Dec. 23, 1958 T. L. ROSS 2,865,834

ELECTROLYTIC ALKALI HALOGEN CELL

Filed Feb. 24, 1953 2 Sheets-Sheet 1

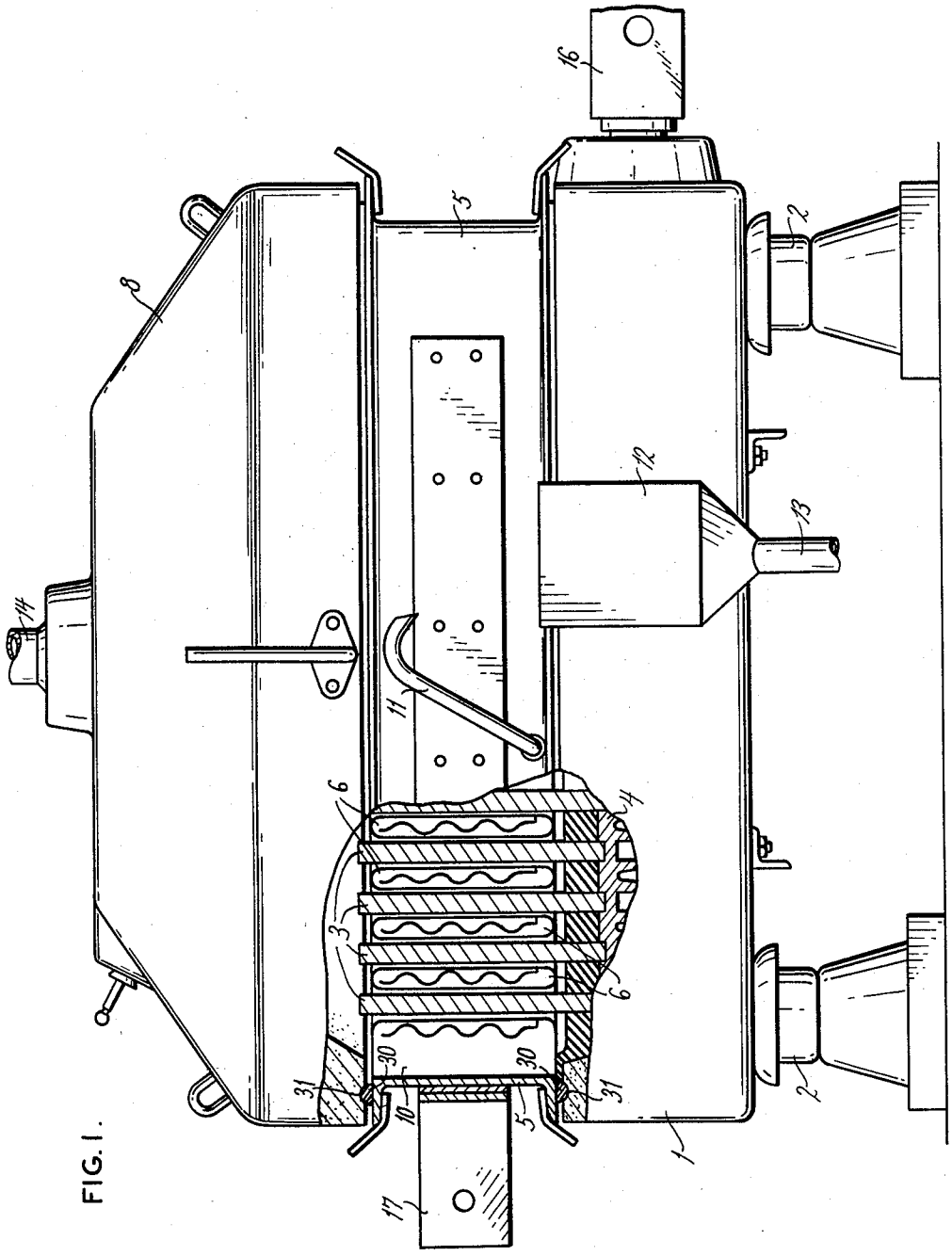


FIG. 1.

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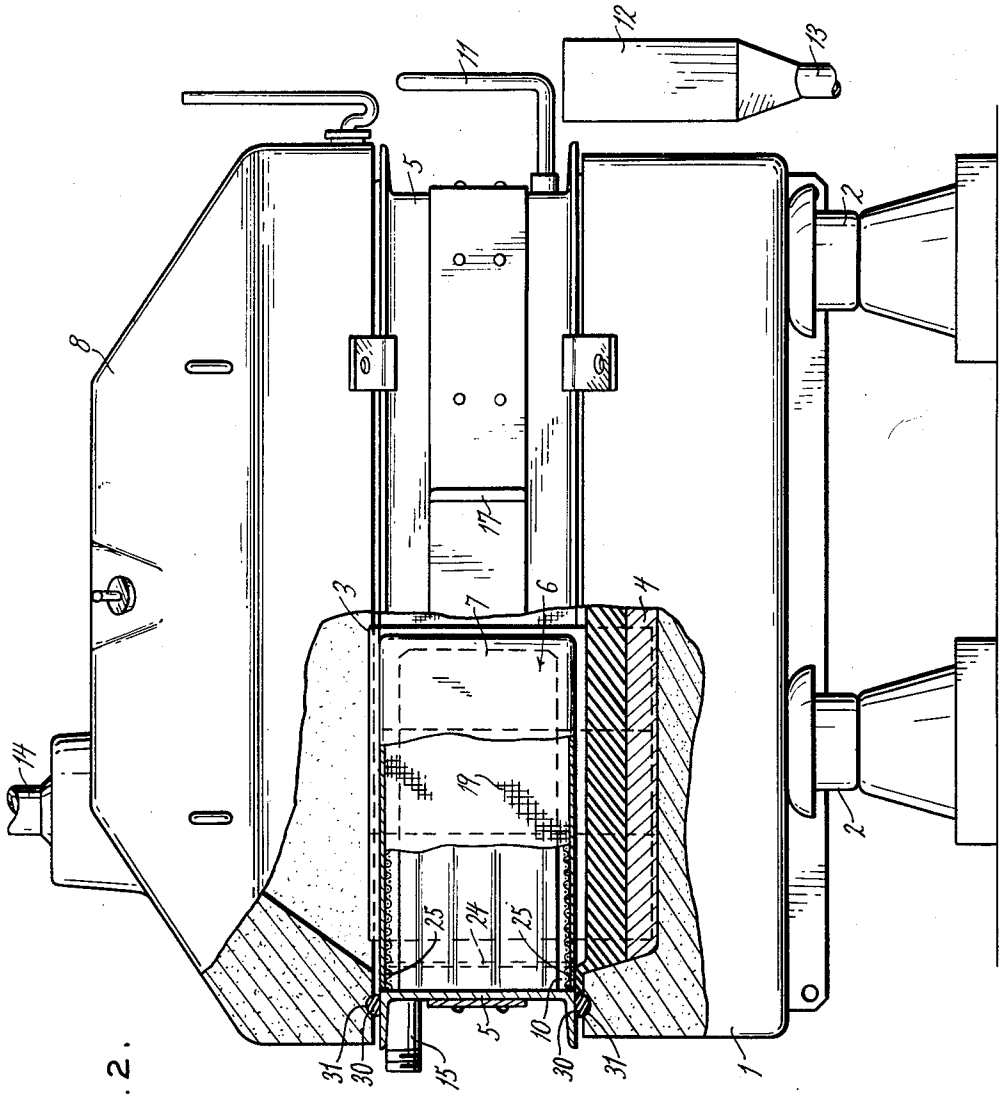


FIG. 2.

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ELECTROLYTIC ALKALI HALOGEN CELL

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Application February 24, 1953, Serial No. 338,260

7 Claims. (Cl. 204—266)

This invention relates to electrolytic alkali halogen cells and more specifically pertains to an improved halogen gas collecting cover or cell top for an electrolytic alkali halogen cell.

Electrolytic alkali halogen cells are widely used in the industrial preparation of caustic soda, chlorine and hydrogen by the electrolysis of sodium chloride brines. The sodium chloride brines are continuously fed into the electrolytic cells and contacted with the cell electrodes. Electric current of from 5,000 to 25,000 amperes or higher at 500 to 1000 volts is supplied to the cell to electrically decompose the sodium chloride brine. Wet chlorine gas is generated at the anode and collects at the cell top through which it is drawn. Hydrogen is collected at the cathode and is withdrawn through the side of the cell. An aqueous mixture of caustic and undecomposed sodium chloride is withdrawn as effluent from the cell.

One type of electrolytic cell to which this invention pertains is illustrated in the accompanying drawings which are made a part hereof. In reference to the drawings:

Fig. 1 is a side elevation of an electrolytic alkali chlorine diaphragm cell partially in section to reveal the electrodes, some of the cathodes in section to reveal the supporting structure within them, the foraminous walls of the cathodic electrodes and diaphragm covering them being indicated conventionally by single lines.

Fig. 2 is an end elevation of an electrolytic alkali chlorine diaphragm cell partially in section, the section passing between an anodic electrode and a cathodic electrode and parallel thereto to reveal a side of the diaphragm covering the cathodic electrode.

Heretofore the electrolytic alkali halogen cell tops and bottoms have been molded from a concrete mixture prepared from Portland cement and a mixture of siliceous aggregates and cured for at least 30 days before assembling the cells and using them. In industrial practice, such concrete cell tops are a source of constant trouble. The concrete cell top is constantly exposed to wet chlorine gas from the time the cell is first placed in operation. Almost immediately after being placed in operation, the inner surface of the cell top starts to disintegrate. By the third to the fifth day, the deteriorated concrete inner surface is sloughing off quantities of disintegrated concrete. The heavier particles of concrete dropped to the bottom of the cell but the final particles which settle slowly in the cell liquor are drawn to the chlorine resistant pervious diaphragms around the cathode thereby reducing the efficiency of the diaphragms. After a week or two of operation, the cathode diaphragm is completely plugged with concrete particles and must be removed and replaced with a new diaphragm. After the original diaphragms have been replaced, the rate of disintegration of the concrete decreases. However, it is necessary to replace the diaphragms again after an additional 60 to 90 days. These diaphragms again usually require replacement in about 50 to 70 days or after the cell has been in operation 110 to 160 days from startup. At this time, the graphite electrodes require replacement. Normally the cell tops can

be used again on a cell with new graphite electrodes. Generally, the diaphragms installed at the time of installation of new graphite electrodes will become plugged by fine concrete particles and require replacement only once during the life of the second set of electrodes. By the time the second set of electrodes have been consumed, the cell tops are usually so badly cracked and corroded that they too must be replaced.

In addition to the labor and materials cost for these frequent diaphragm and top renewals, the operation of electrolytic alkali halogen cells with cell tops molded from mixtures of Portland cement and siliceous aggregates is exceedingly costly in that the diaphragm plugging causes the cells to operate at higher temperatures thereby causing an excessive consumption of electrical power per ton of chlorine produced. The corrosion of the cell top inner surface is not the only factor which reduces the cell top life. Two to five days after new cell tops have been placed in service, the external surface of the cell top develops a number of small cracks. These cracks usually penetrate through the cell top within 15 to 30 days. The external surface of the cell top is usually patched from time to time. However, after the second set of graphite electrodes have been consumed, there are a great number of cracks through the cell top. Further patching of the external surface is useless since the cell top has by now become so weak as to be unsafe for further use.

The cell bottoms constructed in accordance with the prior art practices are also molded from a mixture of Portland cement and siliceous aggregates. Such cell bottoms although not attacked by hot wet chlorine are substantially weakened by the hot aqueous caustic solution formed in the cell and usually require replacement after only one to two years of service.

It is an object of this invention to provide improved tops and bottoms for electrolytic alkali halogen cells.

It is also an object of this invention to provide a top for an electrolytic alkali halogen cell which is resistant to attack by hot wet chlorine.

It is an additional object of this invention to provide a top for an electrolytic alkali halogen cell which will not slough off particles thereof and plug the cathode diaphragm.

Still another object of this invention is to provide an electrolytic cell of greatly increased production capacity and longer production life.

Other objects of this invention will be apparent from the detailed description hereinafter appearing.

Referring to Figs. 1 and 2, 1 is a bottom member which in this case is shown as rectangular and constructed in accordance with this invention. Bottom member 1 rests upon non-conducting members 2, 2, and houses the anode assembly, comprising rolls of upright elongated graphite anodic electrodes 3, 3, in the form of flat sided blades and having their lower ends conductively affixed to a metallic plate 4 preferably of lead.

Resting upon bottom member 1 is the cathode assembly, comprising a normally level liquid retaining and enclosing frame including walls 5 of metal plate, in this case, of channel section, adapted to carry the cell current and conforming in plan to bottom member 1 and projecting perpendicularly with respect to walls 5, and with their outer ends conductively attached thereto, as hereinafter described, two banks of thin, parallel, flat-sided, elongated, horizontally aligned, foraminous cathodic electrodes 6, 6, alternating with anodic electrodes 3, 3, and adapted to be covered by permeable chlorine resistant diaphragm 7. This diaphragm is generally constructed from asbestos fiber and formed as a seamless cover over the entire foraminous cathodic structure in a manner well known to the art.

The cathodic electrodes are of a foraminous structure housed in enclosing walls 5. This structure is generally of woven wire screen as indicated by face 19 in Fig. 2. The side walls or active faces 19 of adjacent cathodic electrodes are joined at their butt end by walls 24 which are preferably arcuate. These butt end walls are spaced from walls 5 leaving corridors 10 between for the reception of liquid and gaseous products issuing from the open butt ends of the cathodic electrodes. Corridors 10 are closed at top and bottom by walls 25 which are shaped to fit the butt end walls 24. The outer edges of walls 25 are conductively affixed to the inner faces of walls 5 flush with their upper and lower edges generally by welding. The current flow from walls 5 to the active faces of the cathodic electrodes is therefore inward and edgewise through walls 25, then through walls 24 and then inward and edgewise through active faces 19 of the cathodic electrodes. The vertical wires of the active faces form closed flattened loops. These vertical wires receive current from the horizontal wires of the active faces by pressure contact therewith.

Surmounting the cathodic assembly conforming therewith and resting upon enclosing walls 5 is the chlorine gas collecting cover or cell top 8 which is constructed in accordance with this invention. The joints between bottom member 1 and walls 5 and between the latter and cover member 8 may be made liquid tight by the sealing means comprising gasket 30 and grooves 31. The electrolyzed brine after percolating through the diaphragm is received into the hollow cathodic electrodes and delivered by them at their outer ends into corridors 10 as hereinbefore stated. Hence, it issues through effluent pipe 11 to be caught in funnel 12 and carried away to a header (not shown) through pipe 13. Chlorine gas is carried away from cover 8 through exit 14 to a header (not shown). Hydrogen gas is carried away from the upper part of the corridor 10 through pipe 15 to a header (not shown). Direct electric current is passed through the electrolyte between the anodic and cathodic electrodes from a generating source (not shown) by means of bus bars 16 and 17.

According to the practice of the prior art, cell top 8 and bottom No. 1 have been constructed by molding a concrete mixture containing Portland cement, gravel and water in the ratio of from 2 to 3 parts by volume of screened gravel or sand, from 1 to 2 parts by volume of coarse gravel aggregate for each part by volume of cement and from ½ to ⅔ parts by volume of water. The preferred size of the gravel aggregate used is from 3/16" to ¾". The concrete members thus formed must be cured for at least 30 days and preferably 60 days before they can be put into service. Cell tops prepared in this manner when subjected to hot wet chlorine begin to disintegrate shortly after being put into service. The disintegration and deterioration of the cell top causes the cathodic electrode diaphragms to become plugged which in turn lowers the productivity of the cell per unit of electric energy input. This plugging also causes the cell to operate at a much higher temperature than normal further hastening the cell top deterioration.

However, it has now been discovered that cell top 8 and bottom No. 1 can be constructed from a concrete-like mixture which sets to chlorine resistant mass. The use of such cell tops completely eliminates the difficulties heretofore encountered with cement structures containing Portland cement and siliceous aggregate. The improved cell top and bottom members are prepared by molding them from a mixture comprising calcium aluminate cement, a sharp, irregular, impervious chlorine resistant aggregate and water. Such cell tops will cure to full strength in 24 to 48 hours after being poured. The cell top shown in the drawing has been prepared in such a mixture. Cell tops prepared according to this invention have given hundreds of days of trouble-free service.

The preferred aggregate for use according to the practices of this invention are the sharp, irregular, impervious aluminum oxide aggregates generally referred to as emery aggregates. The term "emery aggregates" as employed herein is intended to include the natural occurring corundum as well as similar synthesized aluminum oxide compositions such as "Alundum." Aggregates other than emergy aggregates may also be employed. Obviously, crushed limestone although sharp and irregular and in some cases impervious would not be suitable because of the reactivity of limestone with chlorine. Gravel is not sufficiently sharp to be of any utility with the aluminate cement. Sharp quartz sand and ground granite can be employed as the aggregate in preparing cell top and bottom members according to this invention. In general, the concrete-like mixtures containing calcium aluminate cement and sharp, irregular, impervious chlorine resistant aggregates are prepared by combining from about 1 to about 3 parts by volume of aggregate having a maximum particle size of 3/8" with each part by volume of calcium aluminate cement and then adding sufficient water to make a pourable plastic mass.

The following will illustrate a preferred chlorine resistant concrete-like mixture and the use thereof to prepare the improved cell top and bottom members of this invention.

In the pouring of a bottom member, there were prepared six batches calcium aluminate cement and emery aggregate mixes. Each of these batches was prepared by first dry mixing 200 pounds (about 1.5 cubic feet) of emery aggregates having a maximum particle size of 3/8" with one sack of calcium aluminate cement (1 cubic foot). To each of the first two batches there was added 4 gallons of water to form a pourable mass. To each of the next two batches there was added 3.5 gallons of water and to each of the last two batches there was added 2.25 gallons of water. The concrete-like mixture was allowed to set for about 4 hours after the pouring had been completed. The mold was then stripped off and the bottom member was allowed to cure before being used to build an alkali chlorine cell. Several additional cell bottom members were prepared by the procedure described above.

A cell top was poured from 10 batches each containing 200 pounds of the emery aggregate described above and one sack calcium aluminate cement with water as follows: to each of the first three batches there was added 4 gallons of water; to each of the next four batches there was added 3.5 gallons of water and to each of the last three batches there was added 2.25 gallons of water. The mold was stripped from the cell top about 4 hours after pouring had been completed. Several additional cell tops were prepared by the procedure described above.

Several caustic soda chlorine cells of the type hereinbefore described were assembled using cell top and bottom members made as described above after the cell top and bottom members had cured for about two days after the molds had been stripped off. These cells were placed in service together with cells prepared from Portland cement and siliceous gravel aggregates. After about 10 days, the diaphragms in the cells prepared from the Portland cement mixture had plugged with concrete particles and had to be replaced. These replacement diaphragms became plugged with concrete particles after about 70 days of operation and had to be replaced. The cells assembled from cell top and bottom members prepared according to this invention were inspected at this time and found to be in excellent condition. There was no evidence of deterioration of the inner surface of the cell top. Cells having cell top and bottom members prepared according to this invention have been in operation for many months and have not had to be taken out of service because of diaphragms plugging by particles sloughed off from deteriorating cell tops. Although diaphragms in these cells have had to be replaced because of impurities in the brine feed, in general, the diaphragms in the improved alkali chlorine cells of this invention

will last 1½ times longer than those in the cells with tops of Portland cement concrete. It has been found that the graphite electrodes used in the improved cells of this invention will last 1½ times longer than those in the cells having tops of Portland cement concrete.

What is claimed is:

1. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member being prepared from a concrete mixture whose solid components consist essentially of a minor proportion of an aluminous cement and a major proportion of a sharp, irregular, impervious, chlorine resistant aggregate.

2. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member being prepared from a concrete mixture consisting essentially of a minor proportion of aluminous cement and a major proportion of emery aggregate.

3. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member and said bottom member being prepared from a concrete mixture consisting essentially of a minor proportion of aluminous cement as the binder for a major proportion of a sharp, irregular, impervious, chlorine resistant aggregate.

4. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member and said bottom member being prepared from a concrete mixture consisting essentially of a minor proportion of aluminous cement as the binder for a major proportion of emery aggregate.

5. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member being prepared from a mixture consisting essentially of aluminous cement and from 1 to 3 volumes of emery aggregate for each volume of said cement.

6. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said top closure member and said bottom member being prepared from a mixture consisting essentially of aluminous cement and from 1 to 3 volumes of emery aggregate for each volume of said cement.

7. In an electrolytic alkali chlorine cell comprising a cathode assembly including foraminous cathodic electrodes housed in an upright liquid retaining wall; an anode assembly cooperative therewith including upright anodic electrodes having their lower ends embedded in a slab of low melting metal; a top closure member for said retaining wall; and a bottom member for said retaining wall and support for said cathode and anode assemblies; said bottom closure member being prepared from a concrete mixture consisting essentially of aluminous cement as a binder for emery aggregate.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,865,834 December 23, 1958

Theodore L. Ross

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 59, for "final" read -- finer --; column 4, line 7, for "emergy" read -- emery --.

Signed and sealed this 7th day of June 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents