New concepts in the scale-up of chlorine-caustic mercury cells

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Mercury cells of conventional design embody an elongated cathode, with a length which is a multiple of the width. For commercial cells installed to date this multiple is never less than 5 and for most models it is greater than 7. This elongated configuration has also been retained for cell sizes of highest current rating (up to 500 kA) and highest current density (up to 15 kA m^{-2}) as allowed by activated titanium anodes. While being in conformity with tradition, such geometry, when applied to the largest cells, neglects some fundamental rules based on hydrodynamics. New requirements must in fact be fulfilled to obtain optimum mercury flow at the highest current capacities and the highest current densities that characterize the ultimate trend. When the length-to-width ratio is kept below the present typical range, the cell performance also improves because of a decrease of the harmful effects due to accumulation of mercury butter on the cathode surface.

List of symbols

I = current capacity (kA)
i = cathode current density (kA m^{-2})
C = amalgam concentration (% Na)
L = cathode length (m)
W = cathode width (m)
S = cathode area (m^2)
Q = mercury flow-rate (1 min^{-1})
Re = thickness Reynolds number ([3])
t = mercury cathode thickness (mm)
J = cathode slope (mm m^{-1})
k,m,n = constants
ρ = amalgam density (13·6 g cm^{-3})
μ = amalgam dynamic viscosity ($\approx$0·015 P)

1. Introduction

Mercury cathode cells for the electrolysis of sodium chloride in aqueous solution offer the most outstanding example of scaling-up in the electrochemical industry. Whereas, no longer than about twenty years ago, the largest unit capacities did not exceed 50 kA, models are now available with current ratings of 600 kA and more. No other electrolytic process has shown a development trend comparable with this, if unit size is to be taken as a term of comparison. For example, aluminum cells, which were still the giants of the family during the early fifties, with capacities up to 100 kA, have meanwhile grown to 200 kA or slightly more, according to the latest design.

This rapid rise of mercury cell capacity, as promoted by economic opportunities, was made possible by increasing the cell geometry as well as the current density (which has been raised from the value of 4 kA m^{-2}, prevailing twenty years ago, to more than 10 kA m^{-2}) without appreciably affecting the cell voltage and current efficiency. The replacement of graphite anodes with activated titanium anodes [1] was of outstanding importance for such progress.

This kind of revolutionary cell scale-up might be considered as the outcome of an equally revolutionary approach in applying the ultimate knowledge of electrochemical engineering. Yet, it is the purpose of this paper to highlight an aspect of the problem that does not seem to have, so far, received the attention it deserves. In fact, the traditional configuration that has been generally retained for the latest develop-

ments shows that, in solving the problem, one has mostly relied on mere extrapolation, that is on the empirical approaches of the past. This applies in particular to some models of largest capacity and current density.

2. Current state of the art

The prototype of all industrial models working to date is the well-known Solvay cell, developed at the turn of the century. It consisted of an elongated trough, with a sloping bottom which embodied a cathodic surface about 12 m long and 0·5 m wide. All subsequent models have retained an elongated shape, although the length:width ratio was diminished in the course of time to values substantially smaller than 24, the value in the prototype. One advantage inherent in an oblong geometry can be immediately realized, in that the flowing mercury layer must be kept as thin as possible, in order to economize in mercury inventory. In fact, whatever the area of the cathode surface, established by the quotient of current rating by current density, the accuracy required in machining and crosslevelling the cathodic plate admits a tolerance that is directly proportional to the *nominal*, or average, value pre-established for mercury thickness and inversely proportional to the cell width. Since the whole bottom surface must be covered with mercury, the
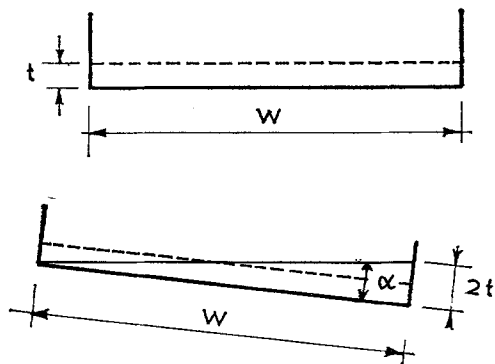

Fig. 1. Maximum permissible tilt for complete bottom coverage as a function of cell width W and average mercury thickness t (Equation 1).

maximum allowable tilt, or unevenness, (Fig. 1) is given by

$$\tan \alpha < \frac{2t}{W} \qquad (1)$$

Another advantage afforded by a relatively small width resides in the fact that it becomes easier to provide a uniform mercury distribution at the inlet end; in addition, the anode connecting system can be considerably simplified, and this is particularly important for cells of largest capacity and current density.

None the less, if the L/W ratio were merely dictated by constructional convenience, as resulting from the above-mentioned aspects of the problem, one would lose sight of another requirement that must also be satisfied by an adequate cell geometry and is even more fundamental than the former, as it involves the hydrodynamic conditions of the mercury flow.

3. Cell geometry and mercury Reynolds number

When the alkali metal is allowed to reach the maximum admissible concentration in the amalgam, which may be conservatively set at 0·25% Na [2], the mercury flow-rate is dictated only by the rated current capacity. For sodium discharge, assuming a current efficiency of 95%, the equation is

$$Q = \frac{I}{10\,C} \qquad (2)$$

Therefore, once the design capacity has been established, the 'thickness Reynolds number', affecting the turbulence of motion in open channel flow [3], will only depend on cell width, according to a law of inverse proportionality

$$Re = \frac{\rho}{\mu} \frac{Q}{W} \qquad (3)$$

Between the cathode surface and other magnitudes the following relations hold

$$S = WL = \frac{I}{i} \qquad (4)$$

From the combination of Equation (2) and (4) one obtains

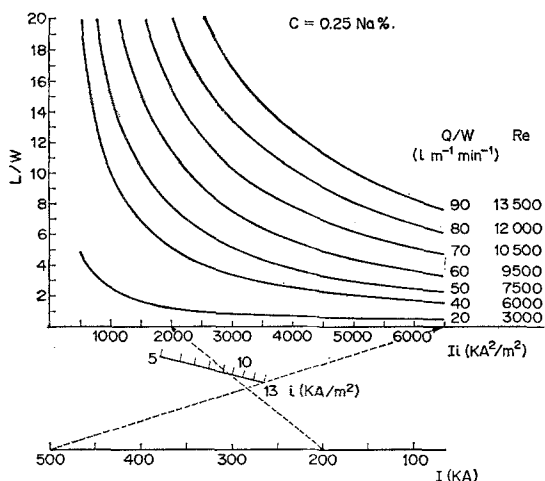$$\frac{L}{W} = 100 \quad \frac{C^2}{Ii} \quad \left(\frac{Q}{W}\right)^2 \qquad (5)$$

Fig. 2. Diagrammatic representation of Equation (5) for $C = 0.25\%$ Na.

This equation is represented diagrammatically in Fig. 2, where each hyperbola is the plot of L/W as a function of the product Ii, for a given parametric value of Q/W or Re and for $C = 0.25\%$ Na.

If, as one main requirement of cell design, it is established that Re shall not exceed a limit beyond which the mercury flow would be affected by excessive turbulence, it can be seen from this graph how drastically L/W must be reduced if one wants to concentrate production in relatively few units of large size, that is by adopting high values for current density as well as current rating.

4. Influence of cell slope

Table 1 shows the characteristics of a few cell models, which typically represent the evolution in capacity and size that has taken place through the years. It is pertinent to remark that, from the Solvay prototype up to the models developed in the fifties, the ratio Q/W never exceeded the value of 40, corresponding to $Re \approx 6000$. This is sufficiently high to cause a mild turbulence, whereby the alkali metal is moved by convective transport into the bulk of the mercury stream, as soon as it undergoes cathodic discharge. This particularly favourable Q/W value, characterizing the less recent models, is to be considered as a mere empirical consequence of an L/W ratio selected according to constructional convenience, rather than hydrodynamic concepts. In fact, at the current ratings and densities for which the old models were designed, any L/W ratio, however great, was never so great as to involve an excessively high Re. But the situation has rapidly changed with the latest trend toward ever higher loads, or Ii values. In fact, since the L/W ratio has not been *substantially* modified, this has involved a substantial increase in Q/W, until values as high as 95 and corresponding Reynolds numbers up to 14 000 have been reached.

This trend is reflected by the gradual increase in cell slope that also has characterized some recent installations. For a pre-established value

Table 1.

Cell model	Year	Capacity (kA)	Current density (kAm⁻²)	Length (m)	Width (m)	Area (m²)	Na%	Q/W (1 m⁻¹min⁻¹)	L/W Actual value	L/W Calculated for Q/W = 50
1. Solvay	1900	10	1·66	12	0·5	6	0·05	40	24	36·5
2. De Nora 18 SGL	1956	160	4·6	15	2·3	34·5	0·2	35	6·5	13·6
3. Kureha HD-4	1965	150	7·5	16·5	1·2	20	0·25	50	13·8	13·8
4. Uhde 300–100	1966	300	10	13·3	2·25	30	0·25	53	5·9	5·2
5. Olin Mathieson E–8–12	1965	288	10	14·8	1·94	28·8	0·25	60	7·6	5·4
6. Uhde	1970	518	15	13·3*	2·6*	34·5	0·25	80	5·1	2
7. De Nora 33 M 2	1969	500	13·5	17·7	2·1	37	0·25	95	8·4	2·3

* Estimated.

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of mercury thickness t, the cell slope J increases for an increase in Q/W according to the equation

$$t = k J^m \left(\frac{Q}{W}\right)^n \qquad (6)$$

where k, m (<0) and n may be taken as constants, since they approximately depend only on the roughness of the underlying steel surface [4].
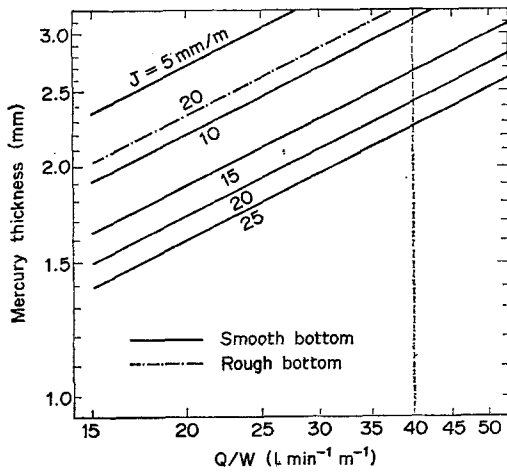

Fig. 3. Mercury layer thickness versus flow-rate per unit width for several slopes (Equation 6).

The graph Fig. 3 represents this function. It illustrates that any increase in slope does not usually serve the purpose of saving in mercury inventory, as erroneously believed in several quarters. Any such increase in slope has indeed the essential purpose of making for an increase in Q/W, so as to keep unaltered the thickness and consequently the mercury inventory, other conditions being equal.

5. New scale-up concepts

The main question that one wants to raise here is the following: is the above noted trend toward higher Q/W values reasonable? Or has it already surpassed a limit beyond which the operating conditions are adversely affected? Indeed, some troubles recently reported from plants equipped with cell models of highest capacity are of such a nature as to justify this sort of question.

From current experience it is well-known that,

for a mercury thickness of between 2 and 3 mm, the continuity of the flowing layer becomes unstable for $Q/W>60$. Under such conditions adhesion is lost between the steel bottom and the amalgam layer, which tends to tear apart and form ripples, or so-called 'solitary waves', involving a transport of matter as well as local and transient increases in thickness. These may be harmful, especially when metallic anodes are used, since any short circuit between such anodes and the cathode, irrespective of its extension and duration, inevitably involves destructive effects not only on the active coating, whatever its nature, but on the anode structure itself [5].

If the mercury thickness is kept down to less than 2 mm, which in principle can only be achieved by increasing the cell slope, the unsteadiness of the mercury layer sets in for Q/W values even lower than 60. This phenomenon is aggravated by the greater difficulty of securing complete bottom coverage even when keeping the amalgam layer stationary (Equation 1).

The last column of Table 1 shows, against the actual design values for the several models, those that would result from applying Equation (5), so as not to exceed the conservative value of $Q/W = 50$.

The foregoing considerations concern cell geometry only with regard to the hydrodynamic conditions it implies. None the less, operation at high current density involves another difficulty, arising from the relatively fast and dangerous accumulation of mercury butter, with effects that can also be forestalled to a large extent by judicious cell design as regards the L/W ratio.

6. Origin and harmful influence of mercury butter

Mercury butter essentially consists of a suspension of insoluble and microscopic iron particles, each enveloped in a thin coating of sodium amalgam. The persistency of such a suspension is due to the outstanding surface-active, or 'wetting' properties of the alkali metal, so that its concentration at the iron-mercury interface is considerably greater than in the mercury bulk [5]. Less than 1% Fe in the sus-

pension is sufficient to make mercury completely lose its fluidity and agglomerate in clumps that dam up the amalgam stream, thus causing local short circuits with the anodes.

Butter formation by iron particles is the result of an erosion-corrosion action exerted by the amalgam on the steel bottom, with the well-known effect of a gradual roughening of its surface [4], due to removal of iron particles. This proceeds at a rate increasing not only with sodium concentration and temperature, but also with current density. Since sodium concentration increases from the mercury inlet end to the amalgam outlet end, the clumps of butter being formed by local particle build-up and coalescense grow at a faster rate in the downstream regions and are therefore dragged by mercury at a lower speed than the smaller clumps forming upstream. It ensues that the former are overtaken by the latter and thus gather in chunks big enough to come to a standstill and then increase indefinitely, until a short-circuiting bridge is thereby established between the cathode and the anode system.

From the foregoing description it can be easily inferred that the magnitude of butter formation and its effects could be considerably reduced by reducing the L/W ratio. It would thus be possible to keep a constant distance between anodes and cathode, within the narrow limits required to prevent the cell voltage rising beyond an economically acceptable maximum even at the highest current densities that have been advertised by some engineering companies. On the other hand, it is hardly credible that, with the cell geometries now in use, it is possible, even with metallic anodes and a not exceedingly high current density of 10 kA m^{-2}, to keep the d.c. power consumption within the claimed limit of 3040 kWh per metric ton of chlorine [6]. In fact, according to the same reference, this would require that the interelectrode gap be kept within 2 mm, i.e. a value that is certainly less than allowed by the combined effect of mercury rippling and mercury butter build-up, besides the inevitable unevenness arising in anode fabrication and adjustment.

7. Economic considerations and conclusions

Despite the preceding arguments, which all point to the benefit obtainable from adopting smaller L/W values than those characterizing the latest trend, an objection might be raised on the ground of economy in cell fabrication. In fact, for a given cathode surface, it might turn out that the investment would be higher for wider and shorter cells, on account of the more complicated anode connections and the larger quantity of copper involved, besides the increase in the mercury inventory requirement (Equation 1). However, such problems would hardly arise by adopting cathode sizes not exceeding 25 m^2 and reasonably high current densities up to 12 kA m^{-2}, corresponding to a cell capacity of 300 kA. For cell sizes and ratings not above these values, it would be sufficient for the L/W ratio not to exceed the value of 5, in order to keep Q/W within a safe value below 60.

On the other hand, with regard to overall manufacturing cost, including capital and fixed charges, it is likely that no considerable advantage would be attainable by increasing the cathode area above 25 m^2, even when metallic anodes are used. (See the previous conclusions for mercury cells equipped with graphite anodes [7].)

In conclusion, if these problems are tackled with an approach which considers optimization of operation as well as first cost (that is an approach following sound engineering principles), the biggest may not necessarily be the best in this particular case.

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