Utility of an Empirical Method of Modeling Combined Zero Gap/Attached Electrode Membrane Chlor-Alkali Cells

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ABSTRACT
An extensive survey of the Doktor-Ingenieur Dissertationen of Jakob Jörissen and Klaus-R. Menschig, both originally from the Universität Dortmund, is presented in regard to the empirical modeling of membrane chlor-alkali cells and how it can be applied to a combined zero gap/attached porous electrode layer membrane cell. Particular emphasis is placed on Menschig’s work on zero gap (ZG) and attached porous electrode layer (APEL) membrane chlor-alkali cells, the first such research to appear in the open literature. Menschig developed various computer programs to characterize these ZG and APEL membrane chlor-alkali cells. He characterized these cells by using the following parameters: the current density distribution over the membrane, the species concentrations on the membrane surfaces, and the potential of the membrane electrodes. With prior knowledge of total cell potential and current efficiency for corresponding APEL membrane chlor-alkali cells, Menschig calculated values for the characterizing parameters mentioned above. He used these values and other information (e.g., membrane and porous electrode layer conductivity) to predict the total cell potential for the ZG configuration. With prior knowledge of total cell potential and current efficiency for corresponding APEL and ZG cell configurations, membrane surface concentrations were derived and used in the prediction of total cell potential for a combined zero gap/attached electrode cell.

Background
Electrolysis cells which contain ion selective membranes are constructed in three primary configurations: the gap cell, the zero gap cell, and so-called solid polymer electrolyte (SPE) cell. Figure 1 shows a gap cell version of a chlor-alkali membrane cell (as in Ref. [1]), which has a space (i.e., a gap) filled with electrolyte between the membrane surface and each electrode. Figure 2 shows a schematic of just the electrode-membrane construction of a zero gap (ZG) cell, where both electrode surfaces have been placed directly against the membrane. The electrodes of a zero gap cell are made of expanded metal or wire mesh (which may have a catalytic layer applied to its surface) backed by a expanded metal current collector that enables the gas bubbles to escape from the electrode surface. Figure 3 illustrates what is referred to by some authors in the literature as a SPE electrode construction which is actually two porous catalyzed electrode layers which have been attached to the surface of the membrane itself (this will be called an attached porous electrode layer, or APEL, cell). Pressed against each porous electrode layer is a fine grid mesh backed by a resilient mat of fine wire which is pressed in by a perforated plate current collector. This provides a path for even current distribution across the surface of the entire electrode. Both the ZG and APEL type cells have the immediate advantage of reducing the potential drop across the cell over that found in a gap cell since the distance between opposing electrodes is reduced significantly.

Various methods and models have been developed to evaluate ion exchange membrane behavior and to relate this behavior to the design of membrane chlor-alkali cells. One approach has been to use empirical relations derived from experimental data to describe various characteristics of a membrane cell (2, 3), such as the correlation of caustic current efficiency (that percentage of the applied cell current that goes to the actual production of sodium hydroxide at the cathode) or the loss of OH (from the catholyte through the membrane to the anolyte) to the concentration of sodium hydroxide in the catholyte at the membrane surface (C(NaOH)). These relations are then used in conjunction with additional experimental data to predict such things as the outlet concentrations of a cascade arrangement of electrolytic gap cells (2) or the concentrations on the membrane surface (3).

This paper presents the essence of the empirical approach to membrane cell modeling as done by Jörissen (2) and Menschig (3) and how these methods can be used to evaluate the chlor-alkali cells currently being developed. Jörissen’s primary objective was to develop a computer model which could be used as a basis for economic evaluation and process optimization of a chlor-alkali electrolyzer with cascade connection of membrane cells. Menschig’s goals were to determine experimentally any differences between APEL and ZG cells with respect to the cell voltage and current efficiencies to characterize empirically these cells, and to develop criteria for the selection of a practical electrolyzer for chlor-alkali production. Menschig predicted from his results that a combined porous anode layer (PAL) and zero gap cathode (ZGC) cell (together referred to as a PAL/ZGC cell) had the potential of saving the most energy (3). It is important to note that this proposed configuration was based on earlier, less efficient membrane which allowed excessive loss of OH from the catholyte to the anolyte.

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From his experimentally derived species concentrations on the membrane surface of the ZG and APEL cells, Menschig predicted a current efficiency of only 74.2% based on caustic production for his hypothetical PAL/ZGC cell. Newer bilayer membranes made with perfluorocarboxylic acid functional groups in the layer toward the cathode and perfluorosulfonic acid functional groups toward the anode have greatly reduced the problem of the loss of OH⁻, yielding caustic current efficiencies up to 94% in gap cells (4, 5). These newer membranes could make it possible to use attached porous cathode and/or anode layers. This led to an interest in the combination of zero gap and attached porous electrode layers, either as anode/cathode or cathode/anode combinations, respectively. These will be referred to as the zero gap anode/attached porous cathode layer (ZGA/PCL) or attached porous anode layer/zero gap cathode (PAL/ZGC) configurations. Since Menschig uses many of the relations for gap membrane cell behavior (as derived by Jörisen’s, and later Menschig’s, symbols have been changed to a single consistent set for clarity). The derived expression for the transport of OH⁻ from the catholyte through the membrane to the anolyte (typically called back-migrating OH⁻) is [p. 55 of Ref. (2)]

\[
N_{\text{OH}^-} = 5.42 + 4.44c_{\text{NaOH}} + 0.125c_{\text{H}^+}c_{\text{NaOH}}
\]

\[(0 < c_{\text{NaOH}} < 18)\]  

where \(N_{\text{OH}^-} = \text{OH}^-\) flux through the membrane (mol/h·m²) and \(c_{\text{NaOH}} = \text{bulk NaOH concentration in the catholyte (mol/l)}\). Note Eq. (1) applies only to Nafton 355 at 3000 A/m² and 80°C. Anolyte by-product models include such things as the formation of active chlorine (as hypochlorite) given as [p. 77, 78 of Ref. (2)]

\[
c_{\text{HClO}} = 1.000000 + 0.000407c_{\text{NaOH}} - 0.000449c_{\text{H}^+}\]  

\[(0 < c_{\text{NaOH}} < 12)\]  

where \(c_{\text{HClO}} = \text{HClO concentration in the anolyte (mol/l)}\).

**Jörisen’s Work**

As mentioned previously, Jörisen was interested primarily in developing empirical relations to describe a gap membrane chlor-alkali electrolysis cell in order to construct a material balance program which describes the performance of a cascade of gap cells in various connections, such as concurrent or countercurrent flows of anolyte and catholyte (2). He derived specifically empirical relations from experimental data to describe the chloride and caustic current efficiencies, by-product formation (the accumulation of which is a problem of the cascade arrangement of cells), water transport through the membrane, and the cell potential.

**Development.**—In Jörisen’s experimental work, he used a Nafton™ 355® membrane, which is a bilayer perfluorosulfonic acid membrane with the following construction: 1.5 mil (0.04 mm) 1500 equivalent weight layer (cathode side), 4.0 mil (0.1 mm) 1100 equivalent weight layer, and T-25: Teflon™ scrim with 70% free membrane surface.

All of his experiments were carried out at steady-state conditions, allowing a minimum of 4h to reach that condition and then data were collected over another 4h period. Figure 4 shows a diagram of his experimental apparatus. The inner diameter of the cell was 52 mm, the length of each half-cell was 40 mm (i.e., an electrode to electrode gap of 80 mm), the membrane surface area was 21.2 cm², and the cell volume including the overflow connections were 90 ml for each chamber (2). The anode was a titanium plate coated with mixed ruthenium oxide and the cathode was a plate of V4A steel. Each half-cell was mixed using a magnetic stirrer. The cell was operated at 3000 A/m² and 80°C. Anode, cathode, and membrane potentials were measured using movable Luggin capillaries. The deliberately large interelectrode distance allowed the separation of the cell potential into its individual components (2).

In his analysis, Jörisen used a factorial experimental design to obtain the information needed to formulate empirical models to describe cell behavior based on the assumption that each half-cell was well mixed. This assumption means that there is no effective boundary layer on the membrane surface and therefore the empirical relations describing the membrane can be based on the bulk concentrations of the chemical species. He used regression analysis to determine which effects were significant, while ignoring interactions among more than two parameters. Statistical methods were used to determine the best models, retaining only the effects of the highest significance. Several of the model equations produced did not have a theoretical basis for the relationship obtained by the statistical evaluation (2) (i.e., a standard form, such as a linear or quadratic model, was used rather than a complex relationship derived from theory).

The derived expression for the transport of OH⁻ from the catholyte through the membrane to the anolyte (typically called back-migrating OH⁻) is [p. 55 of Ref. (2)]

\[
N_{\text{OH}^-} = 5.42 + 4.44c_{\text{NaOH}} + 0.125c_{\text{H}^+}c_{\text{NaOH}}
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\[(0 < c_{\text{NaOH}} < 18)\]  

where \(N_{\text{OH}^-} = \text{OH}^-\) flux through the membrane (mol/h·m²) and \(c_{\text{NaOH}} = \text{bulk NaOH concentration in the catholyte (mol/l)}\). Note Eq. (1) applies only to Nafton 355 at 3000 A/m² and 80°C. Anolyte by-product models include such things as the formation of active chlorine (as hypochlorite) given as [p. 65, 66 of Ref. (2)]

\[
c_{\text{HClO}} = 1.000000 + 0.000407c_{\text{NaOH}} - 0.000449c_{\text{H}^+}\]  

\[(0 < c_{\text{NaOH}} < 12)\]  

where \(c_{\text{HClO}} = \text{HClO concentration in the anolyte (mol/l)}\).
or
\[
c_{A} \text{net Cl}_2 = -c_{A} \text{ex H}^+ + (0.00705 - 0.000449 c_{A} \text{Na}) 
\exp (30.3 c_{\text{ex}} \text{H}^+) \quad \text{(for } c_{A} \text{Na} \text{H}^+ < 0) \quad [3]
\]

where \(c_{A} \text{net Cl}_2\) = active chlorine concentration in anolyte (mol/l), \(c_{A} \text{ex H}^+\) = \(H^+\) ion excess in anolyte (mol/l) (OH\(^-\) ion excess is expressed as a negative value of \(c_{A} \text{ex} \text{H}^+)\), and \(c_{A} \text{Na}\) = total concentration of dissolved material in anolyte (mol/l) NaCl + NaClO, HCl + HOCl + Cl\(_2\)(aq)) (calculated from the sum of analyzed values for NaCl + NaClO, HCl + NaOH + Cl\(_2\)(aq)). Additional empirical relations are given for oxygen and chlorate (ClO\(_3^-\)) formation under acidic or alkaline conditions of the anolyte.

Jørgensen also gives relations that fit the water transport through and the potential drop across the membrane. His statistical analysis showed that the water transport was affected significantly by only the Na\(^+\) ion transport across the membrane and the dissolved species concentration in the anolyte. The greatest problem with this approach is that the membrane properties do not influence the net water transport when the maximum water transport has not been attained. That is, when the concentration of Na\(^+\) ions during migration from anode to cathode chamber (mol H\(_2\)O/mol Na\(^+\)), \(h\) = average hydration number for Na\(^+\) ion transport through the membrane (mol Na\(^+\)/h\(^-\)m\(^2\)), \(N_{\text{net}}\text{H}_2\text{O} = \text{net water transport (mol H}_2\text{O/h-m}^2\) (net water transport + water for back-migrating \(\text{OH}^-\) ions).\n
Present Application.—The remainder of Jørgensen’s work deals with his model of systems of cascade cells with various flow configurations using the previously mentioned empirical relations. He hypothesizes that, in their qualitative form, his empirical relations are not dependent on the type of membrane or cell construction (2). If this were true, then the forms of his equations could be applied to available data for zero gap (ZG), and Jørgensen hypothesizes that, in the membrane is high, complete hydration shells cannot be formed, reducing the average hydration number, and therefore the water transport across the membrane is below its maximum (2). His equation for the membrane potential drop is (p. 115 of Ref. (2))

\[
\Delta U_{\text{mem}} = 0.06668 + 0.02555 \cdot c_{\text{NaOH}} \cdot c_{\text{AT}}\]

where \(\Delta U_{\text{mem}}\) = potential drop in and on the membrane under uniform current density (V). He also developed expressions for the electrode overpotential, equilibrium potential, and IR drop in each electrolyte layer.

Development

Figure 5 shows the construction of Menschig’s experimental apparatus. The membrane used was Nafion 390, which is similar to the membrane used by Jørgensen, having the same layers, but a different construction of the sacrum (total thickness was 0.33 mm, determined by micrometer). Two different mesh sizes were used for the ZG and APEL cells. For the APEL cells, corresponding ZG cell meshes were used as intermediate current distributors by being pressed against the porous electrode layers attached to the membrane. All meshes were made of a platinum-10% iridium alloy. Mesh I had a wire diameter of 0.12 mm and 225 openings/cm\(^2\) (open width between wires: 0.55 mm), while Mesh II had a wire diameter of 0.25 mm and 100 openings/cm\(^2\) (open width between wires: 0.75 mm). The two mesh types used are shown in Fig. 6. Both cell configurations used machined metal backing plates (3 mm thick, 70% open) as current collectors which were connected to the terminal leads. The porous electrode layers for the APEL cells were
formed by electroplating platinum onto the membrane surface (6) and were assumed to have an effective surface area of 100 cm$^2$/cm$^2$ of membrane surface (3, 6). (Note the actual surface area of the porous electrode layer was not measured.)

The cells were operated at steady state with the following experimental conditions being maintained: cell temperature, 80°C; superficial current density, 6500 A/m$^2$; anolyte NaCl concentration, 17.5 weight percent (w/o) (3.28 mol/l); OH$^-$ excess in anode chamber, 0.375 (w/o); catholyte NaOH concentration, 20.0 w/o (5.92 mol/l); anode pressure against the membrane, 0.69 bar. The inlet brine feed was a saturated salt solution with concentrations of Ca$^{2+}$ and Mg$^{2+}$ reduced below 0.5 ppm. In order to maintain the OH$^-$ concentration in the anolyte at a constant value, 20 w/o HCl was added by a separate stream at the rate of 40.57 and 24.41 mol/h-m$^2$ for the APEL and ZG configurations, respectively. Measurements were taken continuously over a 3h period after steady state had been reached.

Three computer programs were used to analyze the experimental data in order to obtain values for the characterizing parameters mentioned above. The first program (6MODZ and its subprograms) is used to calculate the current density distribution over the membrane attached to a porous catalytic electrode layer. The second program (ME-NETZP) can be used to calculate a correction factor (what is called $f_{MZ}$ in this paper) for determining the potential drop across the membrane in the ZG cell (see Fig. 8). Menschig also determined equivalent boundary layer thicknesses to represent the porous electrode layers and the mesh electrodes, producing two boundary layers for the ZG cell (one on each side of the membrane) and four for the APEL cell (see Fig. 6). He assumed that the boundary layer representing the mesh against the porous layer of the APEL cell would be the same thickness as that for the same mesh type in the ZG cell configuration. The details of how he derived these boundary layer thicknesses are given under the description of program ME-MODY below.

**Menschig's Programs**

Current density/potential distribution for an APEL cell.—To determine the degree of the nonuniform potential and current distributions over the membrane surface in ZG and APEL cell configurations, Menschig first formulated a mathematical model to calculate the potential and current distributions over a membrane using an equivalent resistance network to simulate the resistances of the mesh wires, porous electrode layer, and membrane (see Fig. 8). He found many difficulties in trying to solve the three-dimensional problem for the ZG configuration and ultimately used a different two-dimensional approach (3, 6). Therefore, program 6MODZ applies only to the APEL configuration. The original program was written using a form of BASIC used by the Hewlett Packard 2000 computer. The program has now been rewritten in FORTRAN 77 for greater portability. The input data consists of membrane conductivity data at the outlet stream conditions, conductivity data for the catalyzed porous electrode layers, wire conductivity data, wire diameter, open width between wires in mesh, and applied mean current density (i.e., current density based on the superficial membrane surface area). Menschig used a specific resistance for platinum at 80°C of 1.18 · 10$^{-4}$ Ω-cm and an assumed value of 20 Ω/cm$^2$ for his porous platinum layer (3).

The program produces the potential and current on the membrane surface at each node point in a 2x mathematical grid plane (parallel to the membrane) which is superimposed on one mesh square (i.e., that square produced by four wires) (see Fig. 9). This is accomplished by using Ohm's law and Kirchhoff's law, with an iterative procedure, while satisfying the defined mean current density and the assumption of uniform potential distribution across the wire mesh and back side of the porous electrode layer. The mathematical grid in the BASIC version is limited to five sections (six nodes) along one side of the mesh square for a total of 36 nodes. The FORTRAN version can use up to nine sections (100 nodes), giving faster convergence and increased accuracy. An example of the input and results from the FORTRAN version of the program is given in Table 1.

Menschig concluded from his calculations that for open wire mesh widths (i.e., open distance between two parallel wires in the mesh) of 3 mm or less, the potential and current density distribution across the APEL cell membrane is essentially uniform. Since all his experi-
mental APEL cells used meshes finer than this, he assumed that the potential and current density distributions across the membrane of his APEL cells were uniform, with current paths traveling straight through the membrane.

Potential correction factor for ZG cell.—Since Menschig could not solve the three-dimensional representation of the ZG cell configuration, he developed a two-dimensional model of parallel wires on opposite sides of the membrane (i.e., he ignored the “cross” wires in the mesh on either side of the membrane). He then formulated an equation to describe the potential drop between two facing wires and extended this to include the interaction of adjacent wires on both sides of the membrane. This results in an analytical solution for the potential drop across the membrane for a ZG configuration, which is (p. 73 of Ref. (3)).

Table I. Example of the current density/potential distribution for an APEL cell

<table>
<thead>
<tr>
<th>Node</th>
<th>Driving voltage (V)</th>
<th>Current through the membrane (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6804725E + 00</td>
<td>0.4944862E - 04</td>
</tr>
<tr>
<td>2</td>
<td>0.6804726E + 00</td>
<td>0.4944862E - 04</td>
</tr>
<tr>
<td>3</td>
<td>0.6804726E + 00</td>
<td>0.4944862E - 04</td>
</tr>
<tr>
<td>4</td>
<td>0.6804726E + 00</td>
<td>0.4944862E - 04</td>
</tr>
<tr>
<td>5</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
<tr>
<td>6</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
<tr>
<td>7</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
<tr>
<td>8</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
<tr>
<td>9</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
</tbody>
</table>

Where \( \Delta U_{\text{ZG}} = \text{potential drop across a ZG membrane for a mesh of configuration } j \) \( (V) \), \( i_p \) = mean current density \( (A/m^2) \), \( L_i \) = mesh width (center to center distance between two parallel wires) \( (m) \), \( ln(K0) \) = geometric factor calculated by program ME-NETZP, and \( \kappa \) = specific membrane conductivity \( (1/\Omega \cdot m) \). When Menschig assumed a uniform potential distribution across the membrane, he used Ohm’s law to obtain his Eq. [G1.15] (p. 50 of Ref. (3)), which is

\[
\Delta U_{\text{ZGCD}} = \frac{b i_p}{\kappa}
\]

which shows that the factor \( f_{MZj} \) can be calculated primarily from physical dimensions and geometric factors.

In order to obtain the value of \( \ln(K0) \) from the program ME-NETZP, the following information is required: membrane thickness, wire conductivity, wire diameter, mesh width \( (L_i) \), relative position of wires on opposite sides of membrane, either center-to-center or offset, and number of parallel wires across the entire electrode face. The program is written in IBM PC compatible BASIC and an example of the prompted program input and result is given in Table II. The number of wires across the electrode is necessary to determine the effect of interaction. Menschig found that there was little change in the value of \( \ln(K0) \) calculated when the number of wires was 100 or more (6).

Thus, the potential drop across the membrane of a ZG cell can be predicted by using Eq. [9] or an empirical correlation for \( \Delta U_{\text{ZGCD}} \) and the correction factor \( f_{MZj} \). Menschig used the latter approach and compared it to his experimentally derived value and found close agreement, thereby indicating that the ZG wire model presented above can be used to produce reasonable results. Using Eq. [10] with the correction factor for his Mesh I and II gives (p. 73 of Ref. (3))

\[
\Delta U_{\text{ZGCD}} = 0.67 \cdot \Delta U_{\text{ZG}}
\]

and

\[
\Delta U_{\text{ZGCD}} = 0.6 \cdot \Delta U_{\text{ZG}}
\]

which shows that the ohmic potential drop of an APEL cell is lower than for a ZG cell using the same mesh, current density, and specific membrane conductivity (e.g., for Mesh I, the membrane potential drop for the APEL cell is 67% of the equivalent ZG cell as shown in Eq. [12]). Also, the potential drop of a ZG membrane increases with increasing mesh spacing (recall that Mesh II has a larger spacing than Mesh I) (3).

Table II. Example of the determination of the correction factor for the membrane potential of a ZG cell

<table>
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<td>0.4944862E - 04</td>
</tr>
<tr>
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<tr>
<td>9</td>
<td>0.6804730E + 00</td>
<td>0.4944863E - 04</td>
</tr>
</tbody>
</table>

Membrane area of mesh square [mm²]: 0.4356000E + 00
Area per node square [mm²]: 0.1210000E - 01
Membrane resistance per node square [Ω]: 1.682314E + 05
Total current through membrane [A]: 0.1456148E - 02
Total current density [A/m²]: 3343.

The following is a simulated run of the program ME-NETZP using the data for Mesh I (with wires center to center on opposite sides of the membrane).

Input for Mesh type I:
Wire diameter in [mm]: 0.12
Gap between wires in [mm]: 0.55
Are nets offset on either side of membrane (Y/N)? n
How many wires across entire electrode (use min 100): 100
Result:
The factor \( \ln(K0) \) is 5.490924.
Characterizing parameters for ZG and APEL cells.—Program development.—Menschig developed the ME-MODV program to analyze his experimental data to determine species concentrations on the membrane surfaces, membrane potential, effective boundary layer thicknesses, and electrode overpotentials and open-circuit potentials based on these surface concentrations. He used the empirical equations developed by Jørgensen to describe the behavior of his membrane, that is, Eq. [1] for the OH− flux through the membrane and Eq. [7] for the membrane potential. Menschig applied a scaling factor to these relations, because Jørgensen used a current density of 3000 A/m² while he used 6500 A/m². Akin (7) found that the caustic current efficiency of Nafion 300 was independent of the current density in the range of 2 ka/m² to 6.5 ka/m², so the flux of OH− across the membrane changes (at least approximately) in proportion to the current density (3), giving [p. 45, of Ref. (3)]

\[ \Delta U_{\text{ZG}}(i) = \frac{i_2}{i_1} \cdot \Delta U_{\text{ZG}}(i_1) \]  

where \( i_1 \) = current density for Eq. [1] (3000 A/m²) and \( i_2 \) = new mean current density (A/m²). Menschig also assumed that his membrane had constant electrical resistance over the range of current density used in his and Jørgensen’s work, so that the membrane potential drop is also scaled as [p. 45 of Ref. (3)]

\[ \eta_{\text{ZG}} = \frac{i_1 + 1000}{45,200} \]  

Equilibrium potentials were calculated using activity coefficients based on local concentrations with only the Cl− discharge reaction considered at the anode. The anode overpotential was calculated from the regression equation (8) [p. 48 of Ref. (3)]

\[ \eta_a = \frac{-\ln (i_1) + 5.34}{8.16} + 0.11 \]

for 80°C, 25 w/o NaCl and the cathode (hydrogen) overpotential was calculated from the regression equation

\[ \eta_c = \frac{-\ln (i_1)}{5.34} + 0.11 \]

where \( \eta_a \) is the anode current density based on the actual electrode surface area (A/m²), obtained using the data presented by Vetter (9).

Menschig obtained the diffusion layer thicknesses from Vogt’s mass transport model (10) for smooth gas-evolving electrodes. Vogt gives the following equation for the diffusion layer thickness (3) [p. 48 of Ref. (3)]

\[ Sh = f_v \cdot 0.925 \cdot Re^{0.3} \cdot Sc^{0.47} \]

where \( f_v \) had a value of 0.3785 [which is 1/FVOGT, the factor which is given by the program ME-MODV (3, 6)]. Menschig assumed that the correction factor was the same for both the anode and cathode sides (for the same mesh type).

An alternate method for determining the diffusion layer thicknesses representing the electrodes can be obtained using the bulk and surface concentrations in the kinetic expressions given by Vetter (9). Under 100% chloride and caustic current efficiencies (8), the anode diffusion layer thickness, \( \delta_a \), formed during the electrochemical reaction due to transport to the anode is approximated by [p. 48 of Ref. (3)]

\[ \delta_a = 2zFD_{\text{Cl}^-} \left( \text{C}_{\text{Cl}^-} - \text{C}_{\text{Cl}^-(s)} \right) i \]

while the diffusion layer thickness for the cathode, \( \delta_c \), is approximated by

\[ \delta_c = zFD_{\text{OH}^-} \left( \text{C}_{\text{OH}^-} - \text{C}_{\text{OH}^-(s)} \right) i \]

where \( \delta_a \) is anode diffusion layer thickness (m), \( \delta_c \) is cathode diffusion layer thickness (m), \( z \) is number of electrons used in the electrode reaction, \( F \) = Faraday constant (96,487 Ås/mol), \( D_{\text{Cl}^-} \) is diffusion coefficient of Cl− (m²/s), \( D_{\text{OH}^-} \) is diffusion coefficient of OH− ions (m²/s), \( c_{\text{Cl}^-} \) is concentration of Cl− at anode (mol/m³), \( c_{\text{OH}^-} \) is concentration of Cl− in bulk anolyte (mol/m³), \( c_{\text{Cl}^-(s)} \) is concentration of Cl− in bulk catholyte (mol/m³), and \( i \) is current density (A/m²). Menschig actually uses Eq. [20] and [21] to solve for the concentrations at the electrode/membrane interface using the diffusion layer thicknesses obtained from Eq. [18] and [19].

Procedure used by program ME-MODV.—In order to determine the characterizing parameters, such as the species concentrations on the membrane surfaces, equivalent diffusion layer thicknesses for the mesh electrodes/current collectors and porous electrode layers, and the electrode overpotentials and equilibrium potentials using the surface concentrations, the program ME-MODV requires appropriate current density, caustic current efficiency, OH− flux through membrane from catholyte to anolyte (derived from the above factors), chloride current efficiency, bulk outlet concentrations, membrane surface area, actual surface area of electrode mesh per unit surface area of membrane, attached porous electrode layer surface area per unit surface area of membrane, and total experimental cell potential, in addition to the two empirical relations of Jørgensen (Eq. [1] and [7] in this paper). The program first solves for the diffusion layer thicknesses according to Eq. [18], then determines the characterizing parameters for the APEL configuration, followed by the determination of those parameters for the ZG configuration.

The calculations for the APEL configuration are begun with the determination of the membrane surface concentration of NaOH on the cathode side, \( c_{\text{NaOH}} \), by solving for \( c_{\text{NaOH}} \) in Eq. [1] in conjunction with Eq. [14]. Note that \( c_{\text{NaOH}} \) is the NaOH concentration on the membrane surface since Eq. [1] was based on the assumption that no diffusion layer existed in the experimental configuration used to obtain the empirical relation. Next the caustic current efficiency, OH− flux through membrane from catholyte to anolyte (derived from the above factors), chloride current efficiency, bulk outlet concentrations, membrane surface area, actual surface area of electrode mesh per unit surface area of membrane, attached porous electrode layer surface area per unit surface area of membrane, and total experimental cell potential, in addition to the two empirical relations of Jørgensen (Eq. [1] and [7] in this paper). The program first solves for the diffusion layer thicknesses according to Eq. [18], then determines the characterizing parameters for the APEL configuration, followed by the determination of those parameters for the ZG configuration.

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potential drop for the APEL cell ($\Delta U_{\text{MC}}$) is determined. Using this value with Eq. [7], modified by Eq. [15], the concentration of NaCl on the membrane surface, $c_{\text{AM:NaCl}}$, is obtained. An iterative procedure is now used to recalculate the equilibrium and overpotentials and $c_{\text{AM:NaCl}}$ until a converged answer is obtained.

Next, the program solves for the characterizing parameters for the ZG configuration, solving for $c_{\text{AM:NaOH}}$ by again using Eq. [1] in conjunction with Eq. [14]. Then an average of the bulk and membrane surface concentration of NaOH is used to determine the physical properties of the electrolyte surrounding the zero gap electrode. These properties are used to calculate the diffusion layer thickness representing the zero gap cathode by Eq. [21], using a value for $i$ obtained by correcting the mean current density by the caustic current efficiency. From this value ($\delta_{\text{ZGc}}$) and the diffusion layer thickness for a flat plate cathode ($\delta_{\text{Plc}}$) obtained from Eq. [18], the correction factor, $f_v$, is obtained from

$$f_v = \frac{\delta_{\text{Plc}}}{\delta_{\text{ZGc}}}$$

and used in Eq. [19] to calculate the diffusion layer thickness related to the zero gap anode ($\delta_{\text{ZGa}}$). (Note the program uses the factors called FVOGT, which is the inverse of $f_v$.) Next, $c_{\text{AM:NaCl}}$ is calculated iteratively using Eq. [20], starting with an initial guess which is averaged with the bulk concentration of NaCl ($c_{\text{AM:NaCl}}$) to determine the physical properties at the zero gap anode. Finally, the zero gap cathode equilibrium and overpotentials are calculated using the concentrations obtained above.

Also, Menschig calculates the membrane potential drop by two methods, one using the correction factor $f_M$, obtained experimentally with those from Eq. [11]. For Mesh I (225 openings/em$^2$), the experimentally derived value was 0.73 and the model value was 0.67, and for Mesh II (100 openings/cm$^2$), the values were 0.63 and 0.60, respectively. Finally, Menschig concluded that there was a significant difference in the behavior of ZG and APEL cells, as described by his characterizing parameters.

**Present application.**—The primary value of Menschig’s work is in the determination of various conditions which exist in a ZG or APEL cell. It has the limited ability of predicting the total cell potential for a ZG configuration, though Menschig never intended it that way (6). Menschig completed his work with a calculation of the total cell potential for a PAL/ZGC cell configuration obtained by taking the corresponding concentrations on the membrane surfaces from Fig. 10 and 11 (i.e., $c_{\text{AM:NaCl}}$ from the APEL cell of Fig. 11 and $c_{\text{AM:NaOH}}$ from the ZG cell of Fig. 10) and using these values in Eq. [7] as modified by Eq. [15] to obtain $\Delta U_{\text{MC}}$, the membrane potential drop assuming uniform current distribution, or for an APEL cell, at these concentrations. Using this

These two values are used to test the reliability of Menschig’s method of modeling the potential distribution of a zero gap mesh.

**Results of ME-MODV program.**—Table III shows Menschig’s input data and results for his average configuration. The concentrations on the membrane surfaces and diffusion layer thicknesses are shown in Fig. 10 and 11 for the ZG and APEL configurations, respectively. Note that the concentration of NaOH on the membrane surface is nearly twice as high for the APEL cell as compared to the ZG cell (12.32 vs. 6.46 mol/l). Menschig also found that his model of the zero gap mesh potential distribution was reasonable by comparing the values for the correction factor $f_M$ observed experimentally with those from Eq. [11]. For Mesh I (225 openings/cm$^2$), the experimentally derived value was 0.73 and the model value was 0.67, and for Mesh II (100 openings/cm$^2$), the values were 0.63 and 0.60, respectively. Finally, Menschig concluded that there was a significant difference in the behavior of ZG and APEL cells, as described by his characterizing parameters.

| Table III. Example of the characterizing parameters for an APEL and a ZG cell |
|-----------------|-----------------|-----------------|
| **Parameter**   | **Value**       | **Value**       |
| Ref. | 17.5 w/o (3.261 mol/l) | 17.5 w/o (3.261 mol/l) |
| NaOH: 20.0 w/o (5.92 mol/l) | NaOH: 20.0 w/o (5.92 mol/l) |
| Total current: 18.38 A | Total current: 18.38 A |
| Mean current density: 6500 A/m$^2$ | Mean current density: 6500 A/m$^2$ |
| Chlorine current efficiency: 0.837 | Chlorine current efficiency: 0.837 |
| Relative area of Mesh I: 1.13 | Relative area of Mesh I: 1.13 |
| Relative area of Mesh II: 1.5708 | Relative area of Mesh II: 1.5708 |
| Back migrating OH$^-$ for APEL cell: 0.252 mol/h | Back migrating OH$^-$ for APEL cell: 0.252 mol/h |
| Experimental total APEL cell potential: 3.94 V | Experimental total APEL cell potential: 3.94 V |
| True surface area of porous electrode per unit membrane area: 100 cm$^2$/cm$^2$ | True surface area of porous electrode per unit membrane area: 100 cm$^2$/cm$^2$ |
| Back migrating OH$^-$ for ZG cell: 0.1769 mol/h | Back migrating OH$^-$ for ZG cell: 0.1769 mol/h |
| True surface area of Mesh I per unit membrane area: 1.131 cm$^2$/cm$^2$ | True surface area of Mesh I per unit membrane area: 1.131 cm$^2$/cm$^2$ |
| True surface area of Mesh II per unit membrane area: 1.5708 cm$^2$/cm$^2$ | True surface area of Mesh II per unit membrane area: 1.5708 cm$^2$/cm$^2$ |
| Experimental total ZG cell potential, Mesh I: 4.22 V | Experimental total ZG cell potential, Mesh I: 4.22 V |
| Experimental total ZG cell potential, Mesh II: 4.41 V | Experimental total ZG cell potential, Mesh II: 4.41 V |

The results are as follows:

**Results for APEL (SPE) cell configuration:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta U_{\text{MC}}$</td>
<td>1.602475 V</td>
</tr>
<tr>
<td>$C_{\text{AM:NaCl}}$</td>
<td>2.142384 mol/l</td>
</tr>
<tr>
<td>$C_{\text{AM:NaOH}}$</td>
<td>12.31547 mol/l</td>
</tr>
<tr>
<td>$\xi_C$</td>
<td>1.354362 V</td>
</tr>
<tr>
<td>$\xi_C$</td>
<td>$-0.983162$ V</td>
</tr>
<tr>
<td>$\eta_C$</td>
<td>0 V</td>
</tr>
<tr>
<td>$\eta_C$</td>
<td>0 V</td>
</tr>
</tbody>
</table>

**Results for ZG cell configuration:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta U_{\text{MC}}$</td>
<td>1.1725 V</td>
</tr>
<tr>
<td>$C_{\text{AM:NaCl}}$</td>
<td>1.68135 V</td>
</tr>
<tr>
<td>$C_{\text{AM:NaOH}}$</td>
<td>2.86934 V</td>
</tr>
<tr>
<td>$\xi_C$</td>
<td>1.346338 V</td>
</tr>
<tr>
<td>$\xi_C$</td>
<td>$-0.923503$ V</td>
</tr>
<tr>
<td>$\eta_C$</td>
<td>0.3932727 V</td>
</tr>
<tr>
<td>$\eta_C$</td>
<td>$0.48351$ V</td>
</tr>
</tbody>
</table>

**Diffusion layer thicknesses:**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_i$</td>
<td>0.00138 cm</td>
</tr>
<tr>
<td>$b_i$</td>
<td>0.00385 cm</td>
</tr>
<tr>
<td>$b_i$</td>
<td>0.00138 cm</td>
</tr>
<tr>
<td>$b_i$</td>
<td>0.00385 cm</td>
</tr>
<tr>
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<td>0.00138 cm</td>
</tr>
<tr>
<td>$b_i$</td>
<td>0.00385 cm</td>
</tr>
</tbody>
</table>

**Summary:**

This example is based on the average operating conditions for the ZG and APEL cells as used by Menschig (3) which are embedded in the program itself.
with the zero gap correction factor, $f_{M^{2}}$, he obtained $\Delta U_{M}$, the potential drop for a ZG membrane, by using Eq. [10]. Menschig then averaged these two membrane potential drops and called the result the membrane potential drop for the combined cell. Using this value with the equilibrium potentials and overpotentials, again from the corresponding APEL and ZG cell configuration, a potential balance predicted a total cell potential of 3.66V for Mesh I (225 openings/cm²) at 6500 A/cm².

Application to Combined Cell Configurations

Menschig’s work has limited application to combined zero gap/attached porous electrode layer configurations. His method can be used to predict the total cell potential of a ZG cell configuration, given the necessary empirical correlations. Also, the cell potential of combined cells can be predicted by first having experimental data on the corresponding ZG and APEL cells, based on Menschig’s assumption that each half of a combined cell will perform like its corresponding half of a ZG or APEL cell. His methods can be used as described previously to characterize the ZG, APEL, and combined cells (ZGA/PCL and PAL/ZGC) in terms of current density distributions (under his limiting assumptions), species concentrations at the surfaces of the membrane, and overpotentials and electrode equilibrium potentials based on local species concentrations near the membrane surfaces.

Menschig’s method requires experimental data for the particular membrane in a gap cell at a set current density and temperature for various combinations of cell outlet concentrations of NaOH and NaCl. Empirical relations describing the flux of OH⁻ across the membrane from catholyte to anolyte (i.e., the caustic current efficiency) and the membrane potential drop must be derived from this data, producing equations corresponding to Eq. [1] and [7]. Since these relations are used to obtain the concentrations on the membrane surfaces, they must be functions of these surface concentrations. As noted previously, Menschig used Jōrissen’s equations which were derived under the assumption that each half-cell of Jōrissen’s gap cell was well mixed and that there was no significant diffusion layer on the membrane surface. Therefore, Jōrissen could construct his correlations using his bulk concentrations, assuming that these were approximately the same as those on the surface of the membrane. Since concentrations on the membrane surfaces cannot be measured directly, the experimental gap cell which is used to obtain the necessary data to develop the correlations must be designed and operated so as to minimize any diffusion layers on the membrane surfaces.

These empirical equations combined with the additional information listed in Table IV allow the prediction of the total cell current for a ZG cell at a specified catholyte caustic and anolyte salt outlet concentration (for the same current density). Next, by knowing the total cell potential for the corresponding APEL configuration, the surface concentrations needed to estimate the membrane potential of a combined cell can be obtained. The surface concentrations from the ZG and APEL cells can then be used with the empirically derived equivalent to Eq. [7] to obtain the equivalent membrane potential for an APEL cell at these surface concentrations. This value, $\Delta U_{\text{mem}}$, is then corrected using $f_{M^{2}}$ derived from the program ME-NETZP and Eq. [11] to obtain $\Delta U_{M}$. These two membrane potentials are averaged and combined with the electrode overpotentials and equilibrium potentials to predict the total cell potential of the combined cell, just as described previously.
Finally, the concentrations on the membrane surfaces, electrode overpotentials, and equilibrium potentials can be summarized for the combined cells.

**Conclusions**

1. The empirical method presented by Jörisen and Menschig has a limited application to describing the behavior of combined zero gap/attached electrode membrane cells.

(i) Extensive experimental data for each type of membrane in a gap cell, at a set current density and temperature, is required in order to derive the empirical relations describing the OH⁻ flux from catholyte to anolyte (Eq. [1]) and the membrane potential drop (Eq. [7]) for a membrane chlor-alkali cell by regression.

(ii) Given the above relations and various caustic current efficiencies (CCE), the total cell potential of a ZG cell can be predicted as a function of current density (CD) and CCE.

(iii) The concentrations on the membrane surfaces for APEL and ZG cell configurations can be estimated given the above relations and cell performance data (total cell potential, CCE, Cl⁻CE, and CD).

(iv) Menschig's method can be used to predict the total cell potential of combined membrane cells (ZA/PAL or PAL/ZZG configurations) given experimental data on both the corresponding APEL and ZG cell configurations.

2. A more theoretically based method is required if combined zero gap/attached electrode membrane cell behavior is to be estimated without extensive experimental work.

**Acknowledgments**

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**LIST OF SYMBOLS**

- \( \Lambda \) electrode surface area (m²)
- \( b \) membrane thickness (m)
- \( c_{ANA} \) active chlorine concentration in anolyte (mol/m³)
- \( c_{ANA,H^+} \) \( H^+ \) ion excess in anolyte (mol/l) (OH⁻ ion excess is expressed as a negative value of \( x \))  
- \( c_{ANA,NaCl} \) local concentration of NaCl in anolyte, bulk value for Jörisen (mol/m³)  
- \( c_{AT} \) total concentration of dissolved material in anolyte (mol/l NaCl + NaClO₃ + HCl + HOCl + Cl₂) (calculated from the sum of analyzed values for NaCl + NaClO₃ + HCl + NaOH + Cl₂)  
- \( C_{ANA} \) concentration of Cl⁻ at anode (mol/m³)  
- \( C_{ANA,NaCl} \) concentration of NaCl at membrane surface, anolyte side (mol/m³)  
- \( C_{ANA,NaClO_3} \) concentration of NaCl in bulk anolyte (mol/m³)  
- \( C_{ANA,NaClO_4} \) local concentration of NaOH in catholyte, bulk value for Jörisen (mol/m³)  
- \( C_{ANA,NaOH} \) concentration of NaOH in membrane surface, catholyte side (mol/m³)  
- \( C_{ANA,NaOH} \) concentration of OH⁻ at cathode (mol/m³)  
- \( C_{ANA,NaOH} \) concentration of NaOH in bulk catholyte (mol/m³)  
- \( C_{ANA,OH^-} \) concentration of OH⁻ in bulk catholyte (mol/m³)  
- \( \Delta \) gas bubble release diameter (m)  
- \( \delta \) diffusion coefficient (m²/s)  
- \( \delta_D \) diffusion coefficient of \( Cl^- \) ions (m²/s)  
- \( \delta_OH^- \) diffusion coefficient of \( OH^- \) ions (m²/s)  
- \( f_{ZG} \) factor relating the membrane potential of a ZG cell to that of a cell with uniform current density across the membrane, see Eq. [10]  
- \( f_c \) correction factor appearing in Eq. [19]  
- \( \chi \) average hydration number for Na⁺ ions during migration from anode to cathode chamber (mol H₂O/mol Na⁺)  
- \( \eta \) current density (A/m²)  
- \( \eta_i \) current density for Eq. [1] (3000 A/m²)  
- \( \eta_0 \) new mean current density (A/m²)  
- \( \eta_i \) current density based on the actual electrode surface area (A/m²)  
- \( \eta_n \) mean current density, based on surface area of membrane (A/m²)  
- \( \eta_b \) geometric factor calculated by program ME-NETZP  
- \( \eta_b \) mesh width (center to center distance between two parallel wires) (m)  
- \( \eta_b \) OH⁻ flux through the membrane (mol/h-m²)  
- \( \eta_b \) water transport through the membrane (mol H₂O/h-m²) (net water transport + water for back-migrating \( OH^- \) ions)  
- \( \eta_b \) Na⁺ ion transport through the membrane (mol Na⁺/h-m²)  
- \( \eta_b \) net water transport (mol H₂O/h-m²) (net quantity of water moving from anode to cathode chamber)  
- \( Re \) Reynolds number = \( \eta_b d_0 / \delta \)  
- \( Sc \) Schmidt number = \( \eta_b / \delta_D \)  
- \( Sh \) Sherwood number = \( \delta_D / \delta \)  
- \( U_{APEL} \) total cell potential for then APEL cell configuration  
- \( U_{APEL} \) potential drop across membrane with a uniform current density distribution, assumed to be value for APEL configuration, \( V \) potential drop across ZG membrane for a mesh of configuration \( J \)  
- \( U_{APEL} \) total cell potential of a ZG cell for a mesh of configuration \( J \)  
- \( V \) gas evolution rate (m³/s)  
- \( \alpha \) number of electrons used in the electrode reaction  

**Greek letters**

- \( \beta \) mass transfer coefficient = \( D_b / \delta \) (m/s)  
- \( \delta \) diffusion layer thickness (m)  
- \( \delta \) diffusion layer thickness representing the wire mesh layer on anode side for both ZG and APEL cells (m)  
- \( \delta \) diffusion layer thickness representing the wire mesh layer on cathode side for both ZG and APEL cells (m)  
- \( \delta \) diffusion layer thickness representing the porous anode layer of the APEL cell (m)  
- \( \delta \) diffusion layer thickness representing the porous cathode layer of the APEL cell (m)  
- \( \delta \) anode diffusion layer thickness (m)  
- \( \delta \) cathode diffusion layer thickness (m)
\( \delta_{PC} \) diffusion layer thickness for a flat plate cathode (m)
\( \delta_{ZGC} \) diffusion layer thickness for the wire mesh cathode of the ZG cell (m)
\( \varepsilon_A \) anode equilibrium potential (V)
\( \varepsilon_C \) cathode equilibrium potential (V)
\( \eta_A \) anode overpotential (V)
\( \eta_C \) cathode overpotential (V)
\( \kappa \) specific membrane conductivity (1/Ω-m)
\( \nu \) kinematic viscosity (m²/s)

REFERENCES
6. Private communications and conversations with K.-R. Menschig while he was visiting Dow Chemical USA, Freeport, TX (May 1986).