May 20, 1969 TSUYOSHI ISHIMATSU 3,445,374

ALKALI CHLORIDE ELECTROLYTIC MERCURY CELLS

Filed Sept. 1, 1965 Sheet 1 of 4

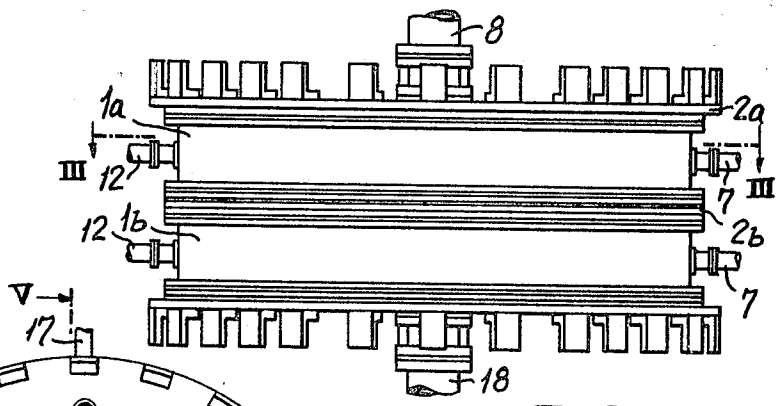


FIG. 1.

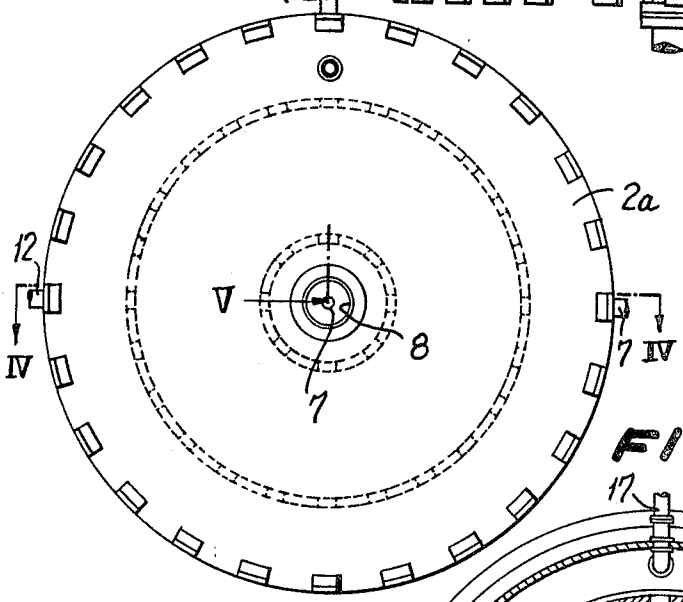


FIG. 2.

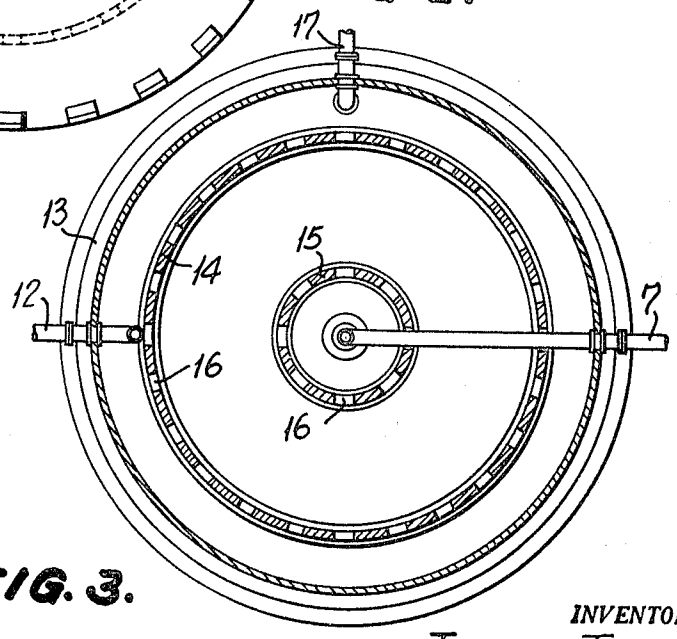


FIG. 3.

INVENTOR.
Tsuyoshi Ishimatsu
BY
Bailey, Stephens & Huettig
ATTORNEYS

May 20, 1969 TSUYOSHI ISHIMATSU 3,445,374

ALKALI CHLORIDE ELECTROLYTIC MERCURY CELLS

Filed Sept. 1, 1965 Sheet 2 of 4

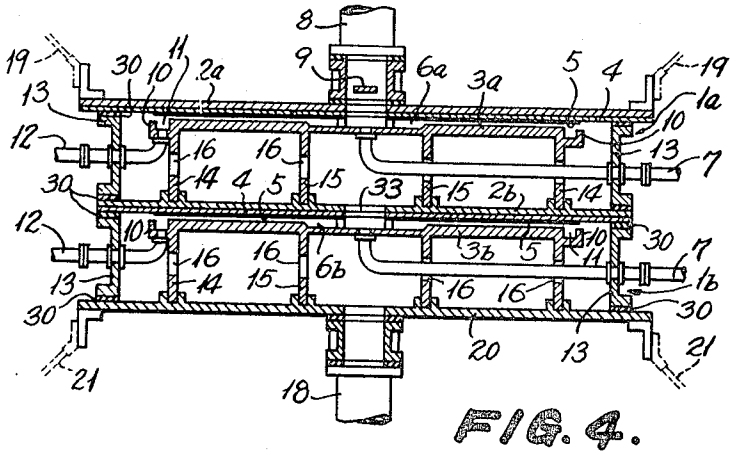


FIG. 4.

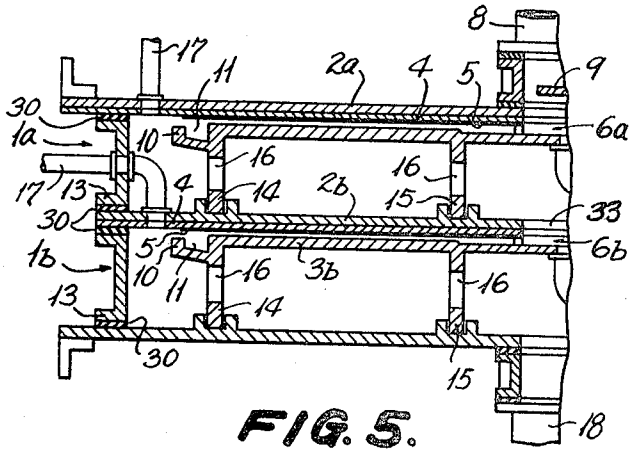


FIG. 5.

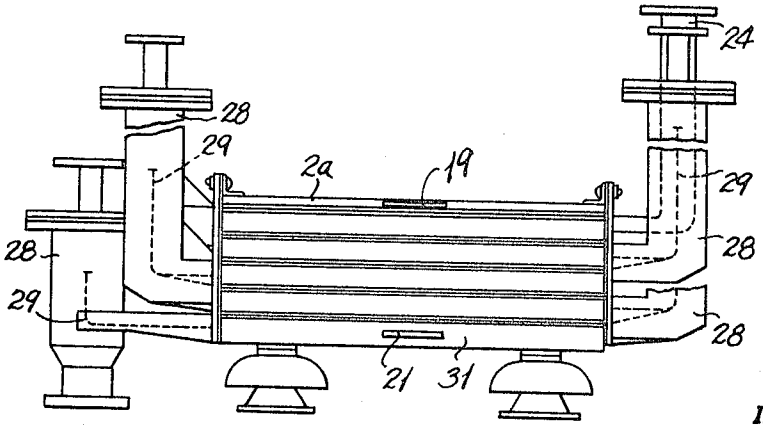


FIG. 6.

INVENTOR.
Tsuyoshi Ishimatsu
BY
Bailey, Stephens & Huettig
ATTORNEYS

May 20, 1969 TSUYOSHI ISHIMATSU 3,445,374

ALKALI CHLORIDE ELECTROLYTIC MERCURY CELLS

Filed Sept. 1, 1965 Sheet 3 of 4

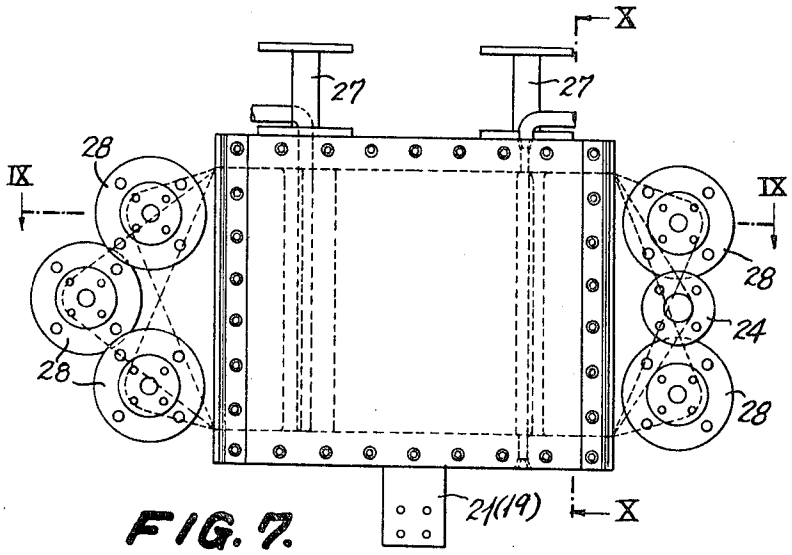


FIG. 7.

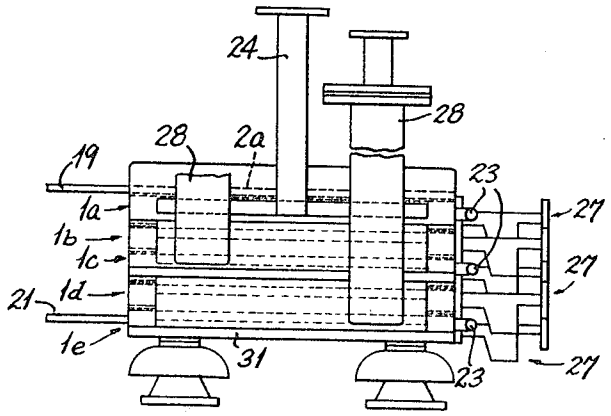


FIG. 8.

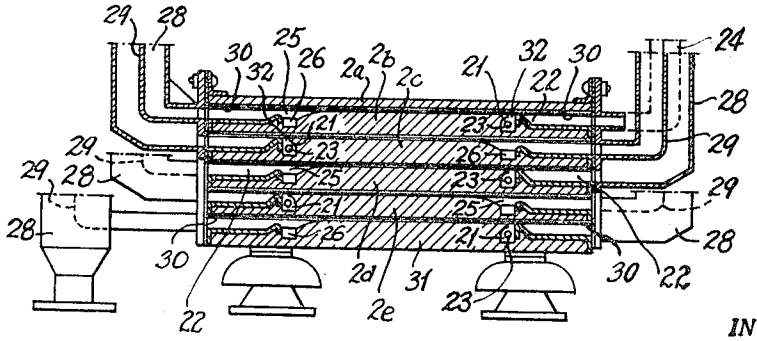


FIG. 9.

INVENTOR.
Tsuyoshi Ishimatsu
BY
Bailey, Stephens & Huettig
ATTORNEYS

May 20, 1969 TSUYOSHI ISHIMATSU 3,445,374

ALKALI CHLORIDE ELECTROLYTIC MERCURY CELLS

Filed Sept. 1, 1965 Sheet 4 of 4

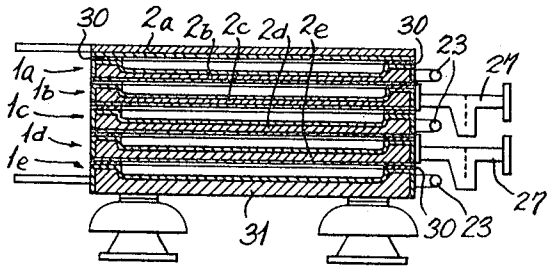


FIG. 10.

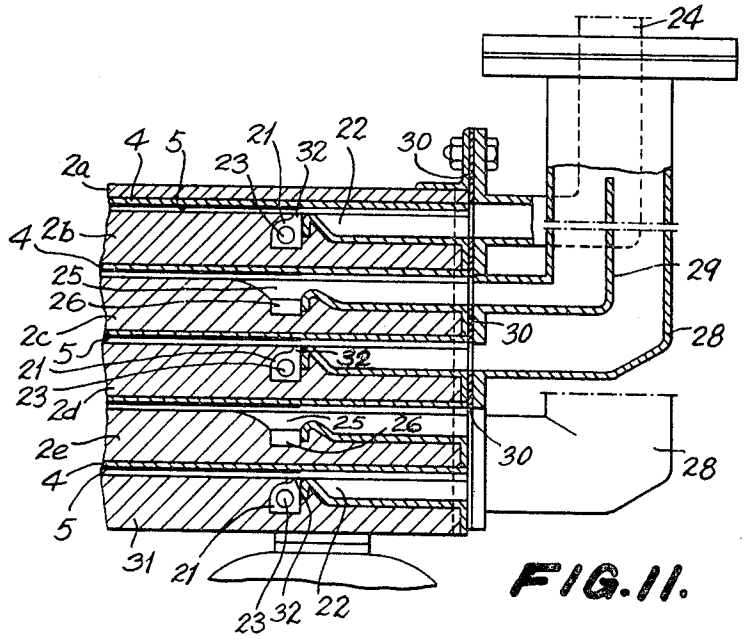


FIG. 11.

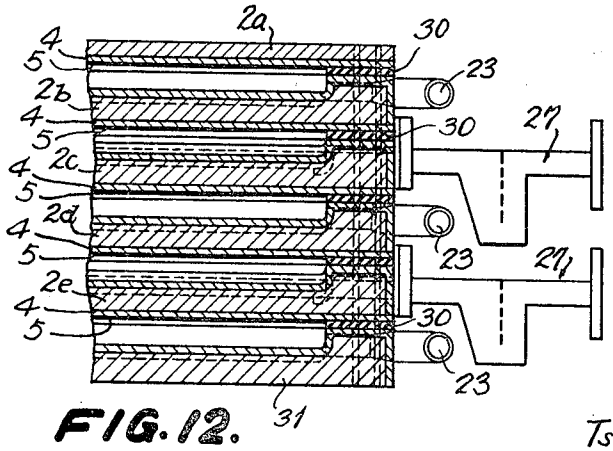


FIG. 12.

INVENTOR.
Tsuyoshi Ishimatsu
BY
Bailey, Stephens & Huettig
ATTORNEYS

United States Patent Office 3,445,374
Patented May 20, 1969

3,445,374

ALKALI CHLORIDE ELECTROLYTIC MERCURY CELLS

Tsuyoshi Ishimatsu 1 of 12 of 4 Sakuragaoka, Tamamura, Minami Tama-gun, Tokyo, Japan

Filed Sept. 1, 1965, Ser. No. 484,268
Claims priority, application Japan, Sept. 5, 1964, 39/50,806; Sept. 13, 1964, 39/70,126
Int. Cl. C23b 5/68; C22d 1/04
U.S. Cl. 204—270 17 Claims

ABSTRACT OF THE DISCLOSURE

Alkali chloride electrolytic mercury cells which are adapted to be superimposed one upon the other, each cell having a metallic cover, the inner face of which is coated successively with a layer of titanium and a layer of a platinum group metal and the latter layer serves as the anode in the cells.

The present invention relates to an alkali chloride electrolytic mercury cell.

The alkali chloride electrolytic mercury cell is widely used for electrolyzing an aqueous solution of alkali chloride, such as sodium chloride, potassium chloride or the like to obtain an amalgam of alkali metals and chloride.

Generally, the electrolyzing voltage necessary for electrolyzing an aqueous solution of alkali chloride is low, but an extremely high electric current is required in an electrolytic cell on a technical scale. In electrolytic plants operating on a technical scale, a large number of the electrolytic cells are used and these electrolytic cells are connected in series.

Since the electrolytic cells are operated with high electric current, the sectional area of a bus-bar used for connecting these electrolytic cells should be extremely large. Consequently, a large amount of bus-bar area becomes necessary. The loss of electric power due to ohmic loss in the bus-bars is considerable.

Since the electrolytic cells are ordinarily arranged on a plane at the spacing necessary for effecting the conversation of the electrolytic cells, wide floor areas are necessary for arranging these cells at the necessary spacings. The spaced arrangement of these electrolytic cells leads to an increase in the lengths of the bus-bars and also leads to an increase in the loss of electric power.

Nowadays, the electrolytic cells used are getting larger in size and the electrolyzing current per unit area of the electrode is also tending to gradually increase.

In ordinary electrolytic cells, anodes are conected to bus-bars through connecting rods. The electric current flows into the anode through the connecting rod. Since the resistance of the current increase with an increase in the length of the rods, the current density of the rods becomes lower with the increase of said lengths.

Since the tendency is to provide larger uniform current densities, however, the electrolytic cells must be made even larger, therefore, in order to provide the higher current densities.

In general, the electrolyzing voltage rises and hydrogen becomes easier to evolve with an increase of the current density. This tendency becomes notable particularly when the current density is non-uniform, because if the current density becomes non-uniform, a higher current density above an average current density occurs locally. Thus, the tendency for the evolution of hydrogen increases with the size of the electrolytic cell as the current density is increased.

It is an object of the present invention to improve

such disadvantages in the existing known alkali chloride electrolytic mercury cell as described above.

Another object of the present invention is to decrease the floor area necessary for arranging alkali chloride electrolytic mercury cells and to diminish the amount or length of the bus-bars necessary for connecting the electrolytic cells.

A further object of the present invention is to decrease the quantity of evolved hydrogen by making uniform the current density of the electrode.

Still another object of the present invention is to provide an alkali chloride electrolytic mercury cell having a construction suitable for use in superimposed installations as set forth hereinafter.

Still another object of this invention is to improve the disadvantages of the above described alkali chloride electrolytic mercury cells by using an electrolytic cell of such a construction in superimposed installations.

Another object of this invention is to provide an alkali chloride electrolytic mercury cell, the rear surface of the cover of which can be utilized as an anode.

Another object of this invention is to provide an alkali chloride electrolytic mercury cell, the outer surface of the cover of which can be utilized as a cathode of another electrolytic cell superimposed thereon .

Another object of this invention is to provide means for supplying, under pressure, chlorine produced by electrolysis.

Other objects, features and advantages of the present invention will become apparent from the following description of the present invention.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:

FIG. 1 is an elevational view showing two circular electrolytic cells superimposed one above another;

FIG. 2 is a plan view of the electrolytic cells shown in FIG. 1;

FIG. 3 is a sectional view on the line III—III of FIG. 1;

FIG. 4 is a sectional view on the line IV—IV of FIG. 2;

FIG. 5 is a sectional, enlarged detail view on the line V—V of FIG. 2;

FIG. 6 is an elevational view of five rectangular cells superimposed one above another;

FIG. 7 is a plan view of the electrolytic cells shown in FIG. 6;

FIG. 8 is a side view of the electrolytic cells shown in FIG. 6;

FIG. 9 is a sectional view on the line IX—IX of FIG. 7;

FIG. 10 is a sectional view on the line X—X of FIG. 7;

FIG. 11 is a sectional, enlarged detail view of a portion of FIG. 9; and

FIG. 12 is a detailed view of FIG. 10 with a part thereof enlarged.

In the drawings, throughout the FIGURES 1 to 12 like reference numerals are used to indicate like parts.

Referring to the drawings, 1 indicates an alkali chloride electrolytic mercury cell which is provided with a metallic cover 2. The cover has a strength sufficient to resist the inner pressure of the cell and is made of metal having a low electrical resistivity. As such a metal there may be used, for instance, steel, aluminum, copper or their alloys, among which steel is the most preferable.

The cover may be of uniform thickness or reinforced with ribs, if required.

The rear or back surface of the cover is covered or coated with a titanium plate. The titanium plate is prefer-

ably to be closely fitted to the rear or back surface of the cover as uniformly as possible. The cover and the titanium plate may be also closely fitted together with vises, but an extremely good result can be obtained in the case where the close fitting is carried out by means of the explosion cladding method. The thickness of the titanium plate ranges preferably from approximately 1 mm. to approximately 10 mm.

It is preferred to cover the whole rear or back surface of the cover with a titanium plate, but it may be permitted to cover only the part of the rear surface of the cover to be used as an electrode. When there is any part of the rear surface of the cover, which is not covered with the titanium plate, it is preferable to cover that part with an anticorrosive material.

To the outer surface of the part of the titanium plate which is used as an electrode there is closely fitted a thin layer of platinum, rhodium, palladium or their alloys (which group is referred to hereinafter as the platinum group of metals), for example, by the electroplating method.

The thickness of the thin layer of the platinum group metal is preferably of the order of from 0.3 to 3 microns.

In an embodiment shown in FIGS. 1 to 5, the cover **2***b* of the electrolytic cell **1***b* is made of a separate material from the cathode **3***a* of the electrolytic cell **1***a* superimposed on the electrolytic cell **1***b*.

In the embodiment illustrated in FIGS. 6 to 12, the outer surface of the cover **2***b* of the electrolytic cell **1***b* is utilized as a cathode of the electrolytic cell **1***a*. The effect of the present invention becomes further notable, when the outer surface of the cover of the electrolytic cell is used as a cathode of another electrolytic cell superimposed on the electrolytic cell.

There is no limit on the shape of the electrolytic cell, and round, sector, rectangular and other shaped electrolytic cells can be used.

In FIGS. 1 to 5, there is shown, by way of example, a round or circular type electrolytic cell.

In these figures, **2***a* and **2***b* are covers, respectively, of electrolytic cells **1***a* and **1***b*. The covers are made of a 10 mm. thick steel plate, the rear surface of which cover is entirely covered with a 3 mm. thick titanium plate **4**. The steel plate and titanium plate are closely fitted or secured to each other by the explosion cladding method.

A platinum layer **5** of approximately 1 to 2 microns in thickness is formed on the surface of said titanium plate **4** by the electroplating method and the part plated with platinum is used as an anode. **3***a* and **3***b* are cathodes respectively made of steel and concentric depressions or recesses **6***a* and **6***b* are provided in the central portions of the cathodes. Mercury is fed from a feeding pipe **7** into said recesses or depressions and the mercury is stored in said recesses. Mercury placed in said recesses is driven in a thin layer by the brine which is fed through a feeding pipe **8** and flows at a high velocity between both electrodes, and this thin mercury layer flows on the cathode plate radially toward the periphery, during which time the mercury is amalgamated, and the amalgam of mercury thus formed flows down from the periphery of the cathode plate together with the brine. **9** is a baffle plate.

In the drawing, there is shown a horizontal cathode plate but the cathode plate may be conical in form in which case a conical cover is used.

To the periphery of the cathode plate there is welded an annular member **10** of L-section to form a groove **11**.

The amalgam falling down from the periphery of the cathode plate is collected in the groove, and withdrawn through a discharging pipe **12** and led to an amalgam decomposer (not shown).

The cathode plate **3***a* of the electrolytic cell **1***a* and the cover **2***b* of the electrolytic cell **2***a* are connected by cylindrical bodies **13**, **14** and **15**, which are located concentrically and said two members are arranged at suitably spaced distance by these cylinders.

The cylinders **14** and **15** are provided with many slits or holes **16** respectively. The brine which falls from the periphery of the cathode plate **3***a* flows into the electrolytic cell **1***b* through the said slits or holes **16** and the center hole **33** of the cover **2***b*.

The chlorine gas generated by the electrolysis emanates from the brine and is collected at the peripheral portion, and discharged through tube **17**. The brine which falls from tne cathode plate **3***b* of the electrolytic cell **1***b* is taken out from the tube **18**, and is reused after the dechlorination process, saturation process and purification process.

The cover **2***a* of the electrolytic cell **1***a* is connected with an anode bus-bar **19**, while the bottom plate **20** of the electrolytic cell **1***b* is connected with a cathode bus-bar **21**.

The cover **2***b* of the electrolytic cell **1***b* and the cathode **3***a* of the electrolytic cell **1***a* are electrically connected by the cylinders **14**, **15** and an electric current passes tnrough the cylinders. Thus, the cylinders accomplish the role of the intercell bus-bars connecting the electrolytic cells **1***a* and **1***b*. Accordingly, in the electrolytic cell of the present invention, there is no need for separate intercell bus-bars. For the purpose of making idle current smaller, decreasing leakage of the brine and at the same time, adjusting the distance between the electrodes, rubber packings **30** are inserted between the cylinder **13**, and the covers **2***a*, **2***b* or the bottom plate **20**.

In FIGS. 6 to 12, there is shown, by way of example, an embodiment of rectangular cells.

The cover **2***a* of the electrolytic cell **1***a* is made of a 7 mm. thick steel plate and the cover **2***b*, **2***c* of the electrolytic cells **1***b*, **1***c* are made of a 37 mm. thick steel plate respectively.

Though the covers **2***b*, **2***c* are shown as solid in the drawings, hollow covers may also be used. The rear surfaces of the covers are entirely covered with a titanium plate **4** of 3 mm. thickness. The steel and titanium plates are closely fitted each other by the explosion cladding method.

The outer surface of the titanium plate is covered with platinum layers **5** of about 1 to 2 microns thickness, and the platinum layer plays the role of anode.

The outer surfaces of the covers **2***b*, **2***c* of the electrolytic cells **1***b*, **1***c* are utilized as cathodes of the electrolytic cells **1***a*, **1***b*.

At the right end of the cover **2***b* of the electrolytic cell **1***b*, grooves **22** are formed.

Mercury is fed to the groove **22** through a pipe **23** and stored in the groove. Mercury stored in the groove is driven in a thin layer through the slit **32** by the brine which is fed to the groove **22** through a pipe **24** and flows at a high velocity between both electrodes and this thin layer of mercury flows over the cathode plate, during which time the mercury is amalgamated and the amalgam thus formed flows into a groove **25** at the left hand side of the said cover.

The inclination of upper stream side of said groove **25** is determined so that it is more lenient than the parabolic locus of the naturally cascading amalgam, said inclination being determined by the flow velocity of the amalgam and the brine, antifriction resistance and the like.

The separation of the amalgam from the brine is completely effected by determining the inclination of the upper stream side of the groove **25** to such a degree as described above. The amalgam is sent to an amalgam decomposer (not shown) by way of a pipe **26** and a sealing device **27**.

The chlorine gas generated during the electrolysis passes from the cells to a separator **28** with the brine. A partition wall **29** is provided in the separator. The brine overflows above the partition wall and is led to another electrolytic cell **1***b* and the chlorine gas is taken out from the upper portion of the separator **28**.

Mercury is fed to the groove **22** of the cover **2***c* of

the electrolytic cell 1*c*. The brine is fed from the separator **28** to the electrolytic cell 1*b* and flows between the anode and cathode at a high velocity in the reverse direction to the electrolytic cell 1*a*. In this way, the brine flows between the anode and the cathode in one cell in a reverse direction from that employed in the preceding or following cell in the system. Thus, the brine flows in series through the cells, being taken out from the separator of the lowest cell, and is reused after the dechlorination process, saturation process and purification process.

The anode bus-bar **19** is connected to the cover 2*a* of the electrolytic cell 1*a*, while the cathode bus-bar **21** is connected to the bottom plate **31** of the lowest cell.

The outer surface of the cover 2*b* of the electrolytic cell 1*b* is used as a cathode of the electrolytic cell 1*a*, and its rear surface is used as an anode of the electrolytic cell 1*b*. As a consequence, an intercell bus-bar is not required. An electric current flows vertically to the electrode surface in the cover of the lower electrolytic cell from the upper electrolytic cell to the lower electrolytic cell. The section of the electrode perpendicular to the current, that is, parallel to the electrode surface, is large in its area and uniform, and consequently, the current density becomes uniform and the voltage drop becomes small.

Rubber packings **30** are inserted in the peripheral end portion of the electrodes and the connecting portion of the separator and the like for the purpose of making idle current smaller, decreasing the leakage of the brine and at the same time, adjusting the distances between the electrodes.

For the sake of simplification, FIGS. 1 to 5 represent an embodiment of two superimposed circular electrolytic cells, and FIGS. 6 to 12 represent an embodiment of five superimposed rectangular electrolytic cells.

It is needless to say that the number of electrolytic cells to be superimposed or piled up is not limited, by the accompanying drawings.

There is no limit for the method of feeding the brine to these electrolytic cells. For instance, the brine may be transmitted to each electrolytic cell in parallel and independently by sending the brine discharged from one electrolytic cell directly to a purifying apparatus or circulating apparatus without feeding it to the next electrolytic cell.

However, as described above, it is appropriate to pass the brine through the superimposed electrolytic cells in series by connecting the brine outlet of one electrolytic cell with the brine inlet of the subordinate electrolytic cell, thus feeding the brine discharged from the upper electrolytic cell to the adjacent electrolytic cell. The following advantages can be obtained by adopting such a brine supplying method as described above. It is also possible to transmit the brine from the lower cell to the upper cell, but it is practical to feed the brine from the upper cell to the lower one.

The amount of the brine to be fed to the cells is so selected that the concentration of the brine discharged from the final electrolytic cell is 200 to 280 g./l. and preferably 240 to 260 g./l.; when the alkali chloride is NaCl, and is 220 to 300 g./l. and preferably 260 to 280 g./l. when the alkali chloride is KCl.

Accordingly, in the case where the brine is fed in series from one to another of a number of electrolytic cells, the amount of the brine flowing through each cell per unit hour becomes extremely large.

Generally, in order to increase the flow rate of the brine, a part of the brine discharged from the electrolytic cell is used as is for recirculation without being sent to the dechlorination process, saturation process and purification process, when the brine is fed in parallel to each electrolytic cell. As a result, for increasing the flow rate of the brine, it becomes necessary to increase the amount of the brine. As a consequence, a huge circulation installation becomes necessary. On the other hand, according to the present invention, it is possible to make the flow rate of the brine high, without the need for such a huge circulation installation. In the method of the present invention, the electrolyzing voltage can be decreased by economically increasing the flow rate of the brine. It is needless to say that a part of the brine discharged from the final cell of the present invention may be circulated without sending it to a dechlorination process and the like.

In the case where the brine is caused to flow in series through the electrolytic cells, the brine in the upper stream side of the electrolytic cell has a higher pressure than that of the brine in the down stream side of the electrolytic cell, for instance, when 20 electrolytic cells are superimposed one above another and the brine is caused to flow from above to below in series, the pressure of the brine in the uppermost electrolytic cell is higher by about 0.6 to 2 atmospheres in pressure as compared with the pressure of the brine of the lowermost cell. Therefore, chlorine gas obtained from the upper electrolytic cells can be taken out in a relatively high pressure state corresponding to the pressure of the brine.

In general, the concentration of the brine in an electrolytic cell is higher at the inlet site for the brine and lower at the outlet site for the brine. The electric resistance of the brine changes with such a change in the concentration of the brine. The change of the electric resistance is one of the causes for rendering the current density non-uniform.

In the electrolytic cell of the present invention, the flow rate of the brine is high and consequently, the change in the brine concentration is smaller.

In the electrolytic cells shown in FIGS. 6 to 12, the direction of the flow of the brine is reversed after it passes through every cell and therefore, the influence of the concentration change of the brine upon the electric resistance is compensated mutually, and the non-uniformity of the current density due to the change of the concentration is extremely small.

As apparent from the foregoing description, in the electrolytic cells of the present invention, the current density is uniform and the flow rate of brine is high. Hence, the amount of the evolved hydrogen is also small, and the chlorine gas can be obtained at high pressure.

Furthermore, the floor area required for arranging the electrolytic cells of this invention and the utilization of bus-bars are both small, and the loss of electric power is also small.

It is possible to operate the electrolytic cells of the present invention without a brine circulation pump of large capacity or without any circulation pump.

This invention is further described in the following examples, which are illustrative but not limitative thereof.

EXAMPLE 1

The following results could be obtained by the use of electrolytic cells as shown in FIGS. 1 to 5.

Number of electrolytic cells superimposed	6
Distance between anode and cathode (mm.)	3
Concentration of sodium chloride solution at inlet NaCl (g./l.)	256
Concentration of sodium chloride solution at outlet NaCl (g./l.)	250
Flow rate of the brine (l./mm./KA)	32.8
Voltage per unit cell (v.)	4.08
Chlorine gas and hydrogen gas concentrations (vol. percent)	96 and 0.2
Current density (amp./dm.^{2})	81.0
Current efficiency (percent)	95

In operating the cells, about 85% of the outlet brine was circulated.

EXAMPLE 2

The following results could be obtained by the use of electrolytic cells as shown in FIGS 6 to 12.

Number of electrolytic cells superimposed	10
Distance between anode and cathode (mm.)	2.8
Concentration of sodium chloride solution at inlet NaCl (g./1.)	255
Concentration of sodium chloride solution at outlet NaCl (g./1.)	250
Flow rate of brine (1./min./KA)	62.8
Current density (amp/dm.^{2})	83.3
Voltage per unit cell (v.)	4.2
Chlorine gas and hydrogen gas concentrations (vol. percent)	96 and 0.2
Current efficiency (percent)	93

In operating the cells, about 67% of the outlet brine was circulated.

What I claim is:

1. An alkali chloride electrolytic mercury cell adapted to be employed in a superimposed relationship with a plurality of such cells and having a metallic cover made of a metal other than titanium, at least a portion of the bottom surface of said cover being closely fitted with a titanium plate covered with a thin layer of an electrode grade metal selected from the group consisting of platinum, rhodium, palladium and alloys thereof, said thin layer adapted to be used as the anode in said cell.

2. An alkali chloride electrolyte mercury cell as defined in claim **1**, wherein the thickness of said titanium plate ranges from approximately 1 mm. to approximately 10 mm.

3. An alkali chloride electrolytic mercury cell as defined in claim **1**, wherein said thin layer of an electrode grade metal has a thickness ranging from 0.3 to 3 microns.

4. An alkali chloride electrolytic mercury cell as defined in claim **1**, which is one of a plurality of such electrolytic cells superimposed one upon another and connected in series electrically.

5. An alkali chloride electrolytic mercury cell as defined in claim **1**, where the outer surface of said cover is made of steel.

6. An alkali chloride electrolytic mercury cell as defined in claim **4**, wherein the outer surface of the cover of each of the superimposed electrolytic cells is made of steel.

7. An alkali chloride electrolytic mercury cell as defined in claim **4**, wherein the outer surface of each of said covers is adapted to be used as a cathode of a superimposed electrolytic cell.

8. An alkali chloride electrolytic mercury cell as defined in claim **4**, wherein the outlet for brine of a superimposed electrolytic cell is connected with the inlet for brine of the superimposed upon electrolytic cell.

9. An alkali chloride electrolytic mercury cell as defined in claim **8**, wherein said cell is adapted to be used so that chlorine gas can be withdrawn therefrom under pressure.

10. An alkali chloride electrolytic mercury cell as defined in claim **4**, wherein said cell is adapted to have the direction of flow of the brine reversed in each successive electrolytic cell.

11. An alkali chloride electrolytic mercury cell as defined in claim **4** wherein each of said cells has a cathode positioned below and planar to the anode in each of said cells.

12. An alkali chloride electrolytic mercury cell as defined in claim **11** wherein said cathodes have recesses in the upper surfaces thereof which are adapted to receive and store mercury therein.

13. An alkali chloride electrolytic mercury cell as defined in claim **11** wherein said recesses are in the center of the upper surfaces of said cathodes.

14. An alkali chloride electrolytic mercury cell as defined in claim **11** wherein said recesses are in the periphery of the upper surfaces of said cathodes.

15. An alkali chloride electrolytic mercury cell as defined in claim **11** wherein each of said cells have means for supplying brine thereto which are adapted to have the flow of brine drive a thin layer of mercury therewith from said recesses over the upper surfaces of said cathodes and between said cathodes and said anodes.

16. An alkali chloride electrolytic mercury cell as defined in claim **15** wherein each of said cathodes are formed by the outer surfaces of said covers.

17. An alkali chloride electrolytic mercury cell as defined in claim **15** wherein the means employed for supplying brine to the cells is adapted to cause the brine to flow in series through the cells.

References Cited

UNITED STATES PATENTS

2,719,117	9/1955	Blue et al.	204—220
3,068,165	12/1962	Messner	204—219
3,271,289	9/1966	Messner	204—219
3,308,043	3/1967	Loftfield et al.	204—219 XR
3,318,792	5/1967	Cotton et al.	204—219

FOREIGN PATENTS

822,665	10/1959	Great Britain.

HOWARD S. WILLIAMS, *Primary Examiner.*

D. R. JORDAN, *Assistant Examiner.*

U.S. Cl. X.R.

204—220, 250