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Generalized expressions for estimating the current efficiency of ion-exchange membrane and diaphragm chlor-alkali cells

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Comprehensive chlorine and caustic current efficiency equations were derived for ion-exchange membrane and diaphragm chlor-alkali cells using material balances that account for all common and significant reactive brine impurities and their respective interactions with Cl_2 and/or NaOH. These generalized equations, formulated in terms of molar flow rates of the species entering, exiting, generated in or consumed in the cells, require a knowledge of the feed and depleted brine compositions to calculate the current efficiency of either an individual electrolyser or an entire circuit. It was shown that the global current efficiency expression can be degenerated to the various currently employed equations in the chlor-alkali industry for estimating the current efficiency with certain assumptions or approximations. These simplified assumptions and approximations, usually involving omission of some brine components or anolyte reactions, were shown to result in differences in the published current efficiency expressions. Disparities between the caustic and chlorine current efficiency of membrane and diaphragm cells were quantified and approaches to achieve either high η_{Cl_2} or η_{OH} were also outlined. Current efficiency equations, based on an analysis of anode gases and anolyte composition, require an accurate measure of all the components in the feed and depleted brine. A simplified method, which is analytically less cumbersome, is also presented to estimate the caustic current efficiency of ion-exchange membrane chlor-alkali cells.

List of symbols

$C_{\text{species}}^{\text{source}}$	concentration of species (noted in the subscript) in the source stream (noted in the subscript) (mol dm^{-3})
F	Faraday number ($96\,487\ \text{C mol}^{-1}$)
I	load (A)
$J_{\text{species}}^{\text{source}}$	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 ($\text{dm}^3\ \text{s}^{-1}$)
q	depleted brine flow rate for membrane cells or cell liquor flow rate for diaphragm cells ($\text{dm}^3\ \text{s}^{-1}$)
R	gas constant
R^*	$= q/p$
T	temperature (K)
$\Delta J_{\text{species}}$	$= J_{\text{species}}^{\text{f}} - J_{\text{species}}^{\text{d}} = pC_{\text{species}}^{\text{f}} - qC_{\text{species}}^{\text{d}}$

Greek letters

η_{Cl_2}	membrane cell chlorine current efficiency
$\eta_{Cl_2}^{D}$	diaphragm cell chlorine current efficiency
$\eta_{Cl_2}^{P}$	diaphragm process chlorine current efficiency
$\eta_{H_2}^{D}$	diaphragm cell hydrogen current efficiency
η_{OH}	membrane cell caustic current efficiency
η_{OH}^{D}	diaphragm cell caustic current efficiency

Subscripts to J, η and C_{species}

a	anolyte
c	catholyte
ch	chemical
d	depleted brine for membrane cells or cell liquor for diaphragm cells
D	diaphragm
e	electrochemical
f	feed brine
o	gases leaving the electrolytic cell
′	feed catholyte
″	exit catholyte

1. Introduction

Worldwide production capacity of chlorine and caustic employing ion-exchange membrane cell technology is currently about 15% and is projected to grow via replacement of the existing diaphragm and mercury cell operations and being the technology of choice in 90% of the planned expansions [1, 2]. One of the criteria commonly used for evaluating the membrane cell operations is energy consumption, P, expressed in kilowatt hours per unit of product, which is calculated from the magnitude of the cell voltage and the current efficiency for chlorine and/or caustic.

Caustic current efficiency can be estimated directly by the caustic collection technique which involves measuring the amount of caustic produced over a known period of time and a knowledge of the coulombs of electricity passed during the same period. Indirect measurement of caustic current efficiency, on the other hand, involves an analysis of the anode gases, feed brine and the anolyte composition, similar to the procedure employed for the measurement of chlorine current efficiency. Several expressions have been published in the literature [3–7] to calculate the caustic and chlorine current efficiency. While these current efficiency equations look similar in format and the authors claim excellent agreement with efficiency results determined independently, they are in fact different from each other as will be shown in the following sections. The purpose of this article is to develop a rigorous generalized equation based on material balance for the various components in the system and examine the nature of the approximations required to degenerate the general expression to the various published current efficiency equations and evaluate the attendant errors. The approach developed here is also extended to diaphragm cells with focus on the assumptions made earlier to arrive at simple versions, and the consequent errors.

2. Theoretical details

2.1. *Process chemistry*

The primary component electrochemical reactions in an ion-exchange membrane chlor-alkali cell are

$$2NaCl \longrightarrow 2Na^+ + Cl_2 + 2e^- \text{ (at the anode)} \qquad (1)$$

and

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \text{ (at the cathode)} \qquad (2)$$

Thus, chloride ions are discharged at the anode to form chlorine and the sodium ions from the anode compartment are exchanged by cation-exchange membrane to form NaOH with the hydroxyl ions generated at the cathode.

When Reactions 1 and 2 only participate during the electrolysis of NaCl solutions and the cation-exchange membrane is ideal, the caustic current efficiency of the electrolyser, η_{OH}, should be 100% whereas the gaseous chlorine current efficiency, η_{Cl_2}, is expected to be <100% because of chlorine losses arising from the finite solubility of Cl_2 in the brine. However, the anodic oxygen evolution, arising from electrochemical discharge of either the H_2O molecules or the hydroxyl ions, following the schemes in Reactions 3 or 4:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (3)$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad (4)$$

not only lowers the chlorine current efficiency but also leads to lowered caustic current efficiency to preserve electroneutrality in the medium.

The back migrating caustic, which also lowers η_{OH}, reveals itself as HOCl, OCl^- and ClO_3^- by reacting with Cl_2 and as O_2 via chemical and thermal decomposition of HOCl (and OCl^-) as follows:

$$NaOH + Cl_2 \longrightarrow NaCl + HOCl \qquad (5)$$

$$NaOH + HOCl \longrightarrow NaOCl + H_2O \qquad (6)$$

$$2HOCl + NaOCl \longrightarrow NaClO_3 + 2HCl \qquad (7)$$

$$2HOCl \longrightarrow O_2 + 2HCl \qquad (8)$$

The presence of OCl^-, HOCl and ClO_3^- in the anode compartment of the electrolyser is not only a result of Reactions 5 to 7 but also a consequence of the presence of NaOH, $NaHCO_3$ and Na_2CO_3 in the feed brine which react with Cl_2 in the anolyte to form HOCl and OCl^- as described by Reactions 9 to 11 followed by Reactions 6 and 7. Thus,

$$NaOH + Cl_2 \longrightarrow NaCl + HOCl \qquad (9)$$

$$Na_2CO_3 + 2Cl_2 + H_2O \longrightarrow 2HOCl + 2NaCl + CO_2 \qquad (10)$$

$$NaHCO_3 + Cl_2 \longrightarrow HOCl + NaCl + CO_2 \qquad (11)$$

Another species in the feed brine involved in Cl_2 consumption in the anolyte, via Equation 12, is Na_2SO_3 which is generally added to remove the active chlorine in the feed brine to the ion-exchange columns to prevent the degradation of the ion-exchange resin by the hypochlorite [1, 4].

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl \qquad (12)$$

$$NaHSO_3 + Cl_2 + NaCl + H_2O \longrightarrow Na_2SO_4 + 3HCl \qquad (12a)$$

While Reactions 12 and 12a are important, the presence of Na_2SO_3 or $NaHSO_3$ is not acknowledged in the material balance equations described in Section 2.2 since their levels in the feed brine are generally controlled in the range of 1 to 10 ppm. However when the feed brine or the anolyte pH is less than 3, it is essential that the material balance accounts for HSO_4^- species because of Reaction 12b.

$$NaHSO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O \qquad (12b)$$

Note that the HSO_4^- ion concentration is only about 10% of the sulfate ion concentration at a pH of about 3, since $\log([SO_4^{2-}]/[HSO_4^-]) = -1.91 + pH$ at 25 °C [10]. The corresponding expression for the SO_3^{2-}/HSO_3^- equilibrium [10] at 25 °C is $\log([SO_3^{2-}]/[HSO_3^-]) = -7.6 + pH$ which indicates the predominant species to be HSO_3^- below a pH of ~ 7 at 25 °C.

2.2. *Derivation of the chlorine and caustic current efficiency expressions*

2.2.1. Ion-exchange membrane cells. The chlorine current efficiency, defined as the ratio of the amount of chlorine leaving the electrolyser to the theoretically expected quantity of chlorine produced, can

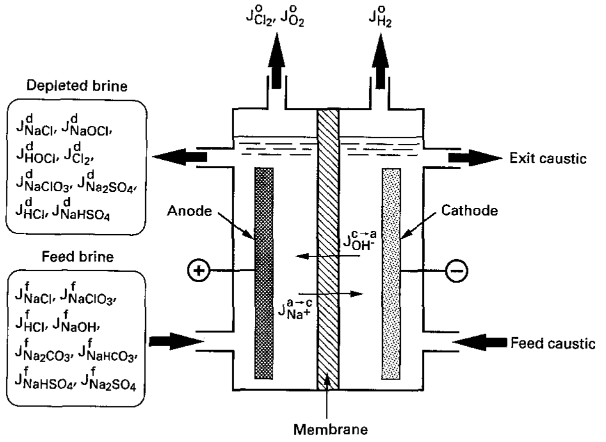

Fig. 1. Schematic of the ion-exchange membrane cell describing the material balance around the electrolyser.

be expressed as

$$\eta_{Cl_2} = \frac{J^{0}_{Cl_2}}{I/2F} \tag{13}$$

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 based species across the anode compartment of the electrolyser (see Fig. 1 for a schematic of the material balance for an ion-exchange membrane cell). From the Cl species material balance described by Equations 14 and 16,

$$\text{Input} = J^{f}_{NaCl} + 2J^{f}_{Cl_2} + J^{f}_{HOCl} + J^{f}_{NaOCl} + J^{f}_{NaClO_3} + J^{f}_{HCl} \tag{14}$$

$$\text{Generation} = \text{Loss} = 0 \tag{15}$$

$$\text{Output} = J^{d}_{NaCl} + 2J^{0}_{Cl_2} + 2J^{d}_{Cl_2} + J^{d}_{HOCl} + J^{d}_{NaOCl} + J^{d}_{NaClO_3} + J^{d}_{HCl} \tag{16}$$

it can be shown that

$$\eta_{Cl_2} = \frac{\Delta Cl}{I/F} \tag{17}$$

where

$$\Delta Cl = Cl^{f} - Cl^{d} = \Delta(J_{NaCl} + J_{HOCl} + J_{NaClO_3} + 2J_{Cl_2} + J_{HCl} + J_{NaOCl}) \tag{18}$$

$$Cl^{f} = J^{f}_{NaCl} + 2J^{f}_{Cl_2} + J^{f}_{HOCl} + J^{f}_{NaOCl} + J^{f}_{NaClO_3} + J^{f}_{HCl} \tag{18a}$$

$$Cl^{d} = J^{d}_{NaCl} + 2J^{d}_{Cl_2} + J^{d}_{HOCl} + J^{d}_{NaOCl} + J^{d}_{NaClO_3} + J^{d}_{HCl} \tag{18b}$$

Similarly, from the material balance of the Cl_2 tracking species (Equations 19 to 22),

$$\text{Input} = J^{f}_{Cl_2} + J^{f}_{HOCl} + J^{f}_{NaOCl} + 3J^{f}_{NaClO_3} \tag{19}$$

$$\text{Generation} = J^{e}_{Cl_2} = I/2F - 2J^{e}_{O_2} \tag{20}$$

$$\text{Loss} = 2J^{ch}_{O_2} \tag{21}$$

$$\text{Output} = J^{d}_{Cl_2} + J^{d}_{HOCl} + J^{d}_{NaOCl} + 3J^{d}_{NaClO_3} + J^{0}_{Cl_2} \tag{22}$$

and noting that the total amount of O_2 collected is from the electrochemical and chemical reactions, described by Equations 3, 4 and 8, as

$$J^{0}_{O_2} = J^{e}_{O_2} + J^{ch}_{O_2} \tag{23}$$

the chlorine current efficiency can be deduced as

$$\eta_{Cl_2} = \frac{1 + (2F/I)\Delta Cl_2}{1 + 2(\%O_2/\%Cl_2)} \tag{24}$$

where

$$\Delta Cl_2 = Cl_2^{f} - Cl_2^{d} = \Delta(J_{Cl_2} + J_{HOCl} + J_{NaOCl} + 3J_{NaClO_3}) \tag{25}$$

$$Cl_2^{f} = J^{f}_{Cl_2} + J^{f}_{HOCl} + J^{f}_{NaOCl} + 3J^{f}_{NaClO_3} \tag{25a}$$

$$Cl_2^{d} = J^{d}_{Cl_2} + J^{d}_{HOCl} + J^{d}_{NaOCl} + 3J^{d}_{NaClO_3} \tag{25b}$$

The term, $\%O_2/\%Cl_2$, in Equation 24 arises from the identity that the mole fraction is equal to the volume fraction (see also [3] for details).

Use of the chlorine current efficiency expressions (Equations 17 and 24) requires a knowledge of the applied load which can be avoided by employing Equation 26, derived by substituting Equation 17 into Equation 24 and rearranging the terms.

$$\eta_{Cl_2} = \frac{1}{1 + 2(\%O_2/\%Cl_2) - 2(\Delta Cl_2/\Delta Cl)} \tag{26}$$

It can also be shown from Equations 17 and 24 that

$$\frac{I}{F} = \Delta Cl + 2\left(\frac{\%O_2}{\%Cl_2}\right)\Delta Cl - 2\Delta Cl_2 \tag{27}$$

or

$$1 = \eta_{Cl_2} + \eta_{O_2} + \eta^{a}_{Cl_2} \tag{28}$$

Thus, the chlorine current inefficiency is a consequence of the chlorine lost because of O_2 evolution and due to the formation of ClO_3^-, OCl^-, HOCl and soluble Cl_2 in the anolyte.

Caustic current efficiency, defined as the amount of caustic collected from the cell, which is also equal to the amount of sodium ions migrated from the anode to the cathode compartment, divided by the theoretically expected quantity of caustic produced, is expressed as

$$\eta_{OH} = 1 - \frac{J^{c\to a}_{OH^-}}{I/F} = \frac{J^{a\to c}_{Na^+}}{I/F} \tag{29}$$

Explicit expressions for the caustic current efficiency can be obtained from either the Na^+ or the OH^- material balance around the anode compartment of the electrolyser (see Fig. 1 for a schematic of the inputs and outputs for Na^+ and OH^-). Thus the caustic current efficiency, deduced from the material balance for the sodium ions, and described through Equations 30 to 32,

$$\begin{aligned}\text{Input} = {} & J^{\mathrm{f}}_{\mathrm{NaCl}} + J^{\mathrm{f}}_{\mathrm{NaClO_3}} + J^{\mathrm{f}}_{\mathrm{NaOH}} + 2J^{\mathrm{f}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{f}}_{\mathrm{NaHCO_3}} + J^{\mathrm{f}}_{\mathrm{NaOCl}} \\ & + J^{\mathrm{f}}_{\mathrm{NaHSO_4}} + 2J^{\mathrm{f}}_{\mathrm{Na_2SO_4}} \end{aligned} \tag{30}$$

$$\text{Generation} = \text{Loss} = 0 \tag{31}$$

$$\begin{aligned}\text{Output} = {} & J^{\mathrm{d}}_{\mathrm{NaCl}} + J^{\mathrm{d}}_{\mathrm{NaClO_3}} + J^{\mathrm{d}}_{\mathrm{NaOH}} + 2J^{\mathrm{d}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{d}}_{\mathrm{NaHCO_3}} + J^{\mathrm{d}}_{\mathrm{NaOCl}} + J^{\mathrm{d}}_{\mathrm{NaHSO_4}} \\ & + 2J^{\mathrm{d}}_{\mathrm{Na_2SO_4}} + J^{\mathrm{a}\to\mathrm{c}}_{\mathrm{Na^+}} \end{aligned} \tag{32}$$

can be shown to be given as

$$\eta_{\mathrm{OH}} = \frac{\Delta\mathrm{Na}}{I/F} \tag{33}$$

where

$$\begin{aligned}\Delta\mathrm{Na} = \mathrm{Na^f} - \mathrm{Na^d} = {} & \Delta(J_{\mathrm{NaCl}} + J_{\mathrm{NaClO_3}} + J_{\mathrm{NaOH}} \\ & + 2J_{\mathrm{Na_2CO_3}} + J_{\mathrm{NaHCO_3}} + J_{\mathrm{NaOCl}} \\ & + J_{\mathrm{NaHSO_4}} + 2J_{\mathrm{Na_2SO_4}}) \end{aligned} \tag{34}$$

$$\begin{aligned}\mathrm{Na^f} = {} & J^{\mathrm{f}}_{\mathrm{NaCl}} + J^{\mathrm{f}}_{\mathrm{NaClO_3}} + J^{\mathrm{f}}_{\mathrm{NaOH}} + 2J^{\mathrm{f}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{f}}_{\mathrm{NaHCO_3}} + J^{\mathrm{f}}_{\mathrm{NaOCl}} + J^{\mathrm{f}}_{\mathrm{NaHSO_4}} \\ & + 2J^{\mathrm{f}}_{\mathrm{Na_2SO_4}} \end{aligned} \tag{34a}$$

$$\begin{aligned}\mathrm{Na^d} = {} & J^{\mathrm{d}}_{\mathrm{NaCl}} + J^{\mathrm{d}}_{\mathrm{NaClO_3}} + J^{\mathrm{d}}_{\mathrm{NaOH}} + 2J^{\mathrm{d}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{d}}_{\mathrm{NaHCO_3}} + J^{\mathrm{d}}_{\mathrm{NaOCl}} + J^{\mathrm{d}}_{\mathrm{NaHSO_4}} \\ & + 2J^{\mathrm{d}}_{\mathrm{Na_2SO_4}} \end{aligned} \tag{34b}$$

Following the same methodology for the hydroxide species, given through Equations 35 to 38, the caustic current efficiency can be deduced easily as expressed in Equation 39.

$$\begin{aligned}\text{Input} = {} & J^{\mathrm{c}\to\mathrm{a}}_{\mathrm{OH^-}} + J^{\mathrm{f}}_{\mathrm{HOCl}} + 2J^{\mathrm{f}}_{\mathrm{NaOCl}} \\ & + 6J^{\mathrm{f}}_{\mathrm{NaClO_3}} + 2J^{\mathrm{f}}_{\mathrm{Na_2CO_3}} + J^{\mathrm{f}}_{\mathrm{NaHCO_3}} \\ & + J^{\mathrm{f}}_{\mathrm{NaOH}} - J^{\mathrm{f}}_{\mathrm{HCl}} - J^{\mathrm{f}}_{\mathrm{NaHSO_4}} \end{aligned} \tag{35}$$

$$\text{Generation} = 0 \tag{36}$$

$$\text{Loss} = 4J^{\mathrm{ch}}_{\mathrm{O_2}} + 4J^{\mathrm{e}}_{\mathrm{O_2}} \tag{37}$$

$$\begin{aligned}\text{Output} = {} & J^{\mathrm{d}}_{\mathrm{HOCl}} + 2J^{\mathrm{d}}_{\mathrm{NaOCl}} + 6J^{\mathrm{d}}_{\mathrm{NaClO_3}} \\ & + 2J^{\mathrm{d}}_{\mathrm{Na_2CO_3}} + J^{\mathrm{d}}_{\mathrm{NaHCO_3}} + J^{\mathrm{d}}_{\mathrm{NaOH}} \\ & - J^{\mathrm{d}}_{\mathrm{HCl}} - J^{\mathrm{d}}_{\mathrm{NaHSO_4}} \end{aligned} \tag{38}$$

$$\eta_{\mathrm{OH}} = 1 - 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}}\right)\eta_{\mathrm{Cl_2}} + \frac{F}{I}\Delta\mathrm{OH} \tag{39}$$

where

$$\begin{aligned}\Delta\mathrm{OH} = \mathrm{OH^f} - \mathrm{OH^d} = {} & \Delta(J_{\mathrm{HOCl}} + 2J_{\mathrm{NaOCl}} \\ & + 6J_{\mathrm{NaClO_3}} + 2J_{\mathrm{Na_2CO_3}} + J_{\mathrm{NaHCO_3}} \\ & + J_{\mathrm{NaOH}} - J_{\mathrm{HCl}} - J_{\mathrm{NaHSO_4}}) \end{aligned} \tag{40}$$

$$\begin{aligned}\mathrm{OH^f} = {} & J^{\mathrm{f}}_{\mathrm{HOCl}} + 2J^{\mathrm{f}}_{\mathrm{NaOCl}} + 6J^{\mathrm{f}}_{\mathrm{NaClO_3}} + 2J^{\mathrm{f}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{f}}_{\mathrm{NaHCO_3}} + J^{\mathrm{f}}_{\mathrm{NaOH}} - J^{\mathrm{f}}_{\mathrm{HCl}} - J^{\mathrm{f}}_{\mathrm{NaHSO_4}} \end{aligned} \tag{40a}$$

$$\begin{aligned}\mathrm{OH^d} = {} & J^{\mathrm{d}}_{\mathrm{HOCl}} + 2J^{\mathrm{d}}_{\mathrm{NaOCl}} + 6J^{\mathrm{d}}_{\mathrm{NaClO_3}} + 2J^{\mathrm{d}}_{\mathrm{Na_2CO_3}} \\ & + J^{\mathrm{d}}_{\mathrm{NaHCO_3}} + J^{\mathrm{d}}_{\mathrm{NaOH}} - J^{\mathrm{d}}_{\mathrm{HCl}} - J^{\mathrm{d}}_{\mathrm{NaHSO_4}} \end{aligned} \tag{40b}$$

It may be noted that the last term in Equation 35 is a result of $\mathrm{OH^-}$ consumption via Equation 12b. Elimination of the F/I term, using Equation 33, and the $\eta_{\mathrm{Cl_2}}$ term with Equation 26, in Equation 39 leads to the expression 41.

$$\eta_{\mathrm{OH}} = \frac{1 - 2(\Delta\mathrm{Cl_2}/\Delta\mathrm{Cl})}{(1 - \Delta\mathrm{OH}/\Delta\mathrm{Na})[1 + 2(\%\mathrm{O_2}/\%\mathrm{Cl_2}) - 2(\Delta\mathrm{Cl_2}/\Delta\mathrm{Cl})]} \tag{41}$$

This version of the caustic current efficiency equation is sometimes preferred by the chlor-alkali producers since it avoids the need for measuring the applied load.

The origin of the caustic current inefficiency may now be probed by rearranging Equations 33 and 39, leading to Equations 42 and 43, which clearly shows that

$$\frac{I}{F} = \Delta\mathrm{Na} + 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}}\right)\Delta\mathrm{Cl} - \Delta\mathrm{OH} \tag{42}$$

or

$$1 = \eta_{\mathrm{OH}} + \eta_{\mathrm{O_2}} + \eta^{\mathrm{a}}_{\mathrm{OH}} \tag{43}$$

It is clear from Equation 43 that the caustic current inefficiency arises from the loss of hydroxyl species to the anode chamber resulting in (i) the generation of $\mathrm{O_2}$, (ii) the formation of $\mathrm{ClO_3^-}$, $\mathrm{OCl^-}$ and HOCl in the anolyte and (iii) neutralization of the feed acidity.

2.2.2. Diaphragm cells. The distinguishing difference in the operation of the membrane and diaphragm cells is the flow direction of the various components in the anolyte which percolates through a porous separator into the catholyte in a diaphragm cell, whereas in a membrane cell, $\mathrm{Na^+}$ and $\mathrm{H_2O}$ are the only major species transported through the membrane from the anolyte to the catholyte. The chlorine current efficiency may now be determined from the material balance of chlorine tracking species*, shown in Fig. 2 and described through Equations 44 to 47.

$$\text{Input} = 3J^{\mathrm{f}}_{\mathrm{NaClO_3}} \tag{44}$$

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* Generally, the feed brine to the diaphragm cells and the exiting caustic liquor do not contain any active chlorine species. However, if these species (i.e., $\mathrm{Cl_2}$, HOCl, $\mathrm{OCl^-}$) are present in the feed brine or cell liquor, the material balance can easily be modified to account for their presence.

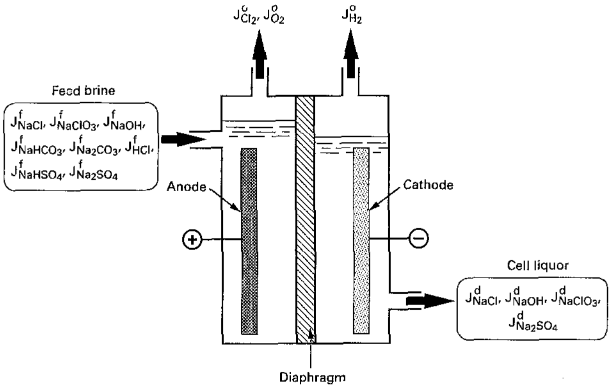

Fig. 2. Schematic of the diaphragm cell describing the appropriate input and output species.

$$\text{Output} = 3J^{d}_{NaClO_3} + J^{0}_{Cl_2} \tag{45}$$

$$\text{Generation} = I/2F - 2J^{e}_{O_2} \tag{46}$$

$$\text{Loss} = 2J^{ch}_{O_2} + (1 - \eta^{D}_{H_2})I/2F \tag{47}$$

It may be noted that the loss term, represented by Equation 47, accounts not only for the oxygen generated chemically via Equation 8 but also for the blind current losses arising from the thermodynamically favoured cathodic reduction of OCl^- and ClO_3^- as described by Reactions 48 to 49.

$$OCl^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^- \tag{48}$$

$$ClO_3^- + 3H_2O + 6e^- \longrightarrow Cl^- + 6OH^- \tag{49}$$

Since these cathodic reactions affect only the amount of current used for the H_2 evolution reaction and not the OH^- formation rate, the magnitude of the blind current losses, quantified from the moles of H_2 evolved, equals $(1 - \eta^{D}_{H_2})I/2F$. Since

$$\eta^{D}_{Cl_2} = \frac{J^{0}_{Cl_2}}{I/2F} \tag{50}$$

and

$$J^{0}_{O_2} = J^{e}_{O_2} + J^{ch}_{O_2} = \left(\frac{\%O_2}{\%Cl_2}\right)\left(\frac{I}{2F}\right)\eta^{D}_{Cl_2} \tag{51}$$

it can be easily shown, from Equations 44 to 47, that

$$\eta^{D}_{Cl_2} = \frac{\eta^{D}_{H_2} + (6F/I)\Delta J_{NaClO_3}}{1 + 2(\%O_2/\%Cl_2)} \tag{52}$$

The caustic current efficiency expression for diaphragm cells can be derived from the NaOH material balance in a similar way employing Equations 53 to 56 (see Fig. 2 for a schematic of the material balance across the cell), taking into account the blind current losses. Thus,

$$\begin{aligned}\text{Input} = {} & J^{f}_{NaOH} - J^{f}_{HCl} + 2J^{f}_{Na_2CO_3} + J^{f}_{NaHCO_3} \\ & + 6J^{f}_{NaClO_3} - J^{f}_{NaHSO_4}\end{aligned} \tag{53}$$

$$\text{Output} = J^{d}_{NaOH} + 6J^{d}_{NaClO_3} \tag{54}$$

$$\text{Generation} = I/F \tag{55}$$

$$\begin{aligned}\text{Loss} &= 4J^{ch}_{O_2} + 4J^{e}_{O_2} + (1 - \eta^{D}_{H_2})I/F \\ &= 4J^{0}_{O_2} + (1 - \eta^{D}_{H_2})I/F\end{aligned} \tag{56}$$

Since

$$\eta^{D}_{OH} = \frac{J^{d}_{NaOH}}{I/F} \tag{57}$$

it can be shown from Equations 53 to 56 that

$$\begin{aligned}\eta^{D}_{OH} = {} & \eta^{D}_{H_2} - 2\left(\frac{\%O_2}{\%Cl_2}\right)\eta^{D}_{Cl_2} + \frac{F}{I}(\Delta 6J_{NaClO_3} \\ & + 2J^{f}_{Na_2CO_3} + J^{f}_{NaHCO_3} - J^{f}_{HCl} \\ & + J^{f}_{NaOH} - J^{f}_{NaHSO_4})\end{aligned} \tag{58}$$

Elimination of $\eta^{D}_{Cl_2}$ from Equation 58, using Equation 52, results in

$$\begin{aligned}\eta^{D}_{OH} = {} & \eta^{D}_{Cl_2} + \frac{F}{I}(J^{f}_{NaOH} + 2J^{f}_{Na_2CO_3} + J^{f}_{NaHCO_3} \\ & - J^{f}_{HCl} - J^{f}_{NaHSO_4})\end{aligned} \tag{59}$$

Thus, Equations 52 and 59 represent the chlorine and caustic efficiency expressions derived rigorously from the appropriate material balances while accounting for the blind current losses. Approximations commonly used to arrive at the equations used in practice are discussed in Section 3.

3. Results and discussion

3.1. *Comparison with the previous published efficiency equations*

3.1.1. Membrane cells. The simple, yet rigorous, approach illustrated in Section 2 shows that there are at least three seemingly different, but actually equivalent expressions, for describing the caustic and chlorine efficiency of the ion-exchange membrane cells. Of these, the commonly used relationships for calculating the chlorine and caustic efficiency are noted below. The reason for the plurality of equations for η_{Cl_2} and η_{OH} stems from the relationship between the efficiency and the individual Cl, Cl_2, Na and OH material balances, elaborated in Section 2. Thus,

$$\eta_{Cl_2} = \frac{1 + (2F/I)\Delta Cl_2}{1 + 2(\%O_2/\%Cl_2)} \tag{60a}$$

$$= \frac{\Delta Cl}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl} \tag{60b}$$

$$= \frac{1}{1 + 2(\%O_2/\%Cl_2) - 2(\Delta Cl_2/\Delta Cl)} \tag{60c}$$

$$\eta_{OH} = \eta_{Cl_2} + \frac{F}{I}(\Delta OH - 2\Delta Cl_2) \tag{61a}$$

$$= \frac{\Delta Na}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl} \tag{61b}$$

Table 1. Current efficiency expressions for ion-exchange membrane cells published in the literature

Authors	*General form of the efficiency equation*	*Δ (Species) used in the efficiency expression*
Tilak *et al.* [4]	$\eta_{Cl_2} = \frac{1 + (2F/I)\Delta Cl_2}{1 + 2(\%O_2/\%Cl_2)}$ $\eta_{NaOH} = \eta_{Cl_2} - \frac{F}{I}(2\Delta Cl_2 - \Delta OH)$	$\Delta Cl_2 = \Delta(J_{Cl_2} + J_{HOCl} + J_{NaOCl} + 3J_{NaClO_3} - J_{Na_2SO_3})$ $2\Delta Cl_2 - \Delta OH = \Delta J_{HCl} - \frac{\Delta(2J_{NaOH} + 4J_{Na_2CO_3} + 2J_{NaHCO_3})}{1 + 2(\%O_2/\%Cl_2)}$
Cowell *et al.* [5]	$\eta_{Cl_2} = \frac{\Delta Cl}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl}$ $\eta_{NaOH} = \frac{\Delta Na}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl}$	$\Delta Cl = \frac{1}{2}\Delta(J_{NaCl} + J_{HOCl} + J_{NaClO_3} + 2J_{Cl_2} + J_{HCl})$ $\Delta Na = \Delta(J_{NaCl} + J_{NaOH} + J_{NaClO_3} + 2J_{Na_2CO_3})$ $\Delta Cl - 2\Delta Cl_2 = \Delta(J_{NaCl} + J_{HCl} - 5J_{NaClO_3} - J_{HOCl})$
Bergner *et al.* [6]	$\eta_{Cl_2} = \frac{1 + (2F/I)\Delta Cl_2}{1 + 2(\%O_2/\%Cl_2)}$ $\eta_{NaOH} = \eta_{Cl_2} - \frac{F}{I}(2\Delta Cl_2 - \Delta OH)$	$\Delta Cl_2 = \Delta[-2(\%O_2/\%Cl_2)J_{HOCl} + 3J_{NaClO_3}]$ $2\Delta Cl_2 - \Delta OH = \Delta(J_{HCl} - 2J_{HOCl} - 2J_{NaOH} - 2J_{Na_2CO_3})$
Masuko *et al.* [7]	$\eta_{Cl_2} = \frac{\Delta Cl}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl}$ $\eta_{NaOH} = \frac{\Delta Na}{(\Delta Cl - 2\Delta Cl_2) + 2(\%O_2/\%Cl_2)\Delta Cl}$	$\Delta Cl = \Delta(J_{NaCl} + J_{HOCl} + J_{NaClO_3} + 2J_{Cl_2} + J_{HCl})$ $\Delta Na = \Delta(J_{NaCl} + J_{NaClO_3})$ $\Delta Cl_2 = \Delta(3J_{NaClO_3} + J_{Cl_2} + J_{HOCl})$ $\Delta Cl - 2\Delta Cl_2 = \Delta(J_{NaCl} + J_{HCl} - 5J_{NaClO_3} - J_{HOCl})$

where

$$\Delta Cl = \Delta(J_{NaCl} + J_{HOCl} + J_{NaClO_3} + 2J_{Cl_2} + J_{HCl} + J_{NaOCl}) \tag{62}$$

$$\Delta Cl_2 = \Delta(J_{Cl_2} + J_{HOCl} + J_{NaOCl} + 3J_{NaClO_3}) \tag{63}$$

$$\Delta Na = \Delta(J_{NaCl} + J_{NaClO_3} + J_{NaOH} + 2J_{Na_2CO_3} + J_{NaHCO_3} + J_{NaOCl} + J_{NaHSO_4} + 2J_{Na_2SO_4}) \tag{64}$$

$$\Delta OH = \Delta(J_{HOCl} + 2J_{NaOCl} + 6J_{NaClO_3} + 2J_{Na_2CO_3} + J_{NaHCO_3} + J_{NaOH} - J_{HCl} - J_{NaHSO_4}) \tag{65}$$

and hence

$$2\Delta Cl_2 - \Delta OH = \Delta(2J_{Cl_2} + J_{HOCl} + J_{HCl} - 2J_{Na_2CO_3} - J_{NaHCO_3} - J_{NaOH} + J_{NaHSO_4}) \tag{66}$$

and

$$\Delta Cl - 2\Delta Cl_2 = \Delta(J_{NaCl} + J_{HCl} - J_{HOCl} - J_{NaOCl} - 5J_{NaClO_3}) \tag{67}$$

Equation (61a) was obtained from Equations 24 and 39 and Equations 60b and 61b were obtained by recasting Equations 39 and 41.

To permit proper comparison of the present equations noted above with the expressions published in the literature, the chlorine and caustic current efficiency equations in [4–7] are rearranged in terms of the differences in the input and outlet mass flow rates of the relevant species and presented in Table 1. Comparison of the Δ(species) noted in Equations 62 to 67 with the corresponding ones in Table 1, shows that the caustic efficiency expressions in [5–7] and the chlorine efficiency equations in [4] and [7] can be obtained from equations 62 to 67 by proper omission of appropriate species in the feed brine. However, the chlorine efficiency relationship in [5] showed a discrepancy in the ΔCl term by a factor of 1/2 which is probably due to either a typographical or an algebraic error.

Errors in η_{OH} in [4] are a result of the assumption that $\eta_{OH} = \eta_{Cl_2}$ which is valid only when the feed brine is neutral and doesn't contain chlorates. Nevertheless calculations show the discrepancy between the calculated η_{OH} and that obtained from Equation 61a to be averaging ±0.3% under normal operating conditions. Comparison of the chlorine and caustic efficiency expressions in [6] with Equations 62 and 67 indicates the deviation of the expressions in [6] to arise from possible algebraic errors and the assumption that $\eta_{OH} = \eta_{Cl_2}$.

3.1.2. Diaphragm cells. Exact expression for chlorine and caustic current efficiency, derived from material balance across a diaphragm chlor-alkali cell, are represented by Equations 52 and 59. To allow comparison of the equations with the earlier results, Equations 52 and 59 were rearranged, expressing the depleted brine flow rate in terms of caustic current efficiency as

$$q = \left(\frac{I}{F}\right)\frac{\eta_{OH}^{D}}{C_{NaOH}^{d}} \tag{68}$$

Thus, the equations describing the caustic and chlorine current efficiency for diaphragm cells can be shown to be given by Equations 69 and 70.

$$\eta_{\mathrm{OH}}^{\mathrm{D}} = \frac{\eta_{\mathrm{H_2}}^{\mathrm{D}} + \frac{F}{I} p \left\{ 6C_{\mathrm{NaClO_3}}^{\mathrm{f}} + \left[1 + 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) \right] (C_{\mathrm{NaOH}}^{\mathrm{f}} + 2C_{\mathrm{Na_2CO_3}}^{\mathrm{f}} + C_{\mathrm{NaHCO_3}}^{\mathrm{f}} - C_{\mathrm{HCl}}^{\mathrm{f}} - C_{\mathrm{NaHSO_4}}^{\mathrm{f}}) \right\}}{1 + 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) + 6\left(\frac{C_{\mathrm{NaClO_3}}^{\mathrm{d}}}{C_{\mathrm{NaOH}}^{\mathrm{d}}} \right)} \tag{69}$$

$$\eta_{\mathrm{Cl_2}}^{\mathrm{D}} = \frac{\eta_{\mathrm{H_2}}^{\mathrm{D}} + \frac{6F}{I} p \left\{ C_{\mathrm{NaClO_3}}^{\mathrm{f}} - \left(\frac{C_{\mathrm{NaClO_3}}^{\mathrm{d}}}{C_{\mathrm{NaOH}}^{\mathrm{d}}} \right) (C_{\mathrm{NaOH}}^{\mathrm{f}} + 2C_{\mathrm{Na_2CO_3}}^{\mathrm{f}} + C_{\mathrm{NaHCO_3}}^{\mathrm{f}} - C_{\mathrm{HCl}}^{\mathrm{f}} - C_{\mathrm{NaHSO_4}}^{\mathrm{f}}) \right\}}{1 + 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) + 6\left(\frac{C_{\mathrm{NaClO_3}}^{\mathrm{d}}}{C_{\mathrm{NaOH}}^{\mathrm{d}}} \right)} \tag{70}$$

where the hydrogen current efficiency, $\eta_{\mathrm{H_2}}^{\mathrm{D}}$, can be shown to be: $\eta_{\mathrm{H_2}}^{\mathrm{D}} = 1 - 2(C_{\mathrm{Av.Cl_2}}^{\mathrm{a}}/C_{\mathrm{NaOH}}^{\mathrm{d}})$ (Appendix 1). Note that the hydrogen inefficiency arises from the blind current losses due to the discharge of available chlorine at the cathode. However, the chlor-alkali industry routinely measures only the chlorine current efficiency of diaphragm cells using the relationship in Equation 71 detailed in [1, 3, 4]:

$$\eta_{\mathrm{Cl_2}}^{\mathrm{D}} = \frac{1}{1 + 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) + \alpha} \tag{71}$$

where

$$\alpha = \frac{6(C_{\mathrm{NaClO_3}}^{\mathrm{a}} - C_{\mathrm{NaClO_3}}^{\mathrm{f}})}{C_{\mathrm{NaOH}}^{\mathrm{d}}} \tag{72}$$

An alternate expression for α used by some chlor-alkali producers is

$$\alpha = \frac{(2\text{ to }8)C_{\mathrm{NaClO_3}}^{\mathrm{d}}}{C_{\mathrm{NaOH}}^{\mathrm{d}}} \tag{73}$$

Comparison of Equation 71 with Equation 70 clearly shows that Equation 71 is a 'crude' approximation for estimating the chlorine current efficiency of diaphragm cells operating with acidic or basic feed brine. It may be noted that the anolyte chlorate term in Equation 72 can arise only from an improper material balancing of the diaphragm cell inputs and outputs.

The F/I term in the numerator of Equations 69 and 70 can, in principle, be eliminated using the Cl or Na material balance across the diaphragm cell, given by Equations 74 and 75.

$$\eta_{\mathrm{Cl_2}}^{\mathrm{D}} = \left(\frac{F}{I} \right) \frac{\Delta \mathrm{Cl}^*}{\eta_{\mathrm{H_2}}^{\mathrm{D}}} \tag{74}$$

where

$$\Delta \mathrm{Cl}^* = \Delta(J_{\mathrm{NaCl}} + J_{\mathrm{NaClO_3}} + J_{\mathrm{HCl}})$$

and

$$\eta_{\mathrm{OH}}^{\mathrm{D}} = \left(\frac{F}{I} \right) \frac{\Delta \mathrm{Na}^*}{\eta_{\mathrm{H_2}}^{\mathrm{D}}} \tag{75}$$

where

$$\Delta \mathrm{Na}^* = \Delta(J_{\mathrm{NaCl}} + J_{\mathrm{NaClO_3}} + 2J_{\mathrm{Na_2SO_4}}) + J_{\mathrm{NaOH}}^{\mathrm{f}} + J_{\mathrm{NaHCO_3}}^{\mathrm{f}} + 2J_{\mathrm{Na_2CO_3}}^{\mathrm{f}} + J_{\mathrm{NaHSO_4}}^{\mathrm{f}}$$

However, the resulting expressions will be unwieldy since the cell liquor flow rate term, q, required for expanding Δ(Species) involves the I/F terms via Equation 68. Equations 69 and 70 can be degenerated to Equation 71 with $\alpha = 6C_{\mathrm{NaClO_3}}^{\mathrm{d}}/C_{\mathrm{NaOH}}^{\mathrm{d}}$ only when the feed brine is devoid of $NaClO_3$, NaOH, Na_2CO_3, $NaHCO_3$, $NaHSO_4$ and HCl, i.e., when the feed brine is neutral and does not contain $NaClO_3$ and the blind current losses are negligible. Feed brine alkalinity and chlorates can be best accounted for only by employing Equation 69 or 70 for calculating the caustic or chlorine current efficiency.

3.2. *Disparity between the chlorine and the caustic current efficiency*

3.2.1. Membrane cells. An analysis of the breakdown of the total current towards the various constituent reactions showed, via Equations 27 and 28 and Equations 42 and 43, that the caustic and chlorine inefficiencies are primarily a result of oxygen evolution and formation of ClO_3^-, OCl^-, HOCl and soluble Cl_2 in the anolyte. The contributing factors towards the origin of some of these inefficiencies may be deciphered by the rearrangement of Equations 24 and 25 and Equations 39 and 40 in terms of the feed and depleted mass flow rates for the various pertinent components. When the feed brine contains no active chlorine species, which is often the situation in membrane cell operations,

$$\eta_{\mathrm{Cl_2}} = 1 - 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) \eta_{\mathrm{Cl_2}} + \frac{2F}{I} [3pC_{\mathrm{NaClO_3}}^{\mathrm{f}} - q(C_{\mathrm{Cl_2}}^{\mathrm{d}} + C_{\mathrm{HOCl}}^{\mathrm{d}} + C_{\mathrm{NaOCl}}^{\mathrm{d}} + 3C_{\mathrm{NaClO_3}}^{\mathrm{d}})] \tag{76}$$

and

$$\eta_{\mathrm{OH}} = 1 - 2\left(\frac{\%\mathrm{O_2}}{\%\mathrm{Cl_2}} \right) \eta_{\mathrm{Cl_2}} + \frac{F}{I} [p(6C_{\mathrm{NaClO_3}}^{\mathrm{f}} + 2C_{\mathrm{Na_2CO_3}}^{\mathrm{f}} + C_{\mathrm{NaHCO_3}}^{\mathrm{f}} + C_{\mathrm{NaOH}}^{\mathrm{f}} - C_{\mathrm{NaHSO_4}}^{\mathrm{f}}) - q(C_{\mathrm{HOCl}}^{\mathrm{d}} + 2C_{\mathrm{NaOCl}}^{\mathrm{d}} + 6C_{\mathrm{NaClO_3}}^{\mathrm{d}} - C_{\mathrm{NaHSO_4}}^{\mathrm{d}})] \tag{77}$$

when there is no acid addition to the feed brine. It follows from Equation 76 that the chlorine current efficiency decreases with increasing formation of active chlorine species and chlorate in the anolyte, increasing active chlorine species being formed not only by the reaction involving Cl_2 and OH species but also by interaction between Cl_2 and Na_2CO_3, $NaHCO_3$ and NaOH present in the feed brine as outlined in Section 2.1. Hence, lowering of the alkalinity of the feed brine should improve the chlorine efficiency.

An examination of Equation 77 shows that the caustic inefficiency, arising from the oxygen discharge and the formation of active chlorine species and chlorate in the anolyte, can be slightly improved by increased alkalinity of the feed brine which will react with the Cl_2 instead of the back migrating caustic binding the Cl_2 to form HOCl, OCl^-, and ClO_3^-.

The disparity between the chlorine and caustic current efficiencies can be quantitatively estimated from Equations 17 and 33 as

$$\eta_{OH} - \eta_{Cl_2} = \frac{F}{I}\Delta(J_{NaOH} + 2J_{Na_2CO_3} + J_{NaHCO_3} - J_{HOCl} - J_{HCl} - 2J_{Cl_2}) \tag{78}$$

Again, Equation 78 reiterates that the disparity between the Cl_2 and NaOH current efficiencies is a result of the alkalinity in the feed brine and the active chlorine species in the anolyte. If the feed brine is neutral and there is no active chlorine in the anolyte, it can be seen that

$$\eta_{OH} - \eta_{Cl_2} = 0 \tag{79}$$

3.2.2. Diaphragm cells. The difference in the chlorine and caustic current efficiency for diaphragm cells can be evaluated from Equation 59, which shows

$$\eta_{OH}^{D} - \eta_{Cl_2}^{D} = \frac{F}{I}p(C^{f}_{NaOH} + 2C^{f}_{Na_2CO_3} + C^{f}_{NaHCO_3} - C^{f}_{HCl} - C^{f}_{NaHSO_4}) \tag{80}$$

According to Equation 80, the differences in these efficiencies are, as noted previously for membrane cells, a result of the presence of alkalinity or HCl in the feed brine. When the feed brine is neutral, it is clear that the caustic current efficiency equals the chlorine current efficiency for diaphragm cells also.

3.3. *Efficiency expressions for* Cl_2 *and* NaOH *for membrane cells*

As noted in earlier sections, a multitude of current efficiency expressions can be derived to calculate the Cl_2 and NaOH current efficiency in ion-exchange membrane cells. The general format of these equations presented in this communication appears simple, but they become unwieldy when expanded to incorporate the feed and depleted mass flow rates of the various relevant constituent species. The main focus of simplification in [4–7] has been towards eliminating the F/I term and/or the depleted brine flow rate term, q, because of practical difficulties associated with its measurement.

The ratio of the feed brine flow rate to the depleted brine flow rate can be determined from the various material balances described earlier. Thus ΔNa can be expressed in terms of ΔCl, ΔCl_2 and ΔOH, employing Equations 17, 27, 33 and 39, as

$$\Delta Na = \Delta Cl - 2\Delta Cl_2 + \Delta OH \tag{81}$$

since

$$\Delta Cl = p[Cl]^f - q[Cl]^d; \qquad \Delta Cl_2 = p[Cl_2]^f - q[Cl_2]^d$$

$$\Delta Na = p[Na]^f - q[Na]^d; \qquad \Delta OH = p[OH]^f - q[OH]^d$$

where $[\,]^f$ and $[\,]^d$ terms refer to the concentration of the non-bracketed molar flow rates described in Equations 18a, 18b, 25a, 25b, 34a, 34b, 40a and 40b.

Equation 81 becomes

$$R^* = \frac{q}{p} = \frac{[Na]^f - [Cl]^f + 2[Cl_2]^f - [OH]^f}{[Na]^d - [Cl]^d + 2[Cl_2]^d - [OH]^d} \tag{82}$$

Following proper substitution of the terms in brackets, using Equations 18, 25, 34 and 40, R^* can be shown to be

$$R^* = \frac{C^{f}_{NaHSO_4} + C^{f}_{Na_2SO_4}}{C^{d}_{NaHSO_4} + C^{d}_{Na_2SO_4}} \tag{83}$$

expressed as a ratio of the $[NaHSO_4] + [Na_2SO_4]$ in the feed and depleted brine, given by Equation 83. This result should not be surprising since the transport of SO_4^{2-} into the catholyte was not allowed in the formulation of the material balance.

It should be noted that anions such as Cl^-, SO_4^{2-} and ClO_3^- are transported through the membrane into the catholyte by diffusion and electro-osmosis. However, this driving force is negated by migration, an electric field effect. Theoretical calculations [11] and experimental studies [12] show that while the transport of these anions is suppressed during the normal operation, maximal carry over of the anions into catholyte occurs only when the applied load is zero. The magnitude of the transport of SO_4^{2-} and ClO_3^- was noted to be proportional to the corresponding anolyte levels, whereas the Cl^- content in the catholyte was found to be decreasing with increasing Cl^- concentration in the anolyte. Overall, the concentration of Cl^-, SO_4^{2-} and ClO_3^- in the catholyte is in the ppm range even though they are in the grams/litre range in the anolyte and hence were not considered in the overall material balance in Section 2.

Use of SO_4^{2-} ratio to estimate the ratio of the depleted brine flow rate and the feed brine flow rate, needed for calculating the efficiencies, requires accurate measurement of SO_4^{2-} in the range of 2 to $15\,g\,dm^{-3}$ in NaCl solution of 200 to $300\,g\,dm^{-3}$. Gravimetric analysis by precipitation of SO_4^{2-} as $BaSO_4$ should, in principle, provide an accuracy of ±0.01%. However, in practice, the accuracy achieved in chlor-alkali plant facilities is ±6 to 8%. Inductively coupled plasma analysis and ion chomatographic technique for sulfate, on the other hand, involves dilution factors of the order of about 10 and provides an accuracy of only ~2 to 3%. Thus, it appears that the use of a 'sulfate ratio' to arrive at the ratio of q/p is not a reliable path to estimate the efficiencies unless a practical and accurate method is developed for determining SO_4^{2-} in brines. Issues related to the adverse effects of SO_4^{2-} on the membrane performance, disclosed in the literature, should be paid close attention, while considering sulfate additions to the feed brine [4, 8].

An alternate approach to arrive at the magnitude of the q/p term is via using the Na or Cl material balance. Thus, the Na material balance from Equation 34 leads to

$$R^* = \frac{q}{p} = \frac{[\mathrm{Na}]^{\mathrm{f}}}{[\mathrm{Na}]^{\mathrm{d}}} - \frac{I\eta_{\mathrm{OH}}}{pF[\mathrm{Na}]^{\mathrm{d}}} \tag{84}$$

or

$$R^* = L - M\left(\frac{I\eta_{\mathrm{OH}}}{pF}\right) \tag{85}$$

where $L = [\mathrm{Na}]^{\mathrm{f}}/[\mathrm{Na}]^{\mathrm{d}}$ and $M = 1/[\mathrm{Na}]^{\mathrm{d}}$. Similarly, the Cl balance results in

$$R^* = \frac{q}{p} = \frac{[\mathrm{Cl}]^{\mathrm{f}}}{[\mathrm{Cl}]^{\mathrm{d}}} - \frac{I\eta_{\mathrm{Cl_2}}}{pF[\mathrm{Cl}]^{\mathrm{d}}} \tag{86}$$

or

$$R^* = X - Y\left(\frac{I\eta_{\mathrm{Cl_2}}}{pF}\right) \tag{87}$$

where $X = [\mathrm{Cl}]^{\mathrm{f}}/[\mathrm{Cl}]^{\mathrm{d}}$ and $Y = 1/[\mathrm{Cl}]^{\mathrm{d}}$. Substitution of Equations 85 and 87 in Equations 39 and 24, followed by algebraic manipulations, leads to the caustic current efficiency expression as

$$\eta_{\mathrm{OH}} = \frac{1 - (F/I)p[2(1-\mathrm{C})(\mathrm{LCl_2^d} - \mathrm{Cl_2^f}) + \mathrm{C}(\mathrm{LOH^d} - \mathrm{OH^f})]}{C - M[2(1-\mathrm{C})\mathrm{Cl_2^d} + \mathrm{COH^d}]} \tag{88}$$

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

Similarly, substitution of Equation 87 in Equation 24 leads to

$$\eta_{\mathrm{Cl_2}} = \frac{1 - (2F/I)p(X\mathrm{Cl_2^d} - \mathrm{Cl_2^f})}{C - 2Y\mathrm{Cl_2^d}} \tag{89}$$

Equation 89 provides an estimate of the cell efficiency for chlorine and does not account for the dissolved chlorine in the anolyte which is generally recovered during the dechlorination operations. The process chlorine efficiency, $\eta_{\mathrm{Cl_2}}^{\mathrm{D}}$, assuming 100% recovery of the dissolved chlorine and the active Cl_2 species from the depleted brine, can be easily determined using Equation 90 where the terms involving the dissolved Cl_2 and the active Cl_2 are omitted from Equation 89.

$$\eta_{\mathrm{Cl_2}}^{\mathrm{p}} = \frac{1 - (2F/I)p[X_0(3C_{\mathrm{NaClO_3}}^{\mathrm{d}}) - \mathrm{Cl_2^f}]}{C - 2Y_0(3C_{\mathrm{NaClO_3}}^{\mathrm{d}})} \tag{90}$$

where

$$X_0 = (C_{\mathrm{NaCl}}^{\mathrm{f}} + C_{\mathrm{NaClO_3}}^{\mathrm{f}})/Y_0$$

$$Y_0 = (C_{\mathrm{NaCl}}^{\mathrm{d}} + C_{\mathrm{NaClO_3}}^{\mathrm{d}} + 10^{-\mathrm{pH}})^{-1}$$

Thus, from Expressions 88 to 90, the chlorine and caustic current efficiency of membrane cells can be determined without any ambiguity in the choice of the operating parameters. The reader is referred to [9] for estimating the concentration of dissolved chlorine in NaCl solutions, required for calculating the chlorine and caustic current efficiencies using Equations 88 and 89.

It is important to note that the process chlorine efficiency is essentially the same as the cell caustic efficiency since, from Equation 78, it can be seen that $\eta_{\mathrm{OH}} - \eta_{\mathrm{Cl_2}}^{\mathrm{p}} = (F/I)\Delta(J_{\mathrm{NaOH}} + 2J_{\mathrm{Na_2CO_3}} + J_{\mathrm{NaHCO_3}} - J_{\mathrm{HCl}})$ which is about 0.7% under normal operating conditions.

3.4. *A simple approach to estimate membrane cell caustic current efficiency*

Current efficiency equations described in earlier sections are solely based on an analysis of anode gases and anolyte composition, which requires an accurate measure of all the components in the feed and depleted brine. A simplified method, which is analytically less cumbersome, is presented below to estimate the caustic current efficiency of ion-exchange membrane chlor-alkali cells.

Caustic current efficiency for the membrane cells can be derived from the material balance of NaOH across the cathode compartment as

$$\eta_{\mathrm{OH}} = \frac{Q'_{\mathrm{NaOH}}(Z^* C''_{\mathrm{NaOH}} - C'_{\mathrm{NaOH}})}{I/F} \tag{91}$$

where the term Z^* represents the concentration ratio of the inert species X^* in the feed to exit catholyte or the flow rate ratio of the catholyte feed rate, Q', to the exit rate Q'', based on material balance for the species X^*.

$$Z^* = \frac{C'_{X^*}}{C''_{X^*}} = \frac{Q''_{\mathrm{NaOH}}}{Q'_{\mathrm{NaOH}}}$$

Potential inert species include borate, sulfate, and K^+, Li^+ if absent in the feed brine. The success of this novel approach depends on analyses of X^* and NaOH to a high degree of accuracy.

3.5. *Error analysis for process chlorine efficiency and energy consumption*

Analysis of errors using the 'propagation of errors' technique (Appendix II) showed the error associated with the process chlorine efficiency calculation to be ±0.25% and the error in the energy consumption, ΔP, calculation to be ±15 kWh/ton Cl_2 (see Table 2) based on the precision achievable by the analytical methods noted in Table 3.

Table 2. Error analysis for current efficiency and energy consumption

Current efficiency/%		Energy consumption/ kWh ton^{-1}Cl$_2$	
η_{Cl_2}	$\Delta\eta_{\mathrm{Cl}_2}$	P	ΔP
(a) Diaphragm cell data from plant I			
98.39	0.17	2634	12
95.84	0.17	2623	12
90.34	0.14	2694	12
(b) Membrane cell data from plant II			
95.33	0.21	2626	13
93.62	0.22	2727	14
93.99	0.22	2741	14

4. Summary and conclusions

Generalized current efficiency expressions were derived for ion-exchange membrane and diaphragm chlor-alkali cells employing a rigorous material balance formalism and accounting for all common reactive brine impurities and their interactions with $\mathrm{Cl_2}$ and/or NaOH. Comparison of the current efficiency relationships deduced in the present study with the published chlorine and caustic current efficiency for ion-exchange and diaphragm cells revealed errors in the earlier versions arising from the manipulations of the basic equation. Rigorous equations for the cell caustic and chlorine current efficiency, and the process chlorine efficiency of ion-exchange membrane cells, without ambiguity in the choice of the operating parameters, were presented. In addition, an analytically simple procedure for estimating the caustic current efficiency of membrane cells was proposed.

Disparity between the caustic and chlorine current efficiency of the diaphragm cells was shown to arise from the alkalinity or the acidity in the cell feed brine, whereas the difference between the caustic and chlorine current efficiency of the membrane cells was noted to stem from not only the acidity or the alkalinity in the cell feed brine but also from the formation of active chlorine species in the anolyte.

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Appendix 1. Derivation of hydrogen current efficiency

Hydrogen inefficiency is a consequence of the blind current losses arising from the discharge of the available chlorine at the cathode forming only NaOH.

$$\mathrm{NaOCl + H_2O + 2e^- \longrightarrow NaCl + 2OH^-} \qquad \text{(A1.1)}$$

Table 3. Analytical methods currently used

Item	Analytical method	Precision
(a) Feed brine		
NaCl	$\mathrm{AgNO_3}$ titration – $\mathrm{Na_2CrO_4}$ indicator	$\pm 2.5\,\mathrm{g\,dm^{-3}}$
$\mathrm{NaClO_3}$	Mix acid – $\mathrm{FeSO_4}$ titration	$\pm 0.005\,\mathrm{g\,dm^{-3}}$
NaOH	Autotitrator – potentiometric	±10 p.p.m.
$\mathrm{Na_2CO_3}$	Autotitrator – potentiometric	±10 p.p.m.
Flow rate	Cell rotameter	$\pm 0.15\,\mathrm{dm^3\,min^{-1}}$
(b) Depleted brine or anolyte		
NaCl	$\mathrm{AgNO_3}$ titration – $\mathrm{Na_2CrO_4}$ indicator	$\pm 2.5\,\mathrm{g\,dm^{-3}}$
$\mathrm{NaClO_3}$	Mix acid – $\mathrm{FeSO_4}$ titration	$\pm 0.02\,\mathrm{g\,dm^{-3}}$
NaOCl	Titration – KI starch indicator	$\pm 0.05\,\mathrm{g\,dm^{-3}}$
pH	Orion – double electrodes	±0.1 unit
(c) Cell liquor		
NaOCl	Titration – KI starch indicator	$\pm 0.5\,\mathrm{g\,dm^{-3}}$
$\mathrm{NaClO_3}$	Mix acid – $\mathrm{FeSO_4}$ titration	$\pm 0.02\,\mathrm{g\,dm^{-3}}$
NaOH	Autotitrator – potentiometric	$\pm 1.5\,\mathrm{g\,dm^{-3}}$
(d) Cell gas		
$\%\mathrm{O_2}$	Carle gas chromatograph – direct with standard	±0.05%
$\%\mathrm{Cl_2}$	Carle gas chromatograph – by difference, no standard	±0.20%

The blind current loss (BCL) can be estimated to be

$$\mathrm{BCL} = 2FqC^{\mathrm{a}}_{\mathrm{Av.Cl_2}} \tag{A1.2}$$

Since the cell liquor flow rate, q, can be expressed as

$$q = \left(\frac{I}{F}\right)\frac{\eta^{\mathrm{D}}_{\mathrm{OH}}}{C^{\mathrm{d}}_{\mathrm{NaOH}}} \tag{A1.3}$$

Equation A1.2 becomes

$$\mathrm{BCL} = 2C^{\mathrm{a}}_{\mathrm{Av.Cl_2}}\frac{I\eta^{\mathrm{D}}_{\mathrm{OH}}}{C^{\mathrm{d}}_{\mathrm{NaOH}}} \tag{A1.4}$$

Thus, the hydrogen inefficiency can be written as

$$1 - \eta^{\mathrm{D}}_{\mathrm{H_2}} = \frac{\mathrm{BCL}/2}{I\eta^{\mathrm{D}}_{\mathrm{OH}}/2} \tag{A1.5}$$

Substitution of equation A1.4 into equation A1.5 gives

$$\eta^{\mathrm{D}}_{\mathrm{H_2}} = 1 - 2\left(\frac{C^{\mathrm{a}}_{\mathrm{Av.Cl_2}}}{C^{\mathrm{d}}_{\mathrm{NaOH}}}\right) \tag{A1.6}$$

Appendix 2. Propagation of errors technique

We consider a quantity Q which is to be calculated from several observed quantities $a, b, c, \ldots$:

$$Q = f(a, b, c, \ldots) \tag{A2.1}$$

The error ΔQ resulting from errors $\Delta a, \Delta b, \ldots$ can be represented as

$$\Delta Q = \left(\frac{\partial Q}{\partial a}\right)\Delta a + \left(\frac{\partial Q}{\partial b}\right)\Delta b + \left(\frac{\partial Q}{\partial c}\right)\Delta c + \ldots \tag{A2.2}$$

and the standard deviation σ_Q resulting from standard deviations $\sigma_a, \sigma_b, \ldots$ can be written as

$$\sigma_Q = \sqrt{\left(\frac{\partial Q}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial Q}{\partial b}\right)^2 \sigma_b^2 + \left(\frac{\partial Q}{\partial c}\right)^2 \sigma_c^2 + \ldots} \tag{A2.3}$$

For simplicity, Equation A2.2 is used to estimate the errors in the chlorine process efficiency and energy consumption calculations. The equation used for the energy consumption calculations is given by

$$\frac{\mathrm{AC\ kWh}}{\mathrm{Ton\ Cl_2}} = \frac{685.834 \times \text{cell voltage}}{\eta_{\mathrm{Cl_2}} \times \eta_{\mathrm{rectifier}} \times \eta_{\mathrm{liquification}}}$$

where the rectifier and liquification efficiencies are the generally accepted values of 0.975 and 0.992, respectively.