

## SHORT COMMUNICATION

**A model for the determination of chloride and chlorate levels in the caustic product of ion-exchange membrane chlor-alkali cells**

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**1. Introduction**

The technology of choice in 90% of the planned expansions in the chlor-alkali industry is the ion-exchange membrane cell process because of the associated ecological and economic advantages [1, 2]. However, the membrane cell process requires ultra pure feed brine to the electrolyzers to avoid damage to the membranes and the anodes, with consequent lowering of current efficiency and escalation of cell voltages. High purity feed brine with less than 10 p.p.b. of Ca + Mg is generally produced by chemically precipitating the Ca + Mg as  $\text{CaCO}_3 + \text{Mg}(\text{OH})_2$ , respectively, from the raw brine, followed by secondary treatment using cation ion-exchange resins of the amino phosphonic or imino diacetic acid type [1, 2].

The caustic produced from the ion-exchange membrane cells is generally pure, although not as pure as the mercury grade caustic. High quality caustic with low  $\text{Cl}^-$  and  $\text{ClO}_3^-$  levels can not be easily achieved by simple chemical treatment of the caustic from the membrane cells. Therefore, it is essential to understand the factors affecting the caustic quality so that caustic with a level of impurities acceptable to the customer can be produced directly from the cells. The purpose of this communication is to present a simple model that can be used as a predictive tool to decipher the effect of the cell operating conditions on the caustic quality produced from a chlor-alkali membrane cell.

**2. Theory**

Acknowledging the complex structural features of the cation-exchange membranes and the associated transport mechanisms [3–6], a classical approach is followed to describe the transport of anions across a cation exchange membrane. The mass transport of an ionic species,  $j$ , across a membrane, governed by the diffusion, migration and electroosmotic water convection, can be described [7] using the Nernst-Planck equation:

$$N_j = -D_j \frac{dC_j}{dx} - \frac{z_j F}{RT} D_j C_j \frac{d\phi}{dx} + C_j v \quad (1)$$

where  $N_j$  is the flux of species  $j$  ( $\text{mol s}^{-1} \text{cm}^{-2}$ ),  $D_j$  is the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $dC_j/dx$  is the concentration gradient at distance  $x$ ,  $d\phi/dx$  is the potential gradient,  $z_j$  and  $C_j$  are the charge and

concentration of species  $j$ , respectively and  $v$  is the electroosmotic water velocity ( $\text{cm s}^{-1}$ ) across the membrane [7]. Since the electric potential gradient,  $d\phi/dx$ , is related to the current density,  $i$  ( $\text{A cm}^{-2}$ ), and membrane conductivity,  $\kappa$  ( $\Omega^{-1} \text{cm}^{-1}$ ), as

$$\frac{d\phi}{dx} = -\frac{i}{\kappa} \quad (2)$$

Equation 1 can be simplified to the form:

$$N = -D \frac{dC}{dx} - (u - v)C \quad (3)$$

where  $u = -z_j D F i / RT \kappa$ . For simplicity, subscript  $j$  is omitted hereafter. The steady-state flux of the ionic species across the membrane can be obtained by solving Equation 3 using the boundary conditions:  $x = 0$ ,  $C = C_b$  and  $x = \delta$ ,  $C = C_0$ . Thus,

$$N = (u - v) \left[ \frac{\gamma C_b - C_0}{1 - \gamma} \right] \quad (4)$$

where  $\delta$  is the thickness of the membrane (cm),  $C_0$  and  $C_b$  are the concentration of the impurity species ( $\text{mol cm}^{-3}$ ) in the cathode and anode compartments, respectively, and  $\gamma = \exp(-(u - v)\delta/D)$ . From the material balance of the species around the cathode compartment:  $qC_0 = pC_i + NS$  (Fig. 1), the concentration of the species of interest in the caustic product,  $C_0$ , can now be expressed as

$$C_0 = \frac{(1 - \gamma)pC_i + \gamma(u - v)SC_b}{(1 - \gamma)q + (u - v)S} \quad (5)$$

where  $p$  and  $q$  are feed and exit flow rates of the caustic ( $\text{cm}^3 \text{s}^{-1}$ ),  $S$  is the total surface area of the membrane in an electrolyser ( $\text{cm}^2$ ) and  $C_i$  is the concentration of the anionic impurity in the feed caustic.

**3. Results and discussion**

It follows from Equation 3 that anions such as  $\text{Cl}^-$  and  $\text{ClO}_3^-$ , present at high concentrations in the anolyte, are transported to the cathode compartment by diffusion and electroosmotic flow and negated by migration. In this Section, the effect of current density, anolyte chloride and chlorate concentration, and the anolyte temperature on the extent of transport of these anions into the cathode chamber is examined.

The electroosmotic water velocity,  $v$ , is calculated employing the following equation:

$$v = \frac{1.8 \times 10^4 i W \eta}{F(10^3 d - C_s)} \quad (6)$$

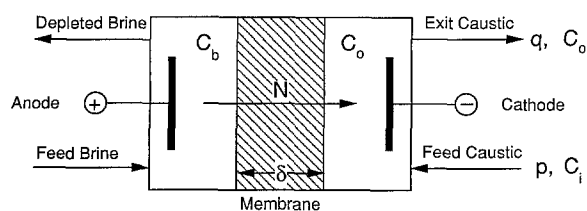


Fig. 1. Schematic of the ion-exchange membrane-cell describing the material balance around the electrolyser.

where  $d$  is the specific gravity of the anolyte ( $\text{g cm}^{-3}$ ) and  $\eta$  is the caustic current efficiency, which can be determined using expressions published previously [8]. The water transport number per sodium ( $W$  in moles of  $\text{H}_2\text{O}$  per mole of  $\text{Na}^+$ ) was estimated from the empirical Equation 7 developed by DuPont [9],

$$W = 11.612 - 5.886 \times 10^{-2} C_s + 1.14 \times 10^{-4} C_s^2 \quad (7)$$

where  $C_s$  is the anolyte salt strength in  $\text{g dm}^{-3}$ .

Equation 7 is based on laboratory data [9] with cells operating at  $3.1 \text{ kA m}^{-2}$  and  $90^\circ\text{C}$  at a catholyte strength of 32%  $\text{NaOH}$  using Nafion<sup>®</sup> 901 membrane. Water transport was nearly constant in these studies performed in the current density range of 1.5 to  $4 \text{ kA m}^{-2}$ . No membrane swelling was observed in the temperature range  $80$  to  $95^\circ\text{C}$ . The water transport characteristics of Nafion<sup>®</sup> 90209 membranes are very similar to that of Nafion<sup>®</sup> 901 series membranes [9]. The water transport number is dependent on the catholyte caustic concentration [10]. However, this dependency was not incorporated in Equation 7, since the caustic strength was fixed at a value of 32%.

The values of the other parameters employed in these calculations are noted in Table 1. The membrane conductivity data employed in the present calculations is that for a carboxylic acid membrane [10, 12], as the overall conductivity of a composite membrane is dictated by the carboxylic layer. Diffusion coefficient data for chloride and chlorate ions across the commercial composite membranes is not available. Hence, an average of the diffusion coefficient data for the chloride ion [13, 14] for carboxylic acid membranes was used in this study, assuming the same temperature dependence as that of membrane conductivity. The diffusion coefficient of the chlorate ion was assumed to be the same as that of the chloride ion because of lack of published data. Variation in

Table 1. Values of parameters used in this study\*

Parameter	Value
Membrane thickness ( $\delta$ )	$1.4 \times 10^{-2} \text{ cm}$
Membrane surface area ( $S$ )	$2.4 \times 10^5 \text{ cm}^2$
Membrane conductivity ( $\kappa$ )	$145.76 \exp(-4000/T) \Omega^{-1} \text{ cm}^{-1}$
Diffusivity of chloride ( $D_{\text{Cl}^-}$ )	$4.27 \times 10^{-3} \exp(-4000/T) \text{ cm}^2 \text{ s}^{-1}$
Diffusivity of chlorate ( $D_{\text{ClO}_3^-}$ )	$4.27 \times 10^{-3} \exp(-4000/T) \text{ cm}^2 \text{ s}^{-1}$
Feed caustic flow rate ( $p$ )	$820 \text{ cm}^3 \text{ s}^{-1}$
Exit caustic flow rate ( $q$ )	$779 \text{ cm}^3 \text{ s}^{-1}$

\* Note that there has been a need to measure these values for each membrane as no such information is presently available in the open literature.

$D_{\text{Cl}^-}$  and  $\kappa$  with anolyte concentration, under the commercial operating conditions, was reported [15] to be weak and hence these dependencies were not considered here.

### 3.1. Effect of current density

3.1.1.  $i \rightarrow 0$  (i.e., during circuit shutdown). From Equation 5, it can be shown that when  $i \rightarrow 0$

$$N = D \left( \frac{C_b - C_o}{\delta} \right) \quad (8)$$

Hence,

$$C_o = \frac{p\delta C_i + DC_b S}{q\delta + DS} \quad (9)$$

Thus, during cell shutdown, the transport of anion is solely governed by diffusion, leading to the maximal influx of anions into the cathode compartment, which can be minimized by lowering the cell operating temperature prior to shutdown, as is evident from Equation 8 via the variations in  $D$  with cell temperature,  $T$ . Significant carry over of anions across the membrane also occurs, during normal operations, in regions where the membrane is inactive (that is  $i \rightarrow 0$ ). Hence it is important that the cells be designed in such a way that the ratio of active membrane area to the peripheral inactive area be high to achieve low anionic impurity content in the caustic product.

3.1.2.  $i \rightarrow$  very high (high current density operation). At high current densities, Equation 5 can be reduced to

$$N = -(u - v)C_o \quad (10)$$

$$C_o = \frac{pC_i}{q + (u - v)S} \quad (11)$$

Hence, at high current densities, the effect of diffusion is maximally negated by the migration and electro-osmotic water flow, resulting in minimal carry over of anions to the catholyte, as shown in Figs 2 and 3. It should be noted that the maximal current density that can be practically employed depends on the cell design and the specifications set by the membrane

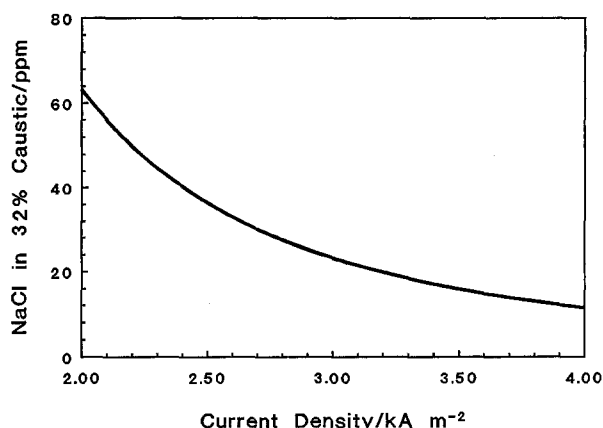


Fig. 2. Effect of current density on the NaCl concentration in the caustic product. Cell operating conditions:  $90^\circ\text{C}$  and  $200 \text{ g dm}^{-3}$  NaCl in anolyte.

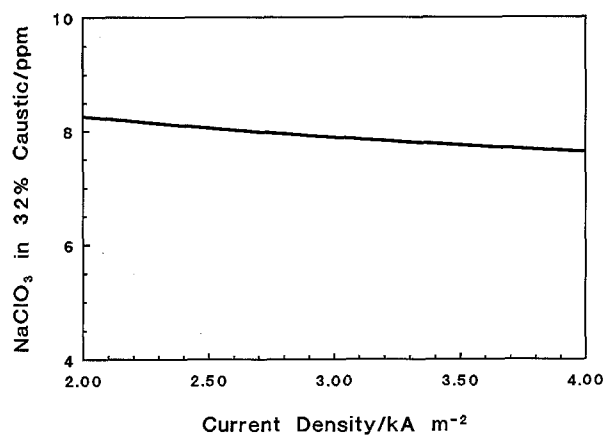


Fig. 3. Effect of current density on the  $\text{NaClO}_3$  level in the caustic product. Cell operating conditions:  $90^\circ\text{C}$  and  $4\text{ g dm}^{-3}$   $\text{NaClO}_3$  in anolyte.

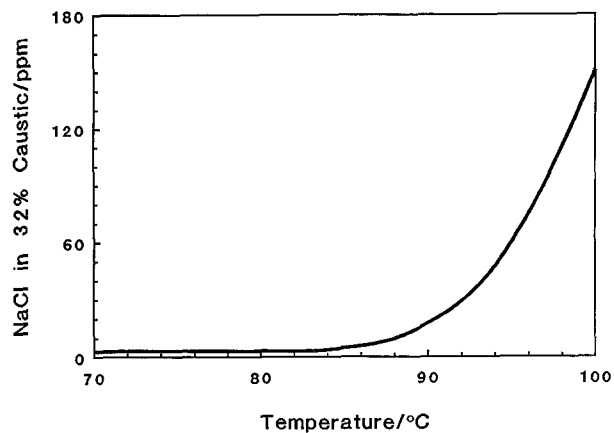


Fig. 6. Effect of temperature on the  $\text{NaCl}$  concentration in the caustic product. Cell operating conditions:  $3.5\text{ kA m}^{-2}$  and  $200\text{ g dm}^{-3}$   $\text{NaCl}$  in anolyte.

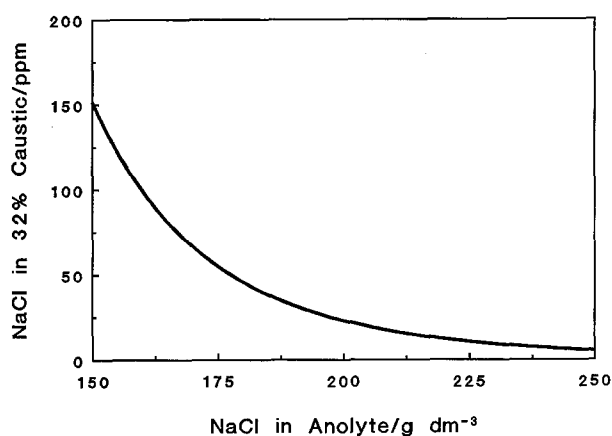


Fig. 4. Effect of anolyte  $\text{NaCl}$  strength on the  $\text{NaCl}$  concentration in the caustic product. Cell operating conditions:  $90^\circ\text{C}$  and  $3.5\text{ kA m}^{-2}$ .

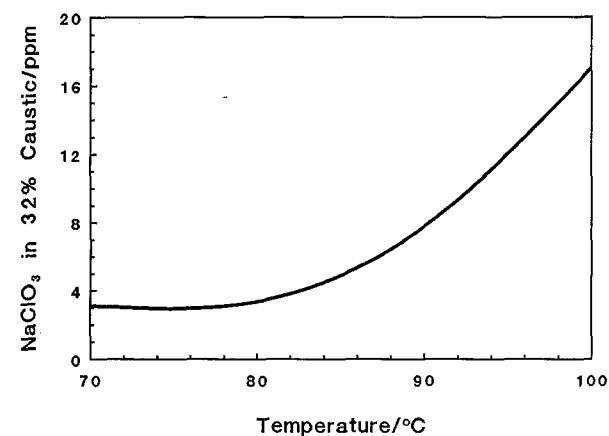


Fig. 7. Effect of temperature on the  $\text{NaClO}_3$  level in the caustic product. Cell operating conditions:  $3.5\text{ kA m}^{-2}$  and  $4\text{ g dm}^{-3}$   $\text{NaClO}_3$  in anolyte.

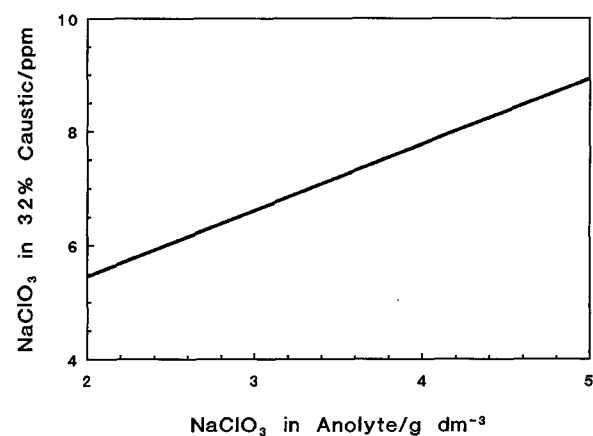


Fig. 5. Effect of anolyte  $\text{NaClO}_3$  concentration on the  $\text{NaClO}_3$  level in the caustic product. Cell operating conditions:  $90^\circ\text{C}$  and  $3.5\text{ kA m}^{-2}$ .

supplier. The trends depicted in Figs 2 and 3 are in general agreement with the published data [9, 11].

### 3.2. Effect of anolyte $\text{Cl}^-$ and $\text{ClO}_3^-$ concentration

As chlorate concentration in the anolyte increases, the diffusion of chlorate ions to the cathode compartment is enhanced, resulting in increased chlorate

concentration in the caustic product. However, a similar pattern does not prevail with chloride ions since the electroosmotic water flow rate decreases as the anolyte salt strength increases, resulting in reduced carry-over of chloride ions into the cathode compartment (Figs 4 and 5). The lack of significant variation of the catholyte  $\text{ClO}_3^-$  level with changes in the anolyte chlorate level is a result of lower chlorate ion concentration in the anolyte, in contrast to the anolyte chloride level which is 70 times higher in molar concentration.

### 3.3. Effect of operating temperature

Increase in temperature lowers the electric field-driven migration rate and increases the diffusion rate. Hence the chloride and chlorate concentrations in the caustic product will increase at elevated temperatures as shown in Figs 6 and 7.

### 3.4. Caustic quality in $\text{NaOH}$ vs $\text{KCl}$ systems

Chloride and chlorate levels in the caustic are expected to be lower during the electrolysis of  $\text{KCl}$  as compared to the  $\text{NaCl}$  system because of the lower

water transport number of 2 to 3 during the KCl electrolysis [9] compared to  $\sim 4$  during NaCl electrolysis. Calculations, using the water transport number only showed the  $\text{Cl}^-$  and  $\text{ClO}_3^-$  levels in the KOH product to be about 2 to 3 ppm, still exhibiting a dependency on current density, temperature and anolyte concentration. This influence should be cautiously interpreted since the  $D_{\text{Cl}^-}$ ,  $D_{\text{ClO}_3^-}$  and  $\kappa$  values used in the calculations are those for the NaCl/NaOH system and not for the KCl/KOH system for which the relevant data are not available.

#### 4. Summary and conclusions

The effect of the cell operating conditions on the ion-exchange membrane cell caustic quality was modelled assuming no pinholes in the membrane and control of the mass transport of ionic species by diffusion, migration and electroosmotic water convection. The theoretical results presented here are in general agreement with laboratory data [9, 11] despite the simplifications adopted. This modelling showed that the caustic product quality from the membrane electrolyser can be adeptly manipulated by adjusting the cell operating conditions. Thus, the chloride content in the caustic can be reduced by (i) increasing the current density, (ii) increasing the anolyte salt strength, and (iii) decreasing the cell operating temperature and the chlorate content in the caustic can be adjusted by (i) increasing the current density, (ii) decreasing the chlorate concentration in anolyte, and (iii) decreasing the cell operating temperature. In addition, the cell operating temperature must be lowered prior to the circuit shutdown, to minimize the diffusion rate of chloride and chlorate ions and hence their levels in the caustic product. Another hitherto neglected important outcome of this study is the influence of the electrolyser design, which

should be configured in such a way that the ratio of active membrane area to the peripheral inactive area be high to achieve low anionic impurity content in the caustic product.

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#### References

- [1] L. C. Curlin, T. V. Bommaraju and C. B. Hansson, 'Kirk-Othmer Encyclopedia of Chemical Technology', Vol. 1, J. Wiley & Sons, New York (1991) p. 938.
- [2] H. S. Burney, 'Modern Aspects of Electrochemistry' (edited by R. E. White, B. E. Conway and J. O'M. Bockris), Plenum Press, New York (1993) p. 393.
- [3] A. G. Guzman-Garcia, P. N. Pintauro, M. W. Verbrugge and R. F. Hill, *AIChE J.* **36** (1990) 1061.
- [4] M. W. Verbrugge and R. F. Hill, *J. Electrochem. Soc.* **137** (1990) 886, 893.
- [5] C. Selvey and H. Reiss, *J. Memb. Sci.* **23** (1985) 11.
- [6] H. Ukihashi, M. Yamahe and H. Miyake, *Prog. Polym. Sci.* **12** (1986) 229.
- [7] A. J. Bard and L. R. Faulkner, 'Electrochemical Methods' J. Wiley & Sons, New York (1980) p. 27.
- [8] C. P. Chen, B. V. Tilak and J. W. Quigley, *J. Appl. Electrochem.* **25** (1995) 95.
- [9] DuPont Technical Bulletin no. 84-3 (1984), no. 88-1 (1989), no. 92-2 (1992).
- [10] J. T. Keating, 'Modern Chlor-Alkali Technology', Vol. 5 (edited by T. C. Wellington), Elsevier Applied Science, London (1992) Chapter. 7, p. 69.
- [11] M. Seko, J. Omura and M. Yoshida, 'Modern Chlor-Alkali Technology', Vol. 3 (edited by K. Wall), Ellis Horwood, Chichester (1986) Chapter 14, p. 178.
- [12] H. Miyake, Y. Sugaya and M. Yamabe, *Reports Res. Lab. Asahi Glass Co., Ltd* **37** (1987) 241.
- [13] A. Herrera and H. L. Yeager, *J. Electrochem. Soc.* **134** (1987) 2446.
- [14] H. Ukihashi, M. Yamabe and H. Miyake, *Prog. Polym. Sci.* **12** (1986) 229.
- [15] J. T. Keating, personal communication (1995).