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SHORT COMMUNICATION

Comments on the estimation of caustic current efficiency of ion exchange membrane chlor-alkali cells

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Nomenclature

$Cl_2(s)$	Soluble chlorine from chlorine hydrolysis (in $g\,dm^{-3}$) following $Cl_2 + H_2O \rightarrow HCl + HOCl$, (calculable from the correlations in [3])
$C_{\text{species}}(a)$	Concentration of species noted in the subscript in the anolyte ($g\,dm^{-3}$)
$C_{\text{species}}(d)$	Concentration of species noted in the subscript in the depleted brine ($g\,dm^{-3}$)
$C_{\text{species}}(f)$	Concentration of species noted in the subscript in the feed brine ($g\,dm^{-3}$)
F	Faraday constant ($96.487\,kA\,s\,mol^{-1}$)
I	load (kA)
q	depleted brine flow rate ($dm^3\,s^{-1}$)
p	feed brine flow rate ($dm^3\,s^{-1}$)
$C_{NaClO_3}(d)$	$NaClO_3$ in depleted brine ($g\,dm^{-3}$)
$C_{NaClO_3}(f)$	$NaClO_3$ in feed brine ($g\,dm^{-3}$)
$Cl_2(d)$	total dissolved chlorine in anolyte ($g\,dm^{-3}$)

1. Introduction

In an earlier publication [1] a generalized current efficiency expression (Equation 1) for estimating the caustic current efficiency (η_{NaOH}) of ion-exchange membrane cells was derived from material balance considerations taking into account the presence of NaOH, Na_2CO_3, and $NaClO_3$ in the feed brine. While the validity and accuracy of this equation was established by comparing the 'anolyte and anode gas' analysis data with the results obtained from caustic collection measurements, Equation 1 does not take into account the presence of Na_2SO_3 in the feed brine and needs the value of the depleted brine flow rate which is generally approximated from the feed brine flow rate. This brief communication addresses these two issues so that potential errors in calculating the caustic efficiencies are avoided.

$$\eta_{NaOH} = \left(\frac{1 - [(2F/I)(qA - pB)]}{C}\right) \times 100\% \tag{1}$$

where

$$A = \left[\frac{3C_{NaClO_3}(d)}{106.45}\right] + \left[\frac{[Cl_2(d) - Cl_2(s)]}{70.91}\right] - \left[\frac{CC_{HCl}(d)}{2(36.5)}\right]$$

$$B = \left[\frac{3NaClO_3(f)}{106.45}\right] + \left[\frac{X}{70.91}\right] - \left[\frac{CC_{HCl}(f)}{2(36.5)}\right]$$

$$C = 1 + (2\%O_2/\%Cl_2)$$

$\%O_2$ and $\%Cl_2$ refer to the volume fraction of O_2 and Cl_2 in the cell gas (see [1] for details).

2. Results and discussion

2.1. *Na_2SO_3 in the feed brine*

The brine fed to ion-exchange membrane cells is sodium chloride, either solution mined or prepared from mined or solar evaporated solid salt, which is first treated with NaOH + Na_2CO_3 to remove Ca^{2+} and Mg^{2+} as $CaCO_3$ and $Mg(OH)_2$ and subsequently subjected to ion-exchange treatment to reduce the metallic impurity levels to the p.p.b. (parts per billion) range, conforming to the specifications of the membrane manufacturers. In some operations, the depleted brine from the membrane cells is first dechlorinated and then resaturated with solid salt before it is sent back to the cells following primary and secondary brine treatments. Since the ion-exchange resins used in the secondary brine treatment are very sensitive to dissolved chlorine or hypochlorite in the brine, Na_2SO_3 is generally added in excess to ensure the total removal of the final traces of chlorine [2].

Since Na_2SO_3 reacts with dissolved chlorine following Equation 2,

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl \tag{2}$$

$$C_{Cl_2}(a) \text{ lost due to } Na_2SO_3 = (70.91/126.0)\,C_{Na_2SO_3}(f) = 0.56266C_{Na_2SO_3}(f) \tag{3}$$

Hence, the term X in Equation 1 will be modified as

$$X = 1.338C_{Na_2CO_3}(f) + 0.844C_{NaHCO_3}(f) + 1.773C_{NaOH}(f) - 0.5626C_{Na_2SO_3}(f) \tag{4}$$

with a density of 1.2 for the feed brine.

2.2. *Calculation of depleted brine flow rate*

The sodium ion material balance around an electrolyser can be described as

$$Na_f^* = Na_d^* + Na_m^* \tag{5}$$

where Na_f^* and Na_d^* refer to the total mass of Na ions going in and out of the electrolyser respectively and

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Na_m to the Na transported through the membrane and out of the cells to form NaOH. Na_f^* and Na_d^* may now be related to the Na containing ionic species in the feed and depleted brine as described by Equations 6 and 7.

$$Na_f^* = p\{Na_f\} \qquad (6)$$

$$Na_d^* = q\{Na_d\} \qquad (7)$$

where

$$\begin{aligned} Na_f = {} & 0.39336C_{NaCl}(f) + 0.3648C_{Na_2SO_3}(f) \\ & + 0.3236C_{Na_2SO_4}(f) + 0.21598C_{NaClO_3}(f) \\ & + 0.4338C_{Na_2CO_3}(f) + 0.27366C_{NaHCO_3}(f) \\ & + 0.5747C_{NaOH}(f) \\ Na_d = {} & 0.39336C_{NaCl}(d) + 0.3236C_{Na_2SO_4}(d) \\ & + 0.21598C_{NaClO_3}(d) + 0.3088C_{NaOCl}(d) \end{aligned}$$

The $C_{species}$ refers to the concentration of the species in the subscript in $g\,dm^{-3}$ and the subscripts f and d refer to the feed brine and depleted brine, respectively.

Na_m is related to caustic current efficiency and the load as

$$Na_m = (I/F)\eta_{NaOH} = 0.23826\ I\eta_{NaOH} \qquad (8)$$

Thus,

$$Na_d^* = Na_f^* - Na_m \qquad (9)$$

or, from Equations 6 and 7,

$$qNa_d = pNa_f - Na_m \qquad (10)$$

Hence

$$q = \left[p\frac{Na_f}{Na_d}\right] - \left[\frac{Na_m}{Na_d}\right] \qquad (11)$$

or

$$q = \left[p\frac{Na_f}{Na_d}\right] - \left[\frac{0.23826\ I\eta_{NaOH}}{Na_d}\right] \qquad (12)$$

Substituting Equation 12 into Equation 1, followed by recasting, results in Equation 13,

$$\eta_{NaOH} = \left(\frac{1 - (2F/I)p[(ANa_f/Na_d) - B]}{[C - (0.47652FA/Na_d)]}\right) \times 100\% \qquad (13)$$

Using a value of F 96.487 $kAs\,mol^{-1}$ in Equation 12 leads to Equation 14,

$$\eta_{NaOH} = \left(\frac{1 - (2F/I)p[(ANa_f/Na_d) - B]}{[C - (45.978A)/Na_d)]}\right) \times 100\% \qquad (14)$$

which is the proper equation for calculating the caustic current efficiency. Equation 14 does not involve q, the depleted brine flow rate and hence, eliminates the need to measure or approximately estimate its magnitude.

It is of interest to note that Equation 12 itself can be used to estimate the caustic efficiencies provided the feed brine and depleted brine flow rates are known. Use of Equation 12 has the advantage of avoiding the anode gas analyses for estimating the caustic efficiency. Alternatively, one may calculate the depleted brine flow rate from the concentration ratio of an inert species in the feed and depleted brine. The inert species should, however, be chemically and electrochemically inactive in the anolyte, should not diffuse/migrate through the membrane, and it should have no adverse effect on the downstream process operations. Such a species could be either borate, perborate, perchlorate or phosphate. It would then be possible to calculate the depleted brine flow rate from the material balance formalism described above for the 'species'. While sodium sulphate may serve the above purpose because of its low diffusivity through the membrane [4], it is not preferred in view of its adverse effects on the membrane resulting in reduced current efficiency and membrane damage [5, 6].

It may be noted that the 'inert species approach' mandates accurate measurement of the feed brine flow rate values to within ±0.01% as these errors are directly reflected in the caustic current efficiency values.

2.3 *Errors involved in current efficiency values arising from approximated versions of Equation 14 for membrane cells and diaphragm cells*

2.3.1. Membrane cells. Caustic current efficiency calculations based on Equation 14 require accurate values of NaCl, Na_2CO_3, NaOH, Na_2SO_4, $NaClO_3$, and $Cl_2(d)$ in the feed brine and the depleted brine, flow rates, total current, $\%O_2$ and $\%Cl_2$ in the cell gas and the pH and temperature of the depleted brine for calculating $Cl_2(s)$. Errors resulting from (a) analytical errors and (b) omission of terms in Equation 14 are addressed below.

The effects of analytical errors are estimated using typical values of Na_f, Na_d, A, B, and C (resulting in a caustic efficiency of 95.1%) and varying these parameters. These calculations showed that an analytical error of 5% in one of the values of Na_f, Na_d, A or B would result in 1% error in the calculated current efficiency, and 1% error in C leads to 1% error in the estimated efficiency values. Thus, it is essential that accurate analytical methods be used for reliably assessing the performance characteristics of ion-exchange membranes and cell technologies.

Simplified versions of Equation 14 have been considered to avoid the extensive analyses of brine components and operating parameters of the cell. These include neglecting the chlorate build-up in the anolyte (ΔClO_3) and soluble Cl_2 and taking into account only the changes of concentration of HCl with acid feed brine or $Cl_2(d)$ with neutral or alkaline brine feed. Efficiency calculations for typical operating conditions showed 1–2% error in efficiency by simple neglect of ΔClO_3 and $Cl_2(s)$ terms.

2.3.2. Diaphragm cells. Equation 14, derived for membrane cells, can be easily extended to estimate the chlorine efficiency of diaphragm cells (η_{Cl_2}) as described in [1]. Thus, the expression for η_{Cl_2} based on material balance considerations is given by Equation (15).

$$\eta_{Cl_2} = \left(\frac{1}{1 + (2\%O_2/\%Cl_2) + \alpha}\right) \times 100\% \tag{15}$$

where $\alpha = 2.2546\ (C^*_{NaClO_3}(a) - C^*_{NaClO_3}\ f)/C_{OH}$, and C_{OH} is the caustic concentration in g dm^{-3} $\cdot$ $C^*_{NaClO_3}(a)$ and $C^*_{NaClO_3}(c)$ refer to the concentration of all chlorine-containing oxidants expressed as $NaClO_3$ in the anolyte and catholyte respectively in g dm^{-3}.

The η_{Cl_2} values calculated employing Equation 15 have been shown in [1] to be in excellent agreement with the measured caustic efficiency values in commercial cells.

Several approximate versions of Equation 15 are employed in the chlor-alkali industry for estimating the chlorine efficiency of diaphragm cells where in α, the [illegible]t term in denominator of Equation 15, is either dropped or simplified as

$$\alpha = \sim 2\,\frac{C^*_{NaClO_3}(a)}{C_{OH}} \text{ or } \frac{6 \text{ to } 18\ C^*_{NaClO_3}(c)}{C_{OH}} \tag{16}$$

These simplifications were found to result in 1–3% higher chlorine efficiency than the actual values based on Equation 15 or direct measurement of caustic efficiency. It may be noted omission of α in Equation 15 implies the absence of dissolved chlorine, OCl^- and ClO_3^- in the anode compartment of a chlor-alkali cell, violating the basic chemistry of the reactions proceeding in a chlorine cell. Furthermore, wrong estimates of current efficiency could result in additional operating costs since errors in efficiency will adversely impact the energy consumption calculations and production capacity, as well as, royalty payments. The details related to the significance and proper determination of α are addressed [1].

The chlorine current efficiency expression for the membrane cells, η^*_{Cl2}, can be easily derived from Equation 1 and the material balance equations for the chloride ions as:

$$\eta^*_{Cl2} = 100\%\ (1 - (5.43844pD/I))/E \tag{17}$$

where

$$D = ([C_{Cl}(f) + 0.33302C^*_{NaClO_3}(f)]Y) - (C^*_{NaClO_3}(f))$$

$$E = 1 + (2\% + O_2/\%Cl_2) - 1.97274Y$$

$$Y = C^*_{NaClO_3}(d)/(C_{Cl}(d) + 0.33302C^*_{NaClO_3}(d)$$

$C_{Cl}(f)$, $C_{Cl}(d)$: chloride ion concentration in the feed brine and depleted brine respectively in g dm^{-3}

η^*_{Cl2} values calculated using Equation 17 are lower by ~2% compared to the η_{NaOH} values in the caustic efficiency range of 94–96% and are within ±0.5% in the caustic efficiency range of 88–90%.

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