel ➢ cells ➢ scrap components : ➢ decomposers ➢ baffles ➢ hydrogen coolers ➢ base plates ➢ mercury pumps ➢ pipe work	0,001 - 1	non-homogeneous contamination
Plastic equipment	<0.1	solid
Miscellaneous:		
➢ copper conductors	0,04	Surface contamination
➢ floor boards	0,05-0,08	
➢ cell sealant (layers concrete)	0,01	
➢ asphalt	1 - 20 %	
➢ decomposer lagging (thermal insulation)	0,03	
➢ concrete and subfloor	variable	non-homogeneous contamination
➢ wood	variable	
➢ soil	variable	

APPENDIX 3 - RECOVERY OF MERCURY: Possible Treatment

Material	**Physical/ mechanical treatment**	**Washing**	**Filtration**	**Chemical treatment**	**Distillation**
Cells	■	■			
Decomposers	■	■			
Sludges from storage tanks and sumps	■	■			
Sludges from settling catch pits, drains etc.	■	■			
Sulphurised or iodised charcoal from hydrogen purification	■	■	■	■	
Carbon from caustic filters	■	■	■	■	
Graphite from decomposers	■	■	■	■	
Rubber/packing	■		■	■	■
Brick work/concrete	■		■	■	■
Ebonite-lined cell components ➢ anode covers			■		■
➢ end boxes			■		■
➢ side walls			■		■
➢ pipe work			■		■
Steel scrap components : ➢ baffles			■		■
➢ hydrogen coolers			■		■
➢ base plates			■		■
➢ mercury pumps			■		■
➢ pipe work			■		■
Plastic equipment			■		■
Miscellaneous: ➢ copper conductors			■		
➢ floor boards			■		
➢ cell sealant (layers concrete)			■		
➢ asphalt			■		
➢ decomposer lagging (thermal insulation)			■		
➢ concrete and subfloor			■		
➢ wood			■		
➢ soil			■		
➢ others			■		

APPENDIX 4 - EUROPEAN LEGISLATION REGARDING MERCURY CONTAINING WASTES

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.

Directive 94/904/EC established under Article 1(4) of Directive 91/689/EEC sets a threshold concentration limit of 3% for hazardous wastes classified as toxic. As yet, no criterion for H14 substances has been established. If and when one is, the most stringent criterion will take precedence.

Therefore, as currently defined under EU legislation, wastes containing more than 3% mercury are classified as hazardous waste.

At national level however it is current practice to consider mercury containing wastes as hazardous for much lower mercury concentration than 3 %.

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.

TRANSFRONTIER MOVEMENT OF WASTES (DIRECTIVE 259/93 EEC)

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 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 have to 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.

LANDFILL DIRECTIVE

A landfill directive is at an advanced stage of discussion and publication is expected in 1999.

Underground storage is covered by the Directive as well as internal waste disposal sites.

Several provisions are due to apply to hazardous wastes such as mercury containing wastes.

- Only hazardous wastes that fulfil the criteria set out in accordance with Annex II of the Landfill Directive are assigned to a hazardous landfill. Annex II provides acceptances procedures and acceptance criteria for mercury containing wastes. Such criteria (not yet fixed at EU level) would consist of a maximum mercury concentration in the eluate after a leaching test or a maximum extractable mercury content.

For the time being, varying national regulations cover such allowable extractable mercury concentrations.

Not all hazardous mercury containing waste will fulfil these acceptance specifications.

- Non hazardous wastes landfill may accept stable non reactive hazardous wastes (e.g. solidified, vitrified), with leaching behaviour equivalent to these of the non hazardous wastes which fulfil relevant non hazardous waste landfill acceptance criteria.

Industrial consumers of chlorine, engineering and equipment supply companies worldwide and chlorine producers outside Europe may establish a permanent relationship with Euro Chlor by becoming Associate Members or Technical Correspondents.

Details of membership categories and fees are available from:

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