JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 21–27

Voltage drop and current distribution using metal anodes in chlorine-caustic cells

L. E. VAALER*

Union Carbide Corporation, Carbon Products Division Research Laboratory, Cleveland, Ohio 44101, USA

Received 3 January 1978

The voltage drop and current distribution in a chlorine-caustic cell using an anode with a titanium substrate was estimated for several geometric arrangements of the titanium mesh and associated supports and conducting elements. The cell was modelled with a three-dimensional grid network and Kirchoff's law applied to each node. Results were applied to the design of anodes for a full-scale cell which was put in operation and showed the anticipated voltage improvement.

1. Introduction

This paper describes a technique for calculating the *IR*-drop of various electrode designs suitable for use in production-type electrolysis cells. The calculations have been useful in optimizing both the performance and cost of the electrodes. The design of metal anodes for chlorine-caustic cells was considered. The problem was to arrange the macroscopic elements of the anode, i.e., expanded metal electrolysis surfaces and bus bars welded onto the expanded metal, in such a manner that the cell voltage would be minimized and the current distribution would be reasonably uniform.

Previous authors have considered the problems of current distribution in electrodes of homogeneous resistance [1–3] considering situations where the symmetry of the electrodes allows the problem to be reduced to a two-dimensional one. Analytical solutions are often not possible and finite difference equations are solved by iterative procedures with the help of a computer. The grid pattern used in setting up the difference equation generally must be fine and involve a large number of points if a solution is to be reasonably accurate. However, with many electrodes used industrially the number of grid points can be substantially reduced. This is because the electrodes must of necessity be designed so that the *IR*-drop through them is small and the current distribution fairly uniform. Thus if a calculation shows that the *IR*-drop is high, it indicates that the design is not useful even though the calculated result with a coarse grid is not very accurate. On the other hand, the relatively small differences, i.e., 0·1 V, between designs exhibiting small *IR*-drops and fairly uniform current densities are of considerable economic interest, and even with a coarse grid these differences can be shown. Furthermore, when the current density is reasonably uniform a linear approximation can be made to the current–polarization curve so that the current can be assumed to go from cathode to anode through a linear resistor. Electrodes used industrially are generally spaced close together and have a relatively large area. This situation allows edge effects to be ignored. The above factors simplify the model used to calculate voltage drop and current distribution. However, when conductive stringers are introduced into the electrode itself the resistance in any direction parallel to the surface is no longer constant. Finite difference equations in three dimensions with resistance changing throughout the network then need to be used to solve the Laplace equation. Instead of pursuing this method it was found more convenient to represent the electrode by resistances connected to grid points and to apply Kirchoff's law to each point.

* Present address: Battelle, Columbus Laboratories, Columbus, Ohio 43201, USA.

Tiedeman, Newman, and DeSua [4] have used this technique to model a battery grid, assuming that the current density is uniform. In the present instance, provision is made for a varying current density.

2. Choice of a model

The two parallel electrodes are divided into elemental areas with a grid point in the centre of each area. A resistance is considered to connect each interior point to the four surrounding points and another resistance connects each grid point on the anode to its corresponding point on the cathode and runs in a direction normal to both. Points adjacent to edges have only three nearest points on the same electrode, and grid points adjacent to corners only two nearest points. Kirchoff's law for each point is

$$\sum_{1}^{n} (E_{\mathrm{i}} - E_{\mathrm{o}})/r_{\mathrm{io}} = 0$$

where E_{o} is the potential of the grid point, E_{i} is the potential at the other end of a resistance attached to the grid point, and r_{io} is the resistance between the two points. The problem is to find the potential needed between the anode and the cathode contacts to drive the desired current through the cell.

3. Solution using the model

If there are m grid points in the x-direction and n grid points in the y-direction on an electrode, $n \times m$ equations can be written. Resistances may be indexed so that they lie in the positive direction from a grid point, i.e., r_{11} is in the x-direction and between E_{11} and E_{21}; R_{11} is in the y-direction and between E_{11} and E_{12}. Then Kirchoff's law for an interior grid point is

$$E_{i,j} = \frac{\dfrac{E_{i+1,j}}{r_{i,j}} + \dfrac{E_{i,j+1}}{R_{i,j}} + \dfrac{E_{i-1,j}}{r_{i-1,j}} + \dfrac{E_{i,j-1}}{R_{i,j-1}} + \dfrac{E_{\mathrm{c}}}{r_{\mathrm{c}}}}{\dfrac{1}{r_{i,j}}\,\dfrac{1}{R_{i,j}}\,\dfrac{1}{r_{i-1,j}}\,\dfrac{1}{R_{i,j-1}}\,\dfrac{1}{r_{\mathrm{c}}}}$$

where E_{c} is the potential of the grid point on the opposite electrode and r_{c} is the effective resistance between the corresponding anode and cathode grid points. In the examples to be cited it is reasonable to assume a constant potential for the cathode, since it is a much better conductor than the typical anode design. In such a case only the $n \times m$ equations for the anode are solved, and the potential of the cathode (the term E_{c} in the above equation) is arbitrarily set equal to zero.

In principle, the equations can be solved by iteration, assuming an initial potential for each grid point and using new values as fast as they are generated by the equations for the preceding grid points. However, the iteration method was abandoned because the convergence of the values to the correct solution was slow, even using so-called 'over-relaxation' techniques. The equations were solved simultaneously by the SIMQ subroutine of IBM. The number of grid points that can be handled will depend upon the size of the computer. With an IBM 1800 computer, using a disc for storage and retrieval of coefficients, a system with up to 160 grid points can be solved. To accommodate to the SIMQ subroutine the program was written so that the subscript variables i and j were converted to a single subscript variable L, and conductivities rather than resistances were used. The single subscript reads from the bottom left corner of the vertical anode in the x-direction and successively reads the next row above so that the final subscript is in the top right corner. Thus, $L = (j-1)m + i$.

To show how a program may be developed to solve the potential distribution a network with 16 grid points has been drawn in Fig. 1. The counter-electrode is assumed to have a much higher conductivity and to be equipotential ($E = 0$). A source of potential equal to 1·0 is connected to the grid through a resistance of conductivity CON. More than one grid point may be so attached. When the equation for an interior point is written with a single subscripted variable

$$E_L = (c_L E_{L+1} + c_{L-1} E_{L-1} + C_{L-m} E_{L-m} + C_L E_{L+m})/k_L$$

where

$$c_L = \frac{1}{r_L}, \quad C_L = \frac{1}{R_L},$$

$$k_L = c_L + c_{L-1} + C_{L-m} + C_L + CE$$

and CE is the anode-to-cathode conductivity.

The coefficients for the potentials in each of the 16 equations that can be written for the network can be tabulated in a matrix as shown in Fig. 2. In-

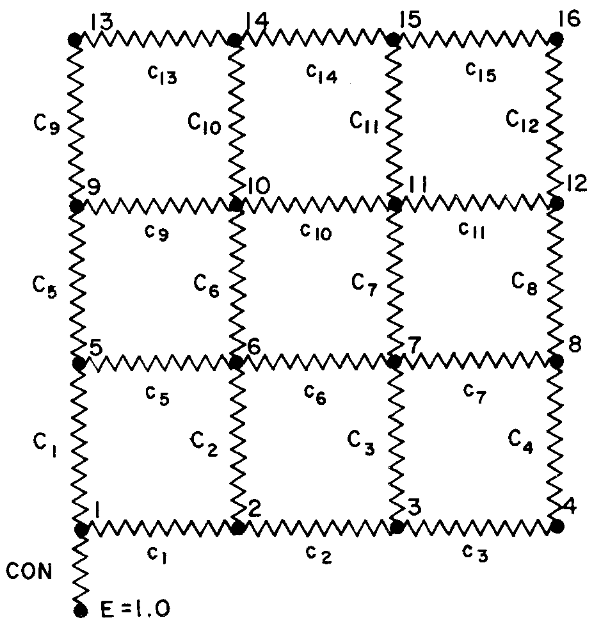

Fig. 1. Grid network.

version of this matrix by SIMQ yields values for the potential at each grid point when the potential at the anode contact is 1·0 and the potential at the cathode is zero. The current flowing from each grid point to the cathode is then calculated and the values are added to give the total current pushed through the anode by one volt. This current is divided into the desired current to give the potential from the anode contact to the cathode necessary to drive through the desired current. Finally, the current density for each grid element area is calculated.

4. Use of the program to design a diaphragm cell anode

A configuration that could be substituted for a graphite anode in an existing cell was chosen. Two

	L-SUBSCRIPT OF VARIABLE																
EQUATION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	Constant
1	$-K_1$	c_1			C_1												$-CON$
2	c_1	$-K_2$	c_2			C_2											
3		c_2	$-K_3$	c_3			C_3										
4			c_3	$-K_4$				C_4									
5	C_1				$-K_5$	c_5			C_5								
6		C_2			c_5	$-K_6$	c_6			C_6							
7			C_3			c_6	$-K_7$	c_7			C_7						
8				C_4			c_7	$-K_8$				C_8					
9					C_5				$-K_9$	c_9			C_9				
10						C_6			c_9	$-K_{10}$	c_{10}			C_{10}			
11							C_7			c_{10}	$-K_{11}$	c_{11}			C_{11}		
12								C_8			c_{11}	$-K_{12}$				C_{12}	
13									C_9				$-K_{13}$	c_{13}			
14										C_{10}			c_{13}	$-K_{14}$	c_{14}		
15											C_{11}			c_{14}	$-K_{15}$	c_{15}	
16												C_{12}			c_{15}	$-K_{16}$	

Fig. 2. Potential coefficient matrix.

expanded metal sheets 6–1/4 in x 25 in are welded to the two edges of a 0·975 in thick stringer so that the stringer bisects each sheet into 3–1/8 in x 25 in halves. The width of the stringer and thus its resistance may be varied. Symmetry allowed consideration of a 3–1/8 in x 25 in area for which a five horizontal x eleven vertical grid pattern was adopted, giving an elemental area of 0·625 in x 2·77 in for each grid point. Contact to the anode was considered to be made to the grid point in the lower left corner by means of a stringer extending 2·77 in below it. Rough calculations showed that the potential drop in the steel screen cathode would be neglible compared to that in the anode at the current density assumed.

Several samples of expanded titanium mesh made from 0·063 in sheet were measured for electrical resistance. Resistance per square in the direction of the long axis of the diamond shape (LWM) was approximately $7{\cdot}50 \times 10^{-4}$ Ω/square. In the direction of the short axis (SWM) the resistance was approximately $2{\cdot}90 \times 10^{-3}$ Ω/square. Specific resistance for the solid titanium in the stringers was assumed to be $2{\cdot}24 \times 10^{-5}$ Ω in. Specific resistance of the electrolyte was assumed to be 0·708 Ω in [5] for a concentration of 250 g l^{-1} of NaCl and a temperature of 90° C. The brine gap was assumed to be 1/4 in. Resistance through the diaphragm was estimated to be 0·3 Ω in^{-2} and anode and cathode effective polarization resistances 0·11 Ω in^{-2} each. Total interelectrode resistance is then: [(0·708/4) + 0·11 + 0·11 x 0.30] /0·625 x 2·27 = 0·492 Ω. Conductance = 1/0·492 = 2·035 Ω.

For an average current density of 1·0 A in^{-2} the total current is: 3·125 x 25 = 78·2 A.

Twenty-four calculations were made on all combinations of the following: mesh thickness [(a) from 0·063 sheet, (b) from 0·0315 sheet assuming half the conductivity of the thicker sheet] ; mesh orientation [(a) LWM in vertical (long) direction, (b) SWM in vertical direction] ; stringer cross-section [(a) 3/16 in x 0·975 in (for two 6–1/4 in x 25 in anode faces), (b) 3/8 in x 0·975 in (for two 6–1/4 in x 25 in anode faces)] ; stringer length [(a) covering two grid points (5·7 in) (b) covering five grid points (12·5 in) (c) covering ten grid points (23·8 in)].

In three further calculations the thinner mesh with vertical SWM was combined with a 3/4 in x 0·975 in stringer 2, 5, and 10 grid points in length. Several calculations were also made using an 8 x 20 grid to determine the effect of the number of grid points on the results.

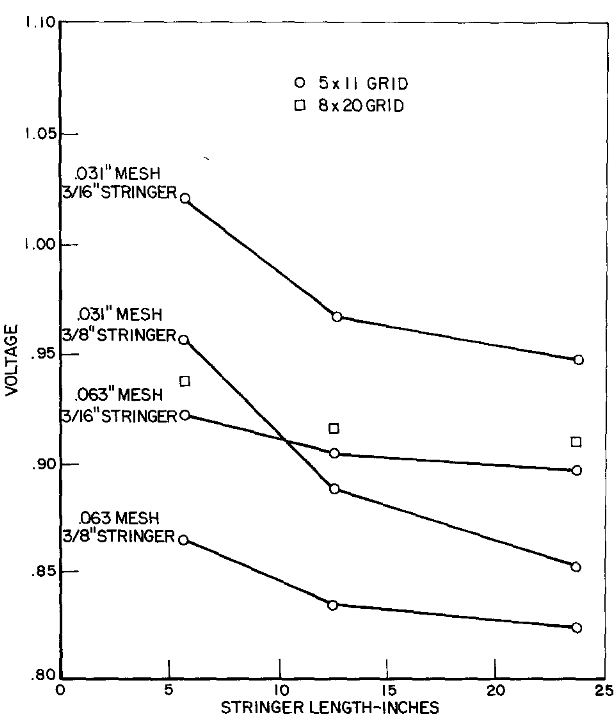

Fig. 3. Voltage as a function of stringer length LWM vertical.

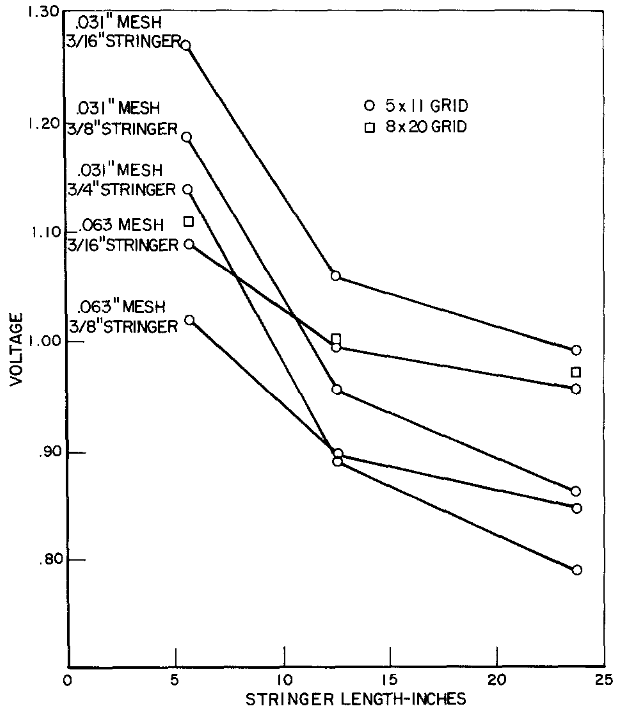

Fig. 4. Voltage as a function of stringer length SWM vertical.

Voltage from the anode contact to the cathode as a function of stringer length is plotted in Figs. 3 and 4. It is obvious that orienting the mesh so that the highest conductivity is obtained in the vertical direction lowers the voltage, but that a sufficiently large stringer can completely override any deficiency in mesh conductivity. If the resistance of the anode were zero, the voltage drop

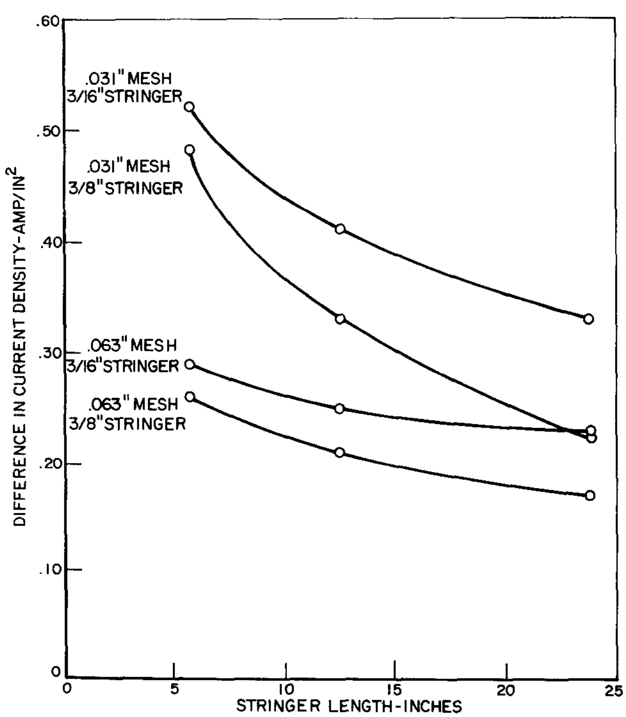

Fig. 5. Current distribution as a function of stringer length LWM vertical.

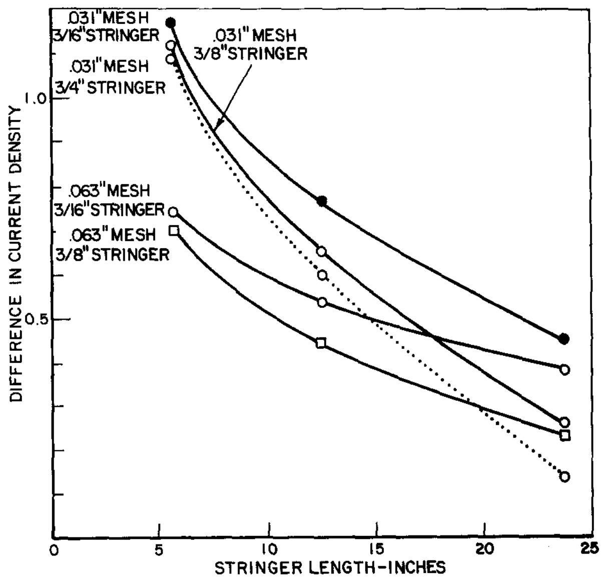

Fig. 6. Current distribution as function of stringer length SWM vertical.

would occur only between anode face and cathode and would be equal to: (0·625) (2·27)/(2·035) = 0·70 V. This is approximately 0·1 V lower than achieved with any of the designs considered.

Increasing the number of grid points from 55 to 160 increased the calculated voltage by 0·02 or less and did not change the trend of the voltage curves. The current density distribution was not significantly affected.

Increasing the conductivity of the anode improves the uniformity of current distribution. The highest current density is invariably found at grid point no. 1, connected to the contact point at the lower left-hand corner of the half-anode. The lowest current density is obtained at the corner grid point diagonally opposite point no. 1. The difference between the maximum and minimum current densities has been plotted as a function of stringer length in Figs. 5 and 6. Again it is apparent that a sufficiently large stringer can overcome a deficiency in mesh conductivity.

Fig. 7 shows plots of the difference in current density between that at point no. 1 and point no. 6 in the lower left-hand corner, which is at the same height. The difference reflects the conductance of the mesh in a horizontal direction and the difference along this bottom row of grid points is higher than in any row above it.

The differences are small compared to the differences between maximum and minimum cur-

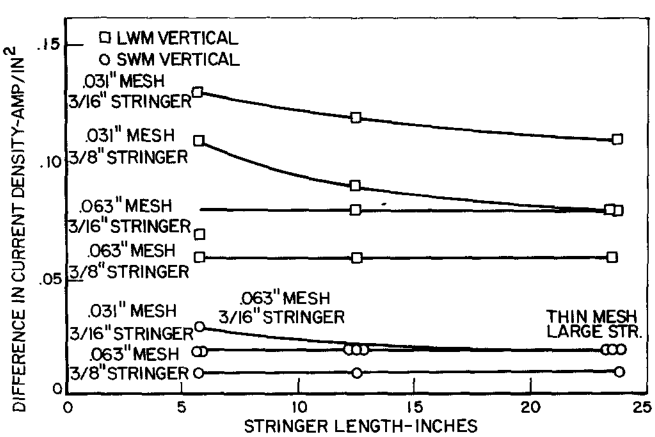

Fig. 7. Horizontal current distribution as a function of stringer length.

rent densities in the anode and indicate that even the thin mesh can adequately carry current in a horizontal direction.

Several combinations of expanded mesh and stringer may be used to provide diaphragm cell anodes of comparable performance. It is obvious that even thinner meshes can be used if augmented by sufficiently heavy stringers, particularly if the SWM is oriented vertically. With the meshes considered it is also possible to space heavier and fewer stringers farther apart in a cell so that fewer contacts to the base are required. Of course, these suggestions do not take account of the structural rigidity that may be required. The reasonably good horizontal conductivity of the mesh suggests that y- or v- shaped stringers are not necessary to distribute current laterally and that the stringers should run only vertically to provide the best conductivity in this direction. Obviously the best way to distribute a given weight of stringers is to have more mass at the bottom than the top of the anode. From a practical standpoint, adjacent stringers going to two or more different heights might be used.

A 25 in × 6–1/4 in expanded mesh anode from 0·063 in sheet weighs 346 g whereas a 3/8 in × 0·975 in × 25 in stringer weighs 676 g. In the design considered half of the weight or 338 g would be allocated to each anode face, so that the weight of the faces and stringers would be nearly equal. The resistance of the anode in the vertical direction with LWM in the same direction is: $(7{\cdot}50 \times 10^{-4})(25/6{\cdot}25) = 3{\cdot}00 \times 10^{-3}\ \Omega$. For the stringer: $(2{\cdot}24 \times 10^{-5})(25/0{\cdot}1827) = 3{\cdot}07 \times 10^{-3}\ \Omega$. Therefore, the resistance of equal weights of anode and stringer are approximately equal and the relative cost of these two would influence the design. A copper-cored stringer should provide equal conductivity with less stringer weight.

The total cell voltage for a current density of $1{\cdot}0\ \mathrm{A\ in}^{-2}$ was roughly estimated as shown in Table 1.

Voltages measured in a full cell of approximately one ton per day capacity were of the order of 3·6 V, including voltage drop through buses and connectors. Thus, the agreement with the above rough estimate was 10% or less. The calculations made possible direct scale-up from small laboratory experiments to a full-scale operation.

Table 1

Parameter	*Value* (V)
reversible cathode potential	0·8
hydrogen overvoltage	0·5
IR-drop, electrolyte	0·2
IR-drop, diaphragm	0·3
anode overvoltage	0·2
reversible anode potential	1·3
total	3·30

The method may also be used for electrode design employing stringers that do not follow orthogonal directions, i.e., diagonal elements on a horizontal anode for a mercury cathode chlorine cell. The diagonal resistances are approximated by orthogonal components which are included in the appropriate grid elements.

Acknowledgement

The author wishes to acknowledge the help of Dr T. A. Lauria who suggested using a matrix to solve the problem of potential distribution, and to Mr Hermann Leggon for adapting the SIMQ program to the desired calculations.

References

[1] C. W. Tobias and R. Wijsman, *J. Electrochem. Soc.* **100** (1953) 459.

[2] J. A. Klingert, S. Lynn and C. W. Tobias, *Electrochim. Acta* 9 (1964) 297.

[3] P. M. Robertson, *ibid* **22** (1977) 411.

[4] W. Tiedeman, J. Neuman and F. DeSua, *10th International Power Sources Symposium*, Brighton, England (September, 1976).

[5] R. S. Karpiuk, paper given at *the Electrochemical Society Meeting* (May, 1962).