JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) 699–704

Estimation of current efficiency in ion-exchange membrane chlor-alkali cells*

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Received 14 October 1987; revised 28 March 1988

A generalized current efficiency equation was derived from material balance considerations to estimate the caustic current efficiency in ion exchange chlor-alkali membrane cells taking into account the presence of $NaHCO_3$, Na_2CO_3, and NaOH in the feed brine. The validity and the accuracy of this equation was established by comparing the 'gas analysis' results with the data obtained from caustic collection measurements. It is also shown that this general expression can be easily extended to deduce the current efficiency applicable for diaphragm cell operations.

Nomenclature

$C_{Cl_2}(s)$	soluble chlorine from chlorine hydrolysis, in $g\,l^{-1}$, following $Cl_2 + H_2O \rightarrow HCl + HOCl$
C species (a)	concentration of the species noted in the subscript in $g\,l^{-1}$ in the anolyte
C species (c)	concentration of the species noted in the subscript in $g\,l^{-1}$ in the catholyte
C species (d)	concentration of the species noted in the subscript in $g\,l^{-1}$ in the depleted brine
C species (f)	concentration of the species noted in the subscript in $g\,l^{-1}$ in the feed brine
C_{OH}	catholyte caustic concentration in $g\,l^{-1}$
F	Faraday Number ($96{,}487\,C\,mol^{-1}$)
I	Load expressed in amps
k	rate constant of Reaction 28
k^1	factor which includes the exchange current density of the chlorate reduction reaction
p	feed brine flow rate in $l\,s^{-1}$
q	depleted brine flow rate in $l\,s^{-1}$
R	gas constant
T	temperature in K
X	$1.338C_{Na_2CO_3}(f) + 0.844C_{NaHCO_3}(f) + 1.773C_{NaOH}(f)$
Y	moles of NaOH consumed s^{-1} with acid feed brine addition
Z	ratio of $C_{NaClO_3}(a)$: $C_{NaClO_3}(c)$
β	transfer coefficient
η	overpotential for the chlorate reduction reaction
η_{Cl_2}	chlorine current efficiency
η_{NaOH}	caustic current efficiency
η^a_{NaOH}	caustic current efficiency with acid feed brine

1. Introduction

One of the most energy consuming electrolytic industries is the chlor-alkali industry which consumes about 2100–$2500\,kWh\,ton^{-1}$ of caustic via diaphragm or ion-exchange membrane cell operations, the latter being the emerging technology. Evaluation of the performance characteristics of membrane cells is best done by comparing the energy consumption information which is calculated from the cell voltage and the caustic current efficiency data.

Current efficiency for caustic production can be estimated from caustic collection which involves collecting a known weight of caustic over a period of time and a knowledge of the number of coulombs of electricity passed during that period of time. While this procedure is accurate, it is a time-consuming and cumbersome measurement. An alternate way of estimating caustic current efficiency is from an analysis of the gases evolved during electrolysis and the anolyte composition as discussed previously for determining the chlorine current efficiency of graphite cells [1–3].

The purpose of this communication is to provide the details related to the calculation of caustic current efficiency (η_{NaOH}) from the data normally collected for

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* This paper was presented at the October, 1987 Honolulu meeting of the Electrochemical Society.

0021-891X/88 $03.00 + .12

estimating current efficiency from 'gas analysis' data. The formalism described here will permit paper evaluation of the performance characteristics of membrane cells under varied operating conditions.

2. Theoretical details

The principal component electrochemical reactions in chlor-alkali cells are:

$$2\text{NaCl} \longrightarrow 2\text{Na}^+ + \text{Cl}_2 + 2\text{e (at the anode)} \tag{1}$$

and

$$2\text{H}_2\text{O} + 2\text{e} \longrightarrow \text{H}_2 + 2\text{OH}^- \text{ (at the cathode)} \tag{2}$$

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

Ideally, it is possible to realize a caustic current efficiency of 100%. However, because of caustic back migration, η_{NaOH} will be $< 100\%$, the back migrating caustic revealing itself in terms of chlorate, hypochlorite and hypochlorous acid in the anode compartment because of the following reactions:

$$\text{NaOH} + \text{Cl}_2 \rightleftharpoons \text{NaCl} + \text{HOCl} \tag{3}$$

$$\text{NaOH} + \text{HOCl} \rightleftharpoons \text{NaOCl} + \text{H}_2\text{O} \tag{4}$$

$$2\text{HOCl} + \text{NaOCl} \longrightarrow \text{NaClO}_3 + 2\text{HCl} \tag{5}$$

$$\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} \tag{6}$$

The total amount of HOCl + OCl^- formed in the anolyte is not only due to the above reactions but also because of the presence of NaOH, NaHCO_3, and Na_2CO_3 in the feed brine, as described by the Reactions 7 to 9, and due to the inherent solubility of chlorine in brine solutions. The latter may be estimated from the chlorine solubility data of Yokota [4] determined in concentrated NaCl solutions at various temperatures, pH values and partial pressures.

$$\text{NaOH} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{HOCl} \tag{7}$$

$$\text{Na}_2\text{CO}_3 + 2\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HOCl} + 2\text{NaCl} + \text{CO}_2 \tag{8}$$

$$\text{NaHCO}_3 + \text{Cl}_2 \longrightarrow \text{HOCl} + \text{NaCl} + \text{CO}_2 \tag{9}$$

It is pertinent to note, in the context of our objective, that oxygen discharge is a parasitic reaction and is a consequence of anodic processes noted in Equations 10 and 11 and/or due to the decomposition of hypo (i.e., HOCl + OCl^-) as described by Reaction 12.

$$4\text{OH}^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \tag{10}$$

$$2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e} \tag{11}$$

$$2\text{HOCl} \longrightarrow \text{O}_2 + 2\text{HCl} \tag{12}$$

It follows from the above reaction schemes that:

(i) formation of one mole of NaClO_3 via Reaction 5 corresponds to a loss of 3 moles of chlorine;
(ii) one mole of Na_2CO_3 in the feed brine will lead to the formation of 2 moles of HOCl (Reaction 8);
(iii) 1 mole of O_2 formation from Reactions 10, 11 and 12 corresponds to a loss of 2 moles of chlorine.

Assuming the absence of blind current losses arising from the discharge of OCl^-, HOCl, and ClO_3^- at the cathode, the chlorine current efficiency (η_{Cl_2}) may be deduced from the following general expression

$$\eta_{\text{Cl}_2} = \frac{\left\{\begin{matrix}\text{Theoretical}\\ \text{amount}\end{matrix}\right\} - \left\{\begin{matrix}\text{Cl}_2\text{ lost due}\\ \text{to O}_2\end{matrix}\right\} - \left\{\begin{matrix}\text{Chlorine lost as}\\ \text{chlorate} + \text{OCl}^- + \text{HOCl}\end{matrix}\right\}}{\text{Theoretical Amount}} \tag{13}$$

The theoretically expected amount of chlorine produced is equal to $I/2\text{F}$ where I is the load expressed in amps and F is the Faraday number (96487 C mol^{-1}). 'Losses' shown in Equation 13 can now be estimated as:

(i) Cl_2 lost due to O_2 formation

Since the mole fraction equals the volume fraction, it follows that:

$$\frac{\text{moles of O}_2}{\text{moles of Cl}_2} = \frac{\%\ \text{O}_2{}^*}{\%\ \text{Cl}_2} \tag{14}$$

The amount of Cl_2 produced (in mol s^{-1}) is $I\eta_{\text{Cl}_2}/2\text{F}$ and hence the moles of Cl_2 lost due to O_2 formation will be $(I\eta_{\text{Cl}_2}/\text{F})$ $(\%\text{O}_2/\%\text{Cl}_2)$, since the number of moles of Cl_2 lost due to O_2 is equal to 2 × moles of O_2.

(ii) Cl_2 consumed as NaClO_3

The amount of sodium chlorate formed in the anolyte can be expressed as

$$\text{Moles of chlorate formed} = \frac{qC_{\text{NaClO}_3}(\text{a})}{106.45} \tag{15}$$

where q is the depleted brine flow rate (l s^{-1}) and $C_{\text{NaClO}_3}(\text{a})$ refers to the anolyte chlorate concentration (in g l^{-1}). Hence,

$$\begin{aligned}\text{Cl}_2 \text{ lost as NaClO}_3 &\\ &= 3 \times \text{moles of sodium chlorate formed}\\ &= \frac{3qC_{\text{NaClO}_3}(\text{a})}{106.45}\end{aligned} \tag{16}$$

(iii) Chlorine lost as dissolved chlorine $C_{\text{Cl}_2}(\text{a})$, i.e. HOCl + OCl^-

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* This is nitrogen free O_2 and is computed from the measured value of % O_2 using the relationship: Nitrogen free O_2 = Measured value of % O_2 − 0.2658 % N_2.

The amount of chlorine lost as dissolved chlorine may be expressed as:

Cl_2 lost as dissolved chlorine in the anolyte

$$= \frac{qC_{Cl_2}(a)}{70.91} \qquad (17)$$

where $C_{Cl_2}(a)$ is the amount of dissolved Cl_2 in the anolyte in $g\,l^{-1}$.

Formation of dissolved chlorine, $HOCl + OCl^-$, is not only due to the back migrating caustic but also due to the presence of Na_2CO_3, $NaHCO_3$ and NaOH in the feed brine as described in Reactions 7, 8 and 9. Since $C_{Cl_2}(a)$ comprises contributions from Reactions 3, 4 and 7 to 9, and also from the hydrolysis of chlorine as, $Cl_2 + H_2O \rightarrow HCl + HOCl$, it is necessary to correct for it for purposes of calculating caustic current efficiency by subtracting $C_{Cl_2}(s)$ from $C_{Cl_2}(a)$, where $C_{Cl_2}(s)$, the solubility of chlorine from chlorine hydrolysis, may be estimated from the data in [4].

It should be pointed out that this correction to $C_{Cl_2}(a)$ is not required for estimating chlorine current efficiency.

The contribution from Na_2CO_3, $NaHCO_3$, and NaOH in the feed brine to $C_{Cl_2}(a)$ can now be expressed as:

g of dissolved Cl_2 due to Na_2CO_3

$$= \frac{141.82C_{Na_2CO_3}(f)}{106}$$

$$= 1.388C_{Na_2CO_3}(f) \qquad (18)$$

where $C_{Na_2CO_3}(f)$ refers to the concentration of sodium carbonate in the feed brine in $g\,l^{-1}$.

g of dissolved Cl_2 due to $NaHCO_3$

$$= \frac{70.91}{84} C_{NaHCO_3}(f)$$

$$= 0.844C_{NaHCO_3}(f) \qquad (19)$$

g of $C_{Cl_2}(a)$ due to NaOH

$$= \frac{70.91}{40} C_{NaOH}(f)$$

$$= 1.773C_{NaOH}(f) \qquad (20)$$

$C_{NaHCO_3}(f)$ and $C_{NaOH}(f)$ in Equations 19 and 20 refer to the concentration of $NaHCO_3$ and NaOH in the feed brine in $g\,l^{-1}$.

Material balance considerations show that chlorine current efficiency must be equal to caustic current efficiency when the feed brine is neutral. In the presence of Na_2CO_3, $NaHCO_3$ and NaOH in the feed brine the caustic efficiency, (η_{NaOH}), values can be calculated by taking into account the contribution of these species to $C_{Cl_2}(a)$. Thus, Equation 13 may be recast as:

$$\eta_{NaOH} = 100\left\{\frac{\left(\frac{I}{2F}\right) - \left(\frac{I\eta}{F}\cdot\frac{\%\,O_2}{\%\,Cl_2}\right) - \left(\frac{3qC_{NaClO_3}(a)}{106.45}\right) - \left(\frac{q[C_{Cl_2}(a) - X]}{70.91}\right)}{I/2F}\right\} \qquad (21)$$

where $X = 1.338C_{Na_2CO_3}(f) + 0.844C_{NaHCO_3}(f) + 1.773C_{NaOH}(f)$. Rearranging the terms in Equation 21 results in:

$$\eta_{NaOH} = 100\left\{\frac{1 - \left(\frac{q}{I/2F}\right)\left(\frac{3C_{NaClO_3}(a)}{106.45} + \frac{[C_{Cl_2}(a) - X]}{70.91}\right)}{1 + \frac{2\%\,O_2}{\%\,Cl_2}}\right\} \qquad (22)$$

When the feed brine contains finite amounts of chlorate, Equation 22 should be appropriately modified by taking into consideration the feed brine flow rate and the depleted brine flow rate, which differs as a consequence of water transport across the ion-exchange membrane. Under these conditions, Equation 22 may be recast as:

$$\eta_{NaOH} = 100\left\{\frac{1 - \left(\frac{2F}{I}\left(\left(\frac{3qC_{NaClO_3}(d)}{106.45}\right) - \left(\frac{3pC_{NaClO_3}(f)}{106.45}\right) + \left(\frac{qC_{Cl_2}(a)}{70.91}\right) - \left(\frac{pX}{70.91}\right)\right)\right)}{\{1 + (2\%\,O_2/\%Cl_2)\}}\right\} \qquad (23)$$

where q refers to the depleted brine flow rate (in $l\,s^{-1}$) and p refers to the feed brine flow rate in $l\,s^{-1}$. $C_{NaClO_3}(f)$ and $C_{NaClO_3}(d)$ represent the concentration of $NaClO_3$ in the feed and depleted brine, respectively. Equation 23 will provide a proper estimate of the caustic current efficiency values taking into account the presence of $NaClO_3$, $NaHCO_3$, NaOH, and Na_2CO_3 in the feed brine. However, when the feed brine is acidic, an additional correction has to be made to Equation 23, as shown in the Appendix.

2.1. *Derivation of current efficiency expression for diaphragm cells*

The main difference between the membrane and diaphragm cell operations is the flow direction of the various components in the anolyte. While water and Na^+ ion transport across the membrane are the main events in a membrane cell, anolyte flows through a porous separator into the catholyte in a diaphragm cell. When the caustic current efficiency is equal to chlorine current efficiency, material balance considerations show [5]:

$$q = \frac{40 I \eta_{NaOH}}{C_{OH} F} \tag{24}$$

where C_{OH} refers to the catholyte caustic strength in $g\,l^{-1}$. Substitution of Equation 24 in Equation 22 results in:

$$\eta_{NaOH} = \frac{100}{1 + \left\{\frac{2\%\ O_2}{\%\ Cl_2}\right\} + \left\{\frac{80}{C_{OH}}\right\}\left\{\frac{3C_{NaClO_3}(a)}{106.45} + \frac{(Cl_2(a) - X)}{70.91}\right\}} \tag{25}$$

Since the primary interest in diaphragm cell operations is the chlorine efficiency and the presence of Na_2CO_3, $NaHCO_3$ and NaOH in the feed brine contribute to Cl_2 losses, the term X in the denominator of Equation 25 must be dropped for calculating the Cl_2 efficiency of diaphragm cells. In the presence of $NaClO_3$ in the feed brine and expressing all the oxidants as $NaClO_3$, Equation 25 can be written as:

$$\eta_{Cl_2} = \frac{100}{1 + \left\{\frac{2\%\ O_2}{\%\ Cl_2}\right\} + 2.2546\left\{\frac{C_{NaClO_3}(a) - C_{NaClO_3}(f)}{C_{OH}}\right\}} \tag{26}$$

where $C_{NaClO_3}(f)$ refers to the $NaClO_3$ concentration in the feed brine, appropriately corrected for the temperature variations of the anolyte and the feed brine and $C_{NaClO_3}(a)$ to the anolyte chlorate concentration.

While all the parameters in Equation 26 are experimentally accessible, anolyte chlorate measurement is cumbersome and tedious. Nevertheless, it can be easily estimated from the catholyte chlorate levels as will be shown below. The difference in the chlorate level in the anolyte and the catholyte arises as a consequence of: (i) electrochemical reduction of chlorate to chloride and (ii) additional evaporation in the cathode chamber because of the higher operating temperature of the catholyte relative to that of the anolyte.

The relationship between the anolyte ($C_{NaClO_3}(a)$) and catholyte ($C_{NaClO_3}(c)$) chlorate levels may be described in general as:

$$C_{NaClO_3}(a) = Z C_{NaClO_3}(c) \tag{27}$$

where Z is a factor which accounts for chlorate reduction at the cathode (in the low current and/or blind current zones) and evaporation which is a function of cell geometry, operating conditions, and caustic strength.

In principle, Z can assume 3 values:

(i) $Z > 1$. This implies that the amount of chlorate in the anolyte is greater than in the catholyte since chlorate is electrochemically reduced at the cathode.

(i) $Z = 1$. This would occur if the anolyte chlorate is equal to the catholyte chlorate and suggests that there is no change in the concentration of chlorate as it is going from the anode to the cathode compartment; in other words, there is neither electrochemical reduction nor evaporation taking place in the catholyte. $Z = 1$ is also possible if the amount of reduction at the cathode is equal to the amount of evaporation.

(iii) $Z < 1$. This would occur if the anolyte chlorate is less than the catholyte chlorate level as the chlorate is becoming concentrated in the cathode compartment because of higher operating temperature (of ~ 5–10° C) of the catholyte against the anolyte. Assuming that no reduction of chlorate occurs, values of Z as low as 0.85 can be accounted for in terms of evaporation in the cathode compartment. However, values of Z less than 0.85 cannot be explained since it would violate the material balance with the known chemistry of the system. It is likely that values of < 0.85 are a consequence of errors in the analysis of the active anolyte chlorine species. $Z \leqslant 1$ will occur only if the current density distribution within the cell is so uniform that the electrochemical reduction of chlorate is not taking place. Uniform current density distribution is a very unlikely situation in the commercial cell geometries and hence, values of $Z \leqslant 1$ have doubtful significance and are attributable to analytical errors.

The amount of chlorate formed in the anode compartment, $C_{NaClO_3}(a)$, may be expressed as (following Reaction 28),

$$3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 3H_2O + 5NaCl \tag{28}$$

$$C_{NaClO_3}(a) = k(C_{OH})^6 \tag{29}$$

where k refers to the rate constant of Reaction 28. The amount of chlorate reduced at the cathode can be formally expressed as

$$\text{Amount of NaClO}_3\text{ reduced} = k^1 C_{\mathrm{NaClO_3}}(\mathrm{a}) \exp(\beta\eta \mathrm{F}/\mathrm{R}T) \quad (30)$$

where k^1 refers to a constant which includes the exchange current density of the chlorate reduction reaction, β to the transfer coefficient and η to the overpotential. It is assumed here that the initial chlorate concentration at the cathode is the same as that in the anolyte. Substitution of Equations 29 and 30 in Equation 27 results in:

$$Z = 1/[1 - k^1 \exp(\beta\eta \mathrm{F}/\mathrm{R}T)] \quad (31)$$

Hence, the ratio of $C_{\mathrm{NaClO_3}}(\mathrm{a})/C_{\mathrm{NaClO_3}}(\mathrm{c})$ should be independent of caustic concentration in the catholyte. Current density is unlikely to have an effect on the ratio, Z, as it would change the overpotential as well as the temperature term in Equation 31. However, if the catholyte temperature varies, Z will vary. Under these conditions,

$$\ln\left(\frac{Z-1}{Z}\right) = \ln k^1 + \beta\eta \mathrm{F}/\mathrm{R}T \quad (32)$$

or a plot of ln $((Z - 1)/Z)$ as a function of $1/T$ should exhibit a linear behaviour.

Thus, from a knowledge of the ratio of $C_{\mathrm{NaClO_3}}(\mathrm{a})/C_{\mathrm{NaClO_3}}(\mathrm{c})$ and the magnitude of $C_{\mathrm{NaClO_3}}(\mathrm{c})$, the current efficiency may be estimated using Equation 33 deduced from Equations 26 and 27.

$$\eta_{\mathrm{Cl_2}} = 100\Bigg/\left[1 + \left\{\frac{2\%\ \mathrm{O_2}}{\%\ \mathrm{Cl_2}}\right\} + 2.2546\left\{\frac{ZC_{\mathrm{NaClO_3}}(\mathrm{c}) - C_{\mathrm{NaClO_3}}(\mathrm{f})}{C_{\mathrm{OH}}}\right\}\right] \quad (33)$$

3. Results

3.1. *Comparison of current efficiency data from gas analysis and caustic collection measurements*

Plant testing of both modified diaphragm type chlorine cells and high performance ion-exchange membrane electrolysers was performed to evaluate the caustic efficiency via 'gas analysis' and 'caustic-collection'. 'Hooker H-4 type diaphragm cells' with polymer modified diaphragms were stabilized for 24 h prior to the test period, stability being defined in terms of constant operating load and caustic strength. Chlorine gas, anolyte, and catholyte samples were collected on 26 selected cells and analysed. The 'gas efficiency' was then calculated using Equation 25.

The average efficiency was found to be 94.97% with a standard deviation of 1.77. On the same H-4 cells, the caustic cell liquor was collected over a 30–40 min period. The total weight collected was determined by direct weighing or by a combination of volume measurement and density determination. The caustic cell liquor was analysed to establish the total weight of caustic collected. The caustic collection efficiency was then calculated by dividing the actual weight of caustic collected by the theoretical amount of caustic produced from Faraday's Law and the number of coulombs of electricity obtained using a calibrated kiloamp-hour (kAh) meter. The caustic collection efficiency determined in this manner averaged 94.71% with a standard deviation of 1.92. Thus, the difference between the two methods of determining caustic efficiency on diaphragm cells was only 0.26%.

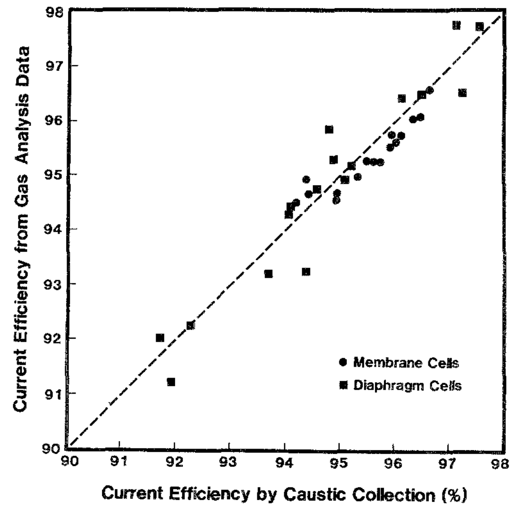

Fig. 1. Comparison of caustic efficiency with the calculated efficiencies from gas-analysis data.

Sixteen separate tests were performed on OxyTech MGC-16 membrane electrolysers. Prior to each test it was ensured that the operating current and the other process parameters remained constant over a 24 h period. During the 1 day test period, chlorine cell gas and anolyte samples were collected every 4 h and analysed. The 'gas efficiency' was then calculated using Equation 23 and the results were averaged for the 24 h period. The average efficiency for all the tests was 95.30% with a standard deviation of 0.54. During the same test period, the actual amount of caustic produced was determined using a magnetic flow totalizer and caustic analysis performed every hour. The caustic collection efficiency was calculated by dividing the actual quantity of caustic produced by the theoretical amount, which was derived using a calibrated kAh meter and Faraday's Law. The average caustic collection efficiency was 95.51% with a standard deviation of 0.72. The difference between the 'gas efficiency' and 'collection efficiency' was only 0.21% for membrane-type chlor-alkali electrolysers.

From all the 42 data points, the average caustic current efficiency via 'gas analysis' was 95.0% ± 1.42 as opposed to 95.02 ± 1.61 using caustic collection data. A comparison of all the data for the membrane and diaphragm cells is given in Fig. 1. The data for the membrane electrolysers indicate a better agreement between 'gas efficiency' and caustic collection efficiency which is primarily attributable to the use of a 24 h test period instead of 30–40 minutes employed during caustic collection with diaphragm cells. This longer test period dampens out errors and upsets that occur in normal plant operations.

4. Conclusions

A generalized current efficiency expression was derived from material balance considerations to permit estimation of caustic current efficiency of ion-exchange membrane chlor-alkali cells from gas-analysis data taking into account the presence of Na_2CO_3, $NaHCO_3$ and NaOH in the feed brine. It was also shown that this general equation can be easily extended to allow calculation of the chlorine current efficiency of diaphragm-type chlor-alkali cells. The validity of these equations was demonstrated by comparing the measured caustic current efficiency data with the calculated efficiencies.

Acknowledgements

The authors wish to thank Occidental Chemical Corporation for permission to publish this communication. The authors are also grateful to R. B. Kaplin and H. Frank for their comments and help during the course of this investigation.

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Appendix: Caustic current efficiency in membrane cells with acid feed brine

When the feed brine is acidic, there will be an additional consumption of back migrating caustic via the reaction:

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad (A1)$$

in addition to the consumption from Reactions 3 to 5 and 7. The number of moles of NaOH consumed from the above reaction may be calculated in a manner similar to the ones described earlier. Thus,

$$\text{Moles of NaOH consumed s}^{-1} = Y$$
$$= \left\{\frac{pC_{HCl}(f)}{36.5}\right\} - \left\{\frac{qC_{HCl}(d)}{36.5}\right\} \qquad (A2)$$

where p refers to the feed brine flow rate in $l\,s^{-1}$, q refers to the depleted brine flow rate in $l\,s^{-1}$, $C_{HCl}(f)$ refers to the amount of HCl in the feed brine in $g\,l^{-1}$ and $C_{HCl}(d)$ refers to the amount of HCl in the anolyte in $g\,l^{-1}$.

Defining caustic efficiency, η^a_{NaOH}, with acid feed brine as:

$$\eta^a_{NaOH} = \frac{\text{Actual amount of NaOH produced}}{\text{Theoretical amount of NaOH}} \qquad (A3)$$

and the actual amount of NaOH produced equals the amount of NaOH estimated using Equation 23 less the amount of NaOH consumed because of Reaction A1; it can be shown that:

$$\eta^a_{NaOH} = \frac{((I/F)\eta_{NaOH}) - Y}{I/F} \qquad (A4)$$

or

$$\eta^a_{NaOH} = \eta_{NaOH} - \left\{\frac{F}{I}\left\{\left\{\frac{pC_{HCl}(f)}{36.5}\right\} - \left\{\frac{qC_{HCl}(d)}{36.5}\right\}\right\}\right\} \qquad (A5)$$

Thus, Equation A5 will permit calculation of caustic efficiency in membrane cells with acid feed brine.