

[54] **ELECTROLYTIC CELL INCLUDING MEANS FOR SEPARATING CHLORINE FROM THE CHLORINE-ELECTROLYTE FROTH FORMED IN THE CELL**

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Related U.S. Application Data

[60] Division of Ser. No. 376,087, July 2, 1973, Pat. No. 3,855,091, which is a continuation-in-part of Ser. No. 219,096, Jan. 19, 1972, abandoned.

[52] U.S. Cl. **204/278; 204/256; 204/266; 204/270**

[51] Int. Cl.² **C25B 9/00**

[58] Field of Search **204/256, 258, 266, 270, 204/278; 55/183, 190, 199**

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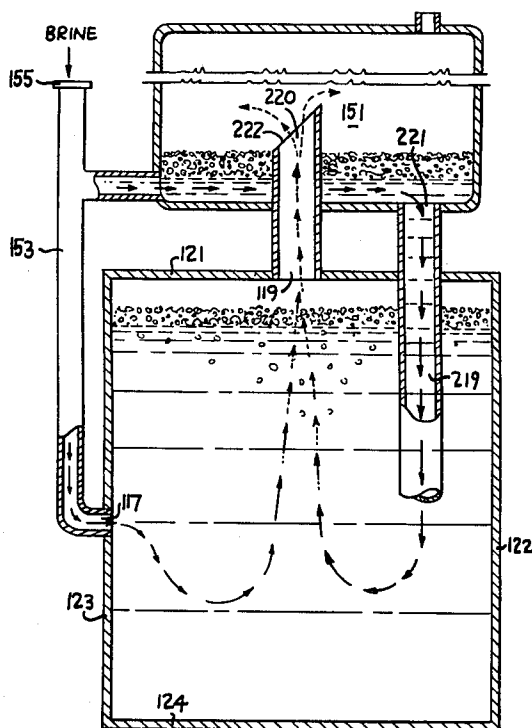
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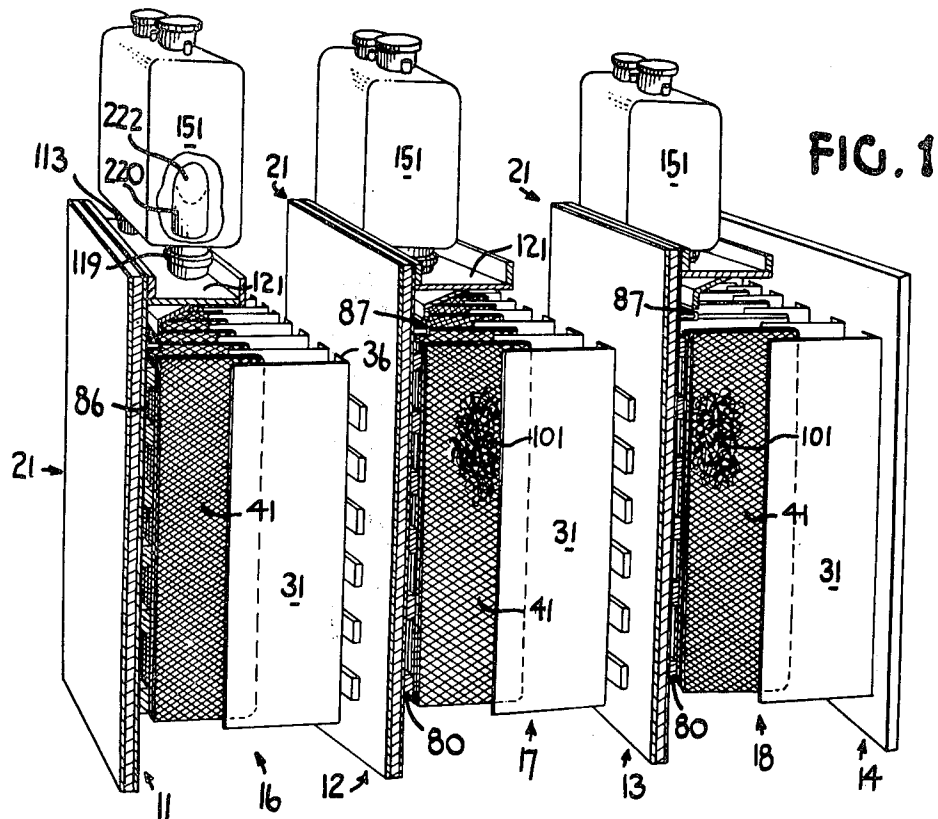
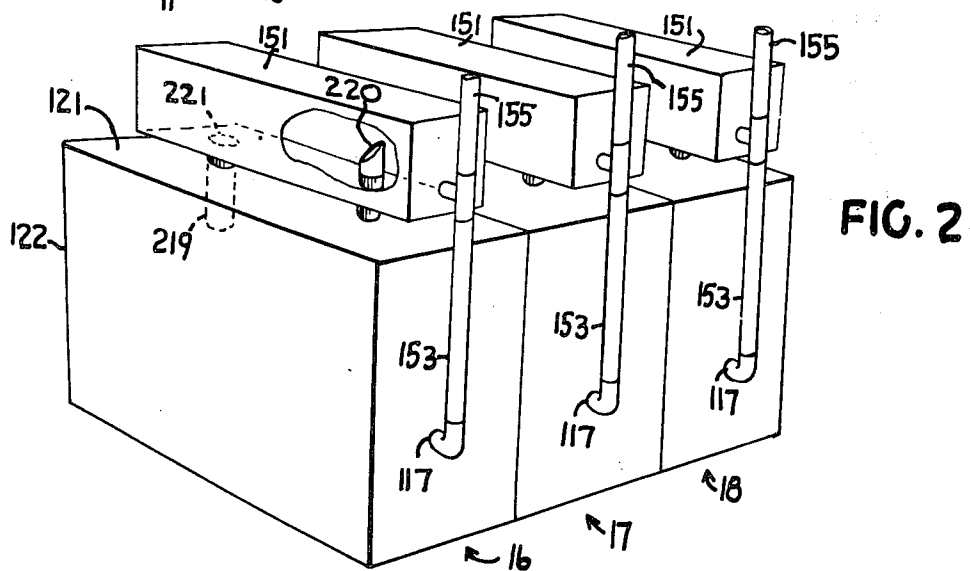
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[57] **ABSTRACT**

An electrolytic cell adapted for the high current density electrolysis of brines is disclosed. The chlorine gas liberated at the anodes is caused to go to a chlorine disengaging tank where the gas is separated from the entrained anolyte, and the anolyte is returned to the cell. Additionally, by taking advantage of the gas uplift in one portion of the cell and the simultaneous return of anolyte to another portion of the cell, a rotary motion of the electrolyte is maintained in the cell. In this way a high concentration of chloride ion and a low concentration of gas are maintained in the anolyte under conditions of high current density electrolysis.

6 Claims, 7 Drawing Figures





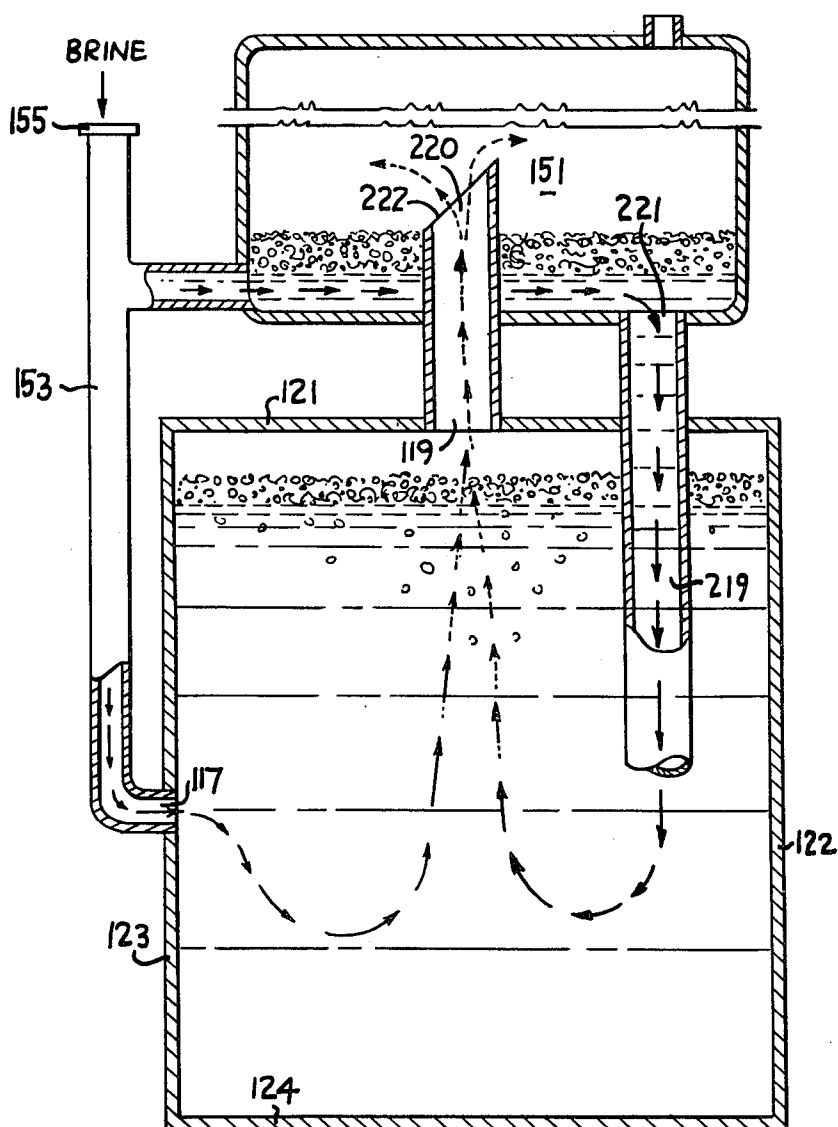
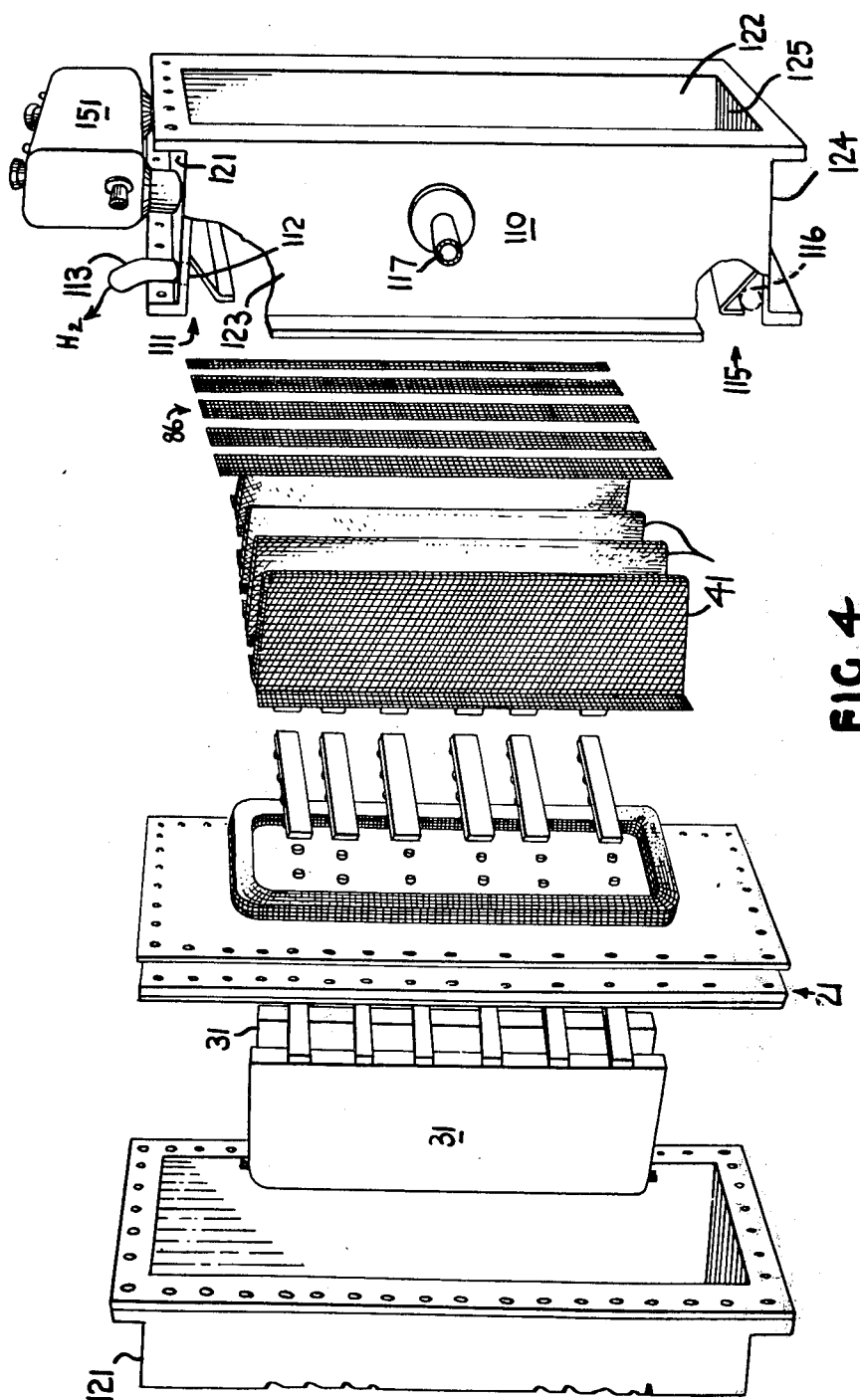
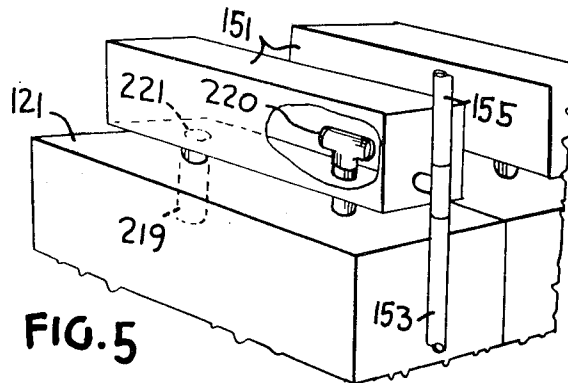
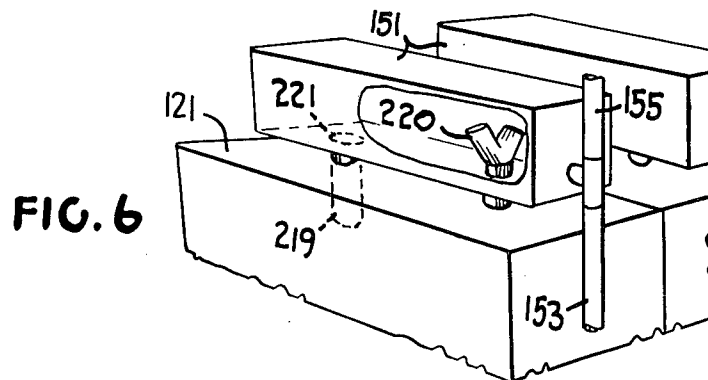
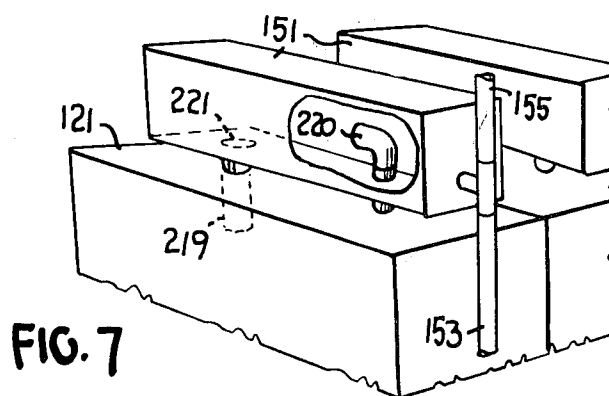


FIG. 3





ELECTROLYTIC CELL INCLUDING MEANS FOR SEPARATING CHLORINE FROM THE CHLORINE-ELECTROLYTE FROTH FORMED IN THE CELL

This is a division of application Ser. No. 376,087, filed July 2, 1973 now U.S. Pat. No. 3,855,091, which is a continuation-in-part of my commonly assigned U.S. application Ser. No. 219,096, filed Jan. 19, 1972 for a "Bipolar Electrolyzer," now abandoned.

BACKGROUND OF THE INVENTION

Previously, electrolysis of brine to yield chlorine has taken place in electrolytic cells having graphite anodes and operating at low current densities. In such cells of the prior art, erosion of the graphite anodes necessitated an anode having an initial thickness of 1 inch or more, thereby dictating an electrode pitch (center line-to-center line distance between electrodes of like polarity) of $3\frac{1}{2}$ or even 4 inches. Diaphragm electrolytic cells of the prior art, operating at low current densities with thick electrodes at large pitches, had low ratios of current per cubic foot of cell volume, frequently as low as $\frac{1}{2}$ or even $\frac{1}{4}$ kiloampere per cubic foot of cell volume.

Newer electrolytic cells use metallic anodes. Such anodes are on a narrower pitch and may be operated at higher current densities. Typically, in order to take advantage of the apparent economies of such diaphragm electrolytic cells, electrolysis should take place at high anode current densities, for example above about 80 amperes per square foot of anodic surface, and preferably above about 100 amperes per square foot of anodic surface. Additionally, the electrodes themselves should be tall, typically 3 feet or more tall, and preferably 4 or more feet tall.

During electrolysis at high current densities (for example, at current densities of about 100 amperes per square foot of anode surface) with tall electrodes (for example, above about 4 feet tall) and narrow interelectrode gaps (for example, with spaces of from about $\frac{1}{8}$ to $\frac{1}{4}$ inch between an anode and the diaphragm of the next adjacent cathode), several problems develop. Large volumes of gas are generated per unit of cell volume, resulting in frothing of the anolyte. The large fraction of gas in the anolyte causes the anolyte IR drop to increase. The concentration of chloride ion in the anolyte becomes non-uniform. According to this invention, the effect of such problems of electrolyzer operation may be diminished.

SUMMARY OF THE INVENTION

It has now been found that the problems associated with frothing of the anolyte, high anolyte electrical resistance, and non-uniform chloride ion concentration may be remedied by rapidly removing the froth containing evolved chlorine gas from the anolyte compartment, separating the evolved chlorine gas from the anolyte, and returning the anolyte, depleted of its chlorine gas content, to the anolyte compartment of the cell.

DETAILED DESCRIPTION OF THE INVENTION

In the electrolytic cells with which this invention is particularly useful, electrolysis normally takes place at high current densities, for example, in excess of 80 amperes per square foot and frequently in excess of 100 amperes per square foot, and between tall elec-

trodes 3 feet high, 4 feet high, and even 6 feet high. The electrodes in these electrolytic cells are close together, frequently having an interelectrode gap (space between an anode and the next adjacent cathode) of $\frac{1}{4}$ inch, and even $\frac{3}{16}$ inch or $\frac{1}{8}$ inch. Such electrodes will have a narrow pitch (center line-to-center line distance between electrodes of like polarity), frequently 3 inches or even less. Such electrolytic cells have large current loads per cubic foot of total internal cell volume, frequently 600 amperes per cubic foot of cell volume, and large current loads per square foot of internal horizontal cell area, frequently 2,500 amperes or more per square foot of horizontal cell area. Such cells generate large quantities of chlorine per square foot of horizontal cell area. The rapid generation of this chlorine results in the formation of an anolyte-chlorine froth.

According to this invention, anolyte froth containing the gas evolved on the anodes is removed to a gas disengaging compartment such as a brine reservoir or a brine feed tank. The froth of chlorine and anolyte is disengaged in the gas disengaging compartment. This disengagement occurs above the level of anolyte in the disengaging compartment and is caused by simultaneously changing the momentum of the froth and discharging the froth into the disengaging compartment. Thereafter, the disengaged anolyte, either mixed with the brine or alone, is returned from the gas disengaging compartment to the cell. The disengaged anolyte is returned to the cell through a downcomer exiting below the level of the electrolyte within the cell. In this way gas is substantially prevented from entering the anolyte return downcomer and is, instead, forced through the riser into the gas disengaging compartment. The liquid return downcomer may be located horizontally away from the gas riser to impart a rotary motion to the anolyte.

The chlorine disengaging apparatus and method of this invention is applicable to both monopolar and bipolar diaphragm cells. However, inasmuch as bipolar cells are more likely to have the combination of high current densities, narrow interelectrode spaces, and tall electrodes resulting in high current loads per square foot of cell horizontal cross-sectional area (for example, in excess of 2,500 amperes per square foot of cell horizontal cross-sectional area looking vertically into the cell), this invention is exemplified with respect thereto. This invention is, however, useful with monopolar electrolytic cells operating under conditions as described hereinbefore where frothing and froth disengaging are serious problems.

The chlorine disengaging apparatus and method of this invention are also useful with diaphragm cells operating at high current densities, narrow interelectrode spaces, narrow electrode pitches, and tall graphite electrodes.

In the drawings:

FIG. 1 is an exploded view showing the general arrangement of the interior of an electrolyzer.

FIG. 2 is an isometric partial cut-away view of an electrolyzer of this invention.

FIG. 3 is a cut-away, front elevation, schematic showing the electrolyte and gas flows in the anolyte compartment.

FIG. 4 is an exploded partial cut-away of an individual bipolar unit.

FIGS. 5, 6, and 7 are isometric, partial cut-away views of the electrolyzer of this invention showing vari-

ous alternative chlorine riser configurations.

An arrangement of bipolar units forming an electrical series of bipolar cells in an electrolyzer is shown in exploded cut-away in FIG. 1 and in partial cut-away in FIGS. 2, 3, and 4. Bipolar units 11, 12, 13 and 14 form bipolar cells 16, 17 and 18. End unit 11 provides a cathodic half cell, while end unit 14 provides an anodic half cell. The intermediate bipolar units 12 and 13 are bipolar units providing both anodic and cathodic half cells.

In addition to the end half units 11 and 14, an electrolyzer will normally include at least one bipolar unit 12 and may be comprised of a plurality (up to 10, or 15, or even more) of bipolar units 12 and 13.

In one type of bipolar electrolyzer with which this invention is useful, each of the bipolar units, as bipolar unit 12, is housed in a channel frame 110. The channel frame 110 is shown in particular detail in FIG. 4. The channel frame 110 comprises sidewalls 122 and 123, top 121, and bottom 124. The channel frame 110 has various openings. Opening 116 in side wall 123 is used to drain the catholyte compartment and thereby recover the liquid catholyte products. The outlet 112 in top wall 121 is used to remove gaseous cathodic products.

Openings 117, 119, and 219 in side walls 122 and 123 and the top 121, respectively, lead into the anolyte compartment. Opening 119, in combination with chlorine riser 220, is a means to remove the froth of gaseous anolyte products, as chlorine and the electrolyte. Opening 117 and opening 219, in combination with the anolyte return downcomer 221, are used to feed brine into the anolyte compartment.

A brine reservoir 151 is above each individual cell, as cell 12, and is hydraulically connected to the anolyte volume of the cell by a gas riser 220 and an anolyte return downcomer 221. While a separate brine reservoir 151 is shown for each individual cell, a single brine reservoir 151 may serve two or more cells or an entire electrolyzer. The brine reservoir, mounted above the cell, and containing the means for removing the froth from the anolyte compartment and separating the froth into liquid and gaseous fractions, and the means for returning the liquid to the cell, is the disengaging tank. While the disengaging tank is also referred to as a brine reservoir, it is to be understood that the disengaging tank need not have brine fed to it.

In the operation of the electrolyzer, brine containing from about 310 to about 325 grams per liter of sodium chloride is fed from a header, not shown, into pipe 155. The brine feed may divide into two streams, one entering the cell through pipe 153 and the other stream entering the brine feed tank 151. Alternatively, all of the brine may enter the cell through pipe 153.

The stream entering pipe 153 enters the cell through opening 117. Opening 117, in side wall 123, is at a horizontal level between the cell bottom 124 and the cell top 121. Typically, the brine feed opening 117 is at a level between one quarter and three quarters of the vertical distance between the cell top 121 and the cell bottom 124, and preferably from about one quarter to about one half of the vertical distance from cell bottom 124 to the cell top 121.

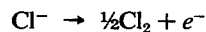
When a portion of the brine enters the brine reservoir 151, the brine entering the brine reservoir 151 is saturated by the chlorine gas entering the brine reservoir tank 151 through the brine riser 220. The chlorine-saturated brine enters the cell through opening 221 in

the brine reservoir 151, thence through anolyte return downcomer 219.

The anolyte return downcomer 219 extends below the upper surface of the anolyte in the cell by an amount sufficient to prevent the chlorine in the gas bubble formed between the cell top 121 and the top of the anolyte and the froth from entering the downcomer 219. The downcomer 219 need only extend to just below the surface of the anolyte, but it will typically extend below the surface of the anolyte by more than six inches and preferably extends as far into the anolyte as possible without washing the diaphragm 101 off of the cathodes 41. In one exemplification of this invention, several electrode pairs, that is, several anodes and cathodes, may be removed and the anolyte return downcomer 219 extended into the space created thereby. In this way, the anolyte return downcomer may extend into the cell by as much as one-half or more of the height (i.e., vertical difference between the cell top 121 and the cell bottom 124) of the cell.

For best results, the anolyte return downcomer 219 is horizontally displaced from the chlorine gas riser 220. In this way, by the horizontal displacement of the brine feed pipe 153 and opening 117, the anolyte return downcomer 219 from each other and from the chlorine gas riser 220, and by the location of the brine feed means below the upper surface of the brine, a rotatory motion is imparted to the brine.

The following reaction takes place at the anodes in the anolyte compartment:



The chlorine liberated at the anode 31 bubbles up the face of the anode. Alternatively, when a perforate anode is utilized having two opposing surfaces separated so as to provide a hollow channel for gas flow and anolyte flow, the chlorine liberated at the faces of the anode facing the cathode 41 passes through the perforation in the face of the anode and bubbles up between the two opposing surfaces of the anode.

The chlorine gas bubbles travel up through the anolyte as shown by the broken arrows in FIG. 3 forming a froth of chlorine and anolyte. The gas lifting effect provided by the liberated chlorine gas carries the froth upward through the cell, through opening 119 in the top of the cell, into and through the chlorine riser 220 into brine reservoir 151. The chlorine gas disengages from the brine in the brine reservoir 151. When the chlorine riser 220 does not extend above the level of the brine and froth in the brine reservoir 151, additional froth is generated in the brine reservoir 151 with recirculation of the gas-laden froth back to the cell, little gas disengagement will occur. Typically, the chlorine riser 220 extends above the bottom of the brine reservoir 151 by a distance equal to the depth of electrolyte and froth in the brine reservoir 151. For best results, the chlorine riser 220 extends to within 2 to 6 inches of the top of the brine feed tank 151.

With the chlorine riser 220 extending above the electrolyte and froth in the brine feed tank as described hereinbefore, moderate gas disengagement occurs. Better gas disengaging occurs when the froth undergoes a change in momentum prior to leaving the riser, for example, when the direction of flow of the gas and liquid are changed. By change in momentum is meant a change in the product of the mass and the velocity vector. By a change in the velocity vector is meant either a change in direction of flow or a change in the

flow rate. This occurs, in one exemplification, when the outlet 222 of the chlorine riser 220 is at a bias as shown in FIG. 3, causing the direction of flow of the froth to change prior to discharge from the riser 220. When the outlet 222 is at an angle of from about 30° to about 75° with respect to the horizontal, good disengaging is achieved. Particularly good gas disengaging is attained when the opening of the outlet 222 is at an angle in excess of 45° to the horizontal.

Even more effective gas disengagement is provided, particularly at the high flow rates contemplated, when the chlorine riser 220 and outlet 222 are in the form of a "Tee," "Wye," or "Elbow" fitting, thereby providing even greater direction and momentum changes to the froth upon leaving the riser 220. Such fittings on the discharge outlet 222 of the riser 220 impose direction and momentum changes in the froth prior to discharge from the riser 220. The chlorine disengaging apparatus of this invention using Tee, Wye, and Elbow fittings are illustrated in FIGS. 5, 6, and 7, respectively.

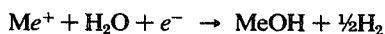
Additionally, there may be used in combination with the chlorine disengaging apparatus of this invention other disengaging means. For example, the froth, after being disengaged by passage through the riser 220 and outlet 222, may be impinged against plates or baffles or caused to pass through screens or mesh.

The chlorine riser 220 should have a cross-sectional area of less than about 0.10 square foot per thousand amperes, and preferably less than about 0.05 square foot per thousand amperes.

The chlorine cells of this invention, having current loads in excess of 600 amperes per cubic foot of cell volume, and frequently in excess of 1,500 amperes per cubic foot of cell volume, will have less than about 0.050 square foot of chlorine riser cross-sectional area per cubic foot of cell volume, and preferably less than about 0.006 square foot of chlorine riser cross-sectional area per cubic foot of cell volume.

In this way a satisfactory froth velocity is maintained in the riser. If the riser cross-sectional area per thousand amperes is greater than about 0.40 square foot, the froth will percolate or bubble into the disengaging tank 151 rather than flow into the tank 151, and the disengaging will not be so effective.

Additionally, in the construction and operation of cells according to this invention the brine reservoir or disengaging tank 151 should have a horizontal cross-sectional area in excess of 0.10 square foot per thousand amperes, and preferably in excess of 0.14 square foot per thousand amperes. Particularly preferred are brine reservoirs or chlorine disengaging tanks 151 having a horizontal cross-sectional area in excess of 0.20 square feet per thousand amperes, e.g., up to about 0.40 square feet per thousand amperes or even 0.50 square feet per thousand amperes or more. The following reaction takes place at the electrically active surfaces within the catholyte compartment:



where Me is a metal, and Me^+ is a metal ion.

The hydrogen gas bubbles up and back through the catholyte compartment and thence into the catholyte backscreen compartment and into compartment 111 of FIG. 4, and finally out through the hydrogen outlet 112 into pipe 113 shown in FIG. 4 in the top of the bipolar unit. The cell liquor containing from about 120 to about 160 grams per liter of sodium hydroxide and about 160 to about 210 grams per liter of sodium chlo-

ride is recovered from the catholyte compartment through opening 116 in wall 122 and discharged through the perc pipe.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

I claim:

1. In an electrolytic cell for the electrolysis of brines at currents above 2,500 amperes per square foot of horizontal area whereby a froth of chlorine and electrolyte is generated, the improvement comprising:

- means having a cross-sectional area of less than 0.050 square feet per cubic foot of cell volume for removing froth from the cell to a disengaging tank;
- means for changing the momentum vector and flow direction of the froth prior to discharging the froth into the disengaging tank;
- means for thereafter discharging the froth into the disengaging tank above the level of liquid therein; and
- means for returning liquid from the disengaging tank to the electrolytic cell.

2. The electrolytic cell of claim 1 wherein said disengaging tank has a horizontal cross-sectional area in excess of 0.06 square feet per cubic foot of cell volume.

3. In an electrolytic cell for the electrolysis of brines at currents above 2,500 amperes per square foot of horizontal area whereby a froth of chlorine and electrolyte is generated, the improvement comprising:

- means having a cross-sectional area of less than 0.050 square feet per cubic foot of cell volume for removing froth from the cell to a disengaging tank;
- means for changing the direction of flow of the froth prior to discharging the froth into the disengaging tank;
- means for discharging the froth into the disengaging tank above the level of liquid therein; and
- means for returning liquid from the disengaging tank to the electrolytic cell.

4. The electrolytic cell of claim 3 wherein said disengaging tank has a horizontal cross-sectional area in excess of 0.06 square feet per cubic foot of cell volume.

5. In an electrolytic cell for the electrolysis of brines at currents above 2,500 amperes per square foot of horizontal area whereby a froth of chlorine and electrolyte is generated, the improvement comprising:

- means having a cross-sectional area of less than 0.050 square feet per cubic foot of cell volume for removing froth from the cell to a disengaging tank having a cross-sectional area in excess of 0.06 square feet per cubic foot of cell volume;
- means for changing the momentum vector and flow direction of the froth prior to discharging the froth into the disengaging tank;
- means for thereafter discharging the froth into the disengaging tank above the level of liquid therein; and
- means for returning liquid from the disengaging tank to the electrolytic cell.

6. In an electrolytic cell for the electrolysis of brines at currents above 2,500 amperes per square foot of horizontal area whereby a froth of chlorine and electrolyte is generated, the improvement comprising:

- means having a cross-sectional area of less than 0.050 square feet per cubic foot of cell volume for

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removing froth from the cell to a disengaging tank
having a cross-sectional area in excess of 0.06
square feet per cubic foot of cell volume;
means for changing the direction of flow of the froth
prior to discharging the froth into the disengaging 5
tank;

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means for discharging the froth into the disengaging
tank above the level of liquid therein; and
means for returning liquid from the disengaging tank
to the electrolytic cell.

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