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MANUFACTURE OF CHLORINE AND CAUSTIC ALKALI IN DIAPHRAGM CELLS

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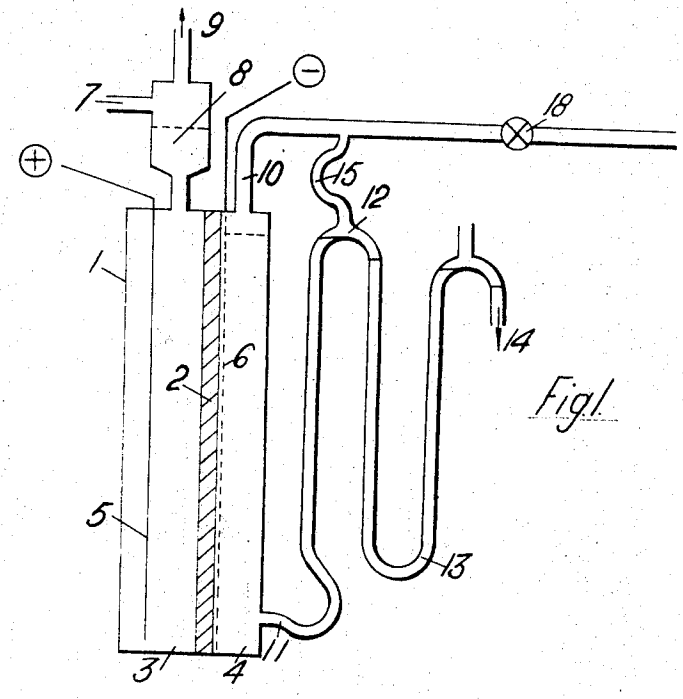

Fig 1

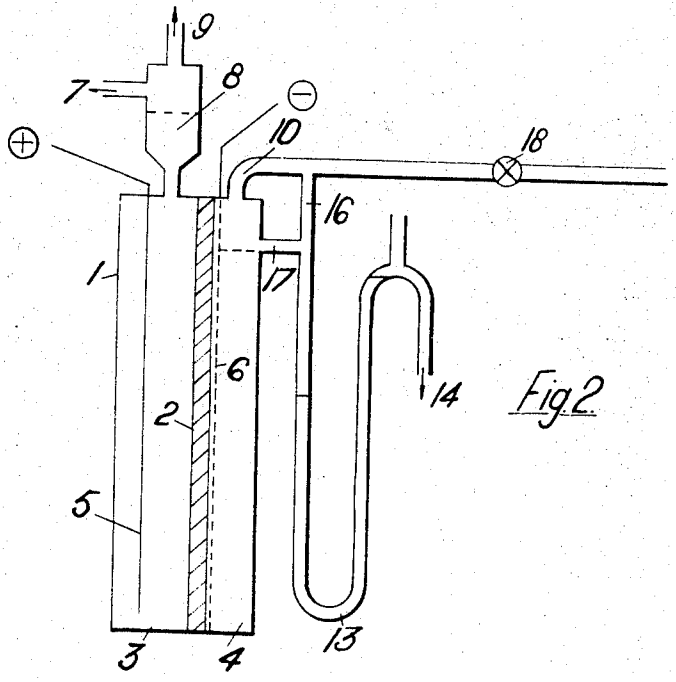

Fig 2

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MANUFACTURE OF CHLORINE AND CAUSTIC ALKALI IN DIAPHRAGM CELLS

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ABSTRACT OF THE DISCLOSURE

Varying electrical loads may be handled during the continuous operation of a chlor-alkali cell which has a percolating asbestos diaphragm by rapidly making changes in the rate of flow of electrolyte through the diaphragm by altering the gas pressure on the anode compartment or cathode compartment each time the current density across the diaphragm is changed. The rate of electrolyte flow is always approximately proportional to the current density.

The present invention relates to the manufacture of chlorine and caustic alkali in diaphragm cells. More particularly it relates to a method of operating cells with percolating asbestos diaphragms under varying electrical load conditions.

Industrial installations of electrolytic cells of various types consume very large quantities of electrical energy so that these installations contribute very significantly to the total energy demand of any highly industrialised country. In order to discourage use of electrical energy at times of peak demand by other consumers, for example domestic consumers, industry is usually penalized by a higher price for energy taken at these times and it has therefore become the custom for industry to practice what is usually termed "load-shedding" wherever possible so as to reduce the use of electrical energy during the part of the day when the cost per unit of energy is high.

Most electrolytic processes cannot be shut down completely without introducing unacceptable troubles, but in some types of cell, for instance in mercury-cathode cells for the electrolysis of brine, the load can be severely reduced when desired and can later be restored to normal without serious effect on the equipment or products. However, when operating cells with percolating asbestos diaphragms between the anodes and the cathodes for the electrolysis of brine, it has heretofore been considered that once steady operating conditions have been reached the current density must be maintained substantially constant throughout the life of the diaphragms in order to avoid chemical changes in the diaphragms which lead to a catastrophic reduction in permeability and consequently to a seriously reduced life. Any load-shedding practised on diaphragm cells has therefore been restricted to very minor proportions and has not been able to affect very significantly the overall factory load.

We have now found that cells with percolating asbestos diaphragms can be operated at current densities varying over at least a ten-fold range without noticeable damage to the diaphragms if the percolation rate through the diaphragms is maintained approximately proportional to the current density by changing the percolation rate rapidly to the new required value each time the current density is changed. We have found that by operating in this way severe load-shedding may be practised and the cells may afterwards be returned to the original high percolation

rate at the original current density without increasing the hydrostatic pressure across the diaphragms. We have furthermore found that the necessary rapid change in percolation rate can be attained by altering the gas pressure on the anode compartment, the cathode compartment or both compartments when the current density is changed.

According to the present invention therefore we provide an advantageous method for the operation under conditions of varying electrical load of a chlor-alkali electrolysis cell which incorporates a percolating asbestos diaphragm, this method comprising rapidly making such change in the rate of flow of electrolyte through the diaphragm by altering the gas pressure on at least one of the anode compartment and the cathode compartment of the cell each time the current density across the diaphragm is changed that the rate of electrolyte flow is always approximately proportional to the current density. The speed of the adjustment of the electrolyte flow to its appropriate new value is of the essence of the invention.

Usually it will be more convenient to alter the pressure on only the anode compartment or the cathode compartment rather than on both. To exercise control by changing the pressure on the anode side one can for example arrange to work the cell with an adequate pressure on the chlorine off-take at maximum current density so that the chlorine pressure can be appropriately reduced when the current density is reduced. Since, however, it is generally undesirable to hold a large volume of chlorine under excess pressure we prefer to control the pressure on the cathode side of the diaphragm by increasing the back-pressure on the cathode compartment when the current density is reduced and returning to the normal working pressure when full-load conditions are restored.

Two suitable arrangements of apparatus for carrying out the method of the invention by rapidly changing the gas pressure on the cathode side of the diaphragm each time the current density is changed are illustrated in the diagrammatic drawings (not to scale), which each illustrates a sectional elevation seen along the line of the diaphragm in a single cell together with pressure-control means, like parts being numbered alike in the two figures.

In the two figures, **1** represents the outer casing of a unit cell which is divided by asbestos diaphragm **2** into an anode compartment **3** and a cathode compartment **4**. The anode is indicated as **5** and the foraminate cathode **6** is set close to the diaphragm. Brine is fed to the anode compartment at a steady rate through pipe **7** to maintain a level of brine as shown in the head tank **8**. **9** is an outlet for chlorine liberated in the anode compartment and **10** is an outlet for hydrogen produced in the cathode compartment.

Referring now to FIG. 1, the outlet for caustic liquor from the cathode compartment is connected towards the bottom of the compartment as shown at **11** and the caustic liquor is delivered by way of a swan-neck **12** and a lute **13** to the delivery pipe at **14**. The swan-neck **12** is connected by a flexible pipe **15** to the hydrogen outlet **10** and the connection at **11** is also made flexible so that the whole swan-neck and accompanying lute can be raised and lowered when desired. This arrangement is most useful when it is desired to have the facility for lowering the liquor level in the cathode compartment gradually during the life of the diaphragm to compensate for the normal slow decrease in diaphragm permeability with age, since these small adjustments of cathode liquor level can be made from time to time as appropriate by lowering the whole swan-neck and accompanying lute. In order to be able to increase the back-pressure quickly on the cathode compartment under load-shedding conditions a pressure-control valve **18** is inserted in the hydrogen delivery pipe. On closing this valve to the required extent

the gas pressure on top of the cathode compartment is increased and the level of liquor in the inner limb of the lute **13** is depressed, thus giving an indication of the amount of pressure applied to the cathode compartment.

The arrangement of FIG. 2 is suitable when it is not desired to be able to change the level of liquor in the cathode compartment. In this case the lute **13** is connected directly to the hydrogen line as shown at **16** and also to the cathode compartment at the normal liquor level as shown at **17**. On closing the pressure-control valve **18** to the required extent an increased back-pressure is applied to the gas space in the cathode compartment and is indicated by depression of the liquor in the inner limb of the lute.

With either of the arrangements illustrated the feed of brine to the head tank **8** must also be adjusted to match the new current density or overflow means must be provided so that the head of liquor in tank **8** remains at approximately the same level when the current density and the back-pressure on the cathode compartment are altered. Furthermore, when it is desired to operate a cell with very severe load-shedding, e.g., 90% reduction in electrical load, it is preferred to arrange for the diaphragm to be completely submerged in the catholyte and in fact to have a few centimetres head of caustic liquor above the top edge of the diaphragm, rather than to have part of the diaphragm exposed as in the schematic arrangements of the drawings. The necessary substantial increase in back pressure can then be applied to the cathode compartment without any danger of forcing hydrogen through the diaphragm from the gas space above the catholyte into the anode compartment.

Very accurate control of the rate of flow of liquor through the cell diaphragm can be achieved if desired by metering the caustic liquor delivery rate or its alkalinity and adjusting the back-pressure on the cathode compartment to bring the delivery rate to the new value or to maintain the alkalinity substantially constant each time the current density is changed. We have found, however, that although the flow of liquor through the diaphragm is not directly proportional to the pressure difference across it, for practical purposes it is quite satisfactory to work the invention by adjusting the pressure difference across the diaphragm so as to be proportional to current density. Although the electrolyte flow rate is not then exactly proportional to current density at all times, the error introduced by working in this way is generally acceptable.

If desired it may be arranged for the back-pressure on the cathode compartment to be controlled automatically when the current density is changed. This can be achieved by operating the control valve by a servo-motor which is fed with a voltage proportional to the electrolyzing current and with an opposing voltage related to the position of the control valve so that whenever there is an error between these two voltages the control valve is moved to a new position until the error is brought to zero. The control valve servo-system may be calibrated to operate on the principle of maintaining the differential pressure across the diaphragm proportional to current density or, if desired, it may be operated in terms of the more accurate parameter of electrolyte flow rate by continuously metering the caustic liquor flow rate by automatic means and feeding this metered data to the servo-system which controls the valve in the hydrogen line. Another alternative is to have the pressure-control valve automatically operated by a servo-system which is responsive to changes in the alkalinity of the caustic liquor produced in the cell, so as to maintain this alkalinity substantially constant. With this arrangement, a slow change or a stepwise change in the alkalinity reference point can be built in to allow for the normal changes in diaphragm percolation rate with ageing.

The invention is further illustrated by the following experimental data obtained on a laboratory-scale cell fitted with a chrysotile asbestos diaphragm and continuously electrolysing a feed brine containing 315 g.p.l. sodium chloride at approximately 80° C. The full-load current was 2 ka./m.^{2} of diaphragm area.

The cell was operated with the electrical load reduced to 34% (66% load-shedding) for 4.5 hours a day on five consecutive days each week up to the twenty-second day shown in the table and thereafter with 90% load-shedding for 4.5 hours a day. Load-shedding was carried out in the manner of the invention by rapidly applying additional back-pressure to the cathode compartment by adjusting a control valve on the hydrogen outlet to show the required depression in a lute connected to the cathode compartment, as in FIG. 1 of the drawings accompanying the Provisional Specification, when the current density was reduced, while keeping a constant head of brine on the anode compartment.

The figures shown in the table are flow rates measured at times when the cell was on full load divided by the effective head of brine across the diaphragm. It will be seen that the permeability of the diaphragm was substantially unchanged during the period of the test.

Day No.	Flow rate/effective brine head (ml./hr./cm.)	Day No.	Flow rate/effective brine head (ml./hr./cm.)
1	36.3	15	39.2
3	40.0	17	37.8
5	41.8	19	38.1
7	38.0	21	37.8
9	37.8	23	37.1
11	40.9	24	36.9
13	44.7	25	37.5

What we claim is:

1. A method for the operation under conditions of varying electrical load of a chlor-alkali cell which incorporates a percolating asbestos diaphragm, which is characterised by rapidly making such change in the rate of flow of electrolyte through the diaphragm by altering the gas pressure on at least one of the anode compartment and the cathode compartment of the cell each time the current density across the diaphragm is changed that the rate of electrolyte flow is always approximately proportional to the current density.

2. A method according to claim **1**, wherein the rate of flow of electrolyte through the diaphragm is rapidly changed each time the current density is changed by altering the gas pressure on the cathode compartment of the cell by means of a pressure-control valve in the hydrogen exit pipe.

3. A method according to claim **2**, wherein the rate of flow of electrolyte through the diaphragm is changed each time the current density is changed so that the alkalinity of the caustic liquor leaving the cell is maintained substantially constant.

4. A method according to claim **3**, wherein the pressure-control valve is automatically adjusted by means of a servo-system responsive to changes in the alkalinity of the caustic liquor leaving the cell.

5. A method according to claim **2**, wherein the rate of electrolyte flow is maintained approximately proportional to the current density by rapidly adjusting the differential pressure across the diaphragm each time the current density is changed so as to maintain the said differential pressure proportional to the current density.

6. A method according to claim **5**, wherein the pressure-control valve is automatically adjusted by means of a servo-system responsive to the cell current density and the differential pressure across the cell diaphragm.

7. A method according to claim 2, wherein the rate of flow of electrolyte through the diaphragm is measured by metering the rate of flow of the caustic liquor leaving the cell and the said rate of flow of caustic liquor is maintained approximately proportional to the current density.

8. A method according to claim 7, wherein the pressure-control valve is automatically adjusted by means of a servo-system responsive to the cell current density and the metered rate of flow of the caustic liquor leaving the cell.

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