Euro Chlor
representing the chlor-alkali industry

GUIDELINES FOR MAKING A MERCURY BALANCE IN A CHLORINE PLANT

Env. Prot. 12

5th Edition

March 2010

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).

****

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 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.

TABLE OF CONTENTS

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

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

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

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.