

Jan. 13, 1970

J. E. COLMAN ET AL
BIPOLAR ELECTROLYTIC CELL

3,489,667

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3 Sheets-Sheet 1

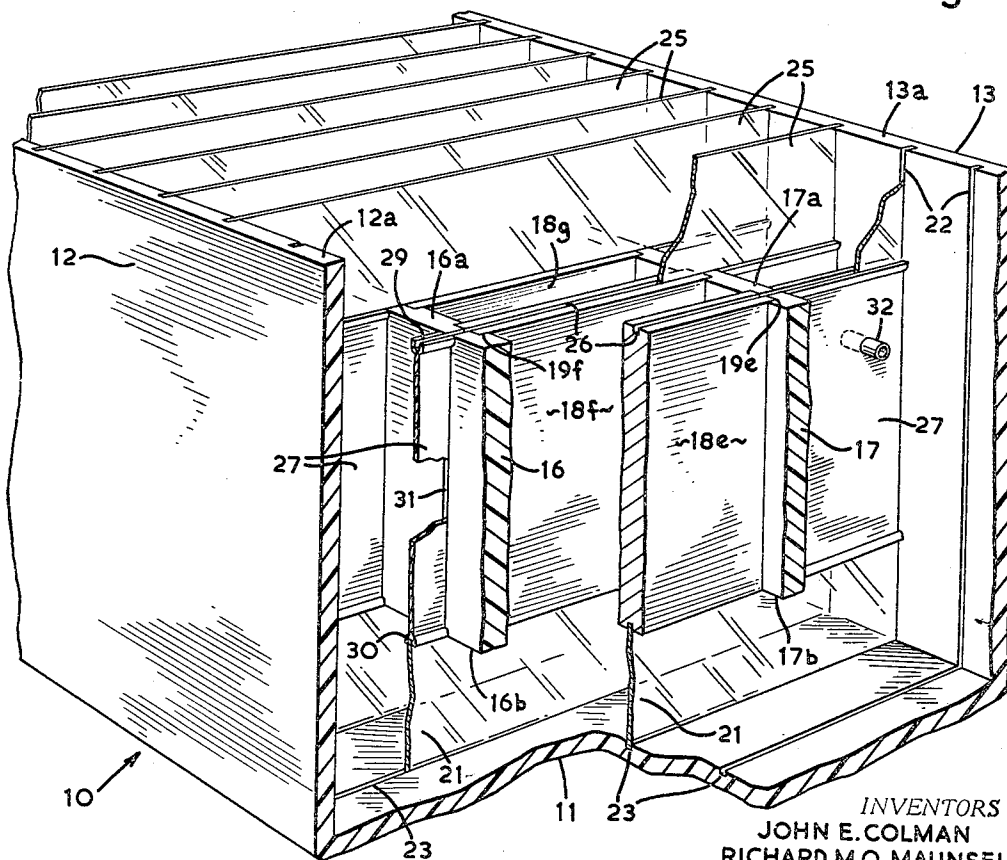
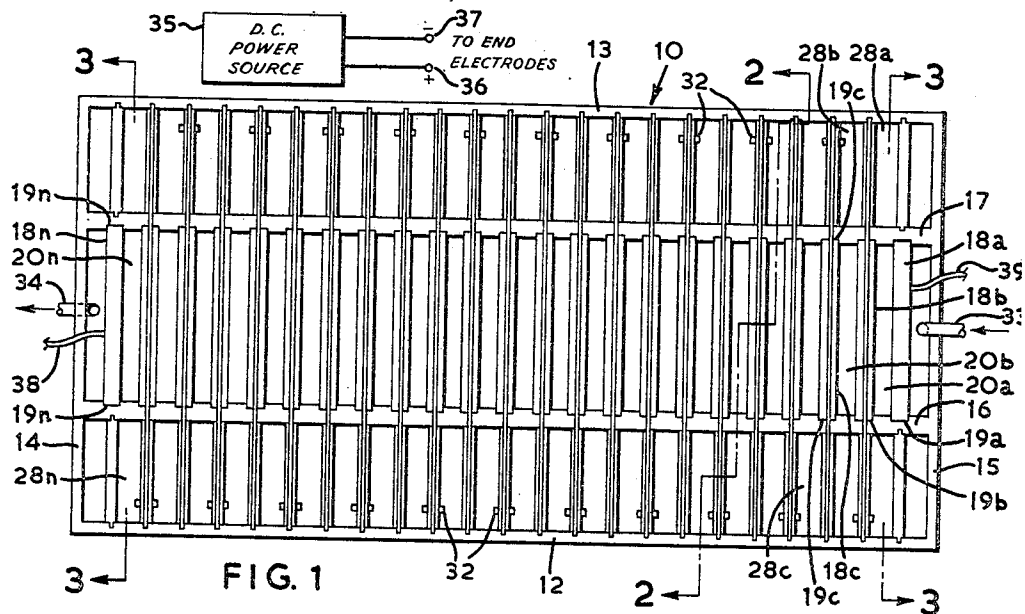


FIG. 2

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3 Sheets-Sheet 2

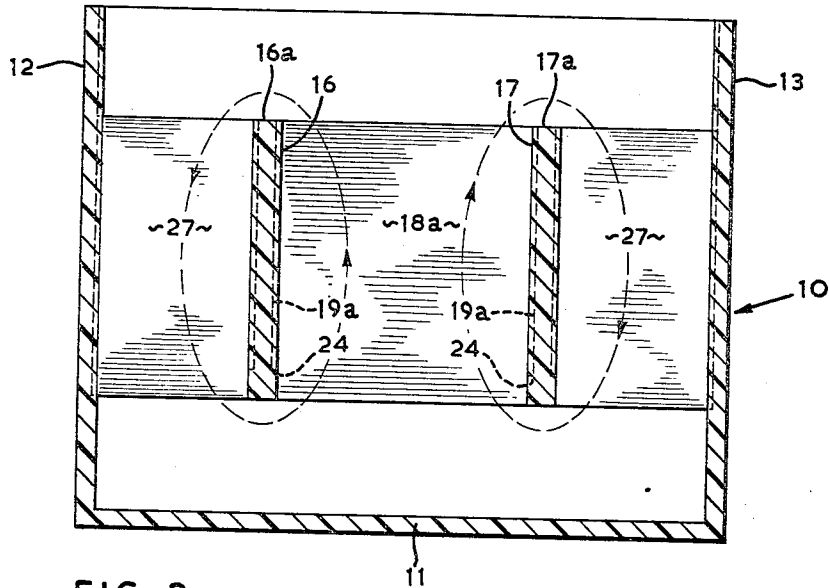


FIG. 3

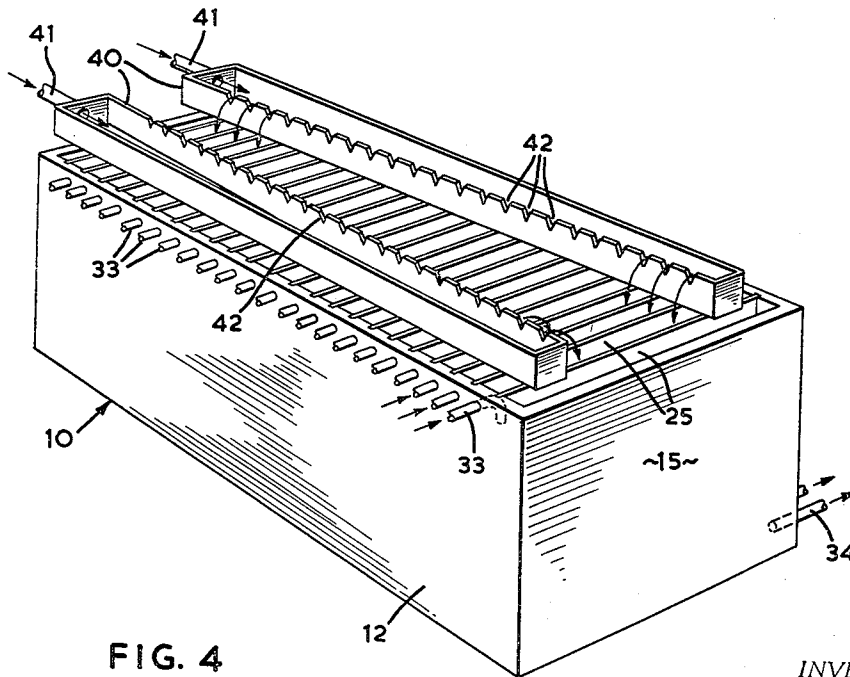


FIG. 4

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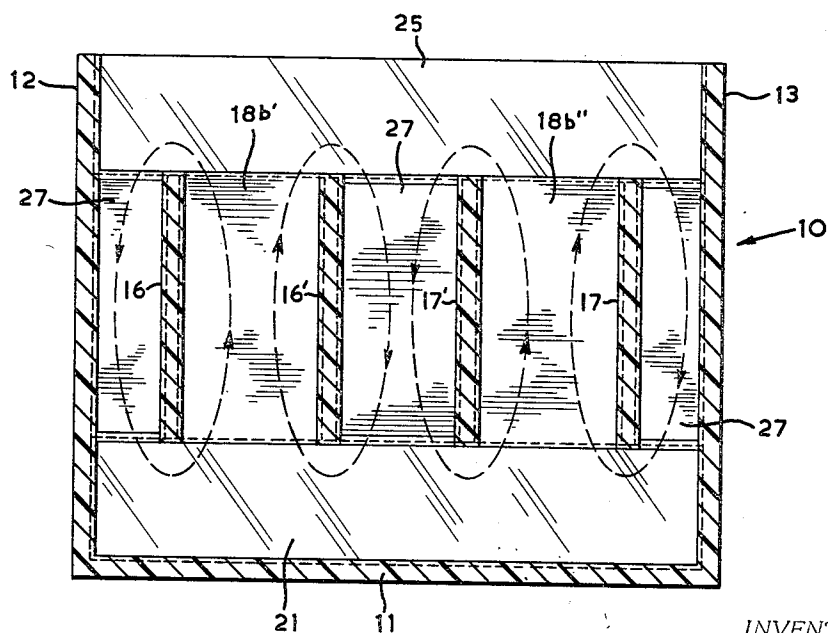
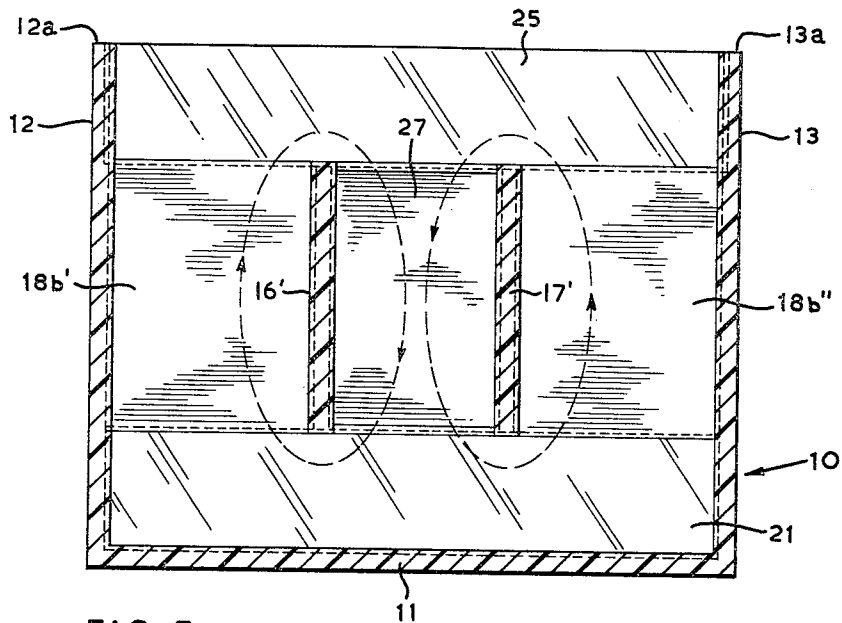
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BIPOLAR ELECTROLYTIC CELL

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3 Sheets-Sheet 3



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3,489,667

BIPOLAR ELECTROLYTIC CELL

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Continuation-in-part of application Ser. No. 490,199, Sept. 27, 1965. This application Feb. 13, 1969, Ser. No. 802,323

Int. Cl. B01k 3/00; C01b 11/26

U.S. Cl. 204-268

12 Claims

ABSTRACT OF THE DISCLOSURE

A bipolar electrolytic cell including a housing for receiving and containing an electrolyte and at least three electrodes, positioned in the housing in spaced-apart relationship with respect to each other. A plurality of individual chambers are connected in liquid flow relationship with different unit cells for passage of electrolyte into respective ones of the unit cells from the individual chambers connected thereto and out of respective ones of the unit cells into the individual chambers connected thereto. The total volume defined by the individual chambers plus the volume of the electrolysis zones constitutes substantially the only volume provided for chemical reactions as a result of electrolysis of the electrolyte to take place in the electrolyte.

This application is a continuation-in-part of application Ser. No. 490,199 filed Sept. 27, 1965, and now abandoned.

This invention relates to bipolar electrolytic cells. More particularly, this invention relates to bipolar electrolytic cells particularly suited for the production of halates and perhalates of alkali metals, especially sodium chlorate and sodium perchlorate.

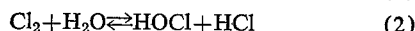
In the past it has been common practice to produce sodium chlorate electrolytically by means of a bipolar electrolytic cell positioned in a large container or tank. A typical prior art bipolar electrolytic cell for such an end use consists of a housing in the form of a box having an open top and in which are positioned a large number of spaced-apart, parallel electrodes, usually of graphite. Electrical connections are made to two or more, but not all of the electrodes for supplying electrical energy to the cell. The electrodes are in effect connected in series electrically through the electrolyte in the cell. At the top and bottom of the housing on both sides thereof are tubes leading into the housing. A sufficient number of these tubes, which constitute inlet and outlet tubes, are provided to communicate with each one of the spaces between two adjacent electrodes. Every two adjacent electrodes and the space therebetween constitutes a unit cell. The housing is supported above the floor of the container or tank, the latter being filled with electrolyte.

The electrolyte enters each unit cell through the lower tubes, these being below the level of the electrolyte in the tank, is electrolysed in the unit cells, and the electrolysed solution is discharged to the tank via the upper tubes, the tank constituting a common reservoir for all unit cells. In many cases, circulation of the electrolyte from the tank to the unit cells and back to the tank is obtained without the use of pumps or other such circulating devices. However, a pump may be employed, if desired. In cases where the tank is positioned remote from the electrolytic cell, rather than having the electrolytic cell in the tank, some form of pumping arrangement is required.

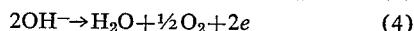
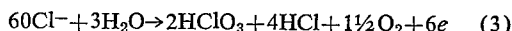
Where sodium chlorate is being produced and the electrolyte is brine, the electrolytic cell usually is operated at an electrolyte temperature of 20° C. to 45° C., when

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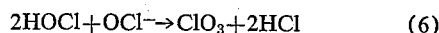
graphite electrodes are employed, cooling of the electrolyte in the tank being required in order to maintain temperatures of this order. The principal desired reactions which take place in the electrolysis zone (each unit cell) are as follows:



Undesirable side reactions which may take place in the electrolysis zone are as follows:



In the reaction zone (tank) the following reaction takes place:



While electrolytic cells of the aforementioned type with their associated tanks are in widespread use, their use is subject to a number of disadvantages. Thus, as aforementioned, inlet and outlet tubes are employed because of the necessity to minimize current leakage between adjacent unit cells. However, the use of tubes creates problems with respect to obtaining good circulation of electrolyte from and to the electrolytic cell when "natural circulation" is relied upon, and this naturally has an effect on efficiency.

Notwithstanding the use of such tubes, current leakage between unit cells of electrolytic cells of the type hereinbefore described and now in use does occur, and, in many cases, it is a significant factor decreasing the efficiency of operation, since the tubes must be reasonably large to promote adequate circulation. Furthermore, the potential between an electrode in the electrolytic cell and the tank may be quite high, e.g., the end electrodes of the cell may be at +60 and -60 volts respectively, while the tank is at 0 volts, and this difference in potential promotes current leakage, the degree of current leakage being greater as the difference in potential increases.

With prior art electrolytic cells of the type hereinbefore described, the maximum voltage drop across the electrolytic cell which normally has been employed is about 120 volts.

From the point of view of current efficiency, in the production of sodium chlorate it is best to electrolyse a liquor having an NaCl concentration of the order of 300 g./l. However, for best chlorate crystal production cost, finished cell liquors normally should have an NaCl concentration of the order of 100 g./l. Consequently, if a prior art electrolytic cell of the type hereinbefore described is operated continuously, in order to produce a cell liquor having an NaCl concentration of the order of 100 g./l., the electrolytic cell must operate in a region of low current efficiency.

In the production of sodium chlorate by electrolysis, it is necessary to add hydrochloric acid to the electrolyte in order to control pH. In the past this has been and is done by adding HCl to the reaction zone. Relatively quiet pockets may be formed in the reaction zones of electrolytic apparatus of the aforementioned type, and because of lack of proper mixing, the addition of HCl may cause the pH of the solution in these pockets to fall quite low. This, in turn, may lead to the evolution of chlorine, which decreases the efficiency of the electrolytic process. Furthermore, the aforementioned pockets or dead zones decrease the effective reaction zone volume.

In electrolytic apparatus of the aforementioned type with graphite electrodes, relatively expensive cooling coils are required to ensure that the solution in the electrolysis zone is kept at a temperature below about 40° C., since,

above this temperature, the rate of attack of oxygen evolved during electrolysis on the graphite electrodes generally will be too high to be tolerated.

In contrast, in accordance with this invention, there is provided a bipolar electrolytic cell in which each unit cell has its own individual reaction zone. Inlet and outlet tubes connecting the reaction zones and unit cells may be eliminated. In fact, subject to the provision of suitable means to support the electrodes in spaced-apart relationship in the electrolytic cell, there is no need, in an electrolytic cell embodying this invention, for there to be any physical member separating the electrolysis zone of a unit cell from its individual reaction zone. This factor can promote considerably improved circulation, a greater flow of electrolyte over the electrode faces and hence improved current efficiency.

When a bipolar electrolytic cell embodying this invention is operated on a batch or continuous basis, the electrolytic cell can be constructed so that there is virtually no current leakage between adjacent unit cells or adjacent reaction zones, because they are essentially isolated from each other. Even when adjacent unit cells are cascaded, which can be done by interconnecting the reaction zones, current leakage can be kept to a minimum, because the passages interconnecting the reaction zones can be made quite small, thereby establishing a path of high electrical resistance.

Because a bipolar electrolytic cell embodying this invention can be arranged to have essentially no current leakage, voltages across the electrolytic cell in excess of 120 volts can be employed. This is advantageous, since rectifier cost and busbar cost decrease with increasing voltage, so that the cost of rectified current decreases with increasing voltage.

When a bipolar electrolytic cell embodying this invention is operated continuously, the various unit cells being cascaded, only the last unit cell need operate with a liquor having an NaCl concentration of the order of 100 g./l. (it will be recalled that such a salt concentration gives the best chlorate production cost), while the liquors in the other unit cells may graduate in NaCl concentration up to 300 g./l., where optimum current efficiency is obtained.

The improved electrolyte circulation which can be obtained in a bipolar electrolytic cell embodying this invention should avoid or reduce quiet pockets or "dead spots" in the reaction zones. Thus, the effective reaction zone volume should be essentially the whole of the available reaction zone volume, chlorine evolution problems due to low pH in quiet pockets and a resultant decrease in efficiency should be eliminated or minimized, and it may be possible, where cooling of the electrolyte is necessary, to employ less expensive cooling equipment in the reaction zones.

A bipolar electrolytic cell embodying this invention is particularly suited for use with bipolar electrodes of the type wherein the anode of the bipolar electrode is platinumised titanium and the cathode thereof is some suitable material such as iron. Where electrodes of this type are employed, no cooling devices need be used, since the electrolyte may be permitted to boil. Under these conditions, the chemical reaction involved in forming chlorinate from hypochlorite will proceed about six times as fast as in prior art apparatus of the type hereinbefore described using graphite electrodes. Hence, for the same amount of chlorate produced, the reaction zone of an electrolytic cell embodying this invention can be about one sixth of that of such prior art electrolytic apparatus.

In brief, in accordance with this invention, there is provided a bipolar electrolytic cell that includes a housing adapted to receive and contain an electrolyte. At least three electrodes are positioned in the housing in spaced-apart relationship with respect to each other, each set of two adjacent electrodes and the space therebetween constituting a unit cell for the electrolysis of an electrolyte occupying the space between the two adjacent electrodes.

Each of the electrodes in a set of two adjacent electrodes are disposed to face each other. Means are provided defining a plurality of individual chambers, each one of these individual chambers being connected in liquid-flow relationship with a different one of the unit cells for passage of electrolyte into respective ones of the unit cells from the individual chambers connected thereto and out of respective ones of the unit cells into the individual chambers connected thereto. The total volume defined by the individual chambers plus that of the spaces between adjacent electrodes constitutes substantially the only volume provided for chemical reactions as a result of electrolysis of the electrolyte to take place in the electrolyte.

This invention will become more apparent from the following detailed description, taken in conjunction with the appended drawings in which:

FIGURE 1 is a plan view of a bipolar electrolytic cell embodying this invention that is designed for cascade operation,

FIGURE 2 is a perspective view, partly in section, of the bipolar electrolytic cell of FIGURE 1, the section being taken along line 2—2 in FIGURE 1,

FIGURE 3 is a section taken along line 3—3 in FIGURE 1,

FIGURE 4 is a perspective view of a bipolar electrolytic cell embodying this invention that is designed for batch operation, and

FIGURES 5 and 6 are sections taken through bipolar electrolytic cells embodying this invention but having electrode arrangements different from those of the cells of FIGURES 1—4.

As used herein, the term "bipolar electrolytic cell" means an electrolytic cell in which, in use, the electrodes are connected in series electrically, and in which some of the electrodes are bipolar, i.e., one face functions as an anode and the other face functions as a cathode. This is in contrast to a monopolar electrolytic cell in which all of the anodes are connected in parallel, and all of the cathodes are connected in parallel, electrical connections being made between each electrode and the positive or negative terminal of a rectifier.

Referring to FIGURES 1 and 2, there is shown a bipolar electrolytic cell having a cell tank that is in the form of a large box having an open top, a bottom wall 11, two spaced-apart, parallel side walls 12 and 13 upstanding from bottom wall 11 at right angles thereto, and two other spaced-apart, parallel side walls 14 and 15 also upstanding from bottom wall 11 at right angles thereto and disposed at right angles to side walls 12 and 13. Tank 10 may be fabricated from any material that is an electrical insulator and that is resistant to chemical attack by the electrolyte that is contained in the tank during its use. Where the electrolytic cell is to be used for the production of sodium chlorate from brine at temperatures of the order of 40° C. or less, tank 10 may be fabricated from a suitable polyvinyl chloride. Tank 10 is made liquid-tight, of course.

While tank 10 has been shown to be rectangular in cross-section, this is not essential, and the tank could assume other shapes.

Extending between the two side walls 14 and 15 and fitting into slots (not shown) therein are electrode positioning walls 16 and 17, those being disposed in spaced-apart, parallel relationship with respect to each other and with respect to side walls 12 and 13. It will be noted that the top edges 16a and 17a of walls 16 and 17 respectively are disposed below the top edges 12a and 13a of side walls 12 and 13 respectively, while the bottom edges 16b and 17b of walls 16 and 17 respectively are positioned above bottom wall 11.

The walls 16 and 17 hold a plurality of electrodes 18a, 18b, 18c . . . 18n in spaced-apart, parallel relationship with respect to each other in the chamber defined by tank 10. As may be seen from FIGURES 1 and 2, this is achieved by means of equally spaced-apart, parallel chan-

nels 19a, 19b, 19c . . . 19n which, except for channels 19a and 19n, extend the full height of both walls 16 and 17. Channels 19a, 19b, etc., are disposed at right angles to bottom wall 11 with the channels in wall 16 facing and aligned with those in wall 17. Walls 16 and 17 hold electrodes 18a, 18b, etc., in spaced-apart, parallel relationship with each other by virtue of the electrodes fitting into channels 19a, 19b, etc., as may be seen from FIGURES 1 and 2.

As best shown in FIGURE 1, because electrodes 18a, 18b, etc., all are of the same thickness with flat, parallel faces, and because adjacent channels are equally spaced apart, interelectrode spaces 20a, 20b . . . 20n of constant width (measured between facing surfaces of adjacent electrodes) are provided. Each set of two adjacent electrodes, for example 18a and 18b, and the interelectrode space therebetween, in this case 20a, constitutes a unit cell for the electrolysis of electrolyte occupying the interelectrode space.

Electrodes 18a, 18b, etc., are shown as rectangular plates having flat, parallel faces. If the electrodes were of graphite, each plate would be most likely made up of graphite "planks" sitting one on top of the other, and the "planks" may be made up of blocks positioned side-by-side, all as known in the art. If the electrodes are of magnetite or of platinised titanium (anode) with an iron backing (cathode), for example, the electrodes may be plates as shown. Of course, it will be appreciated that electrodes fabricated from other materials but suitable for bipolar use may be employed. All of the electrodes with the exception of end electrodes 18a and 18n are bipolar, and the latter two are monopolar.

In order to permit sludge that forms during use of the bipolar cell to accumulate without causing short circuits, and in order to support the electrodes and provide a header for each unit cell, spaced-apart supporting plates 21 (FIGURE 2) are provided. These supporting plates 21 or partitions also help to separate adjacent unit cells and extend across tank 10 between side walls 12 and 13 thereof and upwardly from bottom wall 11 of tank 10, being positioned at right angles to bottom wall 11. Partitions 21 are in the form of flat plates that are parallel with respect to each other and also parallel to electrodes 18a, 18b, etc. As best shown in FIGURE 2, partitions 21 are held in position by being inserted in channels or grooves 22 in both side walls 12 and 13 and channels or grooves 23 in bottom wall 11, channels 22 extending the depth of walls 12 and 13, and channels 23 extending the full width of bottom wall 11. It should be noted, however, as shown in FIGURE 3, that no supporting partitions 21 are provided beneath end electrodes 18a and 18n. These end electrodes are supported by virtue of the fact that channels 19a and 19n do not extend the full height of walls 16 and 17 but terminate at shoulders 24 (FIGURE 3). Electrodes 18a and 18n are notched adjacent shoulders 24 and portions of electrodes 18a and 18n sit on shoulders 24, which thereby support end electrodes 18a and 18n. Partitions 21, which are provided for each electrode except the end electrodes, may be formed from any suitable electrical insulator that is resistant to chemical attack by the electrolyte in the tank and that is sufficiently strong to perform the supporting functions of partitions 21. They may be of the same material as tank 10 or of glass. Since partitions 21 and, in the case of electrodes 18a and 18n, shoulders 24, support the electrodes above bottom wall 11, a space thereby is provided for accumulation of sludge, in the event that electrodes are employed which create sludge, and this sludge is unable to cause electrical short circuits between adjacent electrodes. This space should be sufficiently deep that sludge accumulation will not hinder the flow of electrolyte into each unit cell.

It will be noted that the electrodes, as well as bottom edges 16b and 17b of walls 16 and 17, are grooved to receive partitions 21, the relationship between partitions 21

and these other members being a tongue and groove relationship.

Extending across cell tank 10 between side walls 12 and 13 and positioned in the same grooves 22 as partitions 21 are partitions 25 which may be made from the same material as partitions 21. Partitions 25 are in the form of flat plates positioned in spaced-apart, parallel relationship with respect to each other and parallel to the electrodes. One such partition 25 is provided for each of the electrodes except end electrodes 18a and 18n. As best shown in FIGURE 2, the electrodes for which partition 25 are provided, as well as top edges 16a and 17a of walls 16 and 17, are grooved at 26 to receive partitions 25, the relationship between partitions 25 and these other members being a tongue and groove relationship. Partitions 25 extend upwardly from the electrodes to the top edges 12a and 13a of side walls 12 and 13 respectively of tank 10.

The various unit cells do not occupy all of the chamber defined by cell tank 10, and partitions 21 and 25, or parts thereof, together with partitions designated 27, partition the portion of this chamber that is unoccupied by the unit cells into a plurality of individual chambers 28a, 28b, 28c . . . 28n in which chemical reactions take place forming the desired product. In the embodiment of this invention illustrated in FIGURES 1 and 2, each individual reaction chamber is defined between adjacent ones of partitions 27, 21 and 25.

Partitions 27 may be fabricated from the same material as walls 12 and 13 and are in the form of plates provided with grooves 29 and 30 running along their upper and lower edges respectively. As is best seen in FIGURE 2, these grooves 29 and 30 accommodate partitions 25 and 21 respectively. Partitions 27 are positioned in spaced-apart, parallel relationship and are parallel to the electrodes and extend in alignment with the electrodes between walls 16 and 12 and walls 17 and 13. Partitions 27 are provided with tongues (not shown) that extend into notches 22 and tongues (not shown) that extend into notches or grooves 31 (FIGURE 2) provided in walls 16 and 17, these notches 31 facing the respective side walls 12 and 13 of tank 10 and extending the full height of walls 16 and 17 from the top edges 16a and 17a to the bottom edges 16b and 17b thereof and being parallel to the electrodes. Two partitions 27 are provided for each electrode.

By virtue of the fact that walls 16 and 17 do not extend above the tops of partitions 27 and are spaced above bottom wall 11, each individual reaction chamber 28a, 28b, etc., is connected in liquid-flow relationship over and under walls 16 and 17 with a different unit cell for the passage of electrolyte into the unit cell from the reaction chamber under walls 16 and 17 and for the passage of electrolyte from the unit cell into its individual reaction chamber over the top edges of walls 16 and 17.

When the bipolar electrolyte cell of FIGURES 1 and 2 is used for cascade operation, tubes 32 are employed. As best shown in FIGURE 1, each unit cell, except the last one, and its associated reaction chamber is provided with one of such tubes 32, these tubes passing through partitions 27 to connect the unit cells and their adjacent reaction chambers in series liquid-flow relationship. The position of tubes 32 is not critical, and they could be located more towards the centres of partitions 21, for example.

In order to introduce electrolyte into tank 10, an inlet tube or pipe 33 communicating with the space between end electrode 18a and wall 15 is provided. Electrolysed solution is removed from tank 10 via a tube or pipe 34 (FIGURE 1) extending through bottom wall 11 into the space between end electrode 18n and wall 14.

With a bipolar electrolytic cell of the type shown in FIGURES 1 and 2, except for any minimal current leakage which may occur through tubes 32, there can be substantially no current leakage between adjacent unit

cells if good seals are effected between the various partitions, the various electrodes and walls 11, 12, 13, 16 and 17. In this regard, the various partitions, electrodes and walls 16 and 17 can be so connected to each other that in essence they form a plurality of substantially liquid-tight walls extending across cell tank 10 between side walls 12 and 13 and upwardly from bottom wall 11, and the connections between these former walls and walls 11, 12 and 13 also can be made substantially liquid-tight, thereby having the effect of minimizing current leakage. Current leakage through tubes 32 can be made extremely small by making these tubes of small diameter and/or reasonable length.

As shown in FIGURE 1, a D.C. power source 35 is provided having positive and negative output terminals 36 and 37 respectively. These output terminals are connected to lead-in conductors 38 and 39 respectively which are connected to end electrodes 18n and 18a respectively for the supply of electrical energy to the electrolytic cell. It will be seen that electrodes 18a . . . 18n are electrically connected in series with each other. If desired, more electrodes than just end electrodes 18a and 18n may be connected to D.C. power source 35. Thus, if there are seventeen electrodes, electrodes 1, 9 and 17 may be connected to terminal 36 and electrodes 5 and 13 may be connected to terminal 37.

In the operation of the electrolytic cell of FIGURES 1 and 2 to produce sodium chlorate from brine, the brine solution is introduced into tank 10 via pipe 33, and, because there are no partitions 21 or 25 associated with end electrode 18a, flows into reaction chamber 28a and the interelectrode space 20a between electrodes 18a and 18b. Electrolysis of the electrolyte in this interelectrode space 20a occurs, and reactions in this electrolysis zone 20a of the type hereinbefore noted in Equations 1 and 2 take place. The electrolyte in interelectrode space 20a discharges over walls 16 and 17 into reaction chamber 28a where a chemical reaction of the type hereinbefore noted in Equation 6 takes place, and the electrolyte then is returned to electrolysis zone 20a passing under edges 16b and 17b of walls 16 and 17 respectively. The direction of electrolyte flow is as indicated by the dotted lines in FIGURE 3. A part of the electrolyte is passed into reaction chamber 28b via tube 32 connecting reaction chambers 28a and 28b and is similarly processed in this reaction chamber 28b and the unit cell associated therewith constituting electrodes 19b and 19c and interelectrode space 20b. In this manner the electrolyte passes in series from one unit cell and its associated reaction chamber to the next, and the electrolysed solution finally is removed via pipe 34. Except for any current leakage which may occur through tubes 32, there is substantially no current leakage between adjacent unit cells. In this regard, it will be appreciated, of course, that partitions 25 are sufficiently high to prevent spillage of electrolyte from one unit cell to an adjacent unit cell over the partition 25 dividing the two cells.

The only members separating the individual reaction chambers from their associated unit cells are walls 16 and 17, so that very efficient circulation of electrolyte between a unit cell and its associated reaction chamber is achieved. If other means were devised for holding the electrodes in spaced-apart, parallel relationship with each other, side walls 16 and 17 then could be removed, and it might be possible to obtain even better circulation. In any event, electrolyte circulation is not compromised by considerations affecting current leakage, and the path between each unit cell and its reaction chamber offers a low resistance to the flow of electrolyte, as compared with that offered by the inlet and outlet tubes of prior art electrolytic cells.

In the production of sodium chlorate the cell may be led via pipe 33 with unsaturated or preferably saturated (about 300 g./l.) solutions of sodium chloride, or with solutions containing NaCl plus varying amounts of so-

dium chlorate to produce a cell liquor product containing varying amounts of sodium chloride and sodium chlorate. The sodium chloride concentration through the unit cells to the unit cell defined by end electrode 18n, the electrode adjacent to it, and interelectrode space 20n, decreases progressively so that an electrolyzed solution having a desirable composition can be produced on a continuous basis without sacrificing current efficiency in all of the unit cells. Cell liquors containing about 100 g./l. of sodium chloride and about 450 g./l. of sodium chlorate may be produced, or even higher amounts of sodium chlorate can be produced by the addition of sodium chloride to the liquors in intermediate cells. Liquors particularly suitable for use in generators or plants for the manufacturing of chlorine dioxide can also be produced.

Because of the very minimal current leakage which will occur with a properly constructed cell of the type shown in FIGURES 1 and 2, D.C. power source 35 may be of a type producing a higher voltage than is commonly used with bipolar electrolytic cells for chlorate production, with the consequent advantages hereinbefore noted.

The electrolytic cell of FIGURE 4 is in all respects identical to that shown in FIGURES 1 and 2 with the exception that tubes 32 have been eliminated, so that there are no openings in partitions 27, and tubes 33 and 34 are arranged to introduce electrolyte into and remove electrolyte from each individual unit cell and its associated reaction chamber, each such unit cell and its associated reaction chamber thereby being capable of operating on a batch basis or on a continuous basis. Electrolyte is introduced to each unit cell and its respective reaction chamber by a different one of tubes 33, is processed on a batch or continuous basis in this unit cell and its reaction chamber until the desired product has been formed, and, when a batch process is being used, the solution then is removed via a different one of pipes 34 by opening valves (not shown) connected to these pipes.

During the electrolysis of brine to produce sodium chlorate, it is necessary to add HCl to maintain the pH of the electrolyte at a proper level. It also may be necessary to add water, particularly where the electrolyte is operating at or near its boiling point. As shown in FIGURE 4, these additions can be made to each of the individual reaction chambers by means of troughs 40, one of which is for the addition of water, and the other of which is for the addition of HCl, these being introduced to troughs 40 via pipes 41. Troughs 40 taper inwardly from adjacent pipes 41 and each trough is provided, in one side wall thereof, with V-shaped notches 42, one such notch per trough being aligned with a different reaction chamber. The notches are of the same depth and shape, but, by virtue of the taper of the troughs, deliver the same amounts of water and HCl to each individual reaction chamber. For cascade operation, the first few unit cells require more HCl than the others, so that the first few notches 42 in the trough that delivers HCl can be made deeper than the other notches of this trough.

It should be appreciated that in the embodiments of our invention hereinbefore described, no cooling coils have been indicated, since these devices will not be required if platinised titanium electrodes, for example, are employed. If graphite electrodes are employed, however, cooling coils may be provided and may be inserted in the various reaction chambers, preferably between each set of two adjacent partitions 27. Because of the high degree of electrolyte circulation obtained with a cell embodying this invention between a unit cell and its associated individual reaction chamber, it should be possible to employ less expensive cooling coils than have been employed with prior art bipolar cells for chlorate production.

While it is very preferable for the unit cells and reaction chambers to be incorporated in a single cell tank, this is not essential to the practice of the invention, and the reaction chambers and unit cells may be physically separated from each other with large tubes connecting

each unit cell to its respective reaction chamber, so that there is a low resistance to flow of electrolyte. It should be noted that since current leakage is not a problem, tubes of large diameter that promote good circulation can be employed. It also is not necessary for the electrodes to be disposed centrally in cell tank 10 as shown in FIGURES 1 and 2. Indeed, wall 17, for example, could be eliminated and the edge of the electrodes shown as positioned in the channels in this wall could be positioned in similar channels provided in side wall 13, thereby shifting each reaction chamber to one side of the tank.

It also should be noted that the electrodes may be divided. Thus, in FIGURE 5, electrode 18b is split into two, spaced-apart electrodes 18b' and 18b'', and partition 27 is located between walls 16' and 17'. In other words, the positions of the electrodes and partitions 27 are reversed from the positions thereof shown in FIGURES 1 and 2. Of course, this will require that grooves 22 and 31 be made sufficiently wide to accommodate electrodes 18b' and 18b'' and that a portion of groove 22 adjacent the top edges 12a and 13a of walls 12 and 13 be made of lesser width but deeper than the parts of grooves 22 accommodating electrodes 18b' and 18b'' to accommodate partitions 25. Similarly, channels 19a, 19b, etc., will have to be decreased in width to accommodate partitions 27. A bipolar electrolytic cell employing an electrode arrangement of the type shown in FIGURE 5 would have four electrodes per unit cell, it being understood that all of the electrodes will be split like 18b.

In the embodiment of this invention shown in FIGURE 6, a similar arrangement to that shown in FIGURE 5 is employed, but, in addition, partitions 27 are provided between electrodes 18b' and 18b'' and walls 12 and 13, as in the case of FIGURES 1 and 2. Some advantage may be gained by employing arrangements of the types indicated in FIGURES 5 and 6 because of the mixing which will take part in the portion of the reaction chamber which is between the two electrodes, the direction of electrolyte flow being as indicated by the dotted lines in these two figures. It will be appreciated that the arrangement of FIGURE 6 requires the use of additional walls 16' and 17' as well as walls 16 and 17.

From the foregoing it will be seen that, unlike the prior art, there is no common chamber which receives electrolyte from and delivers electrolyte to all the unit cells. In contrast, each unit cell has its own reaction chamber, so that the unit cells are isolated from each other with respect to any substantial degree of electrical current leakage therebetween. Hence, the path between each unit cell and its reaction chamber can be designed to offer little resistance to the flow of electrolyte. Thus, in a cell embodying this invention, low current leakage but very good electrolyte circulation both can be obtained, whereas, in a prior art cell, one can be obtained only at the expense of the other. In other words, if the inlet and outlet tubes between the unit cells and the common reaction chamber of prior art apparatus are designed to offer less resistance to electrolyte flow by making these tubes shorter and/or larger, current leakage will increase, and if they are designed to offer more resistance to current leakage by making them longer and/or smaller, the resistance that they offer to electrolyte flow will increase. In an electrolytic cell embodying this invention, since the total volume defined by the individual chambers plus the volumes of the electrolysis zones constitutes the only volume (no common reaction chamber) provided for chemical reactions as a result of electrolysis of the electrolyte to take place in the electrolyte, this same problem of having to compromise between electrical current leakage and obtaining good electrolyte circulation is avoided.

For the production of halates and perhalates, particularly sodium chlorate, each unit cell and its associated chamber should be constructed so that the ratio of reaction zone volume occupied by electrolyte to electro-

sis zone volume occupied by electrolyte should be 2:1 or greater. The upper limit for this ratio is governed by practical limitations with respect to size, for example, not by operability, and may be taken as 500:1, but this is not critical. Where graphite electrodes are employed, the preferred range is from 10:1 to 90:1, whereas, with precious metal electrodes, a range from 10:1 to 50:1 is preferred. The term "reaction zone volume" as used in this paragraph excludes the electrolysis zone volume.

A cell embodying this invention is also well suited to the recovery for subsequent use of the hydrogen which is generated in the cells, particularly when platinised titanium anodes are employed.

While preferred embodiments of this invention have been disclosed herein, those skilled in the art will appreciate that changes and modifications may be made therein without departing from the spirit and scope of this invention as defined in the appended claims.

What we claim as our invention is:

1. A bipolar electrolytic cell for the production of halates and perhalates comprising a housing adapted to receive and contain an electrolyte; at least three electrodes positioned in said housing in spaced-apart relationship with respect to each other, at least one of said electrodes being a bipolar electrode, said electrodes of each set of two adjacent electrodes having surfaces facing each other, each set of two adjacent electrodes and the space therebetween constituting a unit cell for the electrolysis of electrolyte occupying the space between said two adjacent electrodes, the space between said two adjacent electrodes constituting an electrolysis zone in which electrolysis of said electrolyte can take place; means defining a plurality of individual chambers, each of said individual chambers being connected in liquid-flow relationship with a different one of said unit cells for passage of electrolyte into respective ones of said unit cells from said individual chambers connected to said unit cells and out of respective ones of said unit cells into said individual chambers connected to said unit cells, the total volume defined by said individual chambers plus the volume of said electrolysis zones constituting substantially the only volume provided for chemical reactions as a result of electrolysis of said electrolyte to take place in said electrolyte, for each of said unit cells the ratio of the volume of the respective individual chamber connected thereto occupied by electrolyte to the volume of the electrolysis zone thereof occupied by electrolyte being at least 2:1.

2. A bipolar electrolytic cell according to claim 1 wherein said ratio is at least 10:1.

3. A bipolar electrolytic cell according to claim 1 wherein said ratio is between 10:1 and 90:1 and said electrodes are graphite electrodes.

4. A bipolar electrolytic cell according to claim 1 wherein said ratio is between 10:1 and 50:1 and wherein at least one of said surfaces of each of said electrodes includes a precious metal.

5. A bipolar electrolytic cell according to claim 1 wherein each of said individual chambers is connected in liquid-flow relationship with a different one of said unit cells via a path characterized by a low resistance to the flow of electrolyte, each unit cell being substantially isolated from every other unit cell with respect to leakage of electrical current between said unit cell.

6. A bipolar electrolytic cell according to claim 5 including means connecting said individual chambers and said unit cells in series liquid-flow relationship with each other.

7. A bipolar electrolytic cell according to claim 6 wherein said means connecting said individual chambers and said unit cells in series liquid-flow relationship with each other are small openings.

8. A bipolar electrolytic cell according to claim 6 wherein said means connecting said individual chambers and said unit cells in series liquid-flow relationship with

each other are passages characterized by a high resistance to current flow during operation of said bipolar electrolytic cell.

9. A bipolar electrolytic cell for the production of halates and perhalates comprising a cell tank having a bottom wall and side walls defining a chamber; at least three electrodes positioned in said chamber in spaced-apart relationship with respect to each other, at least one of said electrodes being a bipolar electrode, said electrodes of each set of two adjacent electrodes having surfaces facing each other, each set of two adjacent electrodes and the space therebetween constituting a unit cell for the electrolysis of an electrolyte occupying the space between said two adjacent electrodes, said unit cells occupying only a portion of the chamber defined by said tank, the space between said two adjacent electrodes constituting an electrolysis zone in which electrolysis of said electrolyte can take place; and means partitioning at least a part of said chamber unoccupied by said unit cells into a plurality of individual chambers, each one of said individual chambers being connected in liquid-flow relationship with a different one of said unit cells for passage of electrolyte into respective ones of said unit cells from said individual chambers connected to said unit cells and out of respective ones of said unit cells into said individual chambers connected to said unit cells, the total volume defined by said individual chambers plus the volume of said electrolysis zones constituting substantially the only volume provided for chemical reactions as a result of electrolysis of said electrolyte to take place in said electrolyte, for each of said unit cells the ratio of the volume of the respective individual chamber connected thereto occupied by electrolyte to the volume of the electrolysis zone thereof occupied by electrolyte being at least 2:1.

10. A bipolar electrolytic cell according to claim 9 including means for introducing an electrolyte into said chamber defined by said tank; means for withdrawing an electrolysed solution from said chamber defined by said tank; and means connected to ones of said electrodes other than bipolar electrodes for supplying electrical energy to said bipolar electrolytic cell.

11. A bipolar electrolytic cell according to claim 10 including means connecting said individual chambers and said unit cells in series liquid-flow relationship with each other.

12. A bipolar electrolytic cell for the production of halates and perhalates comprising a cell tank having a bottom wall and side walls defining a chamber; at least three electrodes, at least one of said electrodes being a bipolar electrode; means holding said electrodes in spaced-apart substantially parallel relationship with respect to each other in the chamber defined by said tank with said electrodes in each set of two adjacent electrodes

having surfaces facing each other, each set of two adjacent electrodes and the space therebetween constituting a unit cell for the electrolysis of an electrolyte occupying the space between said two adjacent electrodes, said unit cells occupying only a portion of the chamber defined by said tank, the space between said two adjacent electrodes constituting an electrolysis zone in which electrolysis of said electrolyte can take place; first spaced-apart partitions corresponding in number to at least the number of said bipolar electrodes and extending across said tank between said side walls thereof and upstanding from said bottom wall of said tank, each of said first partitions supporting a different one of said bipolar electrodes and supporting said bipolar electrode spaced from said bottom wall of said tank, whereby a space is provided between said bottom wall of said tank and said bipolar electrodes; second spaced-apart partitions corresponding in number to at least the number of said bipolar electrodes and extending across said tank between said side walls thereof, each of said second partitions being supported on a different one of said bipolar electrodes and extending from said bipolar electrode away from said bottom wall; third spaced-apart partitions extending between said first and second partitions and with said first and second partitions, said bipolar electrodes and said means holding said electrodes forming a plurality of spaced-apart walls extending between said side walls of said tank and from said bottom wall of said tank to the tops of said second partitions, each individual chamber defined between two adjacent ones of said first, second and third partitions being connected in liquid-flow relationship with a different one of said unit cells for passage of electrolyte into said one unit cell from said latter chamber, the total volume defined by said individual chambers plus the volume of said electrolysis zones constituting substantially the only volume provided for chemical reactions as a result of electrolysis of said electrolyte to take place in said electrolyte, for each of said unit cells the ratio of the volume of the respective individual chamber connected thereto occupied by electrolyte to the volume of the electrolysis zone thereof occupied by electrolyte being at least 2:1.

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