

Sept. 2, 1969

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OF ALKALI CHLORIDES

3,464,910

Filed June 14, 1965

4 Sheets-Sheet 1

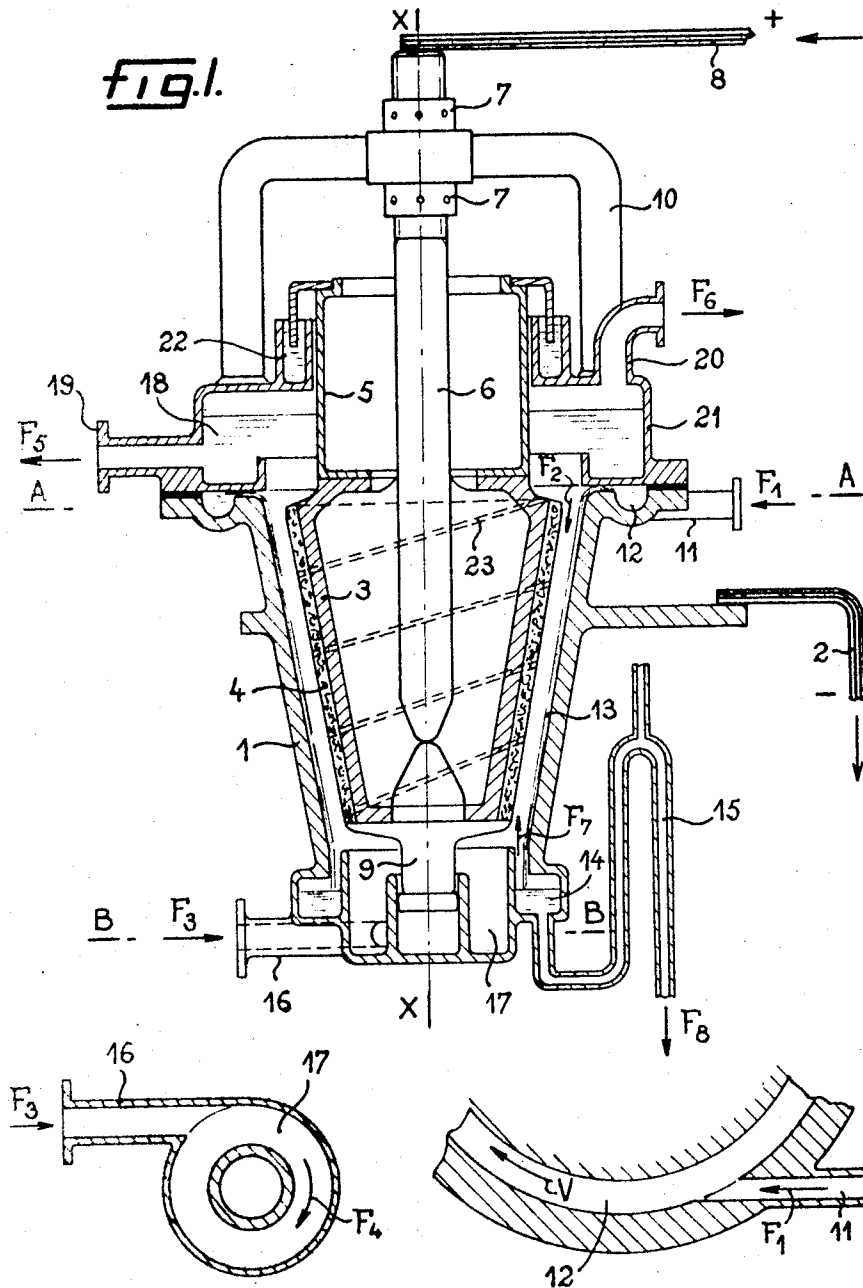


fig.2

fig.3

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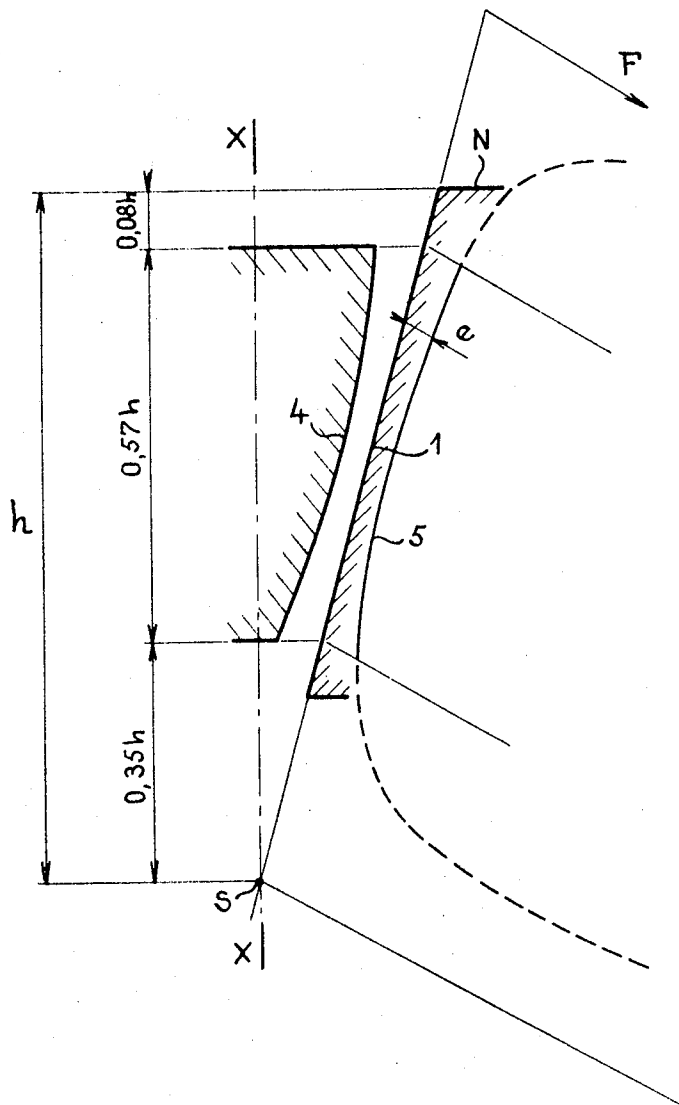


fig. 4

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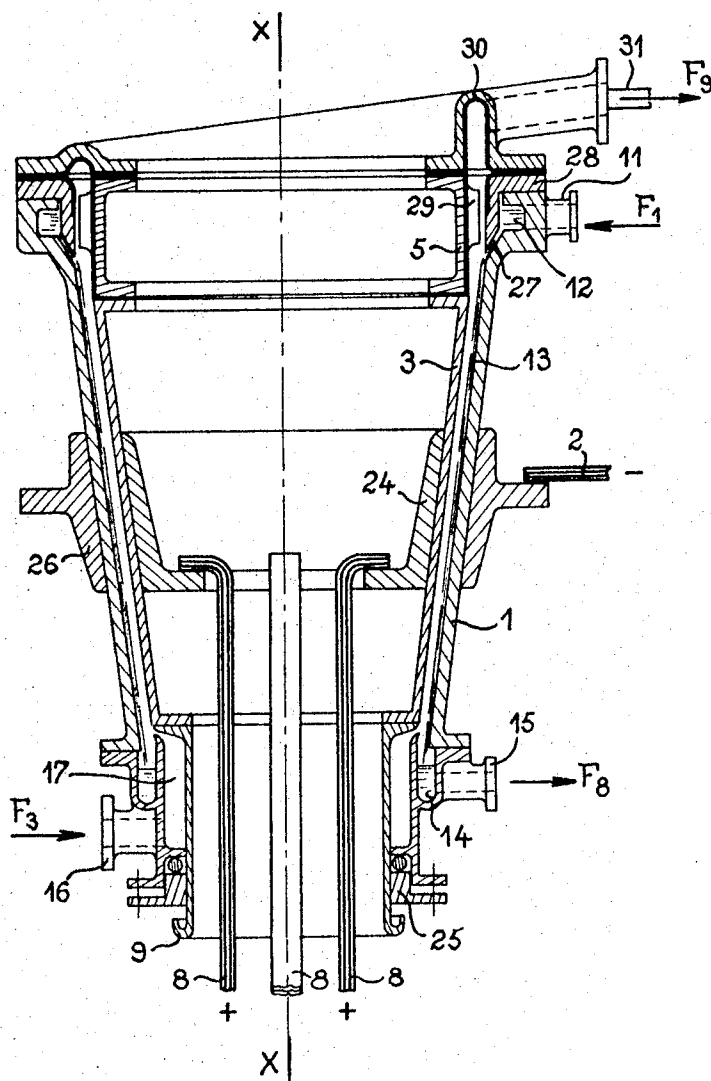


fig. 5

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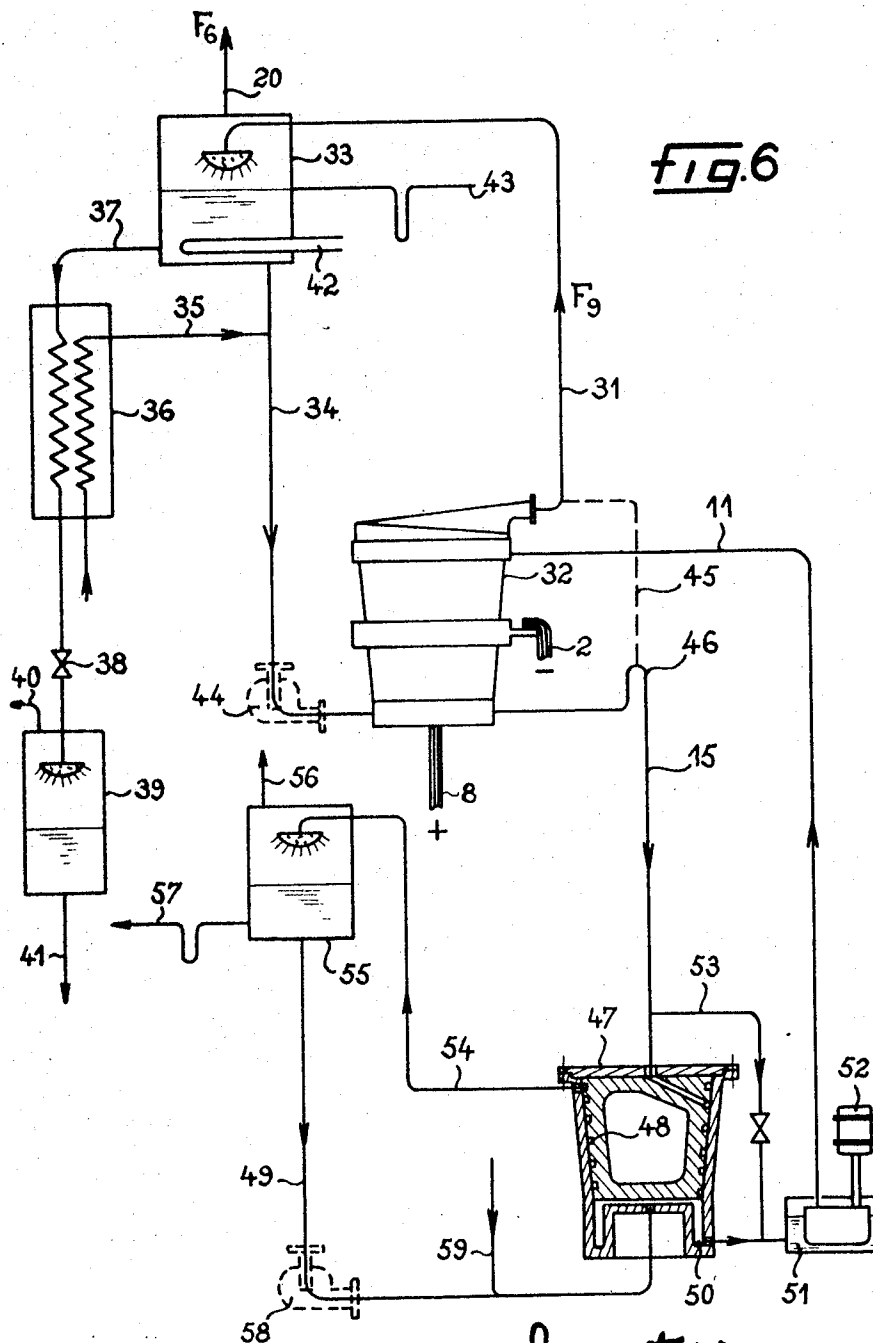


Fig. 6

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AQUEOUS ELECTROLYSIS CELL FOR SALINE SOLUTIONS, ESPECIALLY OF ALKALI CHLORIDES

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Filed June 14, 1965, Ser. No. 463,642
Claims priority, application France, June 15, 1964, 978,330

Int. Cl. B01k 3/04
U.S. Cl. 204—219 13 Claims

ABSTRACT OF THE DISCLOSURE

A device in an installation for electrolysis of saline solutions utilizing a film of mercury introduced tangentially and flowing over the cathode where cathode and anode are coaxially located to each other forming a slanting frustoconical form and a brine solution is introduced with a tangential speed rotating in the same direction as the mercury.

The present invention relates to electrolysis cells for saline solutions (and in particular the aqueous electrolysis of alkali chlorides) in which the electrode surfaces are coaxial surfaces of revolution with a vertical axis.

One of the most usual devices employed for the aqueous electrolysis of alkali chlorides utilizes as a cathode a sheet of mercury flowing slowly over a very slightly inclined plane. The anode is composed of graphite plates brought close to the cathode. The saline solution to be electrolyzed, hereinafter known as brine, flows slowly between the two electrodes, in the same direction as the mercury. Under the action of the electric current, chlorine is liberated at the anode and rises towards the cover of the cell through spaces between the anode plates and passages formed in the plates themselves, while the alkali metal is discharged on the cathode, forming the corresponding amalgam with the mercury. This amalgam is sent into the decomposer supplied with pure water, and reacts with the latter to produce on the one hand hydrogen and on the other the caustic alkali dissolved in water. The metallic mercury thus regenerated returns to the electrolytic cell.

Cells of this design necessitate an absolutely flat mounting of the cathode surface, enabling this surface to be completely covered with mercury and ensuring the uniform flow of the mercury in a layer having a thickness as small as possible. In fact, the volume of mercury in circulation represents a considerable capital outlay and must be reduced to the strictest possible limits. In addition, by reason of the construction of this cell, the bubbles of chlorine formed at the anode are only liberated with difficulty. This results in a reduction of the section of the electrolyte and of the active surface of the anode and in consequence a limitation of the permissible specific load on the anode. A cell intended to produce a given quantity of chlorine thus necessitates a large anode surface and in consequence a corresponding large bulk.

The present invention relates to an electrolytic cell which eliminates these drawbacks.

The cell in accordance with the present invention is essentially characterized by the fact that its electrode surfaces are coaxial surfaces of revolution with a vertical axis, the cathode serving as a support for the flow of the mercury.

This well-defined geometric shape affords numerous advantages and in particular it facilitates the assembly.

The invention also relates to the complete installation formed by an aqueous electrolysis cell and its accessories.

Other characteristic features and advantages of the present invention will be brought out in the description which follows below, prepared with reference to the accompanying drawings, and giving by way of explanation various forms of application of the invention.

In this description, only a solution of sodium chloride is employed, but it will be understood that this choice is in no way limitative.

In the drawings:

FIG. 1 shows in vertical section taken along a plane passing through the axis of revolution, an electrolytic cell in accordance with the invention, working at a pressure of the order of atmospheric pressure;

FIGS. 2 and 3 are cross-sections taken respectively along the lines B—B and A—A of FIG. 1;

FIG. 4 shows in a purely diagrammatic manner, in cross-section taken along the plane passing through the axis of revolution, a particularly advantageous form of construction of the anode-cathode assembly of a cell according to the invention. This anode-cathode assembly can be suitable for a cell of the type shown in FIG. 1; in FIG. 4, there is also shown (represented for greater clearness after folding back in the direction of the arrow F about the centre line of the cathode) the layer of mercury which flows over the wall of the cathode;

FIG. 5 shows in vertical section, along a plane passing through the axis of revolution, a further form of construction of an electrolytic cell according to the invention; as distinct from the cell of FIG. 1, it operates under high pressure; and finally

FIG. 6 shows diagrammatically a view in elevation of a complete installation of an electrolytic cell according to the invention with its various accessories.

In FIG. 1, the cathode 1 of the electrolysis cell according to the invention has the shape of a straight truncated cone. It is made for example of steel; the current departure is effected by a conductor 2. The anode 3, also in the form of a cone but of smaller dimensions, is coated with graphite (reference 4); the current is led-in by a conductor 8, connected on the central rod 6, the longitudinal axis X—X of which is the axis of revolution of the whole of the cell. The anode is suspended in the interior of the cathode 1 by a frame 10. Nuts 7 permit its vertical position to be regulated with respect to the cathode. The anode 3 is guided at its lower portion by a rod 9, so that the two electrodes are perfectly coaxial.

The mercury comes in through a conduit 11 and enters tangentially (arrow F₁, FIGS. 1 and 3) into the annular space 12 from which it overflows onto the cathode 1 (arrow F₂) and covers it completely.

At the bottom the cell, the amalgam formed by the mercury and the alkali metal of the chloride to be electrolyzed is collected in an annular space 14 and is evacuated by a siphon 15 (arrow F₃) intended to counterbalance the column of brine in the cell.

The rich saline solution to be electrolyzed, or brine, comes into the bottom of the cell through a conduit 16 (arrow F₄) and acquires a movement of rotation (arrow F₄) in the annular space 17, in the same direction as the mercury in the space 12. It then rises in the annular space between the film of mercury 13 on the cathode and the graphite 4 of the anode. Part of the sodium chloride contained in the brine is decomposed by the electric current. The weakened brine 18 passes out of the apparatus through a conduit 19 (F₅) and returns to the saturation installation (not shown on FIG. 1).

The gaseous chlorine is separated from the brine in the cover 21 and directed by a conduit 20 (arrow F₆) to the washing and drying installation (not shown in FIG. 1). A hydraulic joint 22 ensures fluid-tightness between the cover 21 and the upper extension 5 of the anode 3.

The design of the electrolysis cell according to the invention offers the following advantages: this cell utilizes anode and cathode surfaces which are perfectly defined and easy to construct, irrespective of the central section which it is desired to give to the space comprised between the two electrodes.

The thickness of the film of mercury which flows over the cathode 1 may be very small. The downward movement of the mercury under the combined effect of gravity and the tangential speed (FIG. 3) which it possesses before overflowing from the space 12 ensures the good distribution of this mercury even in the event of an imperfect assembly or damage to the substructure.

The space between the electrodes 1 and 3 can be easily regulated by lifting or lowering the anode 3. It is thus possible to reduce the distance between these electrodes to a strict minimum and thus to reduce the losses of energy due to the resistance of the electrolyte.

The chlorine produced by the electrolyte rises easily between the electrodes 1 and 3 by reason of the hydraulic thrust; the surface of the anode is thus kept constantly free.

The rotation (arrow F_4) shown in FIG. 2, which is imparted to the brine immediately upon its entry into the annular space 17, ensures the detachment of the bubbles of chlorine from the places on which they are formed on the anode surface 4.

The speed of the brine leaving the annular space 17 so as to rise into the space comprised between the electrodes 1 and 3 is the resultant of a component represented by the speed of this brine in the space 17, which may be called the tangential component (arrow F_4), and a vertical or longitudinal component (arrow F_7 , FIG. 1) due to the upward movement of the brine in the space between the electrodes.

This tangential component may be a multiple of the vertical component. The brine thus rises while executing a kind of helicoidal movement with a small pitch, and it effectively carries away the bubbles of chlorine as soon as they are formed on the anode 3. The higher the resultant speed, the more bubbles of small diameter are carried away by the flow of solution and the better the anode is washed.

In all cells with a mercury cathode, it is of vital importance to prevent any direct contact between the active chlorine and the mercury. The movement of rotation of the brine in the cell according to the invention has as its consequence an automatic separation of dense brine which will accumulate opposite the cathode and light brine containing bubbles of chlorine which will remain confined opposite the anode.

The evacuation of the bubbles of chlorine may be facilitated by providing on the anode coating of graphite 4, essentially helicoidal grooves 23 going in the direction of forward movement of the brine. As the bubbles of chlorine have a rising speed higher than that of the brine, the pitch of these grooves is preferably greater than the pitch of the rising trajectory of the brine.

Whereas the relatively small vertical components are directed in counter-flow between the brine and the mercury, the considerably higher tangential components proceed in the same direction (V , FIG. 3 and F_4 , FIG. 2). More particularly, at the bottom of the cell, the amalgam of which the tangential component of the speed is already partly absorbed by friction, meets the fresh brine having its full tangential component. The movement of rotation of the amalgam is thus ensured during its entire downward movement in the cell.

In FIG. 1, the cathode 1 and the anode 3 have the simple geometric form of straight truncated cones. FIG. 4 shows an anode-cathode assembly (which may be quite suitable for a cell according to the invention, of the type shown in FIG. 1) in which the anode 3 has a particularly advantageous shape with respect to the flow of the mercury over the cathode 1.

In the diagram of FIG. 4, it is assumed that the film of mercury which flows over the cathode is fairly thick (of the order of 1 millimetre).

The mercury arrives horizontally at the level N (coming from 12) with a large tangential component of speed V and falls down freely along the cathode surface 1. While this initial tangential component V maintains itself, the vertical component increases, so that the inclination of the threads of mercury tends to approach the vertical. The thickness of the film of mercury is the result of two opposing factors, namely the increase of the vertical component of the speed of the mercury on the one hand, and the reduction of the diameter of the cathode 1 on the other.

FIG. 4 shows the film of mercury, after folding back about the meridian line of the cathode 1. This film is defined by the curve 5 which indicates the variation of the thickness e as a function of the height of the point considered of the cathode surface.

If h is the distance between the level N of the mercury at its outlet from 12 and the apex S of the geometrical cone on which is applied the inner frustoconical surface of the cathode 1, calculation and tests have shown that it is possible to obtain, opposite the coating of graphite 4 on the anode 1, a film of mercury with a practically constant thickness e if the anode surface 4 extends in the vertical direction between the limiting heights of $0.92h$ and $0.35h$ measured from the apex S of the cone.

The condition which has just been stated is the only one to be satisfied in order to obtain a practically constant thickness e of mercury, and thus the form of the meridian section of the anode-cathode assembly has no particular importance. It is possible for example to adopt with advantage the arrangement shown in FIG. 4, in which the cathode 1 is in the form of a straight truncated cone and in which the anode surface 4 has a meridian section such that the distance between the electrodes is smaller at the mid-height than at the bottom and at the top. Such an arrangement ensures an essentially constant axial speed of the brine in the lower part of the cell, and takes account of the increase in specific volume of the brine in the upper part of the cell, due to its content of bubbles of chlorine.

It will be understood that the cathode 1 may also be given other forms than that of a truncated cone.

Like the majority of known cells, the cell shown in FIG. 1 works at a pressure very slightly different from atmospheric pressure. Now, the cells according to the invention can easily be designed to work under high pressures, for example of 3 to 5 bars or even up to 10 bars.

In addition, the flow of the mercury in a relatively thick layer can be replaced by a flow in a very thin film of a thickness of the order of a few tenths of a millimeter. This results in a further reduction of the volume of mercury in circulation.

FIG. 5 shows precisely an electrolysis cell according to the invention, in which the mercury is in a very thin film. The anode 3 has the shape of a truncated cone. It is of metal plated with a thin coating of metal which resists the action of nascent chlorine. An internal cone 24 (of aluminium for example) distributes the current which is led-in by the conductor 8. The anode 3 is guided at the bottom by its extension 9 and a packing gland 25. The cathode 1 is of steel. It is supported by the ring 26 which leads the current to the negative conductor 2. The very thin layer of mercury 13 on the cathode 1 is supplied by the entry at 11 (arrow F_1) of the mercury, which sets the ring of mercury 12 in movement. The mercury passes into the electrolysis space through the slot 27 between the cathode 1 and the ring 28, plated like the anode 3 with a thin coating of metal resistant to nascent chlorine. The amalgam formed by the mercury and the alkali metal of the chloride to be electrolyzed leaves the

apparatus (arrow F_8) through the conduit 15 after having been collected in the space 14.

The rich brine to be electrolyzed passes into the cell through the conduit 16 (arrow F_3) and gives a movement of rotation to the liquid contained in the space 17. It then rises between the electrodes 1 and 3. In the space between the extension 5 of the anode 3 and the ring 28, it encounters guiding vanes 29 which serve to maintain the rotational movement. The mixture of weakened brine and gaseous chlorine is collected in the annular space 30 and leaves the apparatus through the conduit 31 (arrow F_9) in the direction of a separator (not shown in FIG. 5).

The speed of rotation of the mercury in a thin film falls relatively quickly, so that the mercury has a tendency to flow in an uncontrolled manner into the lower part of the cell and to uncover certain parts of the cathode 1. It is important that the mercury should encounter precisely in this portion, the vortex of rising brine, which ensures its uniform distribution over the entire surface of the cathode 1.

This effect becomes more considerable as the friction of the mercury on the cathode 1 increases. It is possible for example to find an advantage in slowing down the flow of the mercury (and by this fact to increase the duration of its exposure to the electrolysis) by giving the cathode 1 a surface which is not absolutely smooth but on the contrary intentionally rough, either by tool marks, sand-blasting, or by any other method.

The simple construction of the electrolysis cell according to the invention, and in particular that which is shown in FIG. 5, enables the cell to be put under high pressures without necessitating reinforcement at a prohibitive cost.

A first advantage of working under high pressures is the possibility of using the cell to operate at temperatures higher than 100° C. At these temperatures, the solubility of the chlorine in the brine is considerably reduced, so that the weakened brine which returns to saturation is already partly freed from chlorine at its outlet from the separator.

High working pressures in the separator (from 3 to 5 bars or even up to 10 bars) have other advantages, while keeping the temperature of the brine well below the corresponding boiling temperature. In fact, the content of steam in the outgoing gases (in grams per cu. m.) only depends on the temperature and therefore not on the total pressure, whereas this pressure essentially determines the density of the gas. In consequence, at equal temperatures, the steam content of the gases (in grams per cu. m.) becomes smaller as the total pressure increases. In this way, a valuable drying effect is obtained.

Finally, working under high pressure, the volume of the chlorine bubbles in the upper part of the cell becomes smaller as the pressure increases. The section of electrolyte available for the passage of the current will be correspondingly greater, which will reduce the losses of energy due to the resistance of the electrolyte.

For putting into operation, the electrolysis cells according to the invention are first filled with pure water. The mercury pump is then started-up and the circulation of brine is established. As soon as the necessary concentration of sodium chloride is obtained, the electric current can be applied.

A complete system of a cell under pressure with its accessories is shown as an example in FIG. 6 (the electrolysis cell being of the type shown in FIG. 5).

The conductors 8 supply the electric current to the cell according to the invention, indicated generally by the reference 32. The current leaves by the conductor 2. The weakened brine mixed with bubbles of chlorine passes out under pressure through the conduit 31 and reaches the separator 33. The chlorine is drawn-off by the conduit 20 and directed (arrow F_6) to the washing and drying installation. Part of the brine is sent back

to the cell 32 through a conduit 34. It is enriched on the way by an addition of concentrated brine coming from the conduit 35 of the saturation installation 36. A quantity of weakened brine, equal to that coming-in through the conduit 35, is drawn-off at the separator 33 by the conduit 37. This brine can be sent directly to the saturator 36, provided that the latter is equipped for working under pressure. When it is desired to employ an ordinary saturation installation at atmospheric pressure, it is preferable to cool the hot brine from the conduit 37 below 100° C., so as to avoid undesirable evolution of steam during the expansion.

The cooling of the weak brine is advantageously carried out in a heat exchanger and thus provides a heating stage for the fresh brine of the conduit 35. The cooled weak brine is expanded to atmospheric pressure in the pressure-reducing device 38 and passes into a further separator 39. The chlorine is evacuated through the conduit 40 and the weak brine goes to the saturation installation through the conduit 31.

A heating device 42 enables the temperatures of the brine in the separator 33 to be regulated. For example, by heating the brine to a temperature close to its boiling point, the dissolved chlorine can be almost completely separated from the brine. An overflow 43 enables the level of brine to be maintained and to change a charge of brine, if necessary, without stopping the cell.

The brine can very well work with natural circulation without any driving means, since the conduit 31 conveys weak brine which is therefore light and contains a considerable volume of gaseous chlorine, whereas the conduit 34 is filled with rich, heavy and de-gasified brine. However, in the case of high specific loads on the anode, of the order of 10,000 to 15,000 amperes per square metre, it may become necessary to increase this circulation by means of a pump 44. According to local conditions, a pump of this kind can be advantageous, even on small loads.

The mercury reaches the cell 32 through the conduit 11 and the amalgam passes out of the cell through the conduit 15. A conduit 45 permits normal operation of the siphon 46. The amalgam is directed into the decomposer 47 of similar design to that of the cell 32. It passes down into helicoidal grooves 48 and meets in counter-flow the water coming-in from the conduit 49. It decomposes; the metallic mercury collects in the space 50 and is drawn-off into the tank 51, from which the electric pump 52 delivers it to the cell 32 through the conduit 11. In the case where it is desired to increase the concentration of the amalgam passing out of the cell 32 through the conduit 15, a branch connection 53 enables a part of the amalgam to be returned into the electrolysis circuit.

The sodium liberated in the decomposer 47 combines with water and forms hydrogen on the one hand and an aqueous solution of caustic soda on the other. The mixture of liquid and gas passes out through the conduit 54 and separates in the separator 55 into hydrogen, evacuated by the conduit 56, and a solution of caustic soda drawn-off by the conduit 57. In this case also, a re-circulation can be provided through the conduit 49, either naturally or with the assistance of a pump 58. Topping-up with fresh water is effected by the conduit 59.

It will of course be understood that the foregoing description has been given by way of explanation but not in any limitative sense and that modifications can be made to the above forms of embodiment and they can be combined in different ways, without thereby departing from the scope of the invention.

We claim:

1. An installation for the electrolysis of saline solutions, especially of aqueous solutions of alkali chlorides comprising on the one hand an electrolysis cell in which a film of mercury in circulation is utilized as a cathode, and on the other hand, the accessory apparatus necessary for the cycle of operation;

said cell comprising two electrodes, namely an anode and a cathode constituted by two coaxial surfaces of revolution with a vertical axis having spaced apart conical shapes with the apices of the cones in the direction of the bottom of said cell, said surface of revolution farthest away from said vertical axis forming said cathode and serving to support the flow of mercury;

means to impart a tangential speed to the mercury entering the cell and spill it over said cathode;

means to impart a tangential speed to the saline solution to be electrolyzed being fed into the bottom of said cell producing both a tangential component and an upward vertical component to the saline solution passing it between said two electrodes;

each said means to impart a tangential speed to said mercury and said saline solution respectively being on opposite ends of said two electrodes.

2. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by both said means to impart a tangential speed to the mercury and to the saline solution are constituted by annular spaces.

3. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by both said means to impart a tangential speed communicating movements of rotation of the mercury and the saline solution in the same direction.

4. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by said anode having an active surface extending in the vertical direction between approximately 92% and 35% of the distance between the level of the mercury at its arrival on said cathode and the apex of the geometrical cone which defines the surface of said cathode, the distances being taken from the apex of said cone.

5. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by the opening angle of the cone defining the surface of said anode differing from the opening angle of the cone defining the surface of said cathode.

6. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by said electrolysis cell having a high pressure in its interior up to an amount of approximately 10 bars.

7. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by spaced apart means positioned to limit the thickness of the mercury film flowing from said means to impart tangential speed to the mercury and spilling over said cathode

whereby the mercury flows towards the bottom of said cell under the combined effect of gravity and the tangential component of speed.

8. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by said accessory apparatus including separator means operatively connected to said electrolysis cell and working under pressure, by which the

gas normally liberated at said anode is separated from the weakened saline solution;

heating means for ensuring the desired temperature in said separator means;

and means for saturating said weakened saline solution operatively connected to said separator means and said electrolysis cell.

9. An installation for the electrolysis of saline solutions as claimed in claim 8 further characterized by said accessory apparatus further including:

a decomposing device comprising essentially two electrodes formed by coaxial surfaces of revolution with a vertical axis, between which circulates a counter-flow of rising water, by which the mercury contained in amalgam which is formed in the electrolysis cell by the mercury and the metal of the alkali solution, is regenerated;

a further separator means connected to said decomposing device by which the element of the amalgam other than the mercury is separated from the mixture of hydrogen and aqueous solution formed in said decomposing device.

10. An installation for the electrolysis of saline solutions as claimed in claim 9 further characterized by the partial re-circulation of the aqueous solution passing out of said decomposing device without driving means for said accessory apparatus.

11. An installation for the electrolysis of saline solutions as claimed in claim 9 further characterized by pumping means to assist circulation of the aqueous solution passing out of said decomposing device.

12. An installation for the electrolysis of saline solutions as claimed in claim 1 further characterized by said anode having essentially helicoidal grooves winding upward in the direction of forward movement of the saline solution.

13. An installation for the electrolysis of saline solutions as claimed in claim 12 further characterized by said grooves having a greater pitch than the pitch of the rising trajectory of the saline solution.

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U.S. Cl. X.R.

204—272, 250, 275, 220