Technical Paper

Studies on the Electrode Potential and the IR-Drop in a Horizontal Amalgam-Type Chlorine Cell

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The overvoltage and the IR drops in a horizontal amalgam type chlorine cell under working conditions depend on the cell dimension such as the anode-to-cathode spacing, because a considerable amount of chlorine bubble is retained between the two electrodes, and the rate of its escape is affected by the flow of brine in a cell and also by the geometry of the cell. The ratio of the cell length, a , to its width, b , is therefore an important factor of discussion for the optimization of the cell voltage.

1 Introduction

Only few reports have been published on the influences of the cell dimension, i.e. the ratio of cell length to the width a/b , while some experiments^{1)~4)} have been reported on the relationship between the voltage drops and the effective length of the horizontal-type amalgam cell. Operation of large scale chlorine plant using large cells such as 250 kA or more is the world-wide trend today, and the constructive ratio a/b is then slightly decreasing. On the other hand, a large cell has some problems on the construction and practical operation. Therefore the ratio a/b may have an optimum which is not discussed yet in detail.

Many reports on the chlorine overvoltage on the graphite anode and on the IR-drops in the brine are available, but few papers pointed out the effects of the cell dimension on the cell voltage. The overvoltage and the IR-drops as well as the cell voltage will be discussed as a function of the cell dimension in this paper.

2 Experimental Procedure

The effects of the form and dimension of the horizontal-type amalgam cell on the IR-drops and polarization have been studied with over 40 cells under the operation in a commercial scale plant. Of these, six cells labelled in Fig. 1 retained quite stable voltage, i.e. less than ± 15 mV for 17 days, and others were about the same. Each graphite anode was machined in regular way: the slits of 8~10 apertures per dm² with holes of 6 mm diameter. The cell voltage between the copper bolts connected to both anode and cathode was determined with relation to the effective length of the cell, a . Other conditions are as follows:

Current density at cathode	2970 A/m ²
Change of NaCl concentration	
from 311 g/l to 260,2 g/l	50.8 g/l
Temperature of brine-Inlet	64 $\pm$ 1°C
Outlet	68.5 $\pm$ 1.5°C
Cell length, a	12 m
Cell width, b	0.800 m

Cell voltage was measured by a conventional millivoltmeter (0.5% precision) with a mirror. The obtained data plotted against the a/b ratio are shown in Fig. 1.

To know the change of overvoltage at the cathode caused by the enrichment of sodium in the amalgam along the effective length of the cell, one has to determine the sodium content at the inlet and outlet of the cell analytically. In the latter case the sample of amalgam was collected at the outlet from the 1~2 mm thick layer of the amalgam after emptying the cell. The results obtained in working conditions of the cell with which experiments were carried through are shown in Table 1.

The values of the voltage drop through the electrolyte were determined by measuring the conductivity of the electrolyte saturated with chlorine and at different degrees of the suspended chlorine bubbles up to 30 volume%, which corresponded to the cell condition of 10,400 A/m² current density. The IR-drops of the gaseous chlorine-electrolyte mixture was measured in an experimental cell which are shown in Fig. 2. The device consists of a glass tube having a 20 mm inner diameter equipped with reversible electrodes, an aperture for the introduction of the electrolyte and a space for the mounting of a thermometer with a 0.1° precision. At the lower end of the apparatus a Schott filter No. 4 was attached for the dispersion of chlorine gas. The measurement of the resistivity of the electrolyte was carried out according to an improved

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Fig. 1 Dependency of cell voltage on the effective length of the cell

- 1: Representation of the cell voltage according to a line tangential to the points of minimum value
 2: Representation of the cell voltage according to a curve passing through the points of minimum value
 3: Representation of the cell voltage according to a broken line joining all the measured points

Table 1 Examples of analysis of Na-content in the amalgam

Cell number	% content in Na		
	At the inlet	At the outlet	
	Middle sample	Middle sample	Upper layer sample
9	0.032	0.147	0.241
16	0.028	0.138	0.302
21	0.031	0.159	0.311
27	0.016	0.162	0.330
28	0.035	0.152	0.284
40	0.032	0.147	0.262

scheme, as shown in Fig. 3, consisting of a 1,000 Hz oscillator and an inductive system, coupled with a step-down transformer. Differing from the known schemes, one has to measure small values-between 1~5 ohm with a reading error of 0.01 ohm. As the measurements were made with a bridge, the balance was detected with an electronic amplifier having 6G7, 6N9, and EM11, an electronic tube with an image opening.

Temperature was controlled by an ultrathermostat Höppler, with a programmed temperature control.

To make the experimental condition as near as possible to the actual working conditions an industrial brine being used in the mercury process was used and a composition is shown in Table 2.

Fig. 2 Experimental cell used for the measurement of the specific resistivity of electrolyte

Fig. 3 Scheme of the device employed to measure the specific resistivity of the electrolyte

Table 2 Composition of the electrolyte

Composition of the electrolyte	NaCl	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Fe ²⁺	ClO ₃ ⁻	HCl	Hg
g/l	280.5	3.007	0.832	0.0048	0.0002	0.380 0.379	0.102	0.0169 0.017

Table 3 Composition of pure sodium chloride produced by the "Reactivul" Works, Bucharest

Comp.	NaCl	Insoluble	Iodides	N-total	PO ₄ ³⁻	SO ₄ ²⁻	Ba ²⁺	Pb ²⁺	Fe ²⁺	Ca ²⁺	Mg ²⁺	K ⁺
%	99.8	0.001	0.002	0.0005	0.0005	0.005	0.0005	0.0003	0.0001	0.004	0.001	0.005

Fig. 4 Dependency of the specific conductivity of the electrolyte on temperature for chlorine addition of 0.53 g/l ○; 0.391 g/l ▽ and 0.947 g/l □, in the electrolyte

Fig. 5 Dependency of the conductivity and the specific resistivity on the filling degree X of the electrolyte with chlorine bubbles

The cell constant was determined by means of the "Reactivul" Works, Bucharest, with a composition as given in Table 3.

The results obtained for an addition of chlorine up to the limit of solubility at temperatures between 45° and 65° are shown in Fig. 4.

The results are shown in Fig. 5 for the conductivity dependency on the filling degree (Volume ratio of chlorine bubbles in the electrolyte having a size from 1 to 2 mm), at a temperature of 66°.

3 Results and Discussion

The cell voltage under practical working conditions takes different values according to the effective length, a , of the cell and to the constructive factor a/b , as shown in Fig. 1.

The minimal values found can be marked as a line 1 empirically, (tangent at the minimum point) from the inclination of which the value of voltage drops versus the length can be computed. The points placed above the line represent additional voltage drops, chiefly due to the inadequate contact between the copper bolt, which was inserted in the graphite mass to link between the rod and the anode, or to other local causes such as the distance between the electrodes, different flowing conditions of the cathode and the electrolyte, nonuniformity of the perforated graphite electrode or blocking the apertures by salt, and other less known causes.

Practically, the minimal values are drawn as a curve 2, which is parallel to the abscissa for constructive ratios a/b of between 2 and 5 after which the voltage drop increases step-wise from 240 mV (electrolyser 28) to 360 mV (electrolyser 27), of which 10.2 mV represents the voltage drop as a consequence of the decreasing of the electrolyte concentration and the increase of its temperature.

The third interpretation of the results would be to admit a cell voltage according to the broken line 3. The minimum values are inscribed in an increasing order in accordance with the constructive factor a/b .

The conductivity of the medium studied up to the

solubility limit of the chlorine in the electrolyte remains practically constant as shown in Fig. 4.

The conductivity decreases with increase in the amount of chlorine bubbles in the electrolyte as shown in Fig. 5. The filling degree is given by the equation 1

$$\frac{C_{g+e}}{C_e} = 1 - K \cdot X \quad (1)$$

in which

C_{g+e} is the conductivity of the mixture of gaseous chlorine and electrolyte $\Omega^{-1} \text{ cm}^{-1}$.

C_e : Conductivity of the electrolyte $\Omega^{-1} \text{ cm}^{-1}$

K : A constant having the value of 1.695

X : The filling degree of the electrolyte with chlorine bubbles.

Through the interpretation of the experimental results and the data obtained from practical electrolysis, one ascertains that the measured cell voltage shown in Fig. 1 do not limit the zone of solubility to a constructive ratio $a/b=0.3$ as resulting from the calculation of the chlorine quantities produced and absorbed into the electrolyte. This zone could extend practically to a constructive ratio a/b between 2 and 5.

It is supposed that the degree of filling of the electrolyte with chlorine bubbles does not affect the interpolar distance in this zone because are in the free horizontal section of the cell such as the slits and holes of the electrode the spaces between and above the electrodes occupied by the electrolyte. Therefore the constructive form of the cell affects the voltage drops in the electrolyte very slightly—practically no effect. The matter is different in the following zone in which the additional voltage drop through the electrolyte, as a consequence of the formation of chlorine bubbles in the interpolar distance, has to be taken into account and is 31 mV corresponding to a filling degree of $X=0.0812$. In the industrial operation, the formation, association and growth of the chlorine bubbles depends on the technological, hydrodynamic and constructive conditions, especially on the a/b ratio and the electrolyte.

As a consequence of the chlorine bubbles of 1~2 mm in diameter, one finds a relatively small voltage drop through the electrolyte up to 18 mV, experimentally.

By expressing the influence of these factors by dt , the time of the chlorine retained in bubble form in a volume element in the cell, we obtain the relationship:

$$dt = \frac{N_{Cl} \cdot dX_{Cl}}{I_s V} \quad (2)$$

in which

N_{Cl} is the number of moles of the dissolved chlorine in the electrolyte

X_{Cl} is the conversion degree of the chlorine into the bubble form

I_s is the speed of the dissolution process of chlorine evolved at the electrode

V volume unit of electrolyte

The voltage drop through the electrolyte, as a consequence of the filling degree X and of the size of the chlorine bubbles as a function of the constructive ratio a/b from the present work, is shown in Fig. 6.

Fig. 6 Dependency of the IR-drops in the electrolytic medium on the filling degree X and dimension of chlorine bubbles versus the constructive factor a/b 9, 16, 21, 27, 28 and 40 cell number taken into the experiment

4 Cathodic Potential

With increase in the sodium concentration in the amalgam the linear variation of the cathodic potential versus the effective length, and the constructive ratio a/b was obtained. The value of the potential in the vicinity of the electrode with the low sodium content in the amalgam, which is of industrial, is given by equation 3

$$e_{Na^+} = e^0 + \frac{RT}{F} \ln \frac{a_{Na^+}}{a_{Na-Hg}} \quad (3)$$

in which

e^0 is the standard potential, a_i the activity of species i .

Fig. 7 Variation of the cathodic potential as a function of the sodium content of the amalgam versus the constructive factor a/b 9, 16, 21, 27, 28 and 40 cell number taken into the experiment

In the practical cells the activity is very difficult to determine.

Error involved in the concentration instead of the activities, is not serious. In the experimental conditions, the potential difference between the inlet and outlet of the cell as a function of the sodium content of the amalgam took values between 5.87 and 29.4 mV as shown in Fig. 7.

The difference between the Na content in the bulk of the amalgam and the Na content at the amalgam—electrolyte interface (as resulting from the interpretation of the data in Table 1) shifts the value of the cathodic potential towards a more negative value, the limit of this additional voltage drop is of 61.87 mV which is 13.7% of the total measured voltage drop.

5 Anodic Potential

The anodic potential, up to the solubility limit of the chlorine in the electrolyte obtained from the undertaken experiments, does not depend on the constructive form of the cell. In the zone I shown in Fig. 8, the electrochemical polarization and the concentration polarization remain practically constant. The evolution of chlorine bubbles in the interpolar space takes place above the solubility limit and the forma-

Fig. 8 Variation of the anodic potential versus constructive factor a/b 9, 16, 21, 27, 28 and 40 cell number taken into the experiments

tion of a chlorine-electrolyte mixture at the electrode surface gives an unfavourable effect which displaces the value of the anodic potential to more positive values.

This effect differs by density, conductivity, viscosity, flowing regime, and other continually changing features of the electrolyte.

One recognizes thus the existence of a potential step in zone II which is probably due to the formation of the chlorine bubble in the interpolar space. We obtain values between 125 mV (cell 28) and 245 mV (cell 27) as shown in Fig. 8 for the anode potential from the difference between the total voltage drop, measured versus the constructive factor a/b , and sum of the voltage drop through the electrolyte and the cathode potential.

6 Conclusions

The electrode potential and the IR-drops in a horizontal amalgam-type chlorine cell depend also on the constructive form of the cell, besides the known factors²⁾⁻⁹⁾.

In the given working conditions, the conductivity of the studies medium proves to be practically constant up to the solubility limit of chlorine in the electrolyte, and decreasing above this limit as a consequence of the degree of filling with chlorine bubbles and of the other continuous changing features, versus the constructive factor a/b .

The overvoltage expenditure, in practical cells depends on the constructive, technologic and hydrodynamic conditions in which the process takes place.

The knowledge of the influence of the constructive factors on the energy expenditure makes the optimisation of the process possible by the choice, in given working conditions, of an adequate a/b constructive ratio.

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