Guideline for Decommissioning of Mercury Chlor-Alkali Plants

Env Prot 3

5th Edition

September 2009

EURO CHLOR PUBLICATION

This document can be obtained from:

EURO CHLOR - Avenue E. Van Nieuwenhuyse 4, Box 2 - B-1160 BRUSSELS
Telephone: 32-(0)2-676 72 65 - Telefax: 32-(0)2-676 72 41

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).*

****

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	Added references to new Euro Chlor guidelines and presentations to Seminars
2.	Added references to legislation on metallic mercury recovered after shut down
5.2.	Chapter on treatments restructured and completed with new available information
9.	Chapter on health and safety completed from updated Health WG guideline on mercury
10.	Short chapter added on residual contamination, with reference to the related Euro Chlor document
Appendix 1	List of shut down plants updated
Appendices 2 and 3	Materials contaminated and possible treatments lists updated and merged
Appendix 4	Legislations topics removed

Table of contents

Summary

The European chlor-alkali industry has committed that the cell rooms using mercury cell technology should be shut down over the next years (2020 at the latest).

This paper has been drawn up as a reference document for Euro Chlor members on the best tried organisational processes and 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 55 cell rooms in the last 30 years.

See also ***TSEM 05/311 – Decommissioning of a Mercury Chlor-Alkali Plant***.

Other possible contaminants of the shut down installation are not treated is this document.

1. INTRODUCTION

At the present time there are still a bit more than 40 chlorine cell rooms using mercury cell technology in Europe. The European chlor-alkali industry has committed that the chlor-alkali units in EU using this technology should be shut down at the latest for end 2020 and the equipment demolished afterwards.

Depending on 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, as well as the metallic mercury so recovered from the cells.

Since many years, the European chlorine producers who have already faced this problem 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 30 years during which many of cell rooms have been shut down. The actual 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 Regulations and Directives have already been approved or are in preparation.

It is 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 legislation 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, but may be lower in individual countries) are classified "hazardous".
- Hazardous and non-hazardous waste should be separated as much as possible, and mixing of these should be avoided.
- Limitations and obligations apply to trans-frontier movements of wastes, especially of hazardous wastes.
- Wastes sent to disposal have to fulfil acceptance conditions (fixed by the waste management company, based on its permit).

For metallic mercury, a specific legislation (Regulation EC 1102/2008 of October 22 2008) is banning the export from Europe starting March 15 2011 and defines the principal requirements for safe temporary above ground storage or permanent storage in salt mines or deep underground. Details will be confirmed through the Commission comitology procedure; the conclusions are foreseen before end 2010.

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.

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 personnel who are not experienced in mercury handling are to be used, a detailed training and supervision programme will be necessary. Medical supervision and emissions measurements must continue through all stages of the project.

The planning should include:

- provision of a suitable working area and equipment for mercury handling;
- provision of procedures and instructions (see chapter 9 for health and safety aspects);
- determination of the quantity of mercury to be recovered and provision of the number of containers to be used;
- estimation of the quantity of mercury contaminated waste to be disposed of;
- discussions with the operator of the storage facility to ensure that the necessary permits, handling facilities and storage space are available;
- planning and permitting of the transport operation.

Project planning should be framed around the procedures mentioned here below.

3.1. Contact with authorities

The statutory authorities should be informed as soon as possible on environmental, safety and health aspects of the project after the decision to decommission, in particular those involved with the control of waste disposal and liquid/gaseous emissions. 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

If it has been decided to reuse the building, it will 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 them an impermeable surface. Wooden and asbestos structures could be contaminated with mercury as well as concrete floors. Renewal of non-structural materials (including the top layer of the concrete floor) should be considered Furthermore, the cleaning or, if necessary, renewal of the existing sewer systems in or around the plant is recommended.

3.3. Options of re-use of materials and equipment

Equipment in good condition, such as anodes, cell components, cell covers, pumps, etc. can be stored and eventually re-used as spares in existing mercury plants.

As committed by the industry, used and dismantled mercury cells should not be reinstalled to increase the chlorine capacity in another place.

Other materials, for example steel structures, copper or aluminium bus-bars can be recycled as raw materials after appropriate decontamination.

In all case of re-use, a procedure of health risk assessment should allow confirming the success of the decontamination.

3.4. Decontamination

All chemicals must be removed, with special attention paid to those which contain mercury. When this has been done, the cells can be filled with water to prevent mercury emissions. Then, all metallic mercury must be removed as far as practicable.

Several possible techniques can be considered for decontamination, for example:

- retorting on site or external,
- water or chemical cleaning.

A combination of these may be required. This topic is covered in detail in section 5.

Furthermore specialised contractors offer special separation techniques such as melting the metal/rubber lined equipment followed by mercury recovery from the gaseous phase.

Details of the equipment and procedures for emptying the cells into the storage containers is likely to be specific to individual plants, however the following principles should be applied (see also ***Env Prot 19 – Guideline for the preparation for permanent storage of metallic mercury above ground or in underground mines***):

- keep the system closed where possible, to reduce the possibility of vapour emissions and spills; put water in the cells to prevent mercury emissions;
- use gravity transfer where possible;
- check that the mercury is not contaminated and, when necessary, use filtration or decantation to remove solid impurities such as rust and rubber particles;
- avoid transferring other liquids (such as water) into the mercury containers;
- do not fill the container completely (to avoid the danger of over-pressurisation due to thermal expansion). The container should not be filled to more than 80% of its volumetric capacity;
- after filling the containers should be hermetically sealed;
- the containers should then be weighed and labelled appropriately within the EU Directive and international transport regulations (danger signs, quantity of mercury, sender, date and reference number to trace the origin).

In most cases the source plant will have suitable working areas (e.g. the cells room basement), which should be used if possible. The working area should:

- be well defined, if necessary surrounded by kerbing;
- have a smooth, sloped, impervious floor to direct mercury spills to a collection sump;
- be well ventilated but have a roof to exclude rainwater;
- be well-lit to enable easy identification and clean-up of spills;
- be free of obstructions and debris that would absorb mercury and/or hinder the clean-up of spills (e.g. wooden pallets);
- be equipped with a water supply (for washing);
- be connected to an liquid effluent system that allows decantation of the mercury from wash water, and the treatment of the water to remove residual mercury.

Aspiration equipment should be provided so operators can rapidly clean up spills. This equipment should have activated carbon filters to remove mercury vapour from the exhaust air.

3.5. Demolition

Before demolition starts, a survey of all plants, buildings and associated equipment to be demolished should be carried out 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.

Heat input in equipment or structures should be avoided when mercury contamination is present.

Above ground aspects must be considered in the first phase. The possible subsoil contamination and its handling are referred to in the document ***Env. Prot. 15 - Management of Mercury Contaminated Site.***

3.6. Disposal

The case of excess metallic mercury is specifically treated by the Regulation EC 1102/2008 – Banning of mercury exports and safe storage of mercury (see also ***Env Prot 19 – Guideline for the preparation for permanent storage of metallic mercury above ground or in underground mines***).

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.

When possible, the demolition rubble will be segregated into different ranges of mercury contamination levels and types, will allow adapting their disposal in the right landfills (according to relative permits).

Mercury contaminated materials are classified 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.

The company disposing the waste must ensure that the landfill company is competent to handle mercury wastes and that they can demonstrate they comply with the applicable legislations (water and soil protection …).

3.7. Other considerations

The project management team should also consider issues such as:

- Waste water containment and treatment to remove metallic and soluble mercury.
- 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 or containers).
- 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 at least as detailed and stringent.
- Management of individual protection equipment for workers (dressing and undressing location with washing facilities).
- Personnel that may come in contact with mercury need to be medically monitored (registration, type of activities, exposure time, mercury in atmosphere, mercury in urine….)
- Tracing, emptying and sealing of drainage systems.
- Development of systems for tracking mercury recoveries (book-keeping of waste streams, concentration, volumes and destination).
- Washing of mercury from the cell loop to remove residual sodium (hydrogen formation risk).

4. SPECIATION OF MERCURY

4.1. Metallic mercury

During dismantling most contaminated pieces are contaminated in surface with metallic mercury.

The big amounts should be recovered by decantation or vacuum cleaner with appropriate adsorption/condensation system; high pressure water washing is also possible, provided adequate protection is foreseen to avoid dispersion of contaminated water.

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 wash water system for headers and footers
- The degassing system for headers and footers
- The caustic soda system
- The hydrogen pipes and equipment
- The maintenance area of cells and auxiliary equipment
- The retorting area, if any
- The waste water system.

4.2. Solid mercury compounds

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 wash water for headers and footers
- The condensed water from the collecting gaseous system for headers and footers

- The condensed water of the hydrogen network
- 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 personnel who are not experienced in mercury handling are to be used, a detailed training and supervision program will be necessary. Medical supervision and emission measurements 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 a least until all mercury related activities is finished and the mercury content in waste water must comply with statutory requirements.

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

It is usually possible to categorise materials according to the level of mercury content as indicated in Appendix 2 – Types of contaminated materials and possible mercury recovery treatments.

The recommended actions are described below.

5.1. Preliminary measures

A mercury 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 followed by water. Afterwards, it is advisable to keep water in the cells to prevent mercury emissions until the cells are dismantled.

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.

The density of the mercury makes handling difficult. In order to ease the work and minimise the potential for spills and emissions, the systems for emptying the plant and filling the containers should be carefully designed. Designs are likely to be specific to each plant, and should use the experience of the chlor-alkali plant personnel. When possible, gravity transfer should be used.

Cranes and forklift trucks will be required for handling the containers.

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 but can only be applied to certain types of contaminated wastes. Contractors with mobile retorts or fixed retorts on their own premises can be used where there is no on-site retort.

For the mercury in the cells the remaining contaminants can usually be removed by treating each cell in turn:

- circulate the mercury with wash water until the exit wash water stabilises at pH 7 ± 0.5 and the specific gravity at 1.0
- analyse the mercury to ensure that no residual sodium remains (risk of hydrogen formation)

Finally, drain the mercury from the cell into storage containers.

5.2. Available techniques

See Appendix 2 – Types of contaminated materials and possible mercury recovery treatments

Basically, the decontamination techniques are the same as the ones used in mercury plants in production, but some particular aspects must be considered due to the sometime quite huge quantities to be handled in a short period of time (see ***Env Prot 13 - Guideline for the Minimisation of Mercury Emissions and Wastes from Mercury Chlor-Alkali Plants*** for more details).

5.2.1. Treatment of contaminated solids

In each case, and according to the residual mercury concentration and the local requirements, the remaining solid waste is recovered, if possible, or safely disposed of.

5.2.1.1. Mechanical and physical treatments

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

Such treatments are water washing (with or without pressure), ultrasonic technique and vacuum cleaner with appropriate adsorption/condensation system.

The extracted metallic mercury can be recovered in ad-hoc sumps.

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

5.2.1.2. Treatment with hydrogen peroxide (H_2O_2)

In alkaline conditions H_2O_2 is a reducing reagent (pay attention that in acidic condition, H_2O_2 is an oxidant and will dissolve metallic mercury!).

Usually a 5 to 10% weight concentration solution is employed. In contact with fine particles it decomposes with a very positive mechanical effect due to the production of gaseous oxygen.

The effluent containing the dissolved mercury is treated separately.

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.

5.2.1.3. Treatment with hypochlorite solution

Hypochlorite is a strong oxidising agent and dissolves metallic mercury, but the reaction is slow due to the fact that the reaction is a superficial one. By dissolving mercury also iron and other metals are dissolved, reducing the efficiency of a downstream ion exchange unit.

As here above, the liquid effluent is treated separately.

5.2.1.4. 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.

Not all contaminated wastes can be retorted (some produce volatile mercury compounds that can not easily be trapped). In case of combustible material, attention shall be paid to use an inner gas atmosphere.

The excess cooling water (direct contact) is treated as contaminated effluent.

Attention must also be drawn on the energy consumption of this process,

5.2.2. Treatment of contaminated liquid effluents

All washing effluents or liquids coming from other decontamination techniques contain mercury which must be extracted prior purging in the environment.

The techniques usually used work on mercury in ionic form (for example precipitation as sulphur or absorption on resins); if necessary, the metallic mercury that could be present is oxidised in a preliminary phase, for example with active chlorine (like hypochlorite solution).

5.2.2.1. Precipitation of HgS

By adding sulphide, ionic mercury is precipitated as mercuric sulphide. The solid sulphide is filtered from the waste water (plate filters for example) and may be then

- discharged as stabilised mercury sulphide in a secure landfill
- treated thermally for recovering Hg.(see 5.2.1.4)

5.2.2.2. Ion exchange to remove mercury from solution

Depending on the type of resin used, it is possible to regenerate the resins with hydrochloric acid, giving mercury-containing liquor, that must then be treated to extract the mercury or, if possible, recycled in the brine of another mercury electrolysis unit.

Other resins can be treated as solid waste, retorted or sent to underground storage.

5.2.2.3. Other techniques

In some installations, a reducing agent is added to the liquid effluent or an electrochemical process is used to bring back the mercury in metallic form. After mechanical separation, a filtration stage with active charcoal is added to recover the metallic mercury.

There also some other techniques developed, but showing lower performances (fixed bed of micro-organisms absorbing the metallic mercury…).

5.3. Decontamination of materials and equipment

The disposal of non-mercury contaminated material requires cleaning appropriate to the chemicals handled and should not be mixed with mercury-contaminated material. Take into account that sometimes contamination with traces of toxic chlorinated compounds takes place. Also here special treatment and precautions may be necessary.

On dismantling, the parts are preferably transferred in tight drums for storage and handling on the decontamination pad.

During dismantling, a check can be done with a portable device to measure the mercury emission coming from the material. This gives a good indication whether the material is contaminated or not.

5.3.1. Non-mercury contaminated materials

Usually materials and equipment that have only been in contact with dry 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 they 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.

Wood and other materials that can absorb mercury shall be avoided in all decontamination process.

If such material has been contaminated by mercury, it can usually not be decontaminated and should be disposed of as such.

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 most of 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. This waste steel should be cleaned until the level is acceptable by the recycling company, typically 100 mg/kg. No visible mercury should be present (no sweating). This scrap is then usually acceptable 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, if necessary with addition of detergents or hydrochloric acid containing from 0.01 to 0.5% chlorine due to chlorine emission risk, the preparation of this solution requires strong precautions).

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 with water, 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 could not be sufficient. These pieces may then 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 loose 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 (with an adequate gas treatment unit).
- Cryogenic treatment, resulting in mechanical separation due to the thermal shock obtained by vaporisation of liquid nitrogen.
- High pressure water jet can be used to separate the hard rubber coating from the steel; the water contaminated with mercury shall then be treated.
- 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 the resulting waste is 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. Sludge and wet residues

Sludge 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 as mercury sulphur compound followed by landfill, after verifying that the requirements of the Directive 2003/33/CE are respected.

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 (special precautions to be taken due to the risk of chlorine emission).

5.3.2.6. Construction materials

Rough decontamination of construction materials such as bricks, concrete, asphalt or subfloor materials can be done on water-washed vibrating screens, ultrasonic cleaning … before being disposed of.

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 sludge can be done by adding quicklime (calcium oxide) to neutralise the sulphur compounds produced.

After all the equipment has been removed, the walls and ceilings of the building can be washed with water under pressure, depending on its reuse.

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 possible 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 or preferably tight drums are useful and can be suitably colour-coded to indicate content or source of material. The legal requirements for labelling waste are defined by Directive 91/689/EEC. OECD hazardous waste forms must be used.

Transport of the materials should be done in tight drums or in leak-tight containers 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.

The case of excess metallic mercury is specifically treated by the Regulation EC 1102/2008 – Banning of mercury exports and safe storage of mercury (see also ***Env Prot 19 – Guideline for the preparation for permanent stroage of metallic mercury above ground or in underground mines***).

7. DISPOSAL

As far as possible, the quantities and types of all materials to be disposed off should be identified before the unit is shutdown. All mercury contaminated materials must be decontaminated as far as reasonably practicable.

The Directive 2003/33/EC defines the general conditions for disposing off waste. Usually, if the average mercury concentration in the decontaminated materials is less than 100 mg/kg and the leachate limit is respected, it may be possible to send it to a permitted landfill, depending on national and/or local regulations. Even if the mercury content of the material exceeds 100 mg/kg, it may still be possible to landfill it if the leaching test is satisfied (for example after stabilisation); leachate limit requirement does not apply for salt mines disposal, where the acceptance criteria are defined by a site specific risk assessment.

It is therefore important to stabilise the mercury and have the leaching tests satisfied.

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.

The base, walls and final cover of a sealed landfill site or containment site must be impermeable and constructed according to national/local legislations. Appropriate monitoring should be implemented, including for groundwater.

When accepted by the authorities, deposition in an underground salt mine is also a good environmental solution for solid materials which are highly contaminated.

The case of excess metallic mercury is specifically treated by the Regulation EC 1102/2008 – Banning of mercury exports and safe storage of mercury (see also ***Env Prot 19 – Guideline for the preparation for permanent storage of metallic mercury above ground or in underground mines***).

8. ANALYSIS FOR MERCURY

This chapter is based on former experience of Euro Chlor members; the methods described here and in quite old specific guidelines are still valid but currently in updating process with addition of more up-to-date analytical techniques.

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 group of materials 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 pure analytical point of view 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.

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 handling

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 Analytical Chimica Acta 72 (1974), part 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.

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 described in Analytical Chimica Acta 84 (1976), part 2, 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 Analytical Chimica Acta 72 and 84 (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***

9. HEALTH AND SAFETY

9.1. Introduction

Health protection of workers during demolition of chlor-alkali mercury plants is in general much more difficult than during normal production because

- the possible exposure levels tend to be much higher (air concentrations of mercury vapour could increase 10-20 times during clean-up and other operations)
- new procedures have to be defined by management and all workers have to be specifically trained
- demolition is often performed by contract workers who, in general, are less experienced in working with mercury containing materials.

Because the general principles of health protection of workers during demolition are the same as in a production environment, the basic document to use for planning the health protection part of the demolition process stays ***Health 2 – Code of Practice: Control of worker exposure to mercury in the chlor-alkali industry***, although this does not mean that all points of this document are applicable in these special circumstances.

For analysis of mercury in urine, one can refer to the ***Analytical 11 – Determination of Mercury and Creatinine in Urine***.

This chapter summarise what should be the focal points of such a health protection plan.

9.2. General considerations

Due to the higher risk of exposure to mercury during dismantling than during the running of the cell room, the recommendations of Health 2 chapter 3 should be read and strictly followed.

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

It is important to emphasize that new workers should follow a specific training due to the higher risk to be exposed because of their inexperience. To enable them to perform their work in a competent, safe, and environmentally sound manner, this program should approach the topics described in Health 2 chapter 10.

Pregnant women will be of course excluded from works where there is a possible risk of exposure to mercury.

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.

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.

All records, medical, exposures, and training, should be kept according to the principles described in Health 2 chapter 11.

The process of management of health of employees with regard to mercury exposure, as listed in this document, should be monitored and improved by at least an internal audit system. The questionnaire that can be used for this is reflected in a Euro Chlor specific document (***Health 6 – Audit questionnaire - Mercury***). It has to be adapted for dismantling, which is a special circumstance.

9.3. Medical examination before start-up of the demolition

A preliminary medical examination is important for new workers to establish a “zero point” as in some case the contractor company could be specialised in demolition and the workers may have been exposed to mercury before, without having been informed.

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

- Analysis of urinary mercury.
- 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 second point listed here above, should exclude an employee from employment where he or she could be exposed to mercury.

9.4. 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 and, due to the higher level of exposure during demolition than during usual operation, a weekly frequency of urinary mercury measurements is recommended, not only for personnel working in the cell-rooms but also for those handling contaminated waste.

Monthly measurements for personnel working in other areas can be sufficient, but frequency should be increased in case the mercury level rises.

Due to the fact that systematic measurements during a demolition process are difficult and unexpected exposure to mercury can be awaited, it is advised to have portable equipment to do frequently spot measurements of mercury.

9.5. Action levels

After assessment of the risks a written action plan should be made to define clearly, which assessed health risk should be eliminated or diminished. Priorities and a time schedule should be given to the actions.

Additionally, an explanation should be given for situations in which it is not practically possible to comply with internal, or external exposure limits (BEI and/or OEL).

As in Health 2 chapter 8, the proposed action levels based on the outcome of the biological monitoring results are:

< 30 µg/g creatinine	no action
30-50 µg/g creatinine	review of practice
> 50 µg/g creatinine	remove until below 30

The programme (intended to be) implemented should be documented, archived, and published to all whom it concerns. It should be clearly listed whether, where and why exposure to mercury cannot be limited without use of personal protective equipment.

The Medical Advisor may recommend the removal of a worker from further exposure to mercury, on medical grounds, independent of mercury in urine levels.

9.6. 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 30 µg/g creatinine.

9.7. Actions in case of over-exposure

A specific examination (Health 2 chapter 9) should be performed in case an over-exposure to mercury is measured (strong increase of mercury concentration in urine) or even suspected due to the circumstances.

9.8. Safety aspects

There are no safety aspects specific to the fact that the work is done in a chlor-alkali unit but, like all demolition operations, additional precautions need to be taken due to the type of work itself (machines and tool not usual during production phase…) and presence of additional workers on the site, often external to the company.

10. RESIDUAL CONTAMINATION

Even after dismantling the plant there may be residual contamination, which requires ongoing control (for instance, retention of the water treatment plant for operation, air ventilation monitoring …).

The document ***Env Prot 15 - Management of Mercury Contaminated Sites*** give a review of the main techniques used or in development to deal with mercury contaminated sites.

11. REFERENCES

- **Regulation EC 1102/2008 – Banning of mercury exports and safe storage of mercury**
- **Directive 2003/33/EC – Banning of mercury exports and safe storage of mercury**
- **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**
- **Analytical Chimica Acta, (1976) 231-257 Standardisation of Methods of the Determination of Traces of Mercury Part 2 - Determination of Total Mercury in Materials Containing Organic Matter**
- ***Anal 3-7 - Standardization of Methods for the Determination of Mercury Traces***
- ***Analytical 11 – Determination of Mercury and Creatinine in Urine***
- ***Env Prot 13 - Guideline for the Minimisation of Mercury Emissions and Wastes from Mercury Chlor-Alkali Plants***
- ***Env Prot 15 - Management of Mercury Contaminated Sites***
- ***Env Prot 19 – Guideline for the preparation for permanent stroage of metallic mercury above ground or in underground mines***
- ***Health 2 - Code of Practice: Control of Worker Exposure to Mercury in the***

Chlor-Alkali Industry

- ***Health 6 - Audit questionnaire - Mercury***
- ***TSEM 05/311 – Decommissioning of a Mercury Chlor-Alkali Plant***

Appendix 1 – Sites with experience of shutting down mercury cell rooms

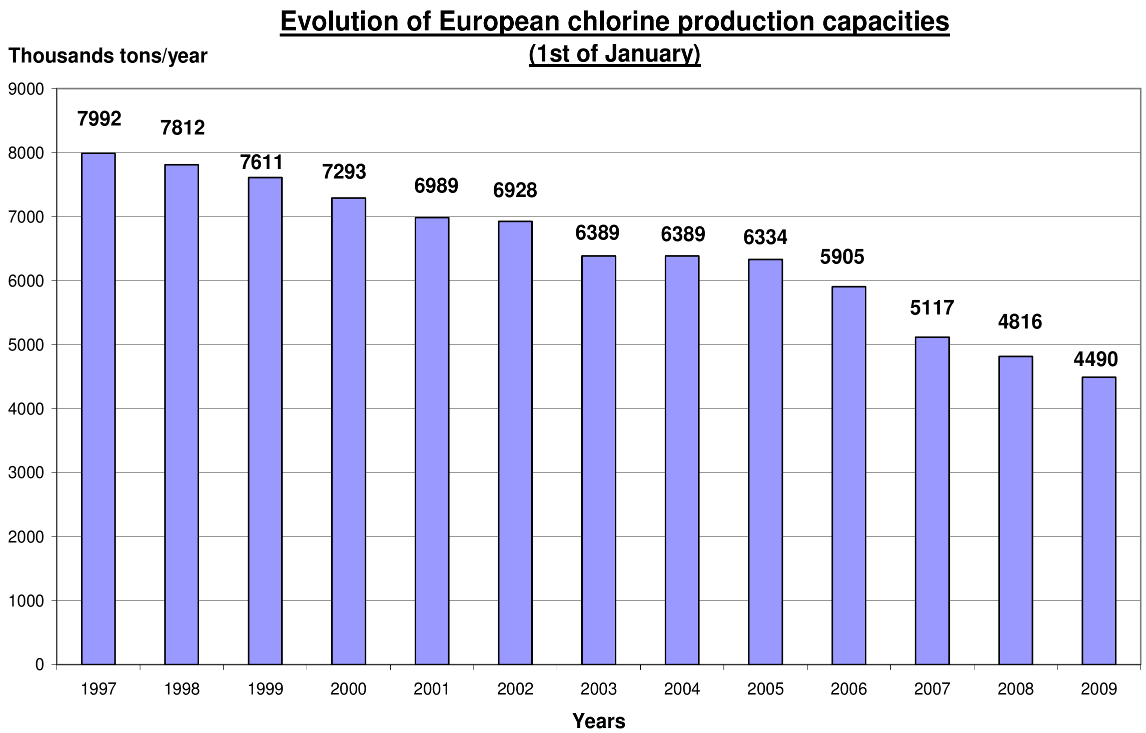
Note: on some sites mercury capacities are still running

Country	Site	Company
AUSTRIA	Hallein	Solvay
	Brückl	Donau Chemie
BELGIUM	Jemeppe	Solvay
	Tessenderlo	Tessenderlo Chemie
DENMARK	Copenhagen	DS Industries
FINLAND	Äetsä	Finnish Chemicals
FRANCE	Jarrie	Elf-Atochem
	Saint-Auban	Arkema
	Tavaux	Solvay
GERMANY	Frankfurt	Hoechst
	Ludwigshafen	BASF
	Dormagen	Bayer
	Leverkusen	Bayer
	Uerdingen	Bayer
	Gerstofen	Clariant
	Skopau	Dow
	Marl	Hüls
	Marl	Vestolit
	Knapsack	Hoechst
	Rheinfelden	Hüls
	Schkopau	Nord BSL
	Bitterfeld	BVV Chemie
	Burghausen	Wacker Chemie

Country	Site	Company
ITALY	Brescia	Caffaro
	Mantova	EniChem
	Gela	EniChem
	Tavazzano	Solvay
	Rosignano	Solvay
	Bussi	Solvay
	Volterra	Altair
	Porto Torres	EniChem
	Priolo	Syndial
NORWAY	Heroya	Norsk Hydro
	Opsund	Borregaard
	Sarpsborg	Borregaard
POLAND	Oswiecim	Dwory
PORTUGAL	Povoa	Solvay
	Estarreja	Uniteca
SPAIN	Torrelavega	Solvay
	Hernani	Electroquimica de Hernani
SWEDEN	Bohus	Akzo Nobel
	Korsnäs	Diacell
	Skutskär	Stora
	Timra	SCA
	Domsjö	SCA-MoDo
	Skoghall	Billerud
SWITZERLAND	Zurzach	Solvay
	Monthey	Syngenta

Country	Site	Company
THE NETHERLANDS	Delfzijl	Akzo Nobel
	Hengelo	Akzo Nobel
	Rotterdam	Akzo Nobel
	Linne Herten	Solvay
UK	Wilton	ICI
	Billingham	ICI
	Runcorn	INEOS
	Hillhouse	ICI
	Baglan Bay	BP Chemicals
	Ellesmere Port	Associated Octel
	Staveley	Rhodia
	Sandbach	Albion Chemicals

The decreasing of capacities of mercury technology in Europe since 1997 is shown in the following chart:



Appendix 2 – Types of contaminated materials and possible mercury recovery treatments

Materials typical contamination			Possible treatments			
Material	**Typical Hg content % w/w**	**Physical state**	**Physical/ mechanical treatment**	**Water washing**	**Chemical washing**	**Retorting**
Sludge from storage tanks and sumps	10 - 30	wet solid	■	■		■
Sludge 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	wet solid	■	■		■
Graphite from decomposers	2	porous solid	■	■	■	■
Rubber/packing	variable	variable	■	■	■	
Brick work/concrete	0.01-0.1	dry solid	■	■	■	■
Ebonite-lined cell components (anodes covers, end boxes, side walls, pipework)	variable	inhomogeneous contamination	■	■	■	
Steel (cells, decomposers, scrap components from baffles, H2 coolers, base plates, Hg pumps, pipework)	0.001 - 1	solid with surface contamination	■	■	■	■
Plastic equipment	<0.1	Solid with surface contamination		■		

Materials typical contamination			Possible treatments			
Miscelaneous material	**Typical Hg content % w/w**	**Physical state**	**Physical/ mechanical treatment**	**Water washing**	**Chemical washing**	**Retorting**
➢ copper conductors	0.04	solid with surface contamination				(for flexibles multi sheets)
➢ cell sealant (layers concrete)	0.01					
➢ asphalt	1 - 20 %	non-homogeneous contamination				
➢ concrete and subfloor	variable	non-homogeneous contamination				
➢ wood	variable	contamination				
➢ soil	variable	non-homogeneous contamination				
➢ decomposer lagging (thermal insulation)	0.03	contamination				
➢ Retort residues	< 0.1 – 0.1	dry porous solid	No treatment before disposing off			
➢ Wooden floor boards	0.05-0.08	non-homogeneous contamination				

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:

Euro Chlor
Avenue E Van Nieuwenhuyse 4
Box 2
B-1160 Brussels
Belgium
Tel: +32 2 676 7211
Fax: +32 2 676 7241
e-mail: eurochlor@cefic.be
Internet: http://www.eurochlor.org