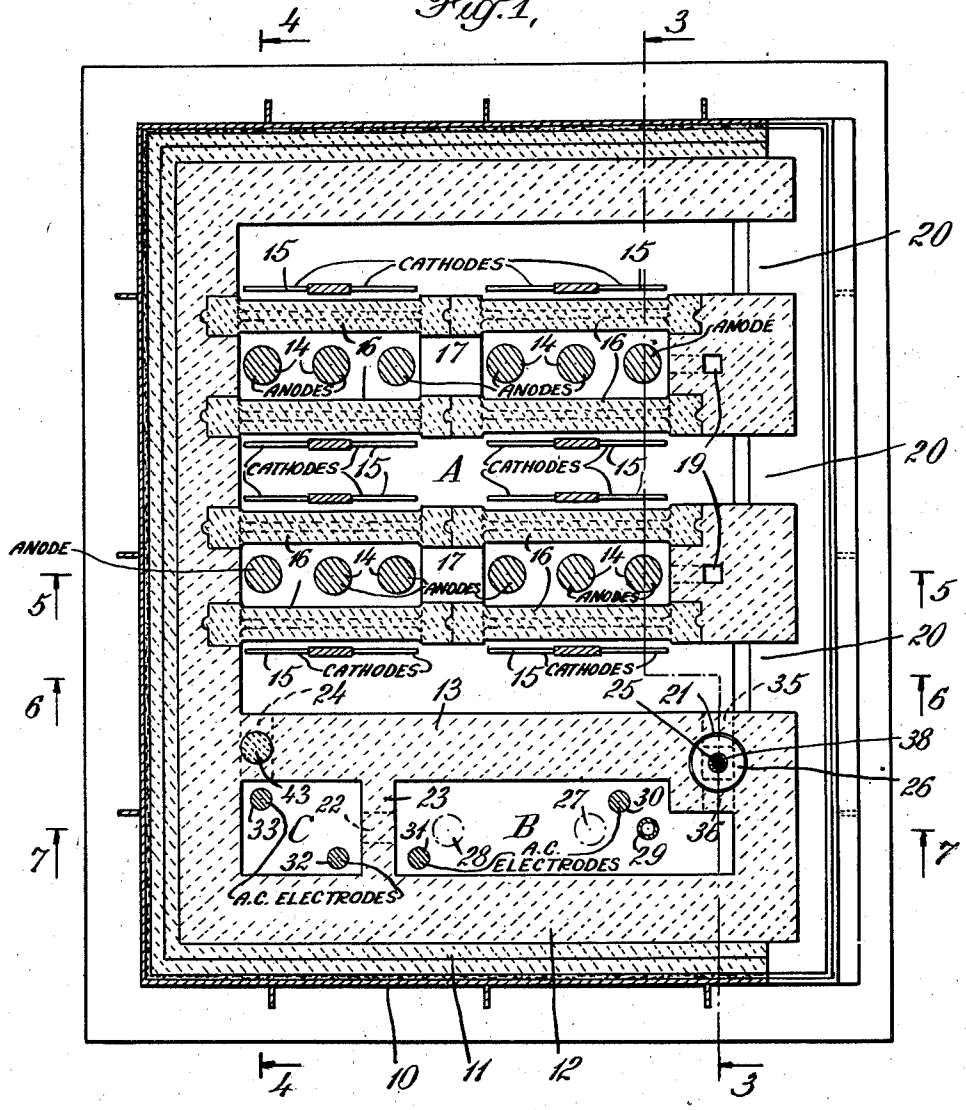
Dec. 9, 1947. R. B. MacMULLIN 2,432,431

CELL FOR THE ELECTROLYSIS OF MAGNESIUM CHLORIDE FUSIONS

Filed Nov. 21, 1942 5 Sheets-Sheet 1

Fig. 1.



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Filed Nov. 21, 1942 5 Sheets-Sheet 2

Fig. 2.

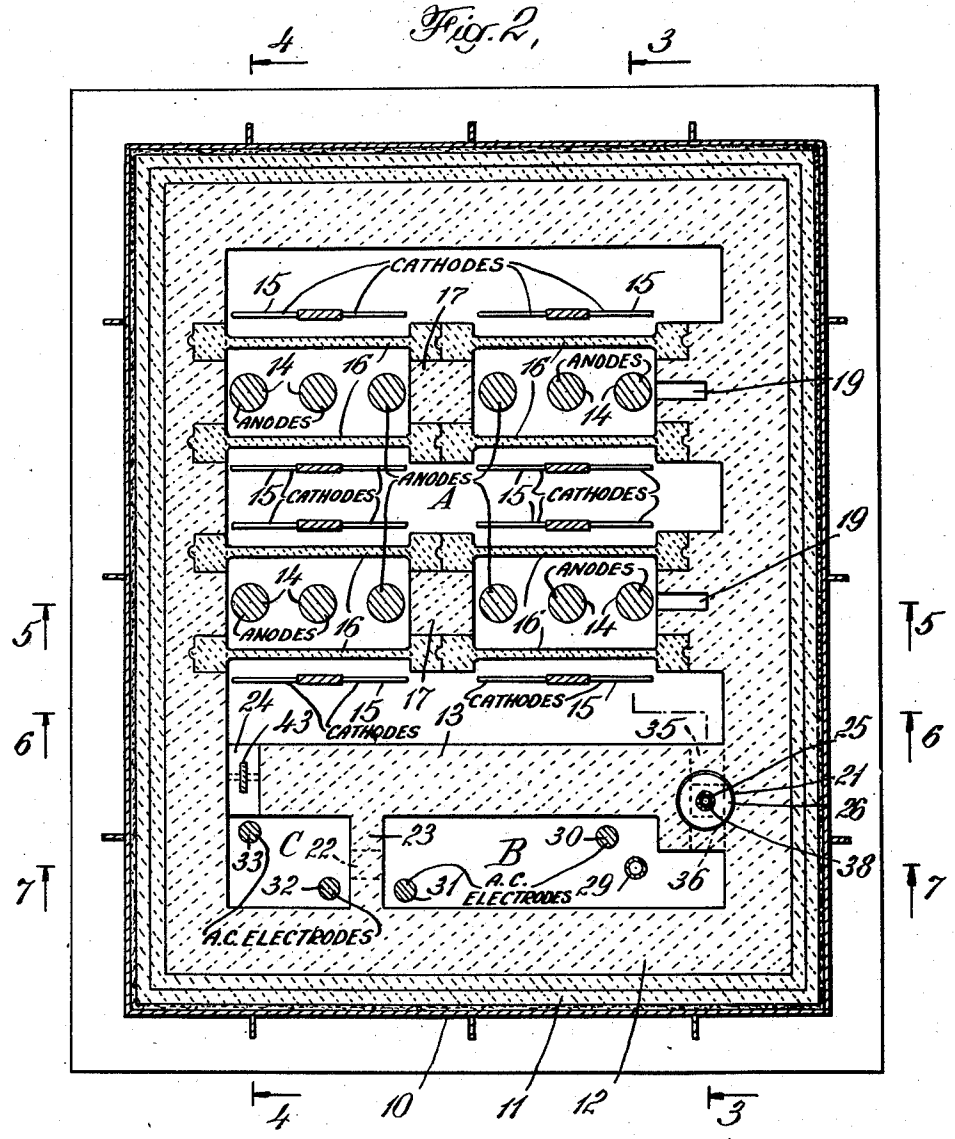

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Fig. 3,

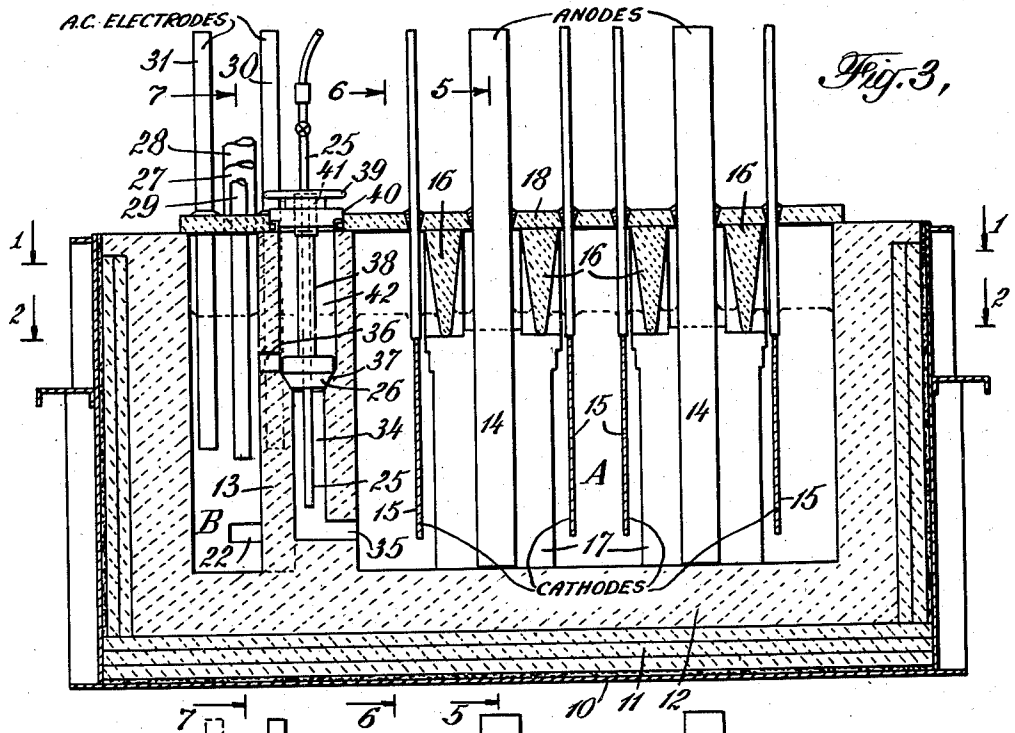

Fig. 4,

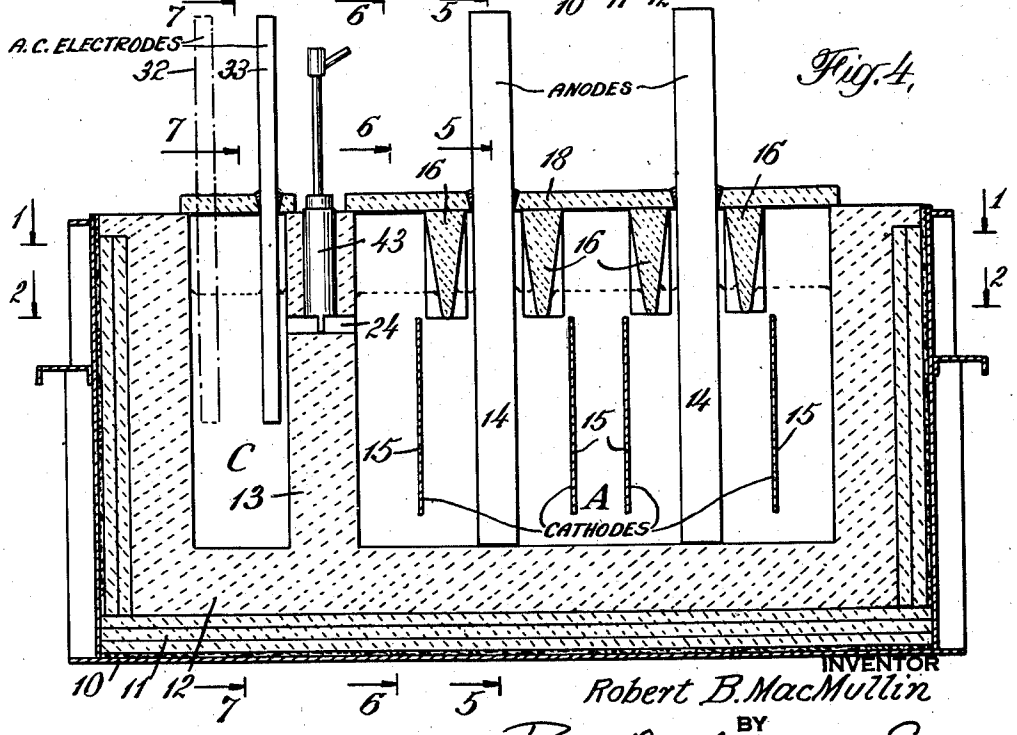

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Fig. 5,

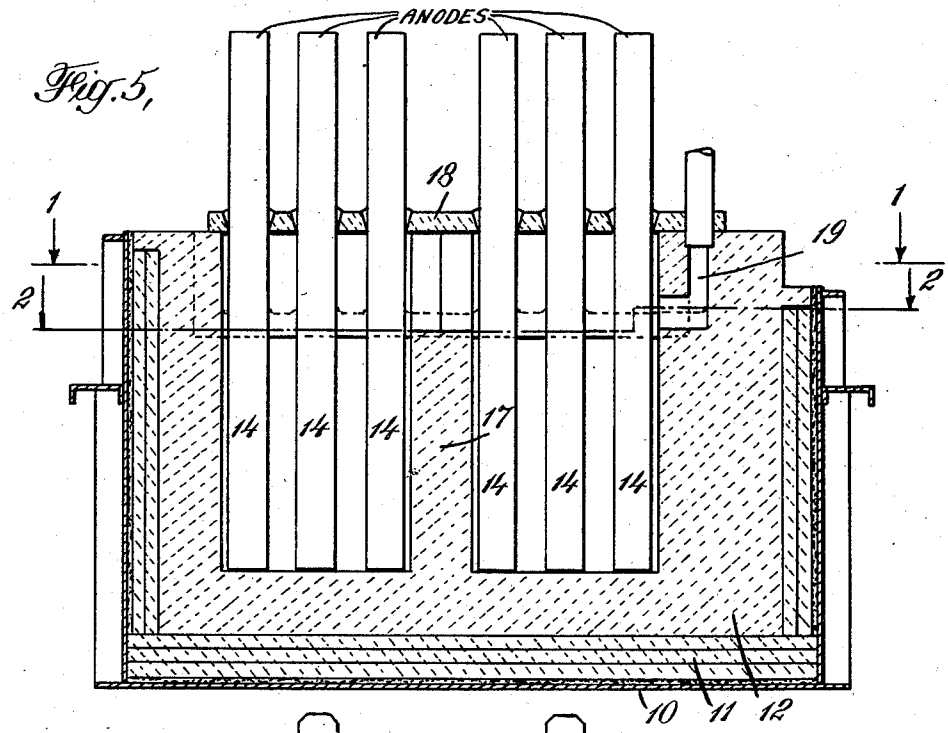

Fig. 6,

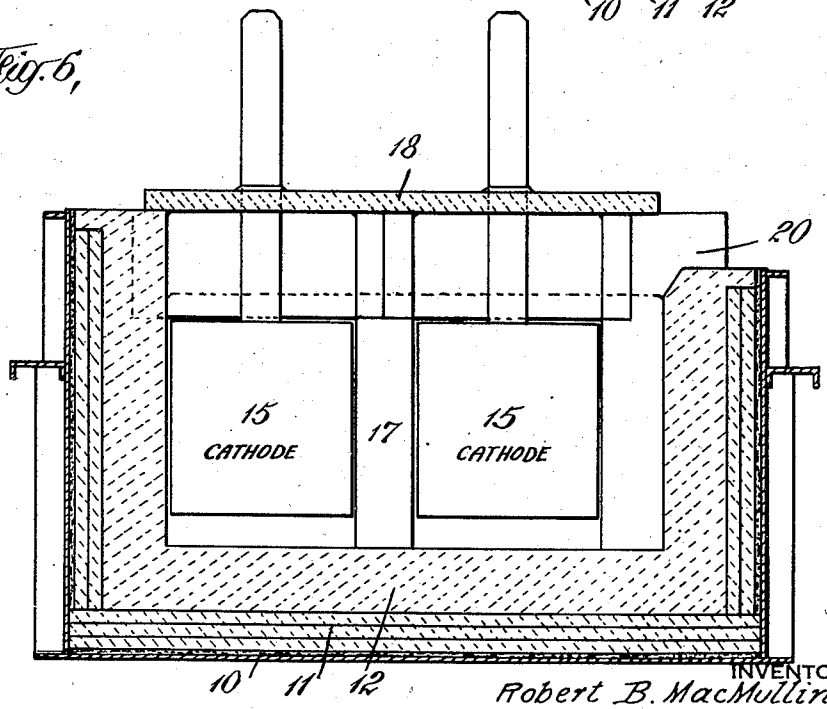

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Fig. 7,

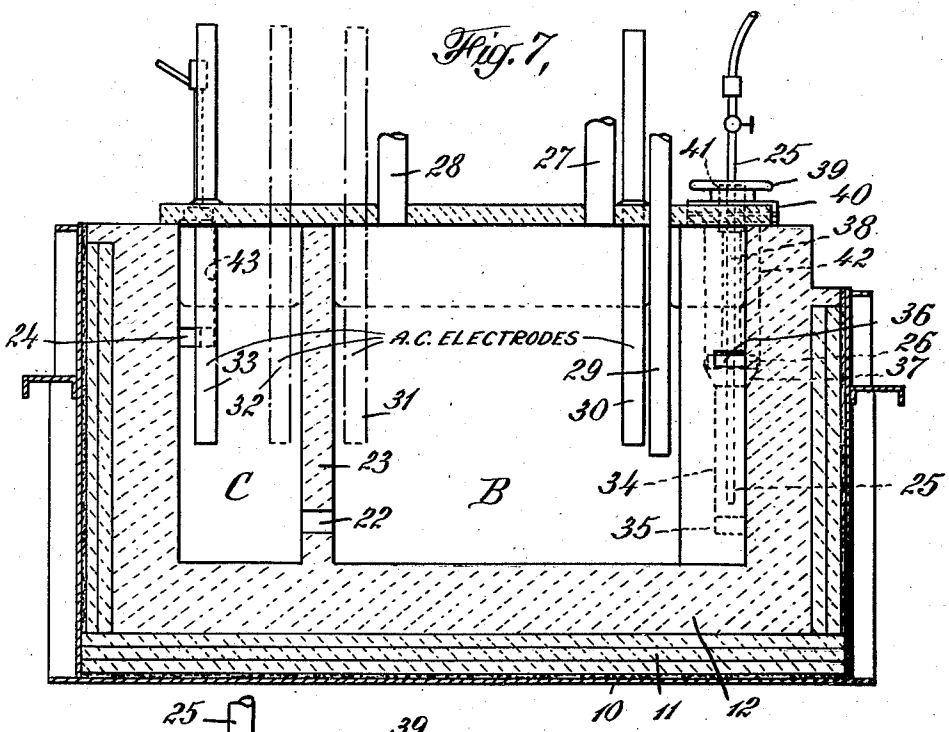


Fig. 10,

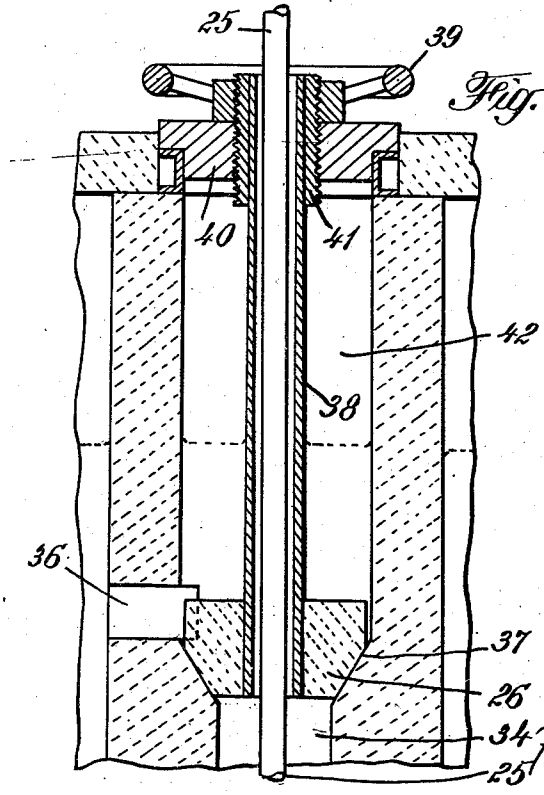


Fig. 8

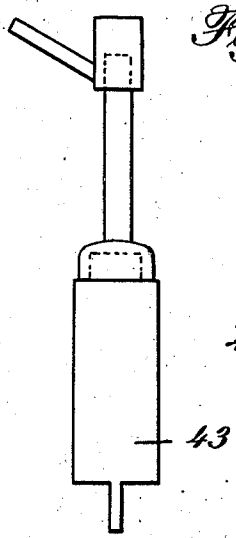
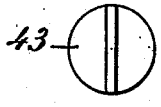


Fig. 9,



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Patented Dec. 9, 1947

2,432,431

UNITED STATES PATENT OFFICE

2,432,431

CELL FOR THE ELECTROLYSIS OF MAGNESIUM CHLORIDE FUSIONS

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Application November 21, 1942, Serial No. 466,456

1 Claim. (Cl. 204—236)

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My invention relates to improvements in cells for the electrolysis of magnesium chloride fusions to which magnesium chloride, to replace that consumed by electrolysis, is supplied in hydrous form. The improved electrolytic cell of my invention is useful particularly for carrying out the process described in my application Serial No. 439,333, filed April 17, 1942.

When hydrous magnesium chloride is added to such fusions at temperatures of the order of 700°–750° C., representative of normal electrolyte temperatures in the operation of such cells, the water component of the make-up salt is not completely eliminated. A part of the hydrous magnesium chloride tends to decompose with liberation of hydrochloric acid and formation of magnesium hydroxy chloride (MgOHCl). The electrolyte thus becomes saturated with the hydroxy chloride. In a fusion consisting essentially of about 25%–50% $MgCl_2$ and the balance of NaCl, for example, the dissolved hydroxy chloride may be equivalent to as much as 0.5% H_2O by weight on the fusion. Additional hydroxy chloride may also be carried in suspension in the electrolyte. Decomposition of the hydroxy chloride in the region of electrolysis, through reaction with the carbon of conventional anodes or with magnesium metal liberated by the electrolysis, impairs the efficiency of the operation, consumes magnesium chloride in the formation of magnesium oxide or magnesium oxy chloride (Mg_2OCl_2) and liberates hydrochloric acid which contaminates the chlorine liberated by the electrolysis. The improved cell of my invention provides for substantially complete dehydration of hydrous make-up magnesium chloride in such magnesium chloride fusions and thus for improvement in the recovery of magnesium metal and of chlorine values, for improvement in chemical efficiency and power consumption, for improvement with respect to the life of carbon anodes and generally for improvement in efficiency, economy and uniformity of operation.

Magnesium hydroxy chloride, as an isolated compound, is probably unstable at temperatures upwards of about 520° C., but when dissolved in a magnesium chloride fusion the dissociation pressure is much reduced depending upon concentrations and temperatures. Such fusions to which magnesium chloride is supplied as a hydrous salt can be demonstrated in many instances to contain a fractional percentage of water, presumably as the hydroxy chloride, at 725° C. for example. This water content can be eliminated to produce a fusion substantially free from water

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or its equivalent as the hydroxy chloride by superheating the fusion, for example to temperatures approximating 800°–850° C. Satisfactory results however are not achieved by generally increasing the temperature of the fusion subjected to electrolysis for if this is done the fusion, at elevated temperatures effective to eliminate water, becomes too thin to provide a maintained chloride film covering liberated magnesium metal, as droplets and coalescing masses, effective to prevent substantial recombination of magnesium and chlorine and burning of the liberated metal.

In the improved electrolytic cell of my invention, the hydrous magnesium chloride is added to the fused electrolyte in a feed chamber, separate from the electrolysis chamber, through which electrolyte depleted with respect to magnesium chloride in the electrolysis chamber circulates and, before it returns to the electrolysis chamber, the electrolyte including added magnesium chloride is circulated through a superheating chamber in which water remaining after the dehydration effected in the feed chamber, present for example as magnesium hydroxy chloride, is eliminated by maintaining a substantially higher electrolyte temperature than in the electrolysis chamber and the feed chamber. The improved electrolytic cell of my invention comprises an electrolysis chamber, a feed chamber and a superheating chamber, anodes and cathodes in the electrolysis chamber, appropriate passages connecting the electrolysis chamber and the feed chamber, the feed chamber and the superheating chamber, and the superheating and the electrolysis chamber below the normal electrolyte level, means for maintaining a higher electrolyte temperature in the superheating chamber than in the electrolysis chamber and the feed chamber, and means for controlling electrolyte circulation from the electrolysis chamber through the feed chamber and the superheating chamber back to the electrolysis chamber.

In the improved electrolytic cell of my invention the means for controlling electrolyte circulation through the cycle just described are arranged in one or more of the passages connecting the electrolysis chamber, the feed chamber and the superheating chamber. These control means may comprise, for example, one or more valves or a forcing means such as a gas lift or both. The primary control means are with advantage arranged in the passage connecting the electrolysis chamber and the feed chamber and may be supplemented by other control means arranged in one or more of the other passages. By thus ar-

ranging the primary control means I secure a number of important advantages. The operation of the cell can be carried out either with continuous controlled circulation of electrolyte from the electrolysis chamber through the feed chamber and the superheating chamber back to the electrolysis chamber or with intermittent circulation through this cycle transferring electrolyte from the electrolysis chamber to the feed chamber, from the feed chamber to the superheating chamber and from the superheating chamber back to the electrolysis chamber at spaced intervals. If, with continuous circulation controlled by means arranged in either the passage between the feed chamber and the superheating chamber or the passage between the superheating chamber and the electrolysis chamber, irregularities occur in the feed chamber, temporary reversal of electrolyte flow through the passage between the electrolysis chamber and the feed chamber tends to carry magnesium hydroxy chloride into the feed chamber and thus to impair the operation as previously described. Since the bulk of the water content of the hydrous make-up salt, $MgCl_2.H_2O$ or $MgCl_2.2H_2O$ for example, is flashed into steam as this salt enters the fused electrolyte in the feed chamber, such irregularities in operation will occur in the feed chamber. However, by arranging the primary control means in the passage connecting the electrolysis chamber and the feed chamber, I avoid difficulties flowing from such irregularities. The same situation prevails with intermittent circulation of the electrolyte. Further, with such intermittent circulation controlled by means arranged in the passage connecting the feed chamber and the superheating chamber or the passage connecting the superheating chamber and the electrolysis chamber, the addition of make-up salt to the electrolyte in the feed chamber increases the liquid head in this chamber and thus directly tends to cause reverse flow through the passage connecting the electrolysis chamber and the feed chamber, a result avoided if the primary control means are arranged in the passage connecting the electrolysis chamber and the feed chamber. Circulation may be that induced by thermal effects or circulation of electrolyte may be effected or assisted by a forcing means such as a gas lift. For effective thermal circulation, the exit port of the passage connecting the feed chamber and the superheating chamber must be below the inlet port of the passage connecting the superheating chamber and the electrolysis chamber. With thermal circulation, a regulating valve may be positioned in any one or more of the three passages. For regularity of circulation, a forcing means such as a gas lift is arranged in one of the several passages, advantageously in the passage connecting the electrolysis chamber and the feed chamber, and one or more valves may be arranged in one or more of the other passages to assist in controlling circulation. With intermittent circulation the forcing means and a valve may be arranged in the same passage for alternate use; with continuous circulation it is advantageous to avoid valves in the gas lift discharge if a gas lift is used as a forcing means.

The accompanying drawings represent an electrolytic cell embodying my invention and my invention will be further described by reference to this illustrative electrolytic cell and its operation. In these drawings:

Fig. 1 is a section in plan on line 1—1 in Figs. 3 and 4;

Fig. 2 is a section in plan on line 2—2 in Figs. 3, 4 and 5;

Fig. 3 is a section in elevation on line 3—3 in Figs. 1 and 2;

Fig. 4 is a section in elevation on line 4—4 in Figs. 1 and 2, except that the position of the alternating current electrode 32 has been indicated in Fig. 4 by dot and dash lines notwithstanding its position to the right of the section line 4—4 in Figs. 1 and 2;

Fig. 5 is a section in elevation on line 5—5 in Figs. 1, 2, 3 and 4;

Fig. 6 is a section in elevation on line 6—6 in Figs. 1, 2, 3 and 4;

Fig. 7 is a section in elevation on line 7—7 in Figs. 1, 2, 3 and 4, except that the position of the alternating current electrodes 31 and 32 have been illustrated in dot and dash lines in Fig. 7 notwithstanding their position below the section line 7—7 as shown in Figs. 1 and 2 and to the left of the section line 7—7 as shown in Figs. 3 and 4;

Figs. 8 and 9 are enlarged details of a valve element also illustrated in Figs. 1, 2, 4 and 7, and

Fig. 10 is an enlarged fragmentary detail of a valve element and gas discharge tube also illustrated in Figs. 3 and 7.

Referring to the drawings: The cell illustrated comprises a rectangular steel shell 10 lined with insulation 11 and refractories 12 and divided by a refractory wall 13 into a major chamber A, the region of electrolysis, and a pair of minor chambers B and C. Anodes 14 and cathodes 15 are arranged in groups in the chamber A. The anodes consist of cylindrical carbon rods resting on the bottom of the chamber. The cathodes are with advantage arranged to permit their elevation while dredging the cell. The anodes and cathodes are connected through busbars arranged immediately over the cell covers to a source of direct current of appropriate potential. Adjacent anodes and cathodes are separated, at and above the normal electrolyte level, by partitions made up of rectangular webbed arch elements 16 supported by pillars 17 and the cell walls. The series of elements 16 along each side of each row of anodes with the covers 18 form closed troughs for collecting the chlorine liberated at the anodes by the electrolysis. Connections 19 are provided for collecting this chlorine from each of the anode troughs and delivering it to an appropriate recovery system. The magnesium metal liberated by the electrolysis collects initially above the cathodes as molten metal floating on the fused electrolyte. The magnesium metal thus collected above the several rows of cathodes is removed from the cell through the several corresponding ports 20. In carrying out my invention in the illustrated cell, the magnesium chloride fusion within chamber A, the region of electrolysis, is maintained substantially free from water although make-up magnesium chloride is introduced as the hydrous salt to the chamber B within the cell structure. The chambers B and C, separated from the electrolysis chamber by the refractory wall 13, constitute, respectively, a feed chamber and a superheating chamber. Fused electrolyte withdrawn from the chamber A through passage 21, the several component parts of which are identified in Fig. 3 by the reference numerals 35, 34 and 36, passes through the chamber B, then, after passing from chamber B into chamber C through passages 22 in refractory wall 23, passes through the chamber C and then through passage 24 back to chamber A. In chamber C, the superheating chamber, the port of

passage 22 is below the port of passage 24. Circulation of fused electrolyte from chamber A through chambers B and C back to chamber A is controlled by regulating either the valve 26 or the gas lift comprising gas discharge tube 25 in the vertical portion of passage 21. This control may be supplemented by regulating the valve 43. Hydrous magnesium chloride is supplied to chamber B through connection 27 and the gas mixture formed in this chamber is discharged through connection 28. Chlorine or hydrochloric acid or a mixture of chlorine and carbon monoxide or carbonyl chloride for example may be introduced into the body of fused electrolyte in chamber B through connection 29 to suppress decomposition of magnesium chloride within the body of electrolyte in this chamber as an incident to the initial dehydration of the hydrous salt. Pairs of electrodes 30, 31, 32 and 33 are arranged within the chambers B and C for supplying heat to these chambers through the fused electrolyte within these chambers as a resistor in each of these chambers with respect to alternating current passing between these electrodes. The desired temperature gradient through the chambers B and C is easily established and maintained for example by providing for separate regulation of alternating current passing (1) between electrodes 30 and 31 with respect to chamber B and (2) between electrodes 32 and 33 with respect to chamber C. Other arrangements for establishing and maintaining this temperature gradient may, however, be used. Individual transformers are with advantage used to supply alternating current for heating the electrolyte in each of the minor chambers of individual cells. With this arrangement the cell side of each such transformer will be at the same direct current potential above ground as the cell and consequently must be insulated with respect to the input side of the transformer to withstand this direct current potential as well as the alternating current potential impressed on the transformer. The primary means for controlling electrolyte circulation through the chambers B and C are either the valve 26 or the gas lift comprising gas discharge tube 25. These means are arranged in the vertical portion 34 of the passage 21 connecting a low point 35 in the electrolysis chamber A with a high point 36 in the feed chamber B (see Fig. 3). The control means illustrated are particularly advantageous. They comprise a valve plug 26 seated in an enlargement 37 in the upper part of the portion 34 of the passage 21 and carried on a tube 38 vertically movable by means of wheel 39 supported by yoke 40 and receiving a threaded collar 41 secured to the upper end of the tube 38. The yoke 40 is removable so that the entire valve assembly can be removed by lifting it out of the cell through the extension 42 of the passage 34 above the discharge port to chamber B. The gas discharge tube 25 can be moved into the vertical portion 34 of the passage 21 from above the normal electrolyte level either through the tube 38 or it can be moved into this passage after removal of the valve assembly permitting alternating use of the valve and the gas lift. Valve 43, arranged in the passage 24 connecting chamber C and chamber A, may be used to supplement valve 26, or this valve 43 may be omitted.

In operation: The cell is charged with fused electrolyte to a level at which the lower edges of the webs in the rectangular arch elements 16 are immersed. The electrolyte may consist for example of a fused mixture of the chlorides of the

alkali metals and alkaline earth metals comprising about 10%–55% by weight of magnesium chloride. The temperature of the electrolyte in the cell is maintained above its fusion point, for example at a temperature approximating 725° C. The heat required to maintain this temperature, in excess of that liberated in conjunction with the electrolysis proper, is supplied to the electrolyte as it passes through the feed chamber and the superheating chamber. The direct current voltage impressed across the anodes and cathodes in the electrolysis chamber will vary with the spacing of these electrodes and the temperature and composition of the electrolyte; it may for example approximate 6–8 volts. Circulation within the electrolysis chamber effective to maintain substantial uniformity, with respect both to composition and to temperature, throughout the major body of electrolyte undergoing electrolysis in that chamber is maintained by the levitating effect of chloride liberated at the anodes and by local thermal cycles of circulation. The additions required to maintain the composition and quantity of electrolyte in the cell, as the electrolysis proceeds, are introduced from time to time into the feed chamber. Magnesium chloride consumed by the electrolysis is thus replaced by the introduction of hydrous magnesium chloride. In the feed chamber, this hydrous magnesium chloride is partially dehydrated, its water content being reduced for example to about 0.3–0.5 mol per mol of added magnesium chloride or less, fused and incorporated into the body of fused electrolyte. Such hydrous magnesium chloride is with advantage introduced into the feed chamber in the form of pellets having a specific gravity of about 1 which may contain a small proportion, about 0.5% for example, of free carbon. The temperature of the fused electrolyte in the feed chamber is maintained at about the same level as that prevailing in the electrolysis chamber by supplying sufficient additional heat as previously described to make up the heat of dehydration and fusion of the hydrous magnesium chloride incorporated into the electrolyte in the feed chamber and any other thermal losses. Thus, with a temperature in the electrolysis chamber approximating 725° C., a temperature of the same order is maintained in the feed chamber. Fused electrolyte depleted with respect to magnesium chloride in the electrolysis chamber moving from that chamber to the feed chamber is thus in the latter chamber replenished with respect to magnesium chloride and moves from the feed chamber to the superheating chamber as a fusion containing added magnesium chloride and a small proportion of water, presumably in the form of magnesium hydroxy chloride. In the superheating chamber a substantially higher temperature is maintained, a temperature of 800°–850° C. for example, and as a consequence this remaining water is eliminated. This superheating of the fused electrolyte after introduction of the hydrous magnesium chloride is effected in the substantial absence of magnesium metal, the magnesium metal liberated by the electrolysis being separated in the electrolysis chamber as previously described from the fused electrolyte moving from the major body in the electrolysis chamber to the minor body in the feed chamber through the submerged passage connecting these chambers. The fused electrolyte stripped of water in the superheating chamber, carrying the added magnesium chloride incorporated in the feed chamber, moves from the superheating chamber into the electro-

lysis chamber where, as a result of the circulation within the electrolysis chamber previously described, its excess of magnesium chloride and its excess of heat are rapidly absorbed by the major body of electrolyte as a whole. The circulation of electrolyte from chamber A through chambers B and C in succession and back to chamber A may, as previously noted, be a continuous controlled circulation or an intermittent circulation. If continuous, the rate of circulation is maintained sufficient to carry into the electrolysis chamber the required make-up magnesium chloride but is limited approximately to the minimum required to accomplish this result since circulation in excess of this minimum tends to increase the additional heat required in the feed chamber and the superheating chamber and involves waste as well as the burden of dissipating such additional heat in the electrolysis chamber. In the particular cell illustrated, the arrangement of the several chambers and connecting passages is such that thermal effects may, at some operating levels, induce circulation rates exceeding this minimum, but generally it is advantageous to force circulation in this cycle to insure effective and regular control and, to this end, the gas lift comprising gas discharge tube **25** is used. If the circulation is intermittent, the valve **26** is closed when circulation is stopped, and during such periods valve **43** may also be closed, and, when transfer of electrolyte is to be effected, valve **26** is opened or removed, valve **43** being open during such periods, and relatively rapid circulation is forced for a limited interval by introducing gas through the gas discharge tube **25** within the vertical portion **34** of the passage **21** as a gas lift. An inert gas such as nitrogen may be used or, since passage **21** discharges into chamber B, a gas such as chlorine to be supplied to the feed chamber may be used.

I claim:

A cell for the electrolysis of magnesium chloride fusions comprising an electrolysis chamber, a feed chamber and a superheating chamber, anodes and cathodes in the electrolysis chamber, a first passage connecting the electrolysis chamber and the feed chamber below the normal electrolyte level, said first passage including a vertical portion connecting a low point in the electrolysis chamber with a high point in the feed chamber, a plug valve in the upper part of said vertical portion of the first passage, a gas discharge tube movable into said vertical portion of the first passage from above the normal electrolyte level, a second passage connecting the feed chamber and the superheating chamber below the normal electrolyte level, a third passage connecting the superheating chamber and the electrolysis chamber below the normal electrolyte level, the second passage connecting the feed chamber and the superheating chamber being positioned below the level of the third passage connecting the superheating chamber and the electrolysis chamber, and means for maintaining a higher electrolyte temperature in the superheating chamber than in the electrolysis chamber and the feed chamber.

ROBERT B. MACMULLIN.

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