Euro Chlor
representing the chlor-alkali industry

GUIDELINES FOR MAKING A MERCURY BALANCE IN A CHLORINE PLANT

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Euro Chlor

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

Euro Chlor is working to:

- improve awareness and understanding of the contribution that chlorine chemistry has made to the thousands of products, which have improved our health, nutrition, standard of living and quality of life;

- maintain open and timely dialogue with regulators, politicians, scientists, the media and other interested stakeholders in the debate on chlorine;

- ensure our industry contributes actively to any public, regulatory or scientific debate and provides balanced and objective science-based information to help answer questions about chlorine and its derivatives;

- promote the best safety, health and environmental practices in the manufacture, handling and use of chlor-alkali products in order to assist our members in achieving continuous improvements (Responsible Care).

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

RESPONSIBLE CARE IN ACTION

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

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

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

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

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1. INTRODUCTION

The importance of accurate, complete and consistent data for the compilation of the annual mercury balance cannot be overstated.

In 1977 the Euro Chlor mercury based electrolysis industry voluntarily established a common and transparent accounting procedure to make an annual mercury balance for every plant, with the corresponding data consolidated and published at the global level. The following balance items are measured and compared:

- the apparent mercury consumption (fresh mercury introduced plus the possible reduction of inventory in the cells/decomposers and storage),
- the sum of all mercury emissions (in products, in air and in liquid effluents), plus the mercury contained in wastes temporarily stored and/or sent to authorised safe disposal.

In 1999, all European chlorine producers operating mercury cells have signed up to several voluntary commitments. One of them is:

"Reporting of individual plant mercury emissions data

Euro Chlor members with chlor-alkali production plants using mercury technology agree to disclose their individual plant mercury emission data in conformity with the OSPAR reporting guidelines. In others words no objection will made because of the confidential nature of this data. The data will be open to audit by the competent national authorities through a designated independent third party (see Reference 1)."

This document has been prepared to be used in conjunction with compilation of the annual calculation form (see appendix 1). It represents the currently available "know how" and references other Euro Chlor publications on sampling, inventory measurement, analytical measurements and housekeeping. All Euro Chlor member companies have committed themselves to follow these best practice guidelines.

A schema of the mercury balance is represented in appendix 2.

1.1. Apparent consumption

The mercury balance is based on the concept of consumption. It is important to recognise that consumption is not the same as purchases. The apparent consumption C_{ap} in any given period is derived from the amount of mercury (M) introduced (or removed) into (from) the plant during the period, corrected by the variation of inventories between the beginning (I_A) and the end of the period (I_B):

$$C_{ap} = M + (I_A - I_B)$$

M is the amount of mercury introduced or removed from stock in the period; it is defined by:

$$M = m - n + t - u$$

with: m = amount of mercury received from other sites

n = amount of mercury sent to other sites

t = mercury purchases (includes mercury from external recovery units)

u = mercury sales

$I_A - I_B > 0$ means decrease of the inventory.

$I_A - I_B < 0$ means increase of the inventory.

1.2. True consumption

The true consumption during a period of one year is the sum of the total losses, composed of the (diffuse) emissions (E) the mercury accompanying the solid waste leaving the plant (S) and the variation of mercury content of the contaminated materials and solid waste temporarily safely stored on the site (ΔF):

$$C_t = E + S + \Delta F$$

E is the total mercury emission calculated as:

$$E = E_1 + E_2 + E_3,$$

with E_1 is Emission in products

E_2 is Emission in waste water

E_3 is Emission in gaseous effluents and cell room ventilation air

S is the mercury content in contaminated materials and solid wastes leaving the plant to be sent to safe and secure final deposit or to external mercury recovery treatment. When the mercury comes back to the plant, it will be considered as purchased.

ΔF is equal to $F_B - F_A$, the difference in the mercury content of contaminated materials and solid wastes temporarily safely stored on site between the previous and the current balance (see Section 5.3).

1.3. Accuracy of the measures

Each mercury inventory I_A (I_B) is the sum of:

- I_{A1} (I_{B1}) mercury in storehouse and
- I_{A2} (I_{B2}) mercury in cells (see Section 4).

However, in practice mercury accumulates progressively in equipment other than cells – for example, in pipes, tanks, traps and in sewers. This accumulation, designated (A), is very difficult to estimate.

Additionally, the methods of making the mercury inventory introduce an error term due to measuring inaccuracies. The mercury inventory values I_A and I_B are of the order of 2000 g/t Cl_2 capacity whilst the other values (S, E, ΔF and M may be 2 to 3 orders of magnitude lower (typically 2 – 50 g/t Cl_2 capacity).

The values of S and ΔF are also difficult to determine with accuracy. An estimation of the magnitude of the corresponding imprecision is shown in Appendix 3.

Hence, the "noise", N, in the accuracy of the inventory measurements can be greater than the sum of the emissions.

1.4. Difference to balance

In theory, the calculation should equal the values of both consumption and emission, but there are disturbing factors, as already mentioned:

- statistical variations and errors coming from the inaccuracies in measurements and the calculation impact of small differences between very large numbers (see the example in appendix 3),
- progressive accumulation of mercury in the equipment like collectors, products storage tanks … (outside cells/decomposers and storage), being sometimes recovered during maintenance works, but usually remaining there until the decommissioning of the plant (not included in the yearly reporting of unit in production),

Due to these effects, both measured terms of the balance show variations from year to year and they usually differ from each other, giving rise to the so called "Difference to Balance" (DB):

DB = consumption - (emissions + mercury in wastes).

The mercury accumulates in tanks, headers, building fabric... (0.5 mm mercury layer in a 20 metre diameter tank represents more than 2 tonnes!); this explains that the annually calculated difference to balance is usually positive (consumption not found in the corresponding emissions or wastes).

When the DB over the lifetime of a plant is considered, a substantial proportion of the historical apparent "losses" can be recovered during dismantling of the installation and equipments, but is nevertheless limited by the degree of efficiency of the final recovery operation (mercury may remain amalgamated in metals or absorbed in building fabric). However, this final DB is not considered as an emission because it is held in safe final deposit (see Reference 7).

This Difference to Balance" DB (where DB = A + N), allows bridging the difference between the measurable apparent consumption C_{ap} and the true consumption C_t, where:

$C_{ap} = C_t + DB$

it follows that

$C_{ap} = E + S + \Delta F + DB$ or $DB = C_{ap} - E - S - \Delta F$

$DB = M + I_{A1} + I_{A2} - I_{B1} - I_{B2} - E - S - \Delta F$

The value of DB, whilst being mainly related to the accumulation (A) of mercury in equipment and pipework, is also largely influenced by the measurement accuracy of cell inventories and mercury in solid waste (sent to external disposal/treatment or temporarily stored on site); it is not a reflection on E which can be measured with a higher accuracy.

2. PLANNING FOR MERCURY BALANCES

In general, the measures which are taken to achieve good housekeeping standards will also provide a solid foundation for a good mercury balance, e.g.:

- Rearrangement of gaseous and liquid effluent streams to minimise the number of mercury outlets,
- Demercurisation of liquid effluent, alkali hydroxide liquor, hydrogen and vent gases,
- Mercury recovery from solid wastes,
- Minimisation of all mercury handling operations,
- Rapid recovery of spilt mercury.

All mercury outlets should be identified (for instance on a map of the plant), avoiding possible double counting (chlorine, hydrogen, caustic and caustic derivatives).

Sampling points must be selected. Sampling frequencies must be fixed, or alternatively, automatic samplers and/or analysers can be installed.

Criteria for obtaining statistically valid results from sampling have been published (see Reference 2) and should be followed.

Standard analysis methods (see References 3, 4, 5, 6 and 8) published by Euro Chlor should also be applied.

All plant personnel need to be aware of the necessity for establishing mercury balances as a means of monitoring the continuous improvement of the plant's environmental performance. All major incidents where mercury losses are involved should be carefully reported and recorded (plant shutdowns, major leaks, maintenance work involving mercury handling, etc.) so that this information can be used when the balance is made.

The date of the balance should be fixed well in advance so that all necessary data is available and all the preparatory work is completed (mercury store inventory, sewer cleaning, mercury recovery from solid wastes, etc.).

The plant should appoint a responsible person who will co-ordinate all the work involved with the establishment of periodic balances. The appointed person will be responsible for maintaining the integrity of all matters pertaining to the administration of the process.

3. OBTAINING DATA FOR MERCURY EMISSIONS (E)

3.1. Products (E_1)

3.1.1. Chlorine

Chlorine, which has been cooled, dried and filtered, contains very little mercury (approximately 1 mg/t).

Most of the mercury entrained by the chlorine from the cells is trapped in the condensates from cooling and, in a lesser extent, in the sulphuric acid from the drying towers. If these liquids are not discharged into the plant effluent treatment system, a sampling and analysis scheme is required.

Moist chlorine (cell gas and waste gases not sent to a drying unit) contains mercury and will contaminate the liquor of caustic absorption towers and/or other products manufactured. In this case, sampling and analysing of the moist chlorine or the reaction products at reasonable intervals may be necessary. However, since flow metering of moist chlorine is not easy, analyses and measurements of the reaction products are often more accurate. Those measurements should be integrated into the balance, taking care to avoid double counting.

3.1.2. Alkali Hydroxide Liquor

After filtration, this liquor contains only small amounts of mercury (10-100 mg/t). Sampling and analysis are not a particular problem and sampling and analysis frequencies are generally high in order to meet customers' specifications.

Sampling lines have to be thoroughly purged in order to be free from accumulation of mercury. An insert liner taking the sample from the centre of the pipe cross Section reduces such problems.

3.1.3. Hydrogen

Hydrogen sampling after a mercury removal unit poses few problems; if there are aerosols from a washing step, iso-kinetic sampling is recommended.

The analysis frequency is normally not relevant to the mercury balance (very low and quite constant concentration) but more to control the performance of the removal process.

However, the mercury concentration in pre-treated hydrogen streams can be high. Any emergency venting of cell hydrogen or by-passing of the treatment plant for, say, maintenance purposes should be noted and an allowance made in the overall balance (in the gaseous effluents section 3.3.3).

Hydrogen released to the atmosphere or used/sold as a fuel is not classed as a "product" and should not be counted in this category. It should be reported as a gaseous effluent (E3) (see Section 3.3.1).

3.2. Waste Water (E_2)

For convenience, all liquid effluent streams containing mercury should ideally be combined in such a way that, after mercury removal, a single sampling point can be used to analyse the entire output from the mercury treatment plant.

Automatic flow proportional sampling together with flow recording is preferred. Automatic sampling and analysing equipment must be frequently checked by approved laboratory methods. Analytical techniques have been developed (see Reference 5).

If solids (for example, from brine purification) are contained in the liquid effluent, special sampling techniques must be applied since automatic analysers may not work properly.

3.3. Gaseous Effluents and Cell Room Ventilation Air (E_3)

3.3.1. Treated Hydrogen to Atmosphere

Mercury removal processes for hydrogen are usually very efficient. Hence the burning of treated hydrogen as a fuel in a power station (or the venting of surplus treated hydrogen) gives rise to very low emissions of mercury. Similarly, during HCl synthesis a very small hydrogen surplus is released with negligible mercury content.

Sampling and analysis procedures are the same as for product hydrogen (see 3.1.3).

3.3.2. Hydrogen at Plant Start-Up

Hydrogen/Nitrogen mixtures emitted during plant start up or emergency situation cannot be treated, but generally result in a very low mercury emission.

Occasional sampling of the flow is necessary, and flow rate and time duration should be recorded to calculate the emission.

3.3.3. Emergency Venting

There are particular occasions when hydrogen must be vented directly from the cells or when the treatment plant must be by-passed. These streams may contain appreciable quantities of mercury. The time duration of this mode of operation should be noted. Generally the flow rate will be known from the production rate.

Mercury concentrations can be estimated from vapour pressure data, provided the temperature is measured.

3.3.4. Weak Hydrogen

Weak hydrogen includes vent gases from end-boxes, wash-boxes, caustic storage tanks, etc.

The flow rate of this emission should be measured periodically, for example with an anemometer, to check the blower capacity. If the vent gas is washed, a demister should be placed before the anemometer.

The emissions are then calculated from the measured mercury concentrations and the measured or, failing this, estimated flowrates.

3.3.5. Brine Vapours

The mercury content of brine vapours is normally very low when the brine purification unit is operated properly by insuring a sufficiently oxidising electrochemical potential in the brine (presence of active chlorine) to keep the mercury in ionic soluble form. For example, the stirring air from precipitation tanks or the vapour from resaturation units usually has low mercury concentration (< 10 µg/m^3).

If, for process reasons, this is not the case, complementary measures need to be taken to avoid emissions to air (for example, closed reactors and tanks, etc.).

3.3.6. Cell Room Ventilation Air

The exact measurement of the mercury losses associated with cell room ventilation air is usually quite difficult. Since air emissions comprise about 80% of all mercury emissions it is extremely important to take considerable care in assessing ventilation flow rates. Euro Chlor has studied this problem and has reviewed the available methods (see References 4 and 8). It is strongly recommended that one of these methods should be used.

Air flow conditions depend on the type of building, the production rates (temperature in the cells room) and climatic conditions. However, mercury concentrations are largely influenced by hydrogen leaks, mercury spillages, uncontained cell cleaning and poor mercury housekeeping conditions. If the Mercury Housekeeping Code of Practice (see Reference 9) is followed, mercury emissions from these sources can be minimised.

3.3.7. Miscellaneous

Other possible sources of mercury emission in air have to be taken into account after a careful analysis of the installation, like exhaust of the mercury waste retorting unit...

3.4. Cell Room Floor and Subsoil

In order to avoid penetration of mercury into the subsoil, it is necessary to construct and maintain the cell room floor and the drainage system so that they are fully impermeable. Recommendations on techniques to be followed are available (see Reference 9).

Mercury spillages should be avoided in accordance with the principles of good housekeeping. Where they do occur, they should be cleaned up directly using the methods prescribed in the Code of Practice (see Reference 9).

4. MERCURY INVENTORY (I)

4.1. Mercury in Storehouse (I_1)

Mercury in the main store as well as any stock kept in the cell room itself should be counted in this category. Mercury contained in shut-down cells should also be included. One should not rely on estimations of the mercury content of such cells; it is necessary to drain the mercury and weigh it.

The weight of mercury can be determined with an accuracy of ± 0.2 %.

4.2. Mercury in Cells (I_2)

Euro Chlor recommends that measurements should be made using radioactive tracer techniques at intervals of no more than every two years as the best approach for obtaining an accurate mercury balance. In case of inventories at intervals more than one year a specific extrapolation procedure has to be defined in order to get annual figures.

The weight of mercury can be determined with an accuracy of ± 0.5%.

One suitable technique has been specified in a Euro Chlor report (see Reference 10).

5. ACCUMULATED MERCURY

5.1. Mercury in Equipment Other than Cells

Mercury accumulated in tank, pits, traps and headers is contained in this category. It should be the aim of the plant to minimise this inventory by recovering this mercury to cells or store wherever possible.

Some equipment can be drained periodically (e.g. tanks, catch-pots, traps). Equipment of this type should be purged just prior to making the balance. The recovered mercury should be weighed and returned to stock. Such mercury would thus be reported as I_1 and will not appear in this category “accumulated mercury”.

The residual amount which cannot be quantified will appear as part of the Difference to Balance.

Sewers, traps and mercury sumps should be cleaned and the mercury recovered shortly before making the balance.

There are other pieces of equipment (headers - mainly wash water, hydrogen, brine, caustic - stock tanks, etc.) which can only be drained during plant stoppages.

For this type of equipment, experience has shown that:

- Very significant quantities of mercury can accumulate in some cases,

- The equilibrium level of mercury in a header is sometimes reached only after several years of operation.

The organisation of plant stoppages for cleaning and recovery of mercury from these items of equipment at the same time as the mercury balance measurements is usually not realistic. That means that recovery of significant quantities of mercury, outside of the normal balancing period, can sometimes give rise to an apparent negative consumption. This does not invalidate the correctness of the balance procedure.

Because of these fluctuations, balance figures should be seen in the context of several years of measurements.

5.2. Mercury sent to Safe Authorised Disposal/Recovery Sites (S)

All mercury-contaminated materials, such as cell components, process equipment, solid wastes from sumps, pits, demercurisation units and the brine purification process, that are sent to authorised deposits, should be included in this category. In some countries, material containing less than 50 or 100 ppm mercury may be disposed of in tips used for mercury-free waste. For the purposes of the balance, all deposits of mercury in whatever concentrations should be accounted for.

It should be the aim of the plant to minimise deposits by recovering mercury to cells or store wherever possible.

Analysis of the mercury content of some of these components may be difficult, due to their non homogeneity, and especially if the mercury is in the metallic form (local agglomeration of drops) Guidance can be found in Euro Chlor documents (see References 2 and 3). It is suggested that a detailed analysis is done on a sample of each type of waste to establish a plant standard and that this is then used in combination with weighing of each load leaving the site to obtain the mercury content.

The waste sent to external treatment unit for mercury recovery will also be included in this item; when the mercury comes back to the plant, it will be considered as “purchased”.

5.3. Mercury in Solid Wastes Temporarily Stored on Site (F)

Dispersed metallic mercury in solid wastes tends to agglomerate and settle. It is therefore very difficult to obtain representative samples from solid wastes such as caustic filtration filter cake, thick mercury and cell room dirt.

The best solution to this problem is to treat, as far as possible, all solid wastes for mercury recovery before making the balance.

However, there may very well be material held on site that, for the following reasons, cannot be recovered or deposited in a registered landfill at the time of the balance:

- Wastes awaiting recovery (F_c), either on-site or off-site,
- Wastes awaiting disposal (F_f)should be included in this category,
- Wastes awaiting a decision (F_i); at the time of the balance, no decision has been taken about the eventual disposal method (recovery, landfill, other).

If a full analysis of the mercury content is not practical, it is suggested that detailed analyses are done on samples of each type of waste to establish a plant standard and that these are then used in combination with weighing to obtain the mercury content. Only the difference in the quantity of mercury in these wastes between this and the previous estimate is relevant to the mass balance. This difference is denoted by ΔF.

6. CHLORINE CAPACITY CALCULATION

All the data obtained should be expressed in "g Hg" and related to the chlorine plant capacity P (t Cl2/year), calculated according to the following agreed formula:

$$P = 1.278 \times kA_{\max} \times (8760 - 150) \times n \times \frac{99}{100} \times 0.001$$

where 1.278 = electrochemical coefficient, assuming a current efficiency of 96.63%, expressed as kg/kA

kA_{max}	=	maximum workable rectifiers' capacity in cell room
8760 – 150	=	production hours, assuming 150 hr/year shut down
n	=	Total number of cells
99/100	=	cell utilisation coefficient
0.001	=	conversion factor to tonnes

The result of this calculation will be compared with the authorised capacity and if higher, replaced by the authorised capacity for recording in the annual questionnaire (see Appendix 1) in the box "Installed capacity".

In case of definitive shut down of the plant during the reporting year, the capacity for mercury balance reporting will be calculated “pro rata temporis”.

7. SUMMARY

The mercury balance (net consumption of mercury) is dominated by the difference between two very large numbers – the inventory of mercury at the beginning and at the end of the reporting period. The accuracy of these inventory measurements is therefore crucial.

Inaccuracies in the inventory measurements (or the ‘noise’, N) and occasional mercury recoveries during maintenance works in the plant are the principal sources of variability in the Difference to Balance figures calculated by an individual plant between one year and the next. The occasional mercury recoveries explain why negative DB values can occur.

It must be recognised that, even with perfect measurement, the Difference to Balance figure is unlikely be zero. During the life of a plant, mercury inevitably accumulates in plant equipment and structures usually resulting in a positive Difference to Balance. This is then offset in the longer term by possible recovery of a substantial proportion of the plant lifetime DB during plant decommissioning (the outstanding balance after final recovery has the characteristic of a deposit and not an emission to the eco-system).

For the industry as a whole, inaccuracies in measurement techniques tend to cancel out. The principal source of Difference to Balance for the industry is therefore this accumulation, A, of mercury in plant equipment. Nevertheless the average DB of West European Euro Chlor plants has reduced by 85 % between 1977 and 2007, due to improvements in technology, analytical methods (accuracy) and in operation procedures

8. REFERENCES

1. OSPAR Commission – Note of Proceedings WOCAI 1999 – WOCAI 99/7/1 – E Annex 5 page 2

2. BITC Mercury Analyses Working Group - Sampling methods and sampling strategy for mercury in alkali chloride electrolysis plants 1977

3. Analytical 3 – –Determination of Mercury in Solids

4. Analytical 6 – Determination of Mercury in Gasses

5. Analytical 7 – Determination of Mercury in Liquids

6. Analytical 10 – Determination of the Total Weight of Mercury in the Electrolysis Cells by Radioisotopes

7. ***Env. Prot. 3 – Guideline for Decommissioning of Mercury Chlor-Alkali Plants***

8. Env. Prot. 5 - Guideline for Measurement of Air Flow and Mercury in Cell-Room Ventilation

9. Env Prot 11 - Code of Practice – Mercury Housekeeping

10. Analytical 10 - Determination of the total weight of mercury in the electrolysis cells by radio-isotopes

9. LIST OF APPENDICES

Appendix 1: Questionnaire on Mercury Balance (used under the form of an Excel sheet sent yearly to all concerned members, with some red cell prefilled with site specific data)

Appendix 2: Schema of a mercury balance

Appendix 3: Worked example of Difference to Balance

APPENDIX 1: Questionnaire on mercury balance

DATABASE FOR THE YEARLY MERCURY BALANCE (values in tonnes)			
Site:		Plant discharge in catchment area of:	
Company:		Atlantic Ocean / North Sea	
Country:		Mediterranean Sea	
		Baltic Sea	
Calculated capacity:	t Cl2/yr	Black Sea	
Code number: (for internal use)		Resaturated brine	
Year	2006	Once through brine	

1 - CELL INVENTORY METHODOLOGY MEASUREMENT

Kind of method used	Previous		Current	
	Date	Amount (tonnes)	Date	Amount (tonnes)
Radiometric method [1]				
Estimation				

2 - INVENTORY OF MERCURY (CELLS + STOREHOUSE)

(I_A) At the beginning of the year (tonnes)		
(I_B) At the end of the year (tonnes)		
Variation on the year (tonnes) $\Delta I = I_A - I_B$ [2]		0.000

3 - TRANSFER OF MERCURY BETWEEN EUROPEAN SITES DURING THE PERIOD* (tonnes)

Site(s) with which the transaction has been made	IN [3]	OUT [4]
TOTAL	0.000	0.000

(1) See Anal 10.

(2) $\Delta I > 0$ means decrease of the inventory; $\Delta I < 0$ means increase of the inventory.

(3) Mercury received from other sites.

(4) Mercury sent to other sites.

4 - MERCURY PURCHASES (tonnes) T [5]	
5 - MERCURY SALES (tonnes) U [6]	

6 - MERCURY CONSUMPTION (tonnes)

Mercury introduced or removed from stock in the period* (tonnes) (M)

M = IN – OUT + T – U	0.000

Apparent consumption: C_{AP} = M + Δ I - Δ F	0.000

7 - AMOUNT OF MERCURY IN WASTES TEMPORARILY STORED

7.1 Wastes awaiting recovery

Wa = Mercury in stock at the beginning of the period* (tonnes)	
Wb = Mercury in stock at the end of the period* (tonnes)	
Change over the period (tonnes) Fc = Fb - Fa*	0.000

7.2 Wastes awaiting disposal

Wd = Mercury in stock at the beginning of the period* (tonnes)	
We = Mercury in stock at the end of the period* (tonnes)	
Change over the period (tonnes) Ff = Fe - Fd*	0.000

7.3 Wastes awaiting a decision for destination

Wg = Mercury in stock at the beginning of the period* (tonnes)	
Wh = Mercury in stock at the end of the period* (tonnes)	
Change over the period (tonnes) Fi = Fh - Fg*	0.000

Total change of mercury in wastes over the period Δ F = Fc + Ff + Fi

Δ F (tonnes)	0.000

* The period has to be one year.

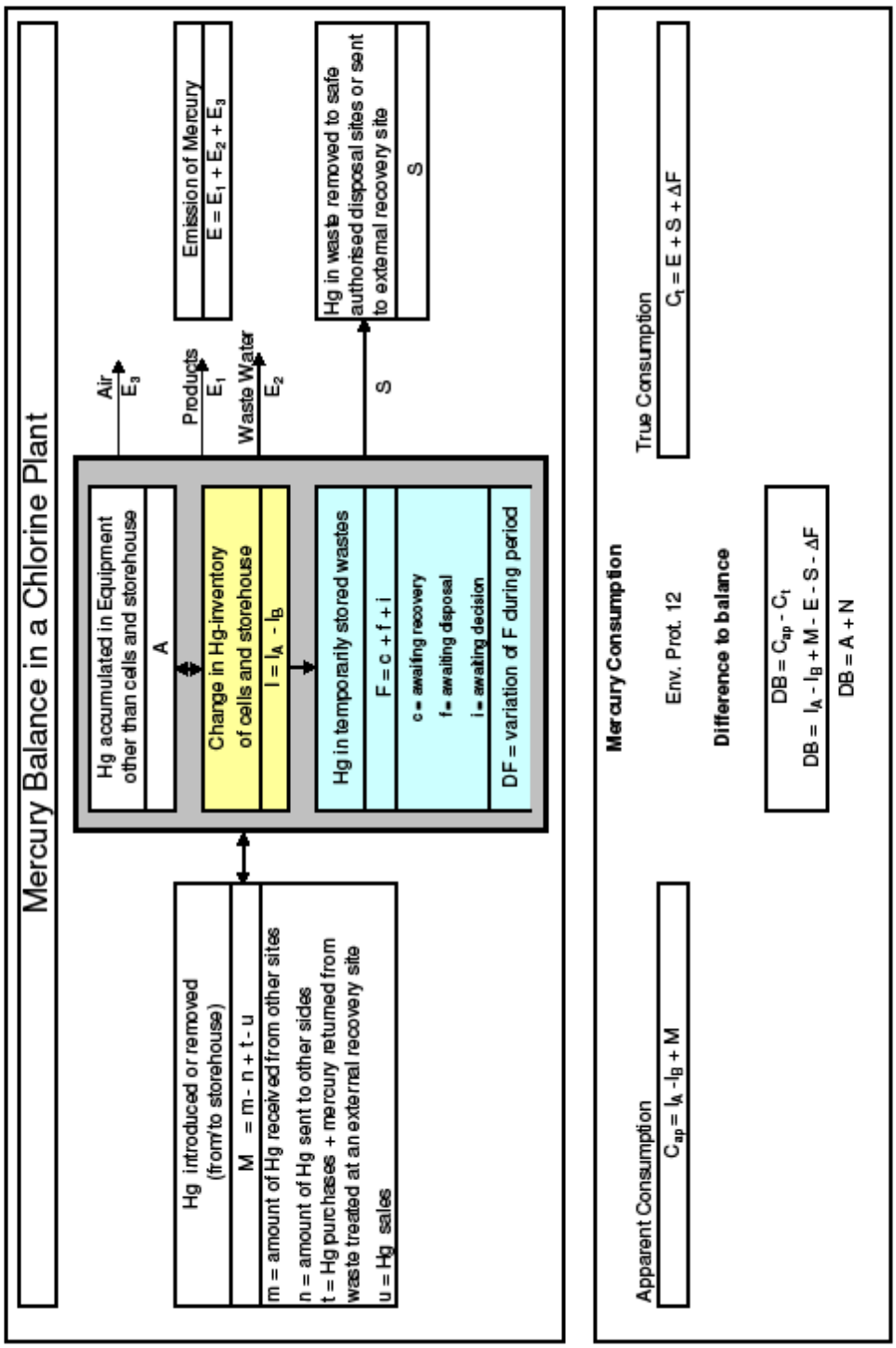
[5] T does not include IN (see section III)

[8] U does not include OUT (see section III)

ALL VALUES IN THE FOLLOWING TABLE ARE IN g Hg/t Cl_2 capacity

SUMMARY OF MERCURY BALANCE (g Hg/t Cl_2 capacity)		
1. Mercury apparent specific consumption (c_{ap})		
2. Mercury emission (e)		
2.1. Products (e1)		
2.2. Waste water [7] (e2)		
2.3. Waste gases (e3)		0.000
2.3.1. Process exhaust		
2.3.2. Cellroom ventilation		
TOTAL (e)		0.000
3. Mercury in the wastes safely disposed of (s)		
4. Difference to balance: db = c_{ap} – e – s (db)		

APPENDIX 2: Schema of a mercury balance



APPENDIX 3: Worked example of difference to balance

A.1. INTRODUCTION

This Appendix details the calculation of the "Difference to Balance" - the annual balance between consumption, emissions and disposals of mercury. It explains the three main reasons for this Difference to Balance, viz:

- A statistical variability due to inaccuracy in measurements, in particular of mercury inventories and of mercury disposal.

- The accumulation of mercury in equipment during the life-time of the plant, and its recovery on decommissioning

- The "noise" due to the inaccuracy in measurements.

Difference to Balance is a well-understood characteristic of mercury cell technology and the use of the term does not in any way indicate that any mercury is not accounted for.

A.2. THE BALANCE METHOD

The apparent consumption of mercury C_{ap} is the difference in the inventories of mercury at the beginning of a balance period, I_A, and the end of the period, I_B, together with M, the mercury introduced or removed from stock in the period.

$$C_{ap} = M + (I_A - I_B) \qquad (1)$$

As was shown in the Introduction to these guidelines, this overall consumption Cap is compared to the emitted losses E plus the quantity of mercury transferred to 'safe deposits or external treatment unit (S) and the variation of mercury in the waste material awaiting treatment ΔF, and is equalised by the Difference to Balance DB, such that

$$C_{ap} = E + S + \Delta F + DB \qquad (2)$$

$$DB = C_{ap} - E - S - \Delta F$$

$$DB = M + (I_A - I_B) - E - S - \Delta F \qquad (3)$$

It should be noted that I_A and I_B are large and similar quantities so that C_{ap} is considerably affected by the small difference of these two large numbers.

The effect on DB of the errors associated with the measurement accuracies of I_A, I_B, S and F is explained in the subsequent sections.

A.2.1 EMISSIONS (E)

Mercury losses are measured in liquid effluents, products and gaseous streams. Emissions are measured regularly and the analytical data are fully documented.

A number of investigations have been carried out by Euro Chlor members to discover all possible paths of emissions. The current combined know-how of the regulatory agencies and industry, together with existing stringent permitting requirements under national legislation, ensures that all emissions are detected and that all significant emissions are quantified to a reasonable accuracy. Emissions are thus not a significant contributor to uncertainty in the mercury balance.

A.2.2 MERCURY IN WASTE SENT TO SAFE AUTHORISED DEPOSITS/RECOVERY (S)

Mercury wastes are strictly regulated and therefore may only be disposed of in designated approved sites under controlled conditions. This can be either in landfills with established, monitored leachate limits or in deep mines. The regulatory conditions governing such disposals ensure that losses or emissions to the environment are precluded. The disposal of mercury waste in this way does not therefore represent a release to the environment.

For the purpose of the overall balance, the quantity of mercury in the waste sent to external recovery site is added to this item.

A.2.3 MERCURY IN WASTE TEMPORARILY STORED (∆F)

In some circumstances, wastes will not have been treated or disposed of at the time of the inventory. This could be because they are waiting for recovery, or are awaiting collection for deposition in a registered landfill or because no decision has yet been taken about their ultimate fate. By their nature, it is unlikely that a full analysis of the mercury content will be practicable. In such circumstances an estimate of the mercury content should be made. The change in inventory of such material across the inventory period is noted as ∆F. This material does not form part of the Difference to Balance and does not represent a release to the environment.

A.3. THE OVERALL BALANCE

The contribution of measurement errors to the balance is best illustrated by a worked example (supposing all measures are independent from each other):

Consider a typical cell-room with a capacity of 200.000 t/yr chlorine consisting of 100 cells and performing with Euro Chlor average mercury emission figures. In 2006, these were:

- Emissions to air, water and products (E) 1.055 g Hg/t Cl_2 capacity
- Mercury transferred to safe deposit (S) 22.924 g Hg/t Cl_2 capacity
- Mercury wastes stored on-site (∆F) 3.807 g Hg/t Cl_2 capacity

A.3.1 VARIATIONS IN APPARENT CONSUMPTION, (C_{ap})

Assume I_A is 372.25 t and that I_B is 370.56 tons, and that mercury purchases (M) are 2.85 tons.

If the inventories I_A and I_B are measured by radio-active tracer methods, the accuracy will be ± 0.5%. A higher accuracy of 0.2% applies to M (weighing), but since this is a small number relative to I_A and I_B, the effect on overall accuracy is small.

Hence, from equation (3)

Absolute $C_{ap} = M + (I_A – I_B)$

Absolute $C_{ap} = (2.85 \pm 0.006) + [(372.25 \pm 1.86) – (370.56 \pm 1.85)]$ t Hg/year,

The global error becomes $\pm 1.86 \pm 1.85 = \pm 3.71$

This absolute value has to be divided by 200 kt Cl_2 capacity/year.

$C_{ap} = [(2.85 \pm 0.006) + (1.69 \pm 3.71)] * 1000000/ 200000$ g Hg/ t Cl_2 capacity

$C_{ap} = 22.7 \pm 18.6$ g Hg/t Cl_2 capacity.

A.3.2 VARIATIONS IN ANNUAL MERCURY MOVEMENT (M)

As shown in the above example, the fact that M is always much smaller than I means that errors in M have an insignificant effect on the overall balance.

A.3.3 VARIATION IN EMISSIONS (E)

In the past years, measurement techniques have improved significantly. Provided the Euro Chlor techniques (see Reference 2) are followed, the overall errors for sampling and analysis should lie between 2 and 10 %.

Assuming the worst case of a 10% global inaccuracy:

$E = 1.055 \pm 0.11$ g Hg/t Cl_2 capacity

A.3.4 MERCURY TRANSFERRED TO SAFE DEPOSITS (S) and VARIATIONS IN AMOUNT OF MERCURY IN TEMPORARILY STORED WASTE (ΔF)

Difficulties persist with solid wastes in obtaining a representative sample, since mercury settles so effectively. Experience indicates errors can be in the range of ± 50 %.

Assuming an error of ± 50% on Hg in waste concentration, this would mean that:

$S = 22.92 \pm 11.46$ g Hg/t Cl_2 capacity

F_A (initial) = 0.3 ± 0.15 t Hg F_B (final) = 1.06 ± 0.53 t Hg

Absolute $\Delta F = F_B - F_A$ = (1.06 - 0.3) ± 0.68 t Hg

ΔF = 3.807 ± 3.403 g Hg/t Cl_2 capacity

A.3.5 THE DIFFERENCE IN BALANCE (DB)

Applying the above, with the estimates of error factors, gives:

DB = $C_{ap} – E – S – \Delta F$

DB = (22.7 ± 18.6) – (1.1 ± 0.1) – (22.9 ± 11.5) – (3.8 ± 3.4) g Hg/t Cl_2 capacity

DB = -5.1 ± 33.7 g Hg/t Cl_2 capacity

However, this assumes that the errors in each measurement occur in the direction that maximises the error in the result. If we assume that the errors occur randomly, then a good estimate of the likely error for the difference to balance is given by the square root of the sum of the squares of the individual errors.

Hence, the likely range of DB for a given plant is:

DB = $-5.1 \pm [(18.6)^2 + (0.1)^2 + (11.5)^2 + (3.4)^2]^{0.5}$ g Hg/t Cl_2

DB = -5 ± 22 g Hg/t Cl_2

This example shows that for a single individual plant, the major source of year-on-year variations in DB is due to statistical error arising from limitations in measurement accuracy, especially the inventory in cells and mercury in wastes.

However, when the results for many plants are consolidated together, the likely error in the consolidated Difference to Balance would be lower (because some errors will balance each other out). For instance, if it were assumed that all the 44 plants in the 2006 Euro Chlor study had the same values for measurements and errors as in the example above, the likely error would be given by:

DB = $\{ 44 * (-5) \pm [(44 * (22)^2]^{0.5} \} / 44$ g Hg/t Cl_2

DB = -5.1 ± 3.3 g Hg/t Cl_2

For the industry as a whole the Difference to Balance will therefore show less variation and is mainly due to accumulation of mercury in plant equipment as described in the following section.

A.3.6 ACCUMULATION OF MERCURY IN PLANT EQUIPMENT

It is well established that mercury accumulates in plant equipment such as steelwork, tanks, headers and building fabric during the operating lifetime of a cell

room. After closure and decommissioning, significant quantities of accumulated mercury are frequently recovered. Figures for recovery of between ten and two hundred tonnes have been reported.

Guidelines on the Best Environmental Practice for decommissioning mercury cell rooms and the final disposal of contaminated plant and equipment are available from Euro Chlor (***Env Prot 3 – Guidelines for the Decommissioning of Mercury Chlor Alkali Plants***).

Sometimes, when previously accumulated mercury is recovered in a plant during a balance period, then the DB for that individual plant can be negative in that balance period. However, due to the sustained accumulation, the average DB for some forty Euro Chlor plants has remained positive; the figure has however been falling steadily in the previous years as a result of the considerable improvements made in decommissioning practice over the years.

Much accumulated mercury is recovered on decommissioning and therefore does not appear in the reported annual balances, since these balances only deal with operating plants. Any that is not recovered is contained in appropriately classified wastes and disposed of to a ‘safe deposit’ in accordance with national regulations in such a way that there are no releases to the environment.

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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