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METHOD OF ADJUSTING INDIVIDUAL ANODES IN A MERCURY CATHODE CELL

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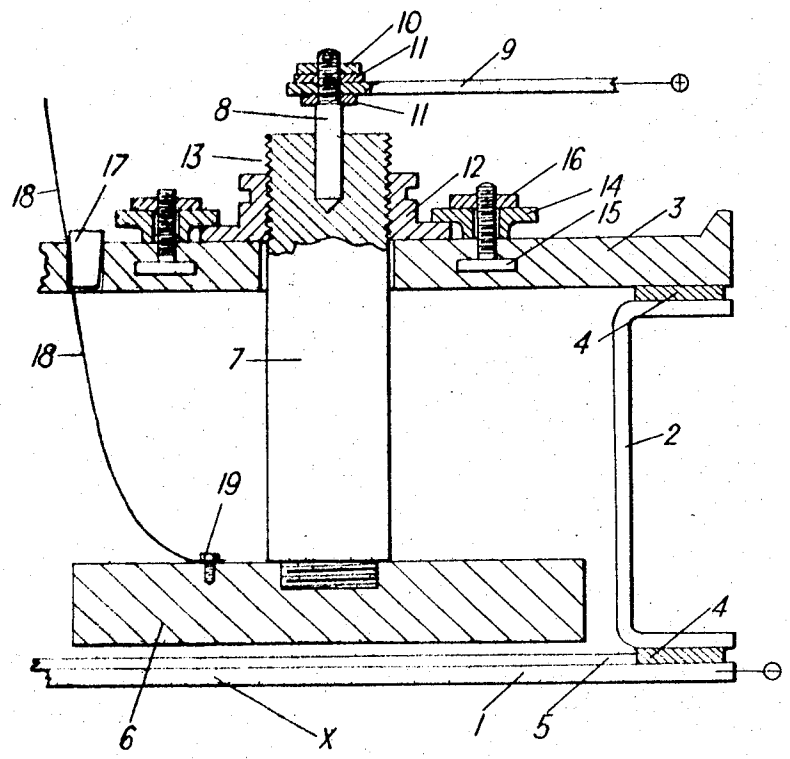

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METHOD OF ADJUSTING INDIVIDUAL ANODES IN A MERCURY CATHODE CELL

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ABSTRACT OF THE DISCLOSURE

There is provided a method of accurately adjusting the gap between the anode and cathode of a mercury cell useful for producing chlorine by electrolysis of alkali metal chloride solutions. The electrical conductance across the electrolyte gap between the anode and cathode is measured and the gap adjusted until the conductance is brought to a predetermined value, e.g. 5000–18,000 mho/m.^{2} of cathode surface. Each anode-cathode gap in the cell is individually adjusted, preferably by use of a probe attached to the anode plate which measures the voltage drop across the electrolyte gap, and from which measured voltage drop is substrated the reversible cell potential and chlorine overvoltage. The so corrected voltage is then related to the current flowing to the anode to obtain a conductance across the electrolyte gap in terms of mho/m.^{2} of cathode surface.

The present invention relates to a process of electrolysis, and more particularly to an improved process for the electrolysis of alkali metal chloride solution in a cell having a flowing mercury cathode.

Cells for the manufacture of chlorine by the electrolysis of alkali metal chloride solutions having a flowing mercury cathode and suspended above the cathode and spaced therefrom in the electrolyte a plurality of solid anodes are widely used in industry. Because there is no diaphragm in this type of cell between the anodes and the cathode it is theoretically possible to bring the anodes and the cathode very close together, and this is very desirable since the consumption of energy in driving the electrolysing current through the resistance of the electrolyte gap reduces the energy efficiency of electrolysis and results only in a heating effect. Every effort in therefore made to adjust the anode-cathode gap to the minimum commensurate with high current efficiency and the avoidance of damage to the anodes.

The anodes may for instance consist of graphite plates or of sheet titanium supports having a platinum metal anode coating, with their underfaces substantially parallel to the mercury cathode. If the gap between an anode and the cathode is too narrow, the current efficiency of electrolysis will be reduced excessively by reaction of chlorine with sodium in the cathode amalgam. Shorting may also occur, causing overheating of the anode and, in the case of titanium-supported anodes, causing severe damage to the platinum-metal coating.

Apart from the desirability of working the cell with an anode-cathode gap close to the allowable minimum, it is found to be of overriding importance in a multi-anode cell to have each anode set accurately to the same anode-cathode gap if the maximum energy efficiency is to be attained. Variations of a fraction of a millimetre between the settings of individual anodes are sufficient to upset the current distribution in the cell and hence to reduce the energy efficiency. Prior art methods of adjustment are not capable of giving reliably the uniform

setting that is needed. One method that has been used for instance with graphite anodes is to lower each one until shorting to the cathode occurs and then to raise the anode a predetermined distance. Apart from the fact that shorting is undesirable, the exact moment of shorting is difficult to determine with reproducibility for each anode. Another method has been to lower the anodes to the baseplate and then raise them a predetermined distance with the cell off load. The accuracy of this method depends, however, on an estimation of the thickness of the mercury cathode during electrolysis.

We have now found that the gap between the anode and the cathode of a mercury cell producing chlorine by the electrolysis of alkali metal chloride solution can be adjusted with great accuracy and reproducibility by measuring the electrical resistance or conductance of the electrolyte gap between the anode and the cathode of the working cell and setting the position of the anode with respect to the cathode so that this resistance or conductance is brought to a predetermined value. We have furthermore found that a multianode mercury cell can be operated at surprisingly high energy efficiency by adjusting the electrolyte gap between each anode and the cathode so that these gaps all have the same electrical resistance or conductance.

According to the present invention, a method of setting an anode in accurately-spaced relationship to the cathode surface of the mercury cathode cell producing chlorine by electrolysis of alkali metal chloride solution comprises measuring the electrical conductance across the electrolyte gap between the said anode and the cathode of the working cell and adjusting the spacing of the anode from the cathode surface so that the said conductance is brought to a predetermined value.

According to a preferred embodiment, the present invention provides a method of operating at high energy efficiency a multianode mercury cathode cell producing chlorine by electrolysis of alkali metal chloride solution which comprises setting each anode in accurately-spaced relationship to the cathode surface by the method described in the preceding paragraph, the predetermined electrolyte gap conductance employed being the same for each anode.

It should be understood that although the present invention provides a method of adjusting an electrolyte gap accurately by setting to a selected conductance value and it is obviously desirable to work the cell at the conductance corresponding to the optimum gap, nevertheless the invention is most valuable in enabling all the anodes in a multi-anode cell to be set to substantially the same electrolyte gap whether or not this gap is exactly the optimum, since such uniform setting has been found to be the most important factor in obtaining the best current distribution between the anodes and hence a high current efficiency.

It will be understood that the conductivity of the aqueous electrolyte in the anode-cathode gap of a working cell varies to some extent with electrolyte concentration, temperature and the effect of the chlorine gas bubble film, the last-mentioned effect being largely a function of anode design. Furthermore it can be determined by varying the gap between the anodes and the cathode of a working cell that the optimum gap with respect to energy and current efficiency and hence the resistance of the gap varies somewhat inversely with respect to electrolysing current density. The conductance to which the anode-cathode gap or gaps should be set for best results will therefore depend on these factors collectively. We have found that in general in mercury cells electrolysing sodium chloride solution the optimum conductance lies in the range 5,000–18,000 ohms per m.^{2}

(5,000–18,000 reciprocal ohms per m.²) of cathode surface, where the said cathode surface is calculated as the cathode surface associated with each anode by dividing the total cathode surface by the number of anodes in the cell. For instance in a typical multi-anode cell electrolysing sodium chloride brine of initial concentration 25.5% and final concentration 17.5% by weight NaCl at 50° C. the optimum electrolyte gap conductance was found to average 7,000 mho/m.² of cathode surface at a cathodic current density of 3 ka./m.² and 8,600 mho/m.² of cathode surface at a cathodic current density of 6 ka./m.². In a cell operating under the same "waste brine" conditions at a cathodic current density of 7 ka./m.² the optimum electrolyte gap conductance ranged from 7,000 to 10,000 mho/m.² of cathode surface, depending on the age of the graphite anodes.

In order to measure the electrical conductance of an anode-cathode gap in a working cell it is necessary to determine the voltage drop due to the electrolysing current passing through this resistance and to relate this voltage drop to the electrolysing current. The voltage drop across the resistance alone cannot be measured directly since it is associated with and inseparable from the reversible cell potential between anode and cathode and the chlorine overvoltage. The reversible cell potential and over-voltage can however be calculate from known data for any given temperature and concentration of electrolyte and cathode amalgam, so that the voltage drop across the ohmic resistance of the electrolyte can be obtained by subtraction from a measured value. In a long multi-anode cell with flowing mercury cathode and flowing electrolyte there will be some variation of reversible cell potential between the different anodes and the cathode with change in amalgam concentration and electrolyte concentration along the cell and if desired this variation can be allowed for in calculating by difference the voltage drop across the ohmic resistance of the electrolyte gap for anodes at different positions along the cell. We have found however that in practice such allowance for these small variations is unnecessary and that excellent results can be obtained by using the same average figure for the reversible cell potential for all anodes in a multi-anode cell.

In making the measurement of voltage between anode and cathode it is undesirable to have measuring probes present in the narrow gap itself. We prefer therefore to connect one measuring probe to the cathodic baseplate in the neighborhood of the anode of the cell and to connect the other probe to a terminal, which may suitably be of titanium, at the upper surface of the anode plate. The voltage drop due to the electrolysing current passing through the anode plate, cathode film and cell baseplate are very small and can in practice be ignored. If a lower order of accuracy can be tolerated in measuring the voltage drop across the electrolyte gap, the probe attached to the anode plate may be omitted and the voltage measurement may be made between the cell baseplate and a point on the anode connector outside the cell, and the ohmic potential drop due to the electrolysing current flowing in the anode connector structure may be subtracted from this measured value in order to arrive at the voltage drop across the electrolyte gap. This method suffers, however, from the disadvantage that the ohmic potential drop is not likely to be exactly the same for each anode connector structure of a multi-anode cell and it is also likely to vary with the passage of time for any one anode connector structure, so that some inaccuracy in calculating the voltage drop across the electrolyte gap is almost certain to arise.

In order to avoid errors due to contact resistance and ohmic resistance in the voltage and current measuring circuits connecting measuring instruments to the cell electrodes it is important to employ a "null" method of measurement wherein there is no flow of measuring currents when the readings are taken. A very suitable instrument for the purpose is the resistance measuring apparatus of our copending application No. 32,850/64. As described in the specification of the said copending application, arrangements can be made with this instrument to subtract automatically from an anode-cathode probe voltage a voltage equal to the sum of the reversible cell potential and the chlorine overvoltage. The instrument then reads resistance of the anode-cathode gap directly by dividing the residual voltage by a factor proportional to the current flowing through the bus-bar to the individual anode. It will be understood that the measuring scale of the instrument may be calibrated in the reciprocals of resistance so as to read conductance directly if desired.

The invention is further illustrated by reference to the accompanying drawing, which shows in diagrammatic vertical section (not to scale) a portion of an electrolytic cell having a flowing mercury cathode, with a voltage probe attached to an anode.

In the drawing, **1** is the baseplate, which is connected to the negative pole of the electrolysing current source, **2** is a side wall and **3** is the cover of the cell. The junctions between these parts are sealed by gaskets **4**. **5** is a flowing mercury cathode in contact with the metal baseplate. The cell will usually have several anodes, which are required to be equally spaced from the cathode, but in the part cell shown in the drawing only one of the anodes is shown by way of illustration. The anode assembly comprises a main anode block **6**, suitably of graphite, a graphite shaft or tup **7** screwed into the anode block and passing through the cell cover, and a copper core **8**, which is force-fitted into a bore in the upper end of the shaft **7** and to which an electrical connection is made from the positive pole of the electrolysing current source by copper bus-bar **9**, which is attached to the threaded upper end of copper core **8** by means of nut **10** and washers **11**. A flanged screw adjuster **12** rests on the cell cover and surrounds the shaft **7**. The screw adjuster is provided with an internal screw thread which engages a screw thread **13** on the upper end of the shaft **7** and thereby supports the anode assembly. Flanged retainers **14** are held on the cell cover by bolts **15** embedded in the cell cover and nuts **16** so that the flanges of the retainers engage the flange of the screw adjuster **12** and locate the adjuster correctly on the cell cover. By rotation of screw adjuster **12** with respect to shaft **7** the anode assembly can be raised or lowered so as to obtain a desired gap between the lower face of the anode block **6** and the upper surface of the flowing mercury cathode **5**. **17** is a bung of resilient material closing a hole in the cell cover through which passes a titanium wire **18** which makes electrical connection with the upper surface of anode block **6** through a titanium terminal screw **19**. In order to measure the conductance of the electrolyte gap between the anode block **6** and the cathode **5** a second terminal connection is provided on the edge of the baseplate nearest the anode and opposite the position marked X on the drawing. When the cell is under load the potential difference between the two terminals can be related to the current flowing to the anode through bus-bar **9**, using for example the instrument of the said copending application and allowing for the known reversible cell voltage and the chlorine overvoltage, so that the conductance of the electrolyte gap is measured. By raising or lowering the anode by means of screw adjuster **12** the required conductance and hence the required electrolyte gap for optimum working can be obtained.

What I claim is:

1. A method of operating at high energy efficiency a multi-anode mercury cathode cell producing chlorine by electrolysis of alkali metal chloride solution which comprises measuring the electrical conductace across the electrolyte gap between each anode and the cathode of the working cell by measuring the voltage drop between a probe attached to the anode plate and the cathodic baseplate of the cell, subtracting from this measurement the calculated value of the reversible cell potential between

anode and cathode and the chlorine overvoltage and relating the residual voltage drop thereby obtained to the measured current flowing to the anode and adjusting the spacing of each anode from the cathode surface so that the said conductance is brought to a predetermined value.

2. A method according to claim 1 wherein the predetermined value of electrolyte gap conductance lies in the range 5,000–18,000 mho/m.^{2} of cathode surface when the said cathode surface is calculated as the cathode surface associated with each anode by dividing the total cathode surface of the cell by the number of anodes in the cell.

3. A method according to claim 1, wherein the predetermined value of electrolyte gap conductance lies in the range 7,000–10,000 mho/m.^{2} of cathode surface.

4. The method of claim 1 wherein said cell contains

a plurality of anodes connected in an electrical parallel manner.

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