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SHORT COMMUNICATION

Determination of the chlorine current efficiency of mercury chlor-alkali cells

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List of symbols

f and d	superscripts refer to feed and depleted brine, respectively.
$C^{\text{source}}_{\text{species}}$	concentration of species (noted in the subscript) in the source stream (noted in the superscript) (mol dm^{-3})
F	Faraday number (96.487 kA s mol^{-1})
I	load (kA)
$J^{\text{source}}_{\text{species}}$	molar flow rate of species (noted in the subscript) in the source stream (noted in the superscript) (mol s^{-1})
p	feed brine flow rate (dm^3 s^{-1})
q	depleted brine flow (dm^3 s^{-1})
$C^{\text{f}}_{\text{Av.Cl}_2}$	total available chlorine in feed brine $(C^{\text{f}}_{\text{Cl}_2} + C^{\text{f}}_{\text{HOCl}} + C^{\text{f}}_{\text{NaOCl}})$(mol dm^{-3})
$C^{\text{d}}_{\text{Av.Cl}_2}$	total available chlorine in depleted brine $(C^{\text{d}}_{\text{Cl}_2} + C^{\text{d}}_{\text{HOCl}} + C^{\text{d}}_{\text{NaOCl}})$ (mol dm^{-3})
%O_2	Nitrogen-free oxygen in the cell gas = Measured value of % O_2 − 0.2658%N_2
$C^{\text{f}}_{\text{Cl}_2}$ and $C^{\text{d}}_{\text{Cl}_2}$	refer to the soluble chlorine in feed and depleted brine.

1. Introduction

Currently, about 14% of chlorine production in North America and 65% in Western Europe is from mercury cells which consume more energy than the diaphragm or membrane chlor-alkali cells [1, 2]. It is, therefore, essential that the energy consumption expressed in terms of kWh ton^{-1} of chlorine is estimated to achieve optimal energy savings.

The purpose of this paper is to develop a chlorine current efficiency expression for the mercury cell operations so that the energy consumption expressed in kWh ton^{-1} of chlorine can be reliably estimated. There is no published current efficiency expression for mercury cell operations. Hence, a material balance approach, similar to that employed for diaphragm and membrane cell operations [3], was followed here.

2. Theory

2.1. *Process chemistry*

The primary electrochemical reactions in a mercury chlor-alkali cell are as follows:
At the anode

$$\text{Cl}^- \longrightarrow \tfrac{1}{2}\text{Cl}_2 + \text{e}^- \tag{1}$$

At the cathode

$$\text{Na}^+ + \text{Hg} + \text{e}^- \longrightarrow \text{Na(Hg)} \tag{2}$$

Chlorine is evolved at the anode and an amalgam with 0.25–0.5% sodium is formed at the mercury cathode. The sodium amalgam produced is then fed to a decomposer, where it reacts with water to form sodium hydroxide and hydrogen gas as

$$\text{Na(Hg)} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \tfrac{1}{2}\text{H}_2 + \text{Hg} \tag{3}$$

The recovered mercury is recycled to the electrolyser. The caustic formed in this process is of high purity and has very low salt content (typically 0.005 wt%). The depleted brine from the electrolyser at a concentration of 21–22% is dechlorinated, resaturated with salt, treated to remove impurities, and returned to the electrolyser.

2.2. *Derivation of chlorine current efficiency expression*

The chlorine current efficiency, defined as the ratio of the amount of chlorine leaving the electrolyser, $J^{\text{o}}_{\text{Cl}_2}$, to the theoretically expected quantity of chlorine produced, can be expressed as

$$\eta_{\text{Cl}_2} = \frac{J^{\text{o}}_{\text{Cl}_2}}{I/2F} \tag{4}$$

Acknowledging the practical difficulties associated with the direct measurement of the amount of chlorine collected at the cell, an indirect approach is followed to estimate it from the material balance (i.e., input + generation − loss = output) of the Cl or Cl_2 species across the anode compartment of the electrolyser (see Fig. 1 for a schematic of the material balance for a mercury cell). From the material balance of the Cl_2 species (Equations 5–8),

$$\text{Input} = 3J^{\text{f}}_{\text{NaClO}_3} + J^{\text{f}}_{\text{Cl}_2} + J^{\text{f}}_{\text{HOCl}} + J^{\text{f}}_{\text{NaOCl}} \tag{5}$$

$$\text{Generation} = J^{\text{e}}_{\text{Cl}_2} = I/2F - 2J^{\text{e}}_{\text{O}_2} \tag{6}$$

$$\text{Loss} = 2J^{\text{ch}}_{\text{O}_2} \tag{7}$$

$$\text{Output} = 3J^{\text{d}}_{\text{NaClO}_3} + J^{\text{d}}_{\text{Cl}_2} + J^{\text{d}}_{\text{HOCl}} + J^{\text{d}}_{\text{NaOCl}} + J^{\text{o}}_{\text{Cl}_2} \tag{8}$$

and noting that the total amount of $\text{O}_2, J^{\text{o}}_{\text{O}_2}$, collected is from the electrochemical, $J^{\text{e}}_{\text{O}_2}$, and chemical reactions, $J^{\text{ch}}_{\text{O}_2}$, as

$$J^{\text{o}}_{\text{O}_2} = J^{\text{e}}_{\text{O}_2} + J^{\text{ch}}_{\text{O}_2} \tag{9}$$

the chlorine current efficiency can be deduced as

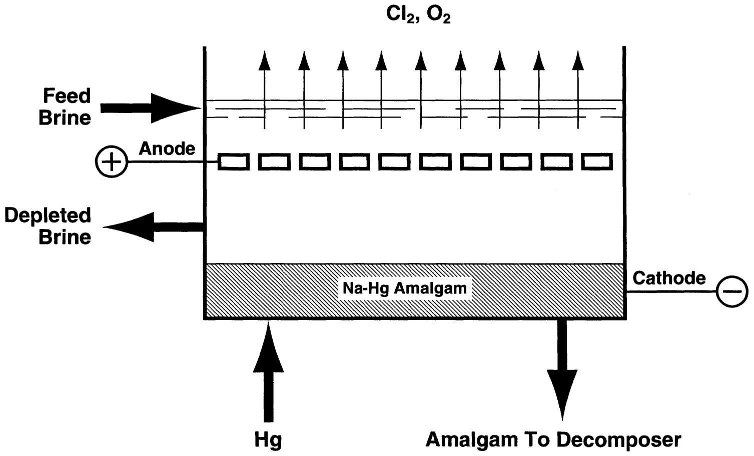

Fig. 1. Schematic of a mercury cell.

$$\eta_{\mathrm{Cl_2}} = \frac{1+\frac{F}{I}\left(6pC^{\mathrm{f}}_{\mathrm{NaClO_3}}-6qC^{\mathrm{d}}_{\mathrm{NaClO_3}}+2pC^{\mathrm{f}}_{\mathrm{Av.Cl_2}}-2qC^{\mathrm{d}}_{\mathrm{Av.Cl_2}}\right)}{1+2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}}\right)} \qquad (10)$$

The term, $\%\mathrm{O_2}/\%\mathrm{Cl_2}$, in Equation 10 arises from the identity that the mole fraction is equal to the volume fraction. Similarly, from the atomic chlorine (Cl) material balance described by Equations 11, 12 and 13,

$$\begin{aligned}\text{Input} &= J^{\mathrm{f}}_{\mathrm{NaCl}} + J^{\mathrm{f}}_{\mathrm{NaClO_3}} + 2J^{\mathrm{f}}_{\mathrm{Cl_2}} + J^{\mathrm{f}}_{\mathrm{HOCl}} \\ &\quad + J^{\mathrm{f}}_{\mathrm{NaOCl}} + J^{\mathrm{f}}_{\mathrm{HCl}} \end{aligned} \qquad (11)$$

$$\text{Generation} = \text{Loss} = 0 \qquad (12)$$

$$\begin{aligned}\text{Output} &= 2J^{\mathrm{o}}_{\mathrm{Cl_2}} + J^{\mathrm{d}}_{\mathrm{NaCl}} + 2J^{\mathrm{d}}_{\mathrm{Cl_2}} + J^{\mathrm{d}}_{\mathrm{HOCl}} + J^{\mathrm{d}}_{\mathrm{NaOCl}} \\ &\quad + J^{\mathrm{d}}_{\mathrm{NaClO_3}} + J^{\mathrm{d}}_{\mathrm{HCl}} \end{aligned} \qquad (13)$$

it can be shown that

$$p[\mathrm{Cl}]^{\mathrm{f}} = q[\mathrm{Cl}]^{\mathrm{d}} + \frac{\eta_{\mathrm{Cl_2}}}{F/I} \qquad (14)$$

where

$$[\mathrm{Cl}]^{\mathrm{f}} = \mathrm{C}^{\mathrm{f}}_{\mathrm{NaCl}} + \mathrm{C}^{\mathrm{f}}_{\mathrm{NaClO_3}} + \mathrm{C}^{\mathrm{f}}_{\mathrm{Cl_2}} + C^{\mathrm{f}}_{\mathrm{Av.Cl_2}} + C^{\mathrm{f}}_{\mathrm{HCl}} \qquad (15)$$

and

$$[\mathrm{Cl}]^{\mathrm{d}} = C^{\mathrm{d}}_{\mathrm{NaCl}} + C^{\mathrm{d}}_{\mathrm{NaClO_3}} + C^{\mathrm{d}}_{\mathrm{Cl_2}} + C^{\mathrm{d}}_{\mathrm{Av.Cl_2}} + C^{\mathrm{d}}_{\mathrm{HCl}} \qquad (16)$$

Use of the chlorine current efficiency expression (Equation 10) requires a knowledge of the depleted brine flow rate which can be avoided by substituting Equation 14 into Equation 10 and rearranging the terms. Thus, the proper expression for chlorine current efficiency for mercury cells operating with NaCl is as follows.

$$\eta_{\mathrm{Cl_2}} = \frac{1+\frac{F}{I}p\left[6C^{\mathrm{f}}_{\mathrm{NaClO_3}}+2C^{\mathrm{f}}_{\mathrm{Av.Cl_2}}-\frac{[\mathrm{Cl}]^{\mathrm{f}}}{[\mathrm{Cl}]^{\mathrm{d}}}\left(6C^{\mathrm{d}}_{\mathrm{NaClO_3}}+2C^{\mathrm{d}}_{\mathrm{Av.Cl_2}}\right)\right]}{1+2\left(\frac{\%\mathrm{O_2}}{\%\,\mathrm{Cl_2}}\right)-\frac{1}{[\mathrm{Cl}]^{\mathrm{d}}}\left(6C^{\mathrm{d}}_{\mathrm{NaClO_3}}+2C^{\mathrm{d}}_{\mathrm{Av.Cl_2}}\right)} \qquad (17)$$

Extension of Equation 14 coupled with Equations 15 and 16 to the KCl system is simple. Estimation of the dissolved chlorine values in NaCl and KCl is shown in Appendix 1.

3. Results and discussion

Equation 10 can be simplified further if the values of the feed brine flowrate (p) and the depleted brine flowrate (q) are known. The brine flowrate in typical mercury cells is generally in the range of 20–35 gal min^{-1}(or 166–290 lb min^{-1}), whereas the water loss is only about 1 lb min^{-1}. Hence, it can safely be assumed that $p = q$. Equation 10 can now be recast as

$$\eta_{\mathrm{Cl_2}} = \frac{1}{1+2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}}\right)-\left(\frac{6\Delta C_{\mathrm{NaClO_3}}+2\Delta C_{\mathrm{Av.Cl_2}}}{\Delta\mathrm{Cl}}\right)} \qquad (18)$$

where

$$\Delta C_{\mathrm{NaClO_3}} = C^{\mathrm{f}}_{\mathrm{NaClO_3}} - C^{\mathrm{d}}_{\mathrm{NaClO_3}} \qquad (19)$$

$$\Delta C_{\mathrm{Av.Cl_2}} = C^{\mathrm{f}}_{\mathrm{Av.Cl_2}} - C^{\mathrm{d}}_{\mathrm{Av.Cl_2}} \qquad (20)$$

$$\begin{aligned}\Delta\mathrm{Cl} &= (C^{\mathrm{f}}_{\mathrm{NaCl}} + C^{\mathrm{f}}_{\mathrm{NaClO_3}} + C^{\mathrm{f}}_{\mathrm{Cl_2}} + C^{\mathrm{f}}_{\mathrm{Av.Cl_2}} + C^{\mathrm{f}}_{\mathrm{HCl}}) \\ &\quad - (C^{\mathrm{d}}_{\mathrm{NaCl}} + C^{\mathrm{d}}_{\mathrm{NaClO_3}} + C^{\mathrm{d}}_{\mathrm{Cl_2}} + C^{\mathrm{d}}_{\mathrm{Av.Cl_2}} + C^{\mathrm{d}}_{\mathrm{HCl}}) \end{aligned} \qquad (21)$$

Equation 18 is the general expression recommended for calculating the chlorine efficiency of mercury cells. However, if the depleted brine pH is ≤ 3.5, Equation 18 can be altered by omitting the terms involving $\mathrm{NaClO_3}$ (see Appendix 2 for the rationale) for estimating and comparing chlorine efficiency of individual cells.

Process chlorine efficiency, $\eta^{\mathrm{P}}_{\mathrm{Cl_2}}$, for a given cell circuit can also be calculated from Equation 18 by omitting the terms, $C^{\mathrm{f}}_{\mathrm{Cl_2}}, C^{\mathrm{f}}_{\mathrm{Av.Cl_2}}, C^{\mathrm{d}}_{\mathrm{Cl_2}}$ and $C^{\mathrm{d}}_{\mathrm{Av.Cl_2}}$ as given by Equation 22.

$$\eta^{\mathrm{P}}_{\mathrm{Cl_2}} = \frac{1}{1+2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}}\right)-6\left(\frac{\Delta C_{\mathrm{NaClO_3}}}{\Delta\mathrm{Cl}^*}\right)} \qquad (22)$$

where

$$\begin{aligned}\Delta\mathrm{Cl}^* &= (C^{\mathrm{f}}_{\mathrm{NaCl}} + C^{\mathrm{f}}_{\mathrm{NaClO_3}} + C^{\mathrm{f}}_{\mathrm{HCl}}) \\ &\quad - (C^{\mathrm{d}}_{\mathrm{NaCl}} + C^{\mathrm{d}}_{\mathrm{NaClO_3}} + C^{\mathrm{d}}_{\mathrm{HCl}}) \end{aligned} \qquad (23)$$

$\eta^{\mathrm{P}}_{\mathrm{Cl_2}}$ includes the chlorine produced from the cells and the chlorine recovered from the dechlorination of the

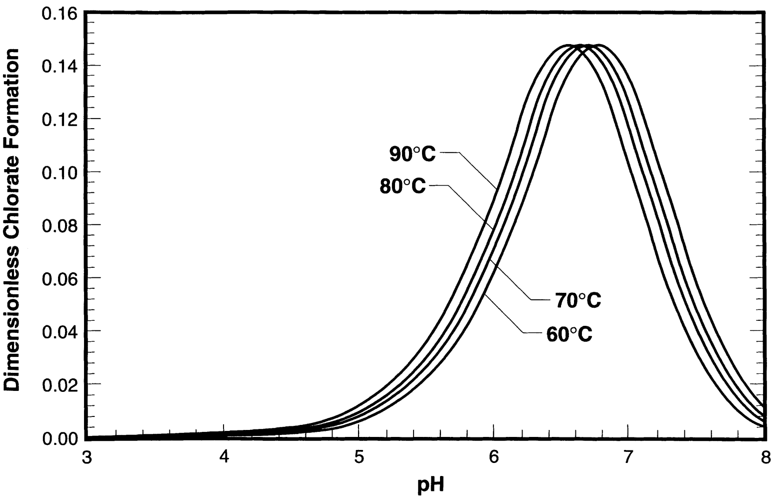

Fig. 2. Chlorate formation rate as a function of pH and temperature.

depleted brine. If the process chlorine efficiency for the circuit is less than 96%, it is essential that individual cell efficiencies be determined using Equation 18, which requires an analysis of the feed brine, depleted brine out of the electrolyser, and average gas analytical data with three to four samples over a 4 h period.

References

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[2] A. Leder, E. Linak, R. Holmes and T. Sasano, CEH Marketing Research Report, SRI International (June 1994).
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Appendix 1: Solubility of chlorine in brine [4]

A. NaCl system

$$C^{\mathrm{f}}_{\mathrm{Cl_2}} \text{ or } C^{\mathrm{d}}_{\mathrm{Cl_2}} = 1.408 \times 10^{-5} P_{\mathrm{Cl_2}} \left[(1.567 - 0.002\,822[\mathrm{NaCl}]^{\mathrm{d}})10^{1000/T} + 70\,906 \times 10^{(\mathrm{pH}-A)}\right]$$

where:

A = $6.01 + 0.001(T - 273.15) - 0.000\,44\,[\mathrm{NaCl}]^{\mathrm{d}}$
G = specific gravity of depleted brine
pH = depleted brine pH
T = anolyte temperature $(K) = t(^{\circ}C) + 273.15$
$[\mathrm{NaCl}]^{\mathrm{d}}$ = depleted brine concentration (g l^{-1})
$P_{\mathrm{Cl_2}}$ = partial pressure of chlorine gas (atm) $= \%\mathrm{Cl_2}(1 - P_{\mathrm{H_2O}})$
$P_{\mathrm{H_2O}}$ = water vapour pressure of depleted brine (atm) $= (1 - R \times S)P^{\mathrm{o}}_{\mathrm{H_2O}}$
$P^{\mathrm{o}}_{\mathrm{H_2O}}$ = vapour pressure of pure water (atm) $= (\frac{1}{760})10^{(7.951\,90\, - \,\frac{1659.793}{T-45.854})}$
R = $(S - 3)[1.9772 \times 10^{-3} - 1.193 \times 10^{-5}(T - 273.15)] + 0.035$
S = $\frac{[\mathrm{NaCl}]^{\mathrm{d}}}{58.44}\left(\frac{1000}{1000G - [\mathrm{NaCl}]^{\mathrm{d}}}\right)$

B. KCl system

$$C^{\mathrm{f}}_{\mathrm{Cl_2}} \text{ or } C^{\mathrm{d}}_{\mathrm{Cl_2}} = 1.408 \times 10^{-5} P_{\mathrm{Cl_2}}[(1.567 - 0.002\,822\,[\mathrm{KCl}]^{\mathrm{d}})10^{1000/T} + 70\,906 \times 10^{(pH-A)}]$$

where:

A = $6.01 + 0.001(T - 273.15) - 0.000\,44\,[\mathrm{KCl}]^{\mathrm{d}}$
G = specific gravity of depleted brine
pH = depleted brine pH
T = anolyte temperature $(K) = t(^{\circ}C) + 273.15$
$[\mathrm{KCl}]^{\mathrm{d}}$ = depleted brine concentration (g l^{-1})
$P_{\mathrm{Cl_2}}$ = pressure of chlorine gas (atm) $= \%\mathrm{Cl_2}(1 - P_{\mathrm{H_2O}})$
$P_{\mathrm{H_2O}}$ = water vapour pressure of depleted brine (atm) $= (1 - R \times S)P^{\mathrm{o}}_{\mathrm{H_2O}}$
$P^{\mathrm{o}}_{\mathrm{H_2O}}$ = vapour pressure of pure water (atm) $= (\frac{1}{760})10^{(7.951\,90\, - \,\frac{1659.793}{T-45.854})}$
R = $7 \times 10^{-4}(S - 2) + 0.0317$
S = $\frac{[\mathrm{KCl}]^{\mathrm{d}}}{74.55}\left(\frac{1000}{1000G - [\mathrm{KCl}]^{\mathrm{d}}}\right)$

Appendix 2: Kinetics of chlorate formation [5]

The dimensionless rate of chlorate formation (Γ), based on the following generally accepted mechanism:

$$2\,\mathrm{HOCl} + \mathrm{OCl^-} \xrightarrow{k} \mathrm{ClO_3^-} + 2\,\mathrm{HCl} \qquad \text{(a)}$$

is given as

$$\Gamma = \frac{r}{kVC_t^3} = \frac{k_{\mathrm{a}}10^{-2\mathrm{pH}}}{(k_{\mathrm{a}} + 10^{-\mathrm{pH}})^3}$$

where:

$r = kV[\mathrm{HOCl}]^2[\mathrm{OCl^-}]$

$V =$ reaction volume

$C_t = [\mathrm{HOCl}] + [\mathrm{OCl}^-]$

$k =$ rate constant for reaction (a)

$= 8.509 \times 10^5 \mathrm{e}^{-4777/T}$ (b)

$k_a =$ equilibrium constant for $\mathrm{HOCl} \rightleftharpoons \mathrm{OCl}^- + \mathrm{H}^+$

$= 3.04 \times 10^{-5} \mathrm{e}^{-2000/T}$ (c)

The dimensionless chlorate formation rate is a function of pH and temperature, the optimal pH values being 6.82 at 60 °C, 6.75 at 70 °C, 6.68 at 80 °C and 6.61 at 90 °C. Chlorate formation rate, R, is calculated as a function of pH and depicted in Fig. 2 which shows that the chlorate formation is almost negligible at pH values of < 3.5.