CODE OF PRACTICE

MERCURY HOUSEKEEPING

Environmental Protection 11

5th Edition

April 2004

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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).

This reference manual is intended to give only guidelines and recommendations. The information is provided in good faith and has been based on the best information currently available. The information is to be relied upon at the user's own risk. Euro Chlor and its members make no guarantee and assume no liability whatsoever for the use and the interpretation of or the reliance on any of the information in this document.

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 that its activities cause the minimum harm to 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 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
1.7.	Plastic pallets were taken into consideration

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The Good Housekeeping Practices detailed in this report result from more than 50 years operating experience from chlorine plants world-wide.

1. Cell Room

1.1. Lighting

Effective lighting (strong, comprehensive, no shadows) is essential for the detection of spilt mercury droplets. Good illumination makes it easier to find and recover mercury and to thoroughly check the state of cleanliness throughout the plant (auxiliary lighting that is not necessarily operated continuously is useful for this purpose). Such lighting should be installed not only in the cellroom but in the cell basements and maintenance areas.

1.2. Cells and Supporting Structures

Mercury leaks can be prevented by good maintenance of cell seals. There should be no breaks in the seals in either the side or end sections of the cell.

The entrapment and accumulation of mercury can be avoided by careful design of the cells' concrete supporting plinths. Sloping surfaces of the plinths and of the beam cross-sections help in this respect and also simplify cleaning.

It is important to prevent corrosion in supporting structures, as the porosity of any corrosion products will result in the formation of mercury sinks. Corrosion can be reduced by judicious use of plastic materials and by coating some exposed steel surfaces with plastics. However, it is necessary to be aware of the danger of coating steel or steel-containing structures- particularly reinforced concrete - as the onset of corrosion may be hidden from view. It is advisable to cover cable support trays as caustic and brine mist can collect on these.

1.3. Vessels/Pumps/End-boxes

Emissions from end boxes and exhaust gas treatment vessels can be avoided by ensuring they are sealed with clamped or bolted gaskets.

To ensure adequately low atmospheric mercury levels, the system vacuum should be set at such a value that suction can be maintained in the end boxes even when 5% of the electrolysers are open. Regular checks of the vacuum efficiency are advisable at various locations throughout the system. Continuous monitoring can simply be achieved by use of a water-filled U-tube with one leg connected to the vacuum system.

Mercury emissions can be reduced if sampling of the amalgam for analysis is minimised. The number of analyses and measurements that involve opening mercury-containing equipment should be carefully studied and limited to those that are necessary for safe operation. A low sampling frequency is only achievable if the operating conditions are constant, brine quality being the critical factor. As well as controlling Ca and Mg levels in the brine, it is important to reduce levels of certain heavy metals that result in the formation of 'mercury butter' (or thick mercury). The frequency of cell cleaning is directly related to the quantity of thick mercury.

Helpful hints

- Do not use rubber hoses for mercury discharge lines.
- Keep the number of flanges in mercury/amalgam pipework as low as possible.
- Install a preventive maintenance schedule on gaskets and valves to avoid leaks.
- Do not design horizontal surfaces on vessel flanges but make them rounded or sloping to prevent mercury hold-ups.
- A vacuum cleaning system is very useful for cleaning mercury spillages. A vacuum pipeline system with frequent mobile attachment connection points is particularly effective.
- Keep vessels containing mercury (for example, front and end-boxes) under slight vacuum.
- Glass or transparent polycarbonate covers on end-boxes give a view of mercury flow without opening the system.

1.4. Floor Areas

Low atmospheric mercury levels in a cell room can only be achieved if high hygiene standards are applied to the general floor area as well as to those areas in the immediate vicinity of the cells.

Except for specific operations, it should be possible to work anywhere in the cellroom without wearing protective apparatus. A general requirement to use protective equipment is a tacit admission that mercury is likely to accumulate and housekeeping standards are inadequate.

Evaporating mercury is drawn through the cellroom by the ventilation fans and/or by rising hot air currents created by the high temperatures in the cells. It is vital to undertake a daily regular and systematic rinsing of the floor with water. Immediate cleaning should be invoked in the event of an accidental spillage.

Helpful hints

- The flooring should be smooth and light coloured to allow detection of mercury droplets. It must be crack-free and impervious.
- Avoid covers on gutters. Mercury will be trapped under them and give rise to extra evaporation.
- Gentle flushing with clean water is advised. High pressure cleaning is likely to scatter the mercury or atomise it.
- Wood, which absorbs mercury, should be avoided in construction materials.

1.5. Flow Gutters

Floor areas should be sloped slightly towards open flow gutters which direct washings to collection vessels from which mercury contaminated materials can settle and be subsequently removed. The vessels should be large enough to contain the entire volume created when rinsing is being carried out. The liquid can then either be transferred to the feed brine circuit or directly to the effluent treatment plant. Untreated liquor should not be discharged to the environment.
The vessels should be cleaned at frequent intervals to remove mercury-contaminated sludge, earth, sand, ash, etc. The fact that these sludges are covered with water is important but is not enough in itself. Water only slows down the evaporation rate but does not stop it (see Note 1). Additionally, if cleaning is not done regularly, any major leak of oxidising agents such as chlorinated brine from an adjacent cell would dissolve all the mercury. There is also the possibility of loss of containment if the brine quantities are too high to be retained in the liquid effluent treatment unit.

1.6. Floor Protection

Any cracks and unevenness that develop in the cell room floor should be filled in and levelled. A continuous and impervious protective coating that is resistant to chemical attack should be applied. This should have a very smooth gloss finish to avoid mercury adhesion and be light in colour to allow easy detection of mercury droplets.
The cellroom should not be used as a storage area. Any materials left lying around the floor area should be cleared away. Unnecessary articles become needlessly contaminated, prevent routine cleaning of floors and are an obstacle to good mercury control schemes. If pallets are used temporarily plastic is preferred.

1.7. Collection of Mercury

Using water jets to clean areas soiled with mercury is not the most suitable technique since it scatters the mercury into small droplets which significantly increase the evaporation rate.
(see Note 2).

Although it is possible to cover the nozzle to minimise the atomising effect, it is preferable to collect the mercury using standard industrial suction equipment for dry and liquid substances. The vacuum system should discharge into a collection vessel fitted with a cyclone and carbon filter.

2. Maintenance

2.1. Work Areas

Maintenance areas should be large enough for work to be carried out easily. Contamination of adjacent areas can be avoided by effective bunding (curbing).

Floor surfaces must be resistant to mechanical shock, which can occur when handling the heavy equipment found in cellrooms. Thick reinforced concrete slabs, covered with steel plates welded together and painted, form an excellent choice.

The recommendations given on floor coverings in section 1.6 are also applicable to maintenance areas.

2.2. Activity Planning

A **s**cheduled programme of preventative maintenance should lead to a decrease in cell opening frequency and time and will therefore reduce mercury emissions.

Some polluting activities, such as dismantling graphite gratings in a decomposer (denuder), cannot be eliminated. In this case the work can be organised to minimise its duration. Another good practice is to purge the decomposer with an inert gas prior to maintenance and send this to the weak gas scrubber for treatment.

It is good practice to decontaminate immediately any mercury-contaminated equipment soiled taken out for maintenance. When this is not possible covering contaminated parts with water or plastic sheeting (when it is impractical to submerge the equipment in water) can reduce the evaporation rates.

Mercury can be recovered from cleaning liquids when the concentration becomes too high by carefully feeding them to the brine loop prior to effluent treatment.

2.3. Hot Work

The application of heat to equipment that has been in contact with mercury is a special problem. Washing with water alone will not remove all contamination, as mercury will continue to 'sweat' out of metal during heating. Consideration should be given to heating the equipment in a decontamination oven to remove and collect mercury. If this is not possible then any work involving heating should be undertaken in a well ventilated area. It may be necessary to wear breathing apparatus when undertaking activities such as welding (mercury monitoring should be undertaken when carrying out such tasks).

2.4. Cell Cleaning

When a cell has to be opened for maintenance, the mercury has to be drained in to the decomposer and the brine removed. The residual visible mercury is removed with a vacuum cleaner.

The cell bottom can be treated with a sodium peroxide solution. The solution is prepared by pouring 1.3 litres of 50% caustic soda and 1.0 litres of 35% sodium peroxide solution into a bucket containing 8 litres of water. The solution is distributed over the entire cell base and the base plate is then brushed. The peroxide treatment is repeated 3 - 5 times. The mercury concentration in the air above the cell base is then checked with a portable mercury analyzer (See **Env Prot 11A - Code of Practice - Mercury Housekeeping - Supplier's References**). If a significant concentration is still detected, the treatment should be repeated with a fresh solution. Finally, the cell bottom is cleaned with water.

2.5. Leak Detection

Systems handling hydrogen are particularly prone to leakage due to the properties of the hydrogen molecule. Additionally, hydrogen streams are generally saturated with mercury at a high temperature. Mercury emissions from these sources are therefore potentially liable to be serious.

After all maintenance activities on systems containing untreated hydrogen gas, leak detection tests should be carried out using equipment sensitive to hydrogen. The presence of hydrogen can be assumed to indicate the presence of mercury. The source of the leakage must be identified and the fault rectified.

3. Mercury Storage

Storage areas should be well lit and floors should slope towards mercury collection systems. The comments that were made in sections 1.4, 1.5 and 1.6 concerning the condition of the floor also apply to the floor areas in mercury storage rooms.

All mercury containers, bottles etc. should be kept closed. Mercury should not be stored in open containers.

Any objects which might adsorb mercury and hinder cleaning must be removed from these areas.

4. Measuring Mercury in the Air

It is the responsibility of management to identify all mercury emission sources, to minimize them and to protect employees should levels become too great.

Both static and portable monitoring methods can be used for regular measurements at specific locations.

Best practice involves regular measurements in a variety of locations throughout the factory, e.g. the electrolysis room, offices, changing rooms, the mercury storage area and the area around the retort(s).

Detailed descriptions of the measurement of air flow and mercury concentrations in cell room ventilation are given in reference 1. However, a summary of important points related to housekeeping is given below:

a) In the case of **closed cell rooms with ventilation fans**, for the measurements to give an accurate assessment of mercury levels, account needs to be taken of the following points:

Mercury levels are not identical at each fan suction inlet, so conditions at more than one fan should be measured.
The number of hours each fan is on work must be recorded.

The flow rate of each fan will vary depending on its wear as well as with other factors associated with the inlet and outlet (walls, columns, tanks, etc.). Therefore the actual flow rate of each fan should be measured regularly.

b) In **closed or semi-closed cell rooms without forced ventilation**, measurements of mercury concentration and air flow rate must be made at the natural air outlets. To obtain a full picture of mercury levels and their variability statistically robust sampling techniques must be employed. Measurements should be taken under a variety of different conditions i.e. in summer and winter; calm and windy conditions; day and night; normal working days and week-ends or holidays; during normal work and during major maintenance. A semi-continuous measurement system for mercury concentration and flow rates is a great help (see reference 1).

c) For **open rooms with natural ventilation**, representative measurements cannot be made using static monitoring devices since air flows change according to prevalent weather conditions. It is common practice to fix a grid of measurement points with a spacing every few meters and at a height of about 160 cm from the floor. To obtain a full picture of mercury emissions measurements should be taken under all possible conditions that can exist in the cell room. A frequency of at least once a month is employed. It is important for a qualified operator to carry out the measurements.

This grid technique gives a clear picture of the origins of mercury losses and their variability with time. It can therefore be used in all types of cell room (open and closed) in order to pinpoint sources of emission and can be particularly useful in evaluating actions taken to reduce mercury emissions.

To obtain a 'base level' it is advised to take the measurements on a Sunday at the end of the day when no maintenance is being carried out which may distort the measurements. Results should be obtained with and without the fans (if any) operating.

Specific activity monitoring should also be carried out to determine exposure levels for particular tasks. The information gathered should be used to determine either correct personal protective equipment or whether the job methodology can be improved.

No rigid correlation has been established between the mercury concentration in the air in the actual place of work and the concentration found in the urine of the workers since this is also affected by personal hygiene standards. However it is certain that the higher the mercury concentration is in the air of the cell room, the higher is the risk of mercury accumulating in the worker's urine. Conversely, high mercury-in-urine figures may indicate an unknown source of leakage. Detailed practices for minimizing worker exposure to mercury are given in reference 2.

Helpful hints

- Make an inventory of all permanent and temporary mercury sources linked both with production and maintenance.
- Measure the concentration levels in the air around these point sources.
- Consider technical or ergonomic measures to minimize or even eliminate these sources
- Communicate the results of all analyses to the production and maintenance staff.
- Involve all staff in the quest for emission elimination.

5. Guide to an Action Programme

5.1. Short Term Actions

The very first action for all plants is to adopt a code of practice which states clearly that no visible mercury is to be tolerated anywhere in the workplace, even in relatively inaccessible places.

Mercury covered with water may only be tolerated when completely unavoidable and for extremely short periods. Successful implementation of this principle will require positive and active co-operation from staff at all levels in the organization.

In particular the following steps must be put in place:

- Treat mercury leaks and mercury incidents in a similar manner to a work accident, i.e. organize a review meeting of the production staff and those involved or who witnessed the incident together with the Safety and Environment Departments so that underlying causes can be identified and corrective action taken.

- Ensure the means are available to see any spilt mercury (illumination, smooth light-colored floor, etc.).

- Make vacuum equipment easily accessible to collect any spilt mercury.

- Define and assign responsibility in the fight against mercury pollution. Overall control of the state of cleanliness of the cell rooms should be the responsibility of all production shifts so that any mercury leak will be dealt with immediately by the working shift. Maintenance staff must intervene quickly in the event of a substantial leak. If the latter are absent, every measure should be put in place to contain the leak until assistance arrives (putty, tanks filled with water to collect mercury, etc.) In short, no case of mercury in prolonged contact with the surrounding air should be accepted.

- Assign responsibility to a “mercury-man” whose main function is to wash the floor area in the cell room every day and purge the mercury from pipes and tanks. The mercury man should remove all the micro-droplets produced in the event of falling mercury.

- Schedule and organize work that involves mercury emissions to be carried out as quickly as possible, thereby reducing contamination.

- Utilize containers where mercury-soiled parts can be immersed in water for transport to the decontamination areas. The parts should be decontaminated as rapidly as possible by the day staff. In their absence, the parts should remain covered with water (or by plastic sheeting if this is not possible) until decontamination can be undertaken.

- Set up tanks for the decontamination of parts. If work involving heating is to be undertaken on mercury contaminated parts consider the use of a decontamination oven.

- Motivate staff on a permanent basis by informing them of improvements that are a result of their efforts. Undertake continual review meetings where specific emission targets are set. Consider incentive schemes.

- Ensure that staff are fully trained in how to undertake the various procedures. This training should include how to use and carry personal protective equipment.

5.2. Long Term Actions

- Identify the places from which mercury could be emitted on a regular or accidental basis. Develop strategies to remove these emission sources.

- Set up a working group to study each operation in as much detail as possible to formalize the procedures. This group should include production, maintenance and safety departments, and especially those people who have a good grasp of the technical issues, in order to find the safest arrangement, procedures and working methods to reduce emissions and accidents.
- When metallic mercury is no longer visible in the workplace, steps should be taken to remove layers of mercury-contaminated encrustation (mainly brine or caustic soda). The prevention of leaks that cause encrustations in the first place should also be undertaken.

- Draw up a complete and accurate internal mercury balance. This activity will provide a strong incentive to improve work practices and reduce mercury emissions.

In conclusion we restate an elementary but fundamental principle: -“The right place for mercury is inside the cell”.

6. References

Env Prot 5 - Measurement of Air Flow and Mercury in Cell Room Ventilation

Env Prot 11A - Code of Practice - Mercury Housekeeping - Supplier's References

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

7. Note 1

It has been stated in various technical documents that mercury evaporation can be stopped by submersion in water.

The experiment described below illustrates that this statement is incorrect and that mercury will continue to evaporate even when it is submerged:

Fill a 1000 ml ground neck conical flask with distilled water. Slowly add 1ml of mercury using a hypodermic syringe fitted with a long enough needle to inject the mercury at the bottom of the aqueous phase. The air in the headspace is slowly purged from the flask with nitrogen or clean compressed air after which the flask is sealed. The headspace is connected to a 10 cm quartz cell located in an UV spectrophotometer, which scans the appropriate wavelength for mercury vapour.

The results of the UV measurements show that after just a few hours the mercury concentration in the headspace is nearly identical to that which would be present in the absence of the water layer. (For a temperature of 20^{O}C this corresponds to 13 mg/m^3.)

Conclusion: submersion in water only slows down the rate of evaporation.

8. Note 2

The following example illustrates how evaporation rates are effected by droplet fragmentation.

Consider 1 ml of mercury in three forms: 1 drop, 1000 droplets and 10000 micro-droplets. It is assumed that the contact surface area with the floor is negligible given the large surface tension of mercury. Simple calculation shows that the total surface area is 4.83 cm^2 for one drop, 48.3 cm^2 for 1000 droplets and 104.2 cm^2 for 10000 micro-droplets. Given that the volatility of mercury at a temperature of 20℃ is 0.056 mg/h.cm^2, the evaporation rates can be calculated for the three cases.

The following table sets out the various evaporation rates as a function of droplet number.

	One drop		***Total***	
Number of drops	**Volume (cm^3)**	**Surface (cm^2)**	*Surface* **(cm^2)**	**Evaporation Rate (µg/h)**
1	1	4.84	4.84	271
1000	0.001	0.0484	48.4	2710
10000	0.0001	0.0104	104.2	5835

Conclusion: the fragmentation of mercury (caused by splashing, brushing or water jetting) is to be avoided since there is an increase of evaporation rate with the number of droplets.

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9. Comment

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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