

March 15, 1938.

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2,111,264

ELECTROLYSIS OF FUSED SALTS

Original Filed Feb. 17, 1933

2 Sheets-Sheet 1

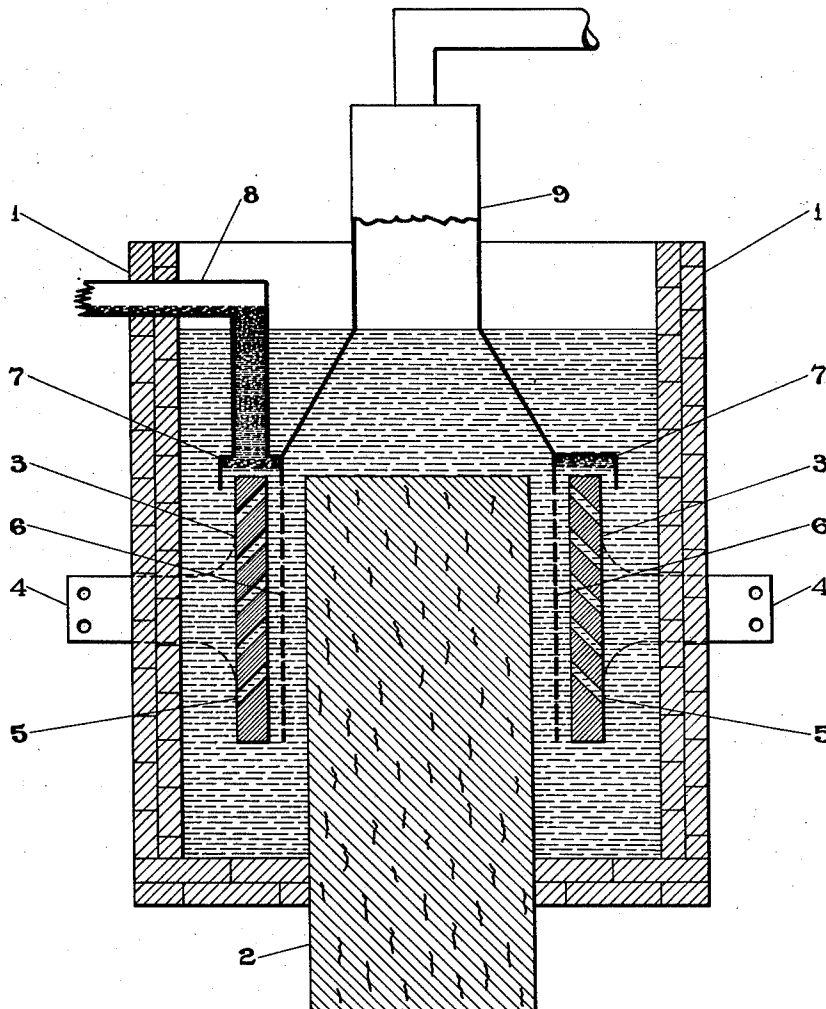


Fig. 1

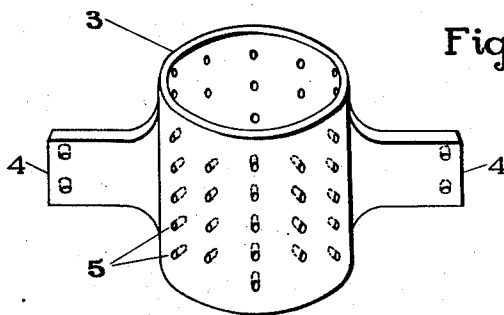


Fig. 2

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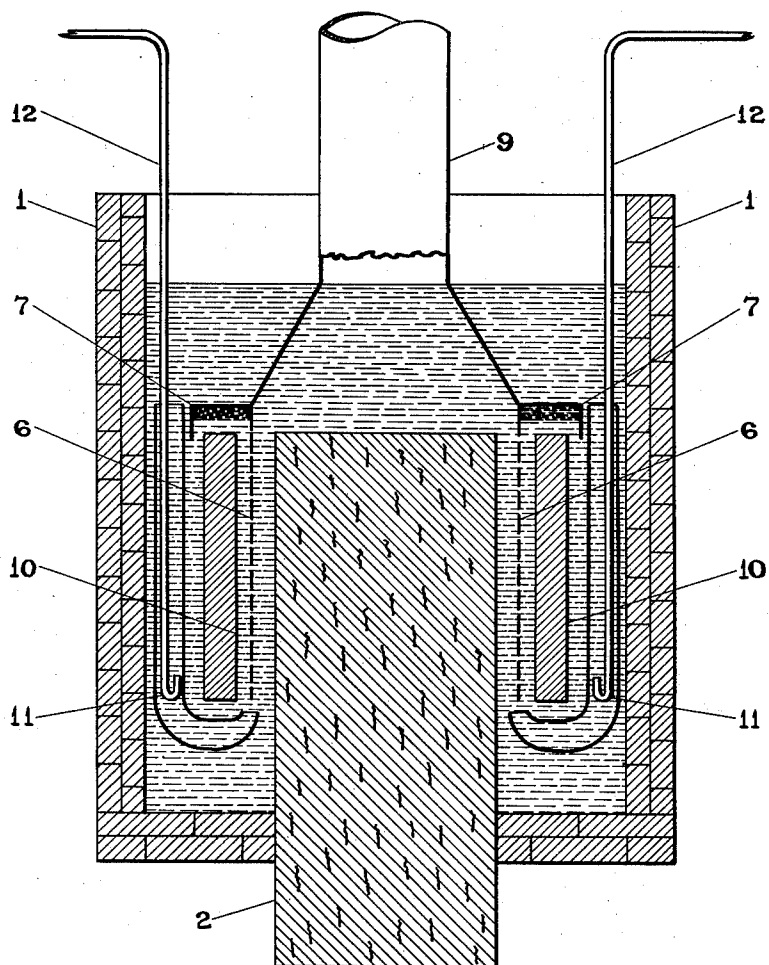


Fig. 3

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UNITED STATES PATENT OFFICE

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ELECTROLYSIS OF FUSED SALTS

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Original application February 17, 1933, Serial
No. 657,235. Patent No. 2,056,184 dated October
6, 1936. Divided and this application October
30, 1935, Serial No. 47,431

10 Claims. (Cl. 204—19)

This invention relates to the electrolysis of fused salts, and more particularly to the production of a light metal by the electrolysis of a fused mixture of metallic halides.

5 This application is a division of my application Serial No. 657,235, filed February 17, 1933.

In the production of metal by electrolysis of molten salts, it is necessary to have a relatively short distance between the electrodes. In the electrolysis of aqueous solutions, the distance between the anode and cathode is of relatively small importance because of the relatively high conductivity of aqueous solutions. However, fused salts are relatively poorer conductors than aqueous solutions of salts, and for this reason the distance between the electrodes must be relatively small in order to avoid undue power consumption per pound of metal obtained.

In the production of a metal by the electrolysis of a fused salt, it is usually necessary to use a mixture of a salt of the metal desired with one or more salt or salts of other metal or metals, in order for the electrolyte to have a suitable melting point. When such a mixture of salts is electrolyzed, the various salts being present in suitable proportions, the desired metal will be produced in predominating amounts. For example, a mixture containing approximately equal parts by weight of sodium chloride and calcium chloride electrolyzed in the molten state will produce metallic sodium with a small amount of calcium in solution. However, if the calcium chloride content is increased to beyond about 70% by weight, the amount of calcium produced will exceed that which can be dissolved by the sodium with the result that calcium will be formed as a separate phase. At the temperatures at which it is desirable to operate this process, the calcium thus separated will be in the solid state and hence will present difficulties where the cell is designed to remove the metal produced by flowing it out in the liquid state. Furthermore, the solid calcium tends to build up on the cathode and eventually will form a bridge across to the diaphragm and/or anode, causing short circuits and lowering the cell efficiency.

When such a salt mixture is electrolyzed in a cell having a relatively short distance between the cathode and anode, especially where the electrode surface is large, the preferential electrolysis of one metal causes an impoverishment of the salt of that metal in the bath in the space between the electrodes. Due to the relatively narrow space between the electrodes, the natural diffusion and/or circulation of the electrolyte is

insufficient to bring fresh electrolyte into the space fast enough to replace the salt of the metal preferentially removed by the electrolysis. This changes the salt composition in the space between the electrodes and causes excessive amounts of the undesired metal to be released. For example, in the above-mentioned production of sodium from a fused mixture of sodium chloride and calcium chloride, the impoverishment of the electrolyte often causes formation of solid calcium on the cathode with the undesirable results noted above. Furthermore, the change in the salt composition between the electrode often results in an increase in the melting point of the bath, which makes it necessary to operate the cell at a higher temperature. This is disadvantageous because more electrical current is then required to keep the cell temperature above the melting point of the electrolyte, and the current efficiency of the cell is correspondingly lowered.

An object of this invention is to provide a means for preventing changes in electrolyte composition between the electrodes of a fused salt electrolytic cell. A further object is to provide means for operating fused salt electrolytic cells with a smaller space between the electrodes, and at lower temperatures than has heretofore been possible without decreasing the efficiency of the cell. Other objects will be hereinafter apparent.

These objects are attained in accordance with the present invention by providing a positive means for circulating the fused salt electrolyte through the space between the cathode and anode of the electrolytic cell, so as to increase the flow of electrolyte into or through said space to a rate sufficient to prevent substantial change in composition of electrolyte within said space.

Two methods of carrying out my invention are illustrated by the appended drawings. Figs. 1 and 3 are diagrammatic sectional views of fused salt electrolytic cells. Fig. 2 is a perspective view of the cathode 3 of the cell illustrated by Fig. 1.

One method of carrying out my invention is illustrated by Figs. 1 and 2 of the appended drawings. The fused salt electrolytic cell illustrated by Fig. 1 has a cylindrical brick-lined, steel casing 1. A cylindrical graphite anode 2 projects upwardly through the bottom of the cell-casing 1. The cathode 3 is a steel cylinder having two diametrically opposed steel arms 4 which project outside the cell casing to serve as electrode terminals. The cathode 3 is pierced with holes 5 at a large number of points uniformly distributed over its surface, these holes 5 slanting upwardly towards the anode at an angle of about 45°. A

perforated cylindrical steel diaphragm 6 is suspended about mid-way in the annular space between the anode 2 and the cathode 3. The annular collector ring 7 serves to support the diaphragm 6 and to collect molten metal which rises in the fused electrolyte from the cathode 3. Outlet tube 8 serves to carry the metal collected in collector ring 7 to the outside of the cell. Gas dome 9 is for the purpose of carrying out gaseous anodic products formed by the electrolysis. The elements 6, 7, 8, and 9 are supported in the cell by means not shown.

Fig. 2 is a perspective view of the perforated cathode 3 of the cell illustrated in Fig. 1. The holes 5 are distributed uniformly over the periphery of the cathode 3, and slant upwardly at an angle of about 45° towards the axis of the cathode.

The cell illustrated by Fig. 1 is similar to that described in U. S. Patent 1,501,756, issued to James C. Downs, with the exception that the cell illustrated by Fig. 1 has the cathode perforated as described, while in the cell described in the Downs patent the cathode has no perforations. In operating the ordinary Downs cell, with a cathode of a given effective area, I have experienced little or no trouble in impoverishment of the electrolyte in the space between the electrodes, provided that the distance between the electrodes is not less than a certain minimum distance. I have discovered, however, that if the space between the electrodes is reduced below the aforesaid minimum, impoverishment of the electrolyte in the space between the electrodes will occur.

I have discovered that the above mentioned disadvantages occurring in fused salt electrolysis may be overcome by increasing the flow of electrolyte into or through the space between the electrodes, to a rate sufficient to prevent impoverishment of electrolyte.

One method of increasing the electrolyte flow between the electrodes, in accordance with my invention, is to provide the cell with a perforated cathode as illustrated by Figs. 1 and 2 of the appended drawings. In a cell thus equipped, the rise of the products of electrolysis in the space between the electrodes, causes a steady flow of electrolyte through the perforations 5 of the cathode 3 into the space between the electrodes, at a rate sufficient to prevent impoverishment therein. The number and size of holes in the perforated cathode will depend upon a number of factors such as the composition of the electrolyte, rate of flow of the electrical current, the distance between the electrodes and the effective area of the cathode. Although, for the purpose of illustrating my invention, I have shown the perforations in the cathodes inclining upwardly at an angle, this is not essential; good results may be secured if the holes 5 are at right angles to the surface of the cathode. However, it is preferable to incline the holes 5 upwardly, especially if the cathode is of substantial thickness.

In prior fused salt electrolytic cells, the relatively slow flow of electrolyte into the space between the electrodes was from the ends towards the middle of the space between the electrodes, and hence fresh electrolyte was brought in only at ends of the effective electrode surfaces, while electrolysis occurred over the entire space. The employment of my perforated cathode insures that fresh electrolyte will be continuously delivered to all parts of the space between the effective surfaces of the electrodes.

Although it might appear obvious that the ef-

fective surface of the cathode would be reduced by making the perforations therein to such extent that the cell efficiency would be lowered, I have found this not to be the case. On the contrary, it appears that possibly the perforations would increase the effective surface of the cathode.

Another method of carrying out my invention is illustrated by Fig. 3 of the appended drawings. Fig. 3 is a diagrammatic cross-section view of a cell similar to that illustrated by Fig. 1 except that the cathode 10 in Fig. 3 has no perforations. A plurality of air-lift pumps, consisting of the elements 11 and 12 are suspended by means not shown in the cell, at equidistant points around the cathode 10. Each of these pumps consists of an air-inlet tube 12 inserted in a wider bent tube 11, open at both ends. The pumps are operated by passing a stream of air or other gas through the inlet tube 12. The passage of the gas upwardly from tube 12 through the long arm of the bent tube 11 causes a rapid flow of the molten electrolyte through tube 11. Since the lower end of tube 11 is situated just below the space between the electrodes 2 and 10, the flow of the electrolyte through tube 11 causes a rapid downward flow of electrolyte in the space between the electrodes. This downward flow is maintained at a rate sufficient to prevent impoverishment of the electrolyte within the space between the electrodes, and yet is not powerful enough to prevent the products of electrolysis from rising upwards into collector ring 7 and gas dome 9, respectively.

In operating fused salt electrolytic cells of the Downs type, for the production of sodium by electrolysis of a mixture of calcium chloride and sodium chloride, I have experienced considerable difficulty with short circuits caused by deposition of calcium on the cathode and eventual bridging of the calcium deposits across to the diaphragm. These difficulties are increased when it is attempted to narrow the space between the electrodes. One effect of these short circuits was to cause serious fluctuations in the cell voltage, for instance, as short circuits occur, the voltage steadily drops. If measures are taken to remove the calcium deposits, for instance, by placing a new diaphragm in the cell, the voltage is brought back to its original value, but in a short time is again decreased by short circuits. These short circuits often cause the voltage to fluctuate as much as 0.6 volts. The short circuits not only cause voltage fluctuation, but also cause the diaphragm to corrode, making frequent diaphragm changes necessary.

I have found that by using a cell equipped with a perforated cathode as illustrated by Figs. 1 and 2 of the appended drawings, the cell voltage remains substantially constant, often not varying by more than about 0.02 volt, diaphragm changes are required much less frequently, and the average cell production is increased by about 30 pounds of sodium per day.

Similar improvements may be obtained by using the air-lift pumps as illustrated by Fig. 3 of the appended drawings. In one case, a fused mixture of calcium chloride and sodium chloride was electrolyzed in a cell of the Downs type, to produce sodium and chlorine. During the first 11 days of operation, the sodium production of this cell maintained a high average, although the voltage fluctuated to some extent, the maximum and minimum readings differing by about 0.32 volt. During the next 14 days, considerable difficulty was

experienced with short circuits. The voltage fluctuated by about 0.66 volt and the average voltage was 0.44 volt less than during the preceding 11 days. In order to prevent the cell production from becoming unduly low, it was necessary to loosen calcium deposits and change diaphragms several times. On the 26th day of operation, a new diaphragm was placed in the cell and four air-lift pumps similar to those illustrated in Fig. 3 of the appended drawings, were installed and put into operation. The cell voltage immediately rose to the normal value and during the next 18 days, while the pumps were operated, the voltage did not vary by more than 0.06 volt. The average daily production also was increased by about 44 pounds per day, during the 18 days that the air-lift pumps were operated.

While I have illustrated my invention by showing two specific devices for causing a flow of the electrolyte into the space between the electrodes in one specific type of fused salt electrolysis cell, my invention is not restricted thereto. Other means for effecting said flow of electrolyte may be employed in the particular type of cell described herein, without departing from the spirit and scope of my invention. Furthermore, similar means may be adapted for other types of fused salt electrolytic cells as will be apparent to those skilled in designing and operating such cells.

I prefer to produce the increased circulation by means of a perforated electrode as illustrated by Figs. 1 and 2 of the appended drawings. This is a simple and effective manner in which to carry out my invention; it avoids the use of complicated apparatus, and requires no especial attention in operation. Furthermore, if this type of device for increasing the cell circulation is used, it is not essential that the cathode be perforated but similar perforations or conduits may be provided in the anode or in both the anode and the cathode. For example, in some types of fused salt electrolytic cells, it may be preferable or more feasible to perforate the anode rather than the cathode. If desired, a pumping device may be used to force electrolyte through such perforations or conduits. Also, other means may be used to flow a stream or streams of the electrolyte into the space between the electrodes. For example, in place of the above described perforated cathode, a series of rings, horizontally disposed one above the other, or a helical cathode may be employed. Many other forms, equivalent to the perforated cathode, will be apparent; for example, such may be found of woven wire construction, or may exist of a grating made of steel bars or rods. Also, a series of tubes leading into the space between the electrodes may be provided, through which the electrolyte is caused to flow by means of one or more suitable pumping devices.

One advantage of my invention is that it makes possible the use of a narrower space between the electrodes of fused salt electrolytic cells than has been heretofore possible. The effect of narrowing the space between the electrodes is to increase the yield of electrolysis products per kilowatt hour of electrical current and thus to increase the overall efficiency of the cell. The positive circulation of electrolyte into the space between the electrodes prevents impoverishment of any constituent of the electrolyte therein, and therefore insures uniformity of cathodic products. For example, in the electrolysis of a mixture of sodium chloride and calcium chloride to produce sodium, my invention

insures uniform production of sodium containing a minimum amount of calcium. Furthermore, my invention makes possible the use of a higher proportion of calcium chloride in this electrolysis, while avoiding the formation of calcium in amounts greater than will dissolve in the sodium released at the cathode. Hence, it prevents the calcium from building up on the cathode and bridging across to the diaphragm and/or anodes to cause short circuits.

A further advantage of my invention is that it enables the electrolysis of fused salt to be carried out at lower temperatures than has been possible heretofore. This is because my invention permits the electrolysis to be carried out with a salt mixture nearer the eutectic point, without producing excessive amounts of undesired metal.

I claim:—

1. A process comprising electrolyzing a mixture of fused salts in a relatively narrow, elongated zone of electrolysis, while flowing the electrolyte in a plurality of streams into said zone, the points of entrance of said streams into said zone being substantially uniformly distributed throughout at least a major portion of said zone.

2. A process comprising electrolyzing a mixture of fused salts in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of electrolyte, while flowing the electrolyte into said zone of electrolysis at a rate sufficiently high to maintain the electrolyte composition throughout said zone substantially identical with the composition of the electrolyte which surrounds said zone and separating a metallic electrolysis product from the electrolyte.

3. A process comprising electrolyzing a mixture of fused salts in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of electrolyte, while flowing the electrolyte from said large body in a plurality of streams substantially uniformly distributed throughout at least a major portion of said zone.

4. A process comprising electrolyzing a fused mixture of calcium chloride and sodium chloride, in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of the electrolyte, while flowing the electrolyte in a plurality of streams into said zone of electrolysis at a rate sufficient to maintain the composition of the electrolyte within said zone substantially identical with the electrolyte composition surrounding said zone.

5. A process comprising electrolyzing a fused mixture of calcium chloride and sodium chloride, in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of the electrolyte, while flowing the electrolyte downwardly through said zone of electrolysis at a rate sufficient to maintain the composition of the electrolyte within said zone substantially identical with the electrolyte composition surrounding said zone, while allowing the products of electrolysis to escape upwardly.

6. A process comprising electrolyzing a fused mixture of sodium chloride and less than 71% by weight of calcium chloride, in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of the electrolyte, while flowing the electrolyte in a plurality of streams into said zone of electrolysis at a rate sufficient to maintain the composition of the electrolyte within said zone substantially identical with the electrolyte composition surrounding said zone.

7. In a process for electrolyzing a mixture of fused salts, the method comprising flowing the electrolyte in a plurality of streams into the space between the anode and cathode, said streams entering said space at a plurality of points substantially uniformly distributed over at least one boundary of said space, which boundary is defined by an electrode face. 5
8. In a process for electrolyzing a mixture of fused salts comprising an alkali metal halide, the method comprising flowing the electrolyte in a plurality of streams into the space between the anode and cathode, said streams entering said space at a plurality of points substantially uniformly distributed over at least one boundary of said space, which boundary is defined by an electrode face. 10
9. In a process for electrolyzing a mixture of fused salts comprising an alkali metal halide, the method comprising flowing the electrolyte in a plurality of streams upwardly, into the space between the anode and cathode, said streams entering said space at a plurality of points substantially uniformly distributed over an area which is substantially parallel to the cathode. 5
10. A process comprising electrolyzing a mixture of fused salts in a relatively narrow, elongated zone of electrolysis, which zone is surrounded by a large body of electrolyte, while flowing the electrolyte downwardly through said zone of electrolysis at a rate sufficient to maintain the electrolyte composition within said zone substantially identical with the electrolyte composition surrounding said zone, while allowing the products of electrolysis to escape upwardly. 10 15

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