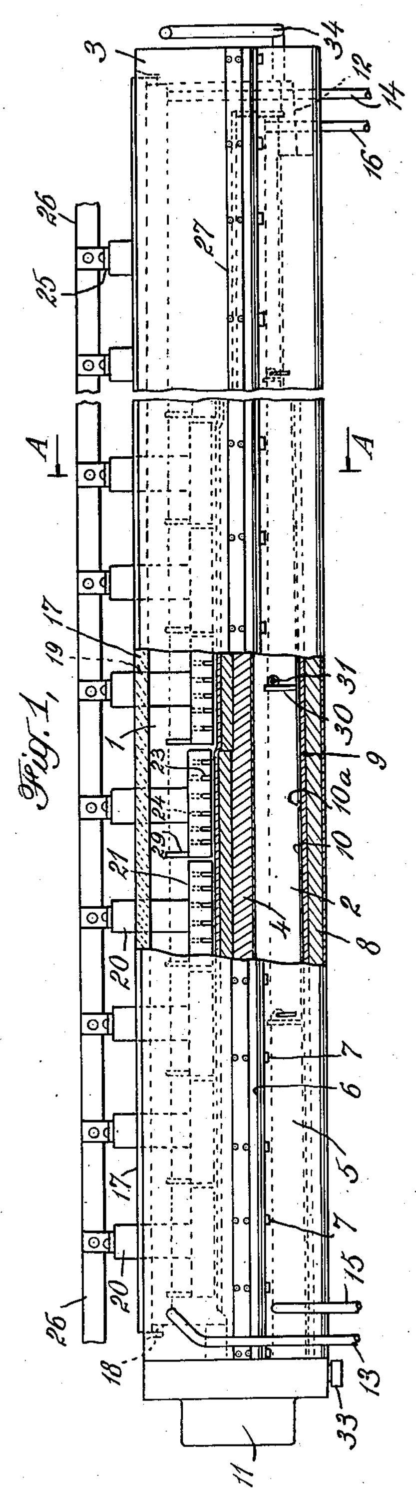
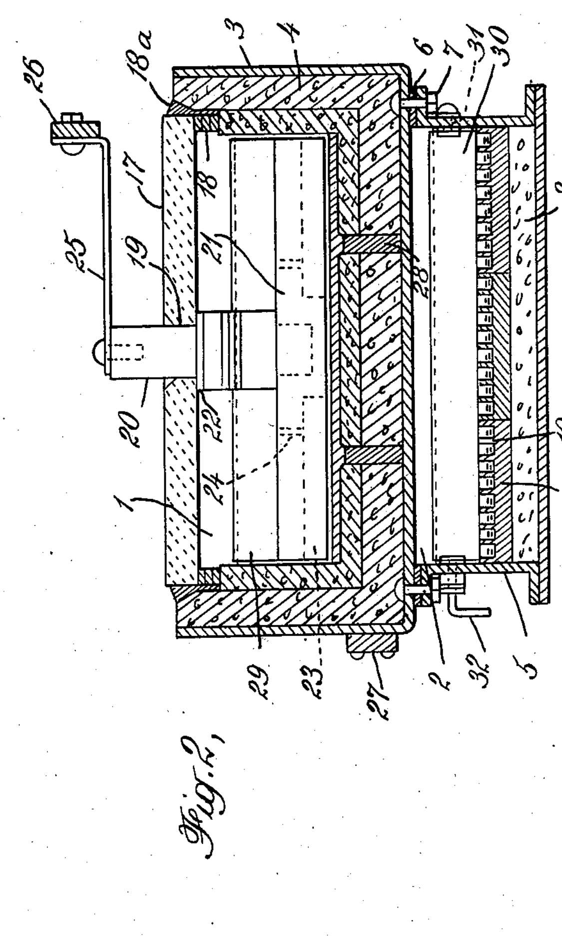
April 19, 1949. R. A. HORST 2,467,892

REGENERATOR CHAMBER FOR MERCURY CATHODE ELECTROLYTIC CELL

Filed Sept. 18, 1942





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Patented Apr. 19, 1949 2,467,892

UNITED STATES PATENT OFFICE

2,467,892

REGENERATOR CHAMBER FOR MERCURY CATHODE ELECTROLYTIC CELL

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Application September 18, 1942, Serial No. 458,844

2 Claims. (Cl. 23—270.5)

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This invention relates to the electrolysis of brine and is particularly concerned with a new and improved mercury cathode apparatus for the conduct of such electrolyses.

In the past various types and designs of mercury cathode electrolytic apparatuses have been proposed.

An early apparatus is the type commonly known as the Castner cell. The Castner cell (U. S. Patent 518,135 of 1894) involves a pair of brine chambers in which brine is electrolyzed to form an amalgam and an intermediate washing chamber in which amalgam is washed with water to remove the active metal and regenerate or reclaim the mercury. The apparatus is so balanced and actuated that by tipping the apparatus first in one direction and then in the other, the mercury is caused to flow from one brine chamber, through the washing chamber, to the second brine chamber and then back in the reverse direction.

Later apparatus substituted stationary brine and washing chambers at different levels and provided various types of elevators for conveying the mercury from the lower to the higher chamber. Such apparatus is illustrated by the Whiting cell of U. S. P. 951,228 of 1910. The Whiting cell involved a brine chamber and a washing chamber situated side by side. The brine chamber was arranged at a slightly higher elevation than the washing chamber so that mercury would flow by gravity from the former to the latter. A bucket-wheel elevator was provided for raising the mercury from the low elevation of the washing chamber to the higher elevation of the brine chamber.

The present invention is concerned with modifications in apparatus of the latter general type, i. e., with electrolytic apparatus having a relatively high brine chamber and low washing chamber and an elevator for raising the mercury.

The apparatus of the invention is applicable to the electrolysis of salts of amalgam-forming metals in general but is especially applicable to the electrolysis of salts of the metals which react with water, for example, the electrolysis of the chlorides and bromides of the alkali-metals. That chamber in which the metal salt is electrolyzed to form an amalgam of the free metal will be referred to herein as the "brine chamber" and that chamber in which the free metal is washed from the amalgam, thus restoring the mercury to its initial condition, as the "regenerator" or, since when water is employed as the washing liquid, as is customarily the case, free hydrogen and metal hydroxide are formed, as the "hydrogen" or "hydroxide" chamber.

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The apparatus of the invention is characterized by a novel arrangement of brine chamber and regenerator each having an approximately horizontal mercury supporting bed or tray, the regenerator tray being directly beneath the brine chamber tray. The two trays are slightly farther apart at one end than at the other and at the end of greater separation an elevator is provided while at the opposite end there is a free flow mercury seal. This arrangement causes the mercury in passing through the cell to follow a path resembling an endless belt about a large drive pulley and a smaller driven pulley.

By the above placement of parts numerous advantages are obtained. Thus the cell occupies a minimal amount of space. If a number of the cells are arranged side by side, the elevators and mercury seals of the entire battery are readily accessible. Since any necessary access to the balance of the cell may be from one side, the cells of the battery may be arranged in juxtaposed pairs and thus placement space may be still further conserved. The brine chamber may be placed directly upon the regenerator, thus serving as a cover to complete the enclosure of the latter and secure the advantages of a closed unit. Moreover, an extremely rigid unitary construction may be employed comprising parallel channel irons or I-beams as side members for the regenerator, so disposed as to serve as a supporting frame for the brine chamber. The inherent rigidity of this assembly permits a lighter weight construction than otherwise necessary, thus permitting not only lower apparatus costs but also lower costs for foundations and supporting structures. As an additional important advantage, the heat generated in the cell is retained in the cell to a substantially greater degree than in previous cells. This feature assists operation of the cell at higher than atmospheric temperatures; in the electrolysis of sodium chloride and potassium chloride brines to produce chlorine and caustic soda or caustic potash, it enables one to secure unusually high concentrations of caustic solutions without application of external heat to the cell, caustic concentrations between 50% and 60% being readily obtainable.

The cell of the invention is preferably at least five times as long as it is wide; i. e., the brine chamber mercury bed has a width not more than one-fifth its length. The brine chamber is provided with a plurality of cross-members or baffles positioned on top of the anodes at more or less regular intervals to confine the flow of brine primarily to the narrow space between the mercury cathode and the anodes disposed thereabove. The regenerator chamber is also provided with cross members or baffles which cooperate with a mercury supporting tray having longitudinal fins to dam the flow of water or other washing liquid above the fins and thus provide a series of pools from which the washing liquid flows in a large number of small parallel streams defined by the mercury on the bottom, the fins on the sides, and the baffles on the top. By this arrangement an orderly and progressive flow of washing liquid from one end of the unit to the other is insured.

The baffle members in the regenerator are preferably pivoted and provided with means outside the cell for moving these baffles to an inoperative position. This construction facilitates flushing of the regenerator, reduces the flushing period, and increases the average efficiency of regeneration and thus, indirectly, the attainable caustic concentration.

The abnormally long brine chamber and the baffles so placed as to concentrate the flow of brine in the zone between the anode and cathode co-operate to provide a high velocity of flow of brine in this zone. This high velocity of the brine scours from the anodes the small bubbles of chlorine which normally tend to adhere to their surface. The prompt removal of these bubbles not only substantially improves the voltage efficiency of the cell but also tends to inhibit irregular erosion of the anodes and thus not only to further increase the voltage efficiency but at the same time to prolong the useful life of the anodes.

In order to secure the greatest advantage from the scouring effect of the brine, it is desirable to provide chlorine escape channels transverse to the flow of brine. This may be accomplished by provision of many spaced anodes, each fairly narrow, so that chlorine is provided with frequent passages for escape upwards between anodes, or it may be accomplished by slotting the anodes vertically to provide even more frequent channels. A preferred form of anode is deeply grooved on its underface to provide gas channels. Chlorine collecting in the channels finds its way out at the ends of the anodes whence it can escape to the gas space above. This escape may be still further facilitated by provision of one or more holes from each channel to the upper face of the anode. The grooved anodes have substantially greater rigidity and substantially less electrical resistance than anodes of comparable size in which slots are cut all the way through.

Another important feature of the apparatus of the invention is the provision of co-current brine and mercury flow, which in combination with the directing effect of the brine chamber baffles sweeps any foreign matter rapidly forward toward the outlet whence it may be removed whenever the accumulation of such material is sufficient to warrant it. Since the efficiency of a mercury cathode electrolytic cell is substantially impaired by the accumulation of foreign material on the surface of the mercury in the zone of electrolysis, the rapid and efficient removal of such material from the zone of electrolysis contributes considerably to the electrical efficiency of the cell.

The practical application of my invention is illustrated by the specific embodiment described in detail below in connection with the accompanying drawing, wherein

Fig. 1 is a side elevation showing a specific embodiment of the invention. The apparatus is shown partly in sectional view and partly phantom view to show more clearly the construction of the apparatus.

Fig. 2 is an enlarged cross-section on line A—A of Fig. 1.

In the apparatus illustrated the cell comprises a brine chamber 1 and a regenerator chamber 2. By reference to Fig. 2 it will be seen that the brine chamber is constructed as a long chamber comprising a steel shell 3 provided with a lining of concrete or other suitable material 4.

For a cell having a capacity of about a half metric ton of chlorine per day and a rated load of 16,000 amperes, chamber 1 may be in the neighborhood of 2½ feet wide by 40 feet long. As will be apparent from Fig. 1, the floor of this chamber is a succession of steps and the depth of the chamber is accordingly somewhat greater at one end than at the other. The floor of the brine chamber 1 may be constructed of concrete or other alkali-resistant materials of construction. A particularly suitable type of construction involves the use of a poured concrete lining supporting precast concrete working surfaces as more fully described in U. S. application Serial No. 458,847 of even date, now abandoned.

A pair of channel-shaped steel structural members 5 form the sides of the regenerator chamber. One side-face of each channel provides a supporting surface for shell 3. The channel irons are separated from shell 3 by sealing gaskets 6 to prevent leakage of hydrogen from or air into chamber 2. The shell may be secured to the members 5 by a series of bolts 7. The floor of regenerator chamber 2 has a gentle slope with its high end beneath the low end of chamber 1 and its low end beneath the high end of chamber 1. This slope, which is at the rate of about $\frac{1}{16}$ inch per linear foot, may be provided by a concrete fill 8. The floor of the regenerator chamber is preferably composed of compressed graphite sections 9 having vertical fins 10 running longitudinally of the chamber and providing channels for flow of mercury from the high end of the regenerator chamber to the low end thereof as more clearly shown in Fig. 2. The ends of sections 9 may be beveled or notched, if desired, to provide transverse channels 10*a*.

At the left end of the cell an elevator 11, which may be of the bucket-wheel type, is provided for elevating mercury from the low end of the regenerator to the high end of the brine chamber. At the opposite end of the cell a mercury seal construction 12 is provided for permitting mercury to flow from the brine chamber down to the upper end of the regenerator chamber.

Flow of brine in the cell illustrated is from left to right and the brine chamber is provided with a brine inlet conduit 13 and brine overflow and chlorine outlet conduit 14. In the regenerator, flow of regenerating liquid, which is normally water or dilute alkali-metal hydroxide when alkali-metal hydroxide is being produced, is also from left to right from inlet 15 to hydroxide overflow and hydrogen outlet 16.

The brine chamber 1 is provided with a removable top or cover 17 supported on spacing elements or shims 18. Spacing elements 18 preferably are composed of a material having very little plasticity since the thickness of these elements determines the position of the anodes with respect to the mercury cathode. Leakage of chlorine from the chamber between the cover 17 and the lining 4 may be avoided by applying a suitable caulking material 18a, such as putty, between the lining 4 and the cover 17.

The cover 17 is provided with a plurality of apertures 19, one for each anode. Projecting through apertures 19 are a series of carbon anode supporting rods 20 to which the carbon anodes 21 are affixed in any suitable manner; they are shown threaded to the supporting rods. A shoulder of supporting rods 20 may rest against the cover 17 or may be separated therefrom by spacing washers 22 to initially adjust each anode so that its underface is the desired distance from the mercury level in the cell. This distance may be in the neighborhood of ¼ inch. The anode supporting rods 20 may be secured firmly to the cover 17 in any suitable manner, for instance by means of clamps or cement. The anodes 21 are graphite blocks which have a length substantially equal to the width of the brine chamber and normally have a width about half of this. Their thickness may be around 3 inches initially and during the operative life of the anode gradually diminishes to about 1 inch.

I prefer to provide the anodes 21 with channels or grooves 23 disposed along the underface of the anodes in a direction substantially perpendicular to the flow of brine and mercury thereunder. These channels, while they may extend to the upper surface of the anodes, preferably extend initially about one-third of the way through and are connected with the space above the anodes by means of apertures 24.

Electrical connection to the anodes is secured by means of electrically conductive supporting rods 20 and metallic connectors 25 and bus bar 26. Connectors 25 may be flexible or rigid and may be affixed to rod 20 by a stud bolt or a poured lead connection, or a clamp.

Electrical contact between the current source and the mercury cathode is obtained through the shell 3 of the brine chamber; electrically conductive bus bar 27 is riveted or otherwise affixed to the shell preferably along its entire length in order to avoid voltage losses through the shell. Conductive rods 28 are welded to the shell 3 and project up to near the upper surface of the floor lining 4. Mercury flowing through the chamber fills the cups formed by the tops of these conductive rods and the lining and thus makes electrical connection with shell 3 and bus bar 27.

Each anode 21 is provided with a baffle 29 extending from the upper edge of the anode to a point above the level of brine in the brine chamber. These baffles may be affixed to the anodes in any suitable manner, for instance by means of dowels. Since the end of each anode and the accompanying baffle present a wall opposing the longitudinal flow of liquid through the cell, liquid is forced beneath the anodes and the primary flow takes place in the space between the lower anode surface and the mercury.

The regenerator chamber 2 is supplied with transverse baffles 30 supported on pivots 31 in side walls 5 and provided with operating handles 32 located outside the cell so that baffles 30 may be manually raised to a horizontal position near the top of the regenerator. Suitable provision, such as valve-stem gaskets or washers, are provided to avoid leakage where handles 32 extend through the side wall 5 of the regenerator. The normal operative position of baffles 30 is as shown in the drawing with their lower edges resting upon fins 10. In this position the baffles, which extend above the normal liquid level in the regenerator, force the liquid in flowing from inlet 15 to outlet 16 to pass under each baffle. This provides a progressive flow of the regenerating liquid essential for securing at the same time high alkali-metal hydroxide concentration and effective removal of alkali-metal from mercury.

It is not necessary that the baffles be pivotally mounted for fixed baffles would perform the function of preventing lengthwise diffusion of the regenerative liquid as well. The pivoted baffles, however, facilitate cleaning as explained below.

A pair of outlets 33 and 34 have been shown at opposite ends of the cell. The outlet 33 preferably is disposed at approximately the mercury level in the cell when the cell is not operating; that is, when mercury in the upper chamber has all collected at the low end of the regenerator. This outlet has been shown as a simple capped pipe. Outlet 34, which is preferably disposed at about the normal mercury level when the cell is operating, is illustrated as a swivel type outlet which may be opened by swinging the high end to a point below the liquid level in the brine chamber.

For the production of highly concentrated alkali-metal hydroxide, it is desirable to limit heat loss by provision of suitable insulation. Since chamber 1 is so constructed that heat loss from this chamber is normally small, it is not necessary to provide additional insulation for this chamber. The primary loss of heat occurs at the seal end of the cell, particularly where mercury contacts the exterior metal walls of the unit. Thus, if the walls of mercury seal 12 are composed of metal considerable loss of heat at this point may occur unless adequate insulation is provided. It is also desirable to insulate side walls 5 of chamber 2 to conserve heat, particularly when caustic soda of about 50% concentration is being produced. Since the shell 3 loses some heat and is an active electrical conductor, it may be advantageously protected by a suitable material serving as both a heat and electrical insulator.

In assembling the above apparatus for operation, the unit is completely assembled and the required amount of mercury introduced with cover 17 removed. Anodes 21 are fixed to the cover with suitable adjustment of distances so that when the cover is placed upon spacers 18, which may be up to ¾ inch thick or, in some cases, up to about 1⅛ inches thick, the underfaces of the anodes are within about $\frac{2}{10}$ of an inch of the mercury surface. Since it is desirable to avoid as much as possible working around the cell, there is an advantage in securing bus bar 26 rigidly to the anodes and treating this bus bar as a part of the cover assembly. Baffles 29 are affixed to the anodes 21 and the cover is then placed on spacing elements 18 of the aforementioned thickness. The cover 17 is then sealed in place by means of putty 18a.

To start operating the cell, elevator 11 is set in operation to provide a sufficient flow of mercury through the cell so that the floor of the brine chamber is covered with a thin layer of mercury. Brine is introduced through inlet 13 until it begins to flow out through overflow outlet 14 and water is introduced at 15 until it begins to flow out through overflow outlet 16.

The following description illustrates the operation of the cell for the production of chlorine and aqueous 50% sodium hydroxide solution from sodium chloride brine.

Aqueous 25% sodium chloride solution is introduced at 13 at an hourly rate of about 355 liters and at a temperature of about 30° C. A sufficient voltage is applied between bus bars 26 and 27 to provide a cathode current density of about 21½ amperes per square decimeter. The flow of water into the regenerator chamber may be controlled to provide the concentration of sodium hydroxide desired, for example 50–52% NaOH. Under normal operating conditions with a cell of the type described, with elevator 11 and mercury seal 12 insulated to avoid heat loss, an adequate removal of sodium from the amalgam is secured in travel of amalgam from the mercury seal 12 to elevator 11. Under these conditions of operation the unit is capable of producing in the neighborhood of 500 kilograms of chlorine gas and a corresponding amount of 52% sodium hydroxide solution per day.

As the operation of the cell continues, the underfaces of anodes 21 are gradually worn or oxidized away and consequently the spacing between the mercury and the active anode surfaces increases. When this spacing has increased to about ½ inch, which may be after 2 to 6 months operation more or less, operation of the cell is discontinued and the spacing of the anodes is readjusted by removal of the required number of shims 18 to lower cover 17 and thus bring the active anode surfaces approximately to their original position. This adjustment may be coincided with the customary cleaning of the cell to remove any accumulation of foreign material from the anodes, the walls of the cell and from the mercury. For removing foreign material from the mercury, the arm on outlet 34 may be swung into a lower position to permit brine and foreign material to flow out through this outlet. For cleaning the regenerator chamber, baffles 30, if of the movable type, are turned to inoperative position to permit washing liquid to flow freely along the floor and sweep any material which has accumulated thereon to the lower end of the chamber where it may be withdrawn through outlet 33. The wash water for this purpose may be introduced through outlet conduit 16 or through a wash liquid inlet specially provided for this purpose. When the cell has been properly cleaned, the outlets are closed, the cover is replaced, and the chambers refilled with brine and water and operation started as before.

I claim:

1. A regenerator chamber, adapted for use in conjunction with a mercury cathode electrolytic cell, having vertical side and end walls and an inclined floor provided with a series of substantially vertical fins arranged to provide a plurality of parallel longitudinal channels, an entrance for liquid at the higher end of said floor and an outlet for liquid at the lower end, whereby flow of amalgam may be maintained longitudinally of the chamber, a second liquid inlet and a second liquid outlet positioned above said first mentioned inlet and outlet and in opposite relation thereto,

whereby aqueous regenerating liquid may be caused to flow longitudinally of the chamber and counter-current to the flow of amalgam, and a plurality of transverse baffles within said regenerator, the upper edges of which are above the levels of the second liquid inlet and outlet and the lower edges of which extend downwardly substantially to the level of the top of the fins, said baffles being disposed so as to provide a plurality of pools of aqueous regenerating liquid and to confine flow of said liquid from one pool to another to the longitudinal channels on the floor of the chamber.

2. A regenerator chamber, adapted for use in conjunction with a mercury cathode electrolytic cell, having vertical side and end walls and an inclined floor provided with a series of substantially vertical fins arranged to provide a plurality of parallel longitudinal channels, an entrance for liquid at the higher end of said floor and an outlet for liquid at the lower end, whereby flow of amalgam may be maintained longitudinally of the chamber, a second liquid inlet and a second liquid outlet positioned above said first mentioned inlet and outlet and in opposite relation thereto, whereby aqueous regenerating liquid may be caused to flow longitudinally of the chamber and counter-current to the flow of amalgam, a plurality of transverse baffles within said regenerator, the upper edges of which are above the levels of the second liquid inlet and outlet and the lower edges of which extend downwardly substantially to the level of the top of the fins, said baffles being disposed so as to provide a plurality of pools of aqueous regenerating liquid and to confine flow of said liquid from one pool to another to the longitudinal channels on the floor of the chamber, and means for pivoting said transverse baffles so as to swing the baffles to an inoperative position while flushing the regenerator.

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