May 26, 1959 E. J. WILLIAMS ET AL 2,888,389

ELECTROLYTIC PRODUCTION OF MAGNESIUM METAL

Filed Sept. 6, 1956 3 Sheets-Sheet 1

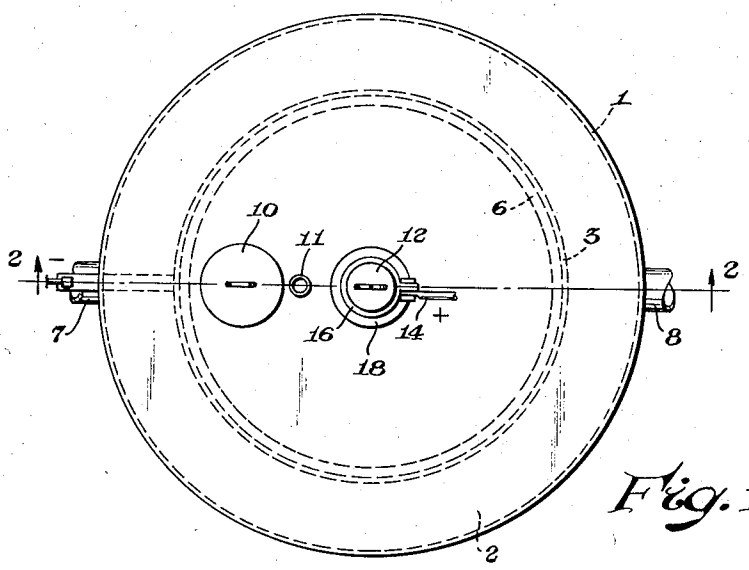

Fig. 1

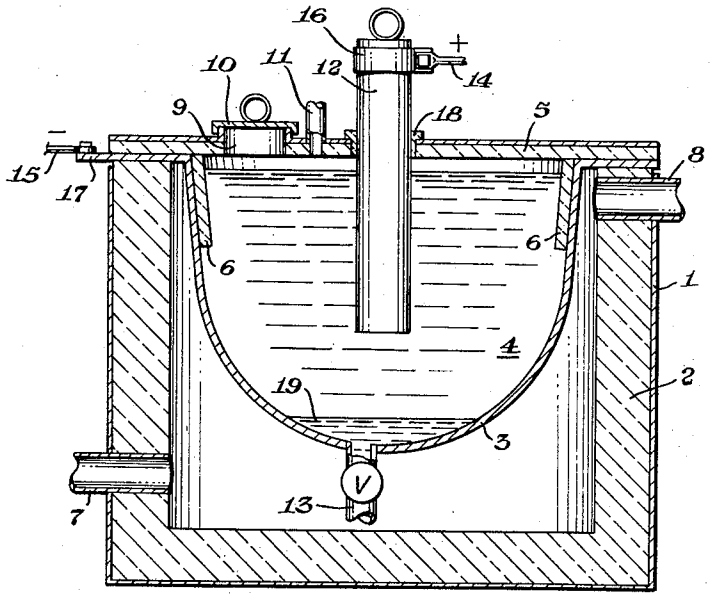

Fig. 2

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Filed Sept. 6, 1956 3 Sheets-Sheet 2

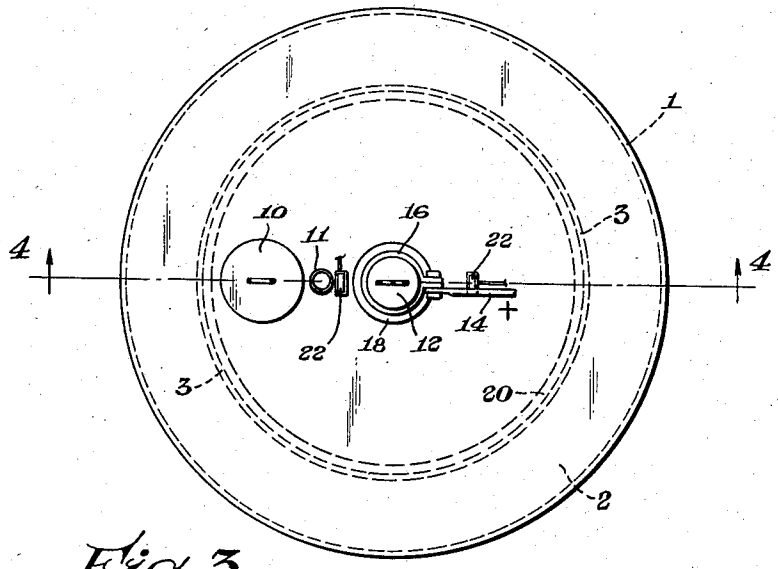

Fig. 3

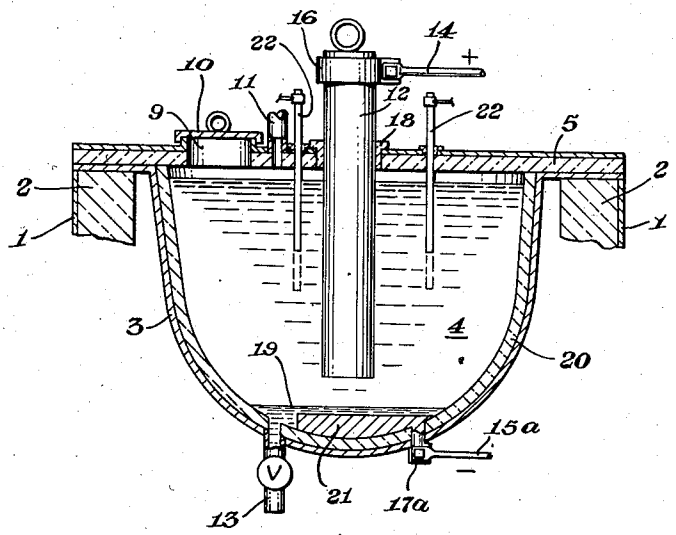

Fig. 4

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ELECTROLYTIC PRODUCTION OF MAGNESIUM METAL

Filed Sept. 6, 1956 3 Sheets-Sheet 3

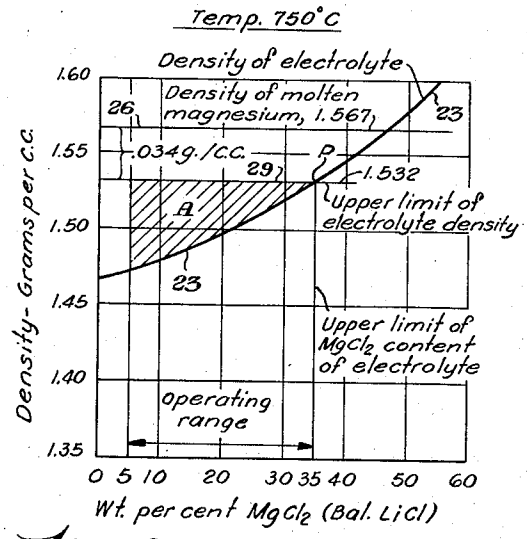

Fig. 5

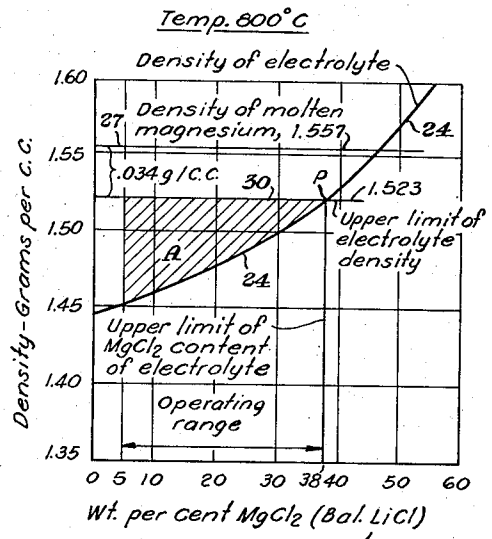

Fig. 6

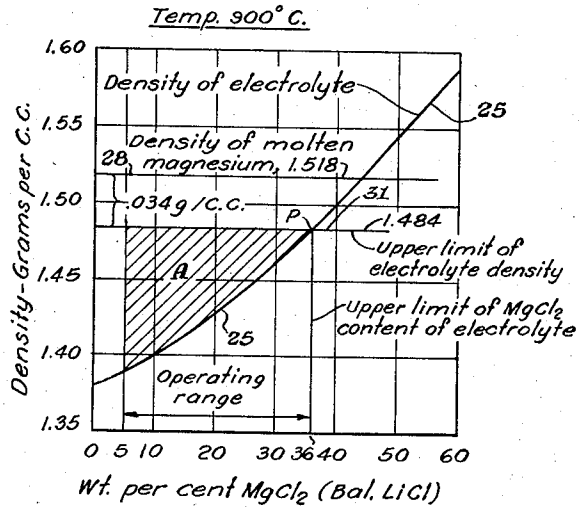

Fig. 7

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2,888,389

ELECTROLYTIC PRODUCTION OF MAGNESIUM METAL

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Application September 6, 1956, Serial No. 608,267

9 Claims. (Cl. 204—70)

The inveniton relates to electrolytes for and methods of electrolytic production of magnesium. It especially relates to molten salt mixtures as electrolytes having a density less than that of molten magnesium and to the method of producing magnesium therefrom.

Magnesium is currently produced on a large scale by the electrolysis of a fused salt bath containing magnesium chloride. The principal source of magnesium chloride at present is the ocean. Formerly the principal sources were the brine of deep wells and the naturally occurring mineral carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$.

These electroyltic baths have a density greater than that of molten magnesium so that generally the magnesium reduced from the electrolytic bath rises to the surface of the bath and is recovered by removal from the surface thereof. One known exception to this is the process wherein magnesium is produced by deposition from a fused bath containing magnesium chloride on a molten alloy containing a minor proportion of magnesium, e.g., a lead-magnesium alloy, and the magnesium is subsequently reduced from the magnesium enriched alloy by a complicated step. This process is of minor industrial importance due to the inconvenience and expense of the subsequent step. Aside from this exception current practice requires that the magnesium rise to the surface of the electrolyte. Since the gaseous products of electrolysis are also lighter than the bath, and therefore rise to and evolve from the surface, elaborate means for preventing recombination of the magnesium with the evolving gaseous products, e.g., chlorine, have been found necessary.

A further difficulty encountered with baths heavier than molten magnesium is that the magnesium, as it collects at the surface of the bath, is exposed relatively unprotected from air and chlorine which gives rise to a constant threat of burning of the magnesium, particularly at higher operating temperatures. As a result, a significant amount of the liberated magnesium is reoxidized and unrecoverable.

An important economic consideration in the production of magnesium by the electrolysis of fused salt mixtures is the conductivity of the electrolyte and rate of power consumption per pound of magnesium produced which reflect the efficiency of the method employed. The efficiency of known electrolytic methods of producing magnesium has not been satisfactory as shown by calculation of the kilowatt-hours required per pound of magnesium produced. A further important economic consideration in magnesium production is the degree of purity of the chlorine in the effluent gas. Chlorine is produced at the anode as a by-product in the electrolysis of magnesium chloride. It was high commercial value if it is in a relatively pure condition.

In view of the difficulties attendant upon conventional methods of electrolytic production of magnesium, it is a desideratum in the art to provide an improved electrolyte for and methods of producing magnesium electrolytically.

We have now formulated a novel improved electrolyte of high conductivity and a highly efficient method of producing magnesium metal by electrolysis thereof whereby substantially pure chlorine is produced at the anode and substantially pure magnesium metal is produced at a submerged cathode out of contact with the atmosphere below the surface of the electrolyte without significant metal loss and at a lower rate of power consumption per pound of magnesium produced than is possible by employing any method heretofore known. The improved electrolyte consists of a fused bath having a density less than that of molten magnesium, at the temperature of the electrolysis, comprising by weight from 5 to 38 percent of magnesium chloride with or without a fluoride of an alkali or alkaline earth metal, wherein the fluoride (F) portion comprises 0.25 to 0.75 percent by weight of the electrolyte, and the balance of the bath is lithium chloride.

It is understood that impurities are tolerated in the electrolyte so long as their presence does not interfere with the electrolysis of the molten salt mixture. For example, other fluorides and chlorides of alkali and alkaline earth metals may be present so long as the density of the electrolyte is less than that of molten magnesium at the temperature of electrolysis or so long as objectionable codeposition of the non magnesium metal does not occur with the magnesium. Traces of water and magnesium oxide may also be present and traces of oxides and salts of metals, which electrodeposit at potentials below that required to deposit magnesium, among which are iron, copper, nickel, silicon, manganese, lead, titanium, boron, aluminum and chromium, may be tolerated. Since these metals deposit at a lower potential than does magnesium, the specification of the magnesium to be produced will predetermined the permissible amounts of such metals. Since the impurities expected to be present are of greater density than lithium chloride, greater tolerance of impurities can be permitted at lower concentrations of magnesium chloride, i.e., higher concentrations of lithium chloride, and less tolerance at higher concentrations of magnesium chloride.

The invention then consists of the improved electrolyte and method of producing magnesium therefrom herein fully described and particularly pointed out in the claims, reference being made to the accompanying drawing.

In said drawing:

Figure 1 is a plan view of one type of electrolytic cell with which the invention may be practiced.

Figure 2 is a sectional elevation along line 2—2 of Figure 1.

Figure 3 is a plan view of a modification of the cell of Figure 1 wherein the cell is fully lined with a refractory ceramic except for openings and electrical contacts as shown and no gas heating means is provided, A.C. electrodes being provided for heating the cell.

Figure 4 is an elevational section of Figure 3 taken along line 4—4.

Figures 5, 6, and 7 are graphs correlating the electrolyte composition with its density at 750°, 800°, and 900° C., respectively.

Referring now to Figures 1 and 2 of the drawing in detail, there is shown steel shell 1 inclosing refractory brick setting 2. Iron pot 3, having a flanged rim, is placed in the brick setting. The pot holds electrolyte 4, formulated in accordance with the invention, and also serves as the cathode of the cell. The top of the cell is provided with ceramic cover 5. About the interior of pot 3 is ceramic lining 6 extending from the flanged rim of the pot downwardly into electrolyte 4 a sufficient distance to fall below the operating level of the electrolyte. This protects the iron pot from interaction with chlorine formed during the electrolysis. Brick setting 2 contains an inlet pipe 7

for introducing heat as from a burner (not shown) and outlet pipe 8 for egress of combustion gases of the heating burner. In cover 5 is opening 9 for admission of feed and for access to the pot. Opening 9 is provided with a removable cover 10. Outlet pipe 11 is provided for egress of chlorine and other gases, if any, formed during electrolysis. Extending through an opening in cover 5 and into pot 3 is anode 12. The degree to which anode 12 extends is controlled by a chain fall (not shown). Drain assembly 13 containing a valve is provided at the lower portion of pot 3. Current leads 14 and 15 are connected to the anode and cathode respectively by suitable terminals 16 and 17 respectively. Packing gland 18 is provided about the anode at the opening in cover 5.

In Figures 3 and 4, the interior surface of the pot is insulated by ceramic lining 20 except for necessary ports and electrical contacts. Instead of pot 3 being the cathode, as in Figures 1 and 2, a steel or graphite plate 21 serves as the cathode. Such an arrangement provides a means for closely controlling the spacing between anode 12 and cathode 21 which is particularly helpful in fully utilizing the electrolyte and method of its use according to the invention. A.C. electrodes 22 provide means for heating the electrolyte prior to electrolysis and supplementing the heat provided by the D.C. passing between anode 12 and cathode 21 if necessary. Terminal 17*a* is shown secured to cathode plate 21 and connected to negative current lead 15*a*. In operating this type of cell, the A.C. electrodes 22 are lowered prior to charging the cell and the initial charge is made a conductor by playing a gas flame on the charge until it becomes sufficiently molten to carry the current between A.C. electrodes 22. Alternatively the pot may be charged with molten electrolyte and its temperature maintained by supplying A.C. to electrodes 22.

In carrying out the invention, the pot is heated, preferably to a temperature above the melting point of magnesium. The heated pot is then charged with electrolyte formulated in accordance with the invention or its separate ingredients. In charging the pot initially as with the separate ingredients it is advantageous to first introduce the lowest melting point ingredient, i.e., LiCl, followed by the other ingredients. If desired, the electrolyte ingredients may be melted in a separate vessel and introduced in the molten condition into the electrolytic cell. After the pot is charged, the electrolyte is brought to a suitable operating temperature above the melting point of magnesium, the electrolyte then being completely molten except for incidental refractory and insoluble impurities normally present in the electrolyte ingredients when not previously purified. The electrolyte has a melting point from between 590° and 595° C. in the preferred concentrations.

A generally desirable operating temperature to produce molten magnesium is in the range of about 660° to 900° C.; a preferable temperature range is about 700° to 800° C. Heretofore it has been believed that operating temperatures in excess of about 720° C. caused disturbances and metal fogging at the cathode due to the perceptible vapor pressure of magnesium. No such difficulties were encountered, even at temperatures of 900° C.

Electrolysis is effected by applying a suitable potential across the anode and cathode of the cell, making the pot the cathode as shown, so as to pass direct current through the electrolyte. The strength of the current is not sharply critical. For example, a current density in the range of about 3 to 30 amperes per square inch of anode cross-sectional area as measured parallel to its lower face may be used. A preferable current density of the anode is 5 to 15 amperes per square inch of cross-section. Corresponding cathode current densities may be somewhat lower than when a cell similar to that shown in Figures 1 and 2 is used, whereas cathode densities may be somewhat higher than at the anode when a cell similar to that shown in Figures 3 and 4 is used. The electrolyzing current may

provide sufficient heat to maintain the electrolyte at operating temperatures, but, if necessary, additional heat may be obtained by gas firing in a cell of the type shown in Figures 1 and 2 or by passing A.C. between electrodes 22 in the type of cell shown in Figures 3 and 4.

As the electrolysis proceeds, the magnesium liberated at the cathode sinks in the electrolyte and accumulates at the bottom of the cell to form the molten body of magnesium 19. Chlorine is liberated at the anode and rises to the surface of the electrolyte where it is withdrawn from the cell, as through outlet pipe 11. The accumulated molten magnesium may be removed by means of a dipper or a siphon inserted through opening 9 or by means of the drain line assembly 13 by opening the valve therein. The utilization of this electrolyte makes it possible to produce an anode gas with a chlorine concentration approaching 100 percent without the increase in power consumption incurred by the use of curtains or other mechanical means of separation of the electrode products. The current efficiency of the cell employing the novel electrolyte is high and the amount of power consumed per pound of magnesium produced lower than for cells employing known electrolytes.

It is understood that the cells shown in Figures 1 to 4 are illustrative of but two forms of cells for use in the practice of the invention and that other forms of cells and modifications of those shown may be used with the novel electrolyte according to the method herein described. The design and construction may vary widely as will appear to those versed in the art. For example, cells may be more complex such as one employing a plurality of anodes and cathodes instead of a single anode and cathode as shown.

The magnesium chloride content of the electrolyte is to be at least 5 weight percent because codeposition of lithium with the magnesium at the cathode becomes objectionably excessive at less than 5 percent by weight of magnesium chloride in the electrolyte. On the other hand, the percentage of magnesium chloride is to be no higher than that which will result in the electrolyte being of lighter density than the molten magnesium. A density differential of at least 0.034 g. per cc. is recommended. If the density of the electrolyte is not at least 0.034 g. per cc. less than that of the molten magnesium at the temperature of electrolysis, the cell operation tends to become somewhat erratic.

The desired density differential is maintained by the inclusion of a sufficient amount of lithium chloride in the electrolyte. Recovery of magnesium at the cell bottom is facilitated, therefore, by maintaining the magnesium chloride content low enough and the lithium chloride content high enough to insure a sufficient density differential between the electrolyte and the produced metal, e.g., at least 0.034 g./cc.

Higher percentages of magnesium chloride in the electrolyte, i.e., percentages resulting in density differentials approaching 0.034 g./cc., are less desirable than percentages of magnesium chloride approaching the 5 percent minimum. Among the reasons for preferring the lower percentages are: better control of the density differential and therefore better settling of the molten magnesium, higher conductivity of the electrolyte, greater tolerance of impurities, smoother operation, and more efficient power utilization.

In Figures 5, 6, and 7 the density of the molten binary electrolyte of $MgCl_2$ and LiCl containing increasing percentages of $MgCl_2$ is given by the curves 23, 24, and 25 for three temperatures 750°, 800° and 900° C., respectively. In each of the fiures there is drawn a horizontal line 26, 27, and 28 at a height corresponding to the density of molten magnesium at the temperature shown for the electrolyte. Below each of the lines 26, 27, and 28, and spaced therefrom an amount corresponding to the density differential of 0.034 gram per cc. are shown the three lines 29, 30, and 31, respectively.

The locus of the point P, the point of intersection of each curve and the line representing 0.034 g./cc. less than the density of molten magnesium at the given temperature, shows the highest percentage of $MgCl_2$ recommended at a given temperature. Shaded area A on each of Figures 5, 6, and 7 represents the allowable increase in density of the binary electrolyte which may be due to the presence of a coalescing agent, such as an alkali or alkaline earth fluoride, and to impurities which may be tolerated as set out hereinbefore.

Referring to Figure 5, it can be seen that at 750° C., the preferred operational range of $MgCl_2$ in the binary electrolyte, is 5 to 35 percent by weight. Referring to Figure 6, it can be seen that the preferred operational range of $MgCl_2$ at 800° C. is 5 to 38 percent by weight. Referring to Figure 7, the preferred operational range of $MgCl_2$ can be seen to be from 5 to 36 percent by weight at 900° C. The presence of other compounds in the electrolyte will lower the permissible upper limit of $MgCl_2$ to some percentage less than that permitted by the pure binary. The allowable density increase represented by shaded area A on each figure shows that the density may increase much more at values approaching 5 percent without affecting smooth operation of the cell than it may when the density values approach the point of intersection P of the curves and the 0.034 g./cc. density differential line. The allowable density increase also shows that greater percentages of impurities may be present when the percentage of $MgCl_2$ is low as compared to when it is high. The preferred range for the magnesium chloride is from 8 to 20 percent by weight of the fused bath.

In electrolysis, as the magnesium chloride in the electrolyte becomes depleted during operation of the cell containing the electrolyte of our invention, it is replenished either at intervals or continuously to maintain the desired proportion of it in the fused bath. Although the feed may contain water, it is preferred that it be substantially anhydrous. Appropriate additions of lithium chloride may occasionally be made to maintain the proper density differential between the bath and the liberated magnesium. Routine tests of the cell bath reveal when there is a need for addition of magnesium chloride, lithium chloride, or a fluoride if the latter is desired. Calcium fluoride, magnesium fluoride, and lithium fluoride are the preferred fluorides, but any fluoride of an alkali or alkaline earth metal may be used, up to 1.0 percent by weight of the fluoride (F) fraction of alkali or alkaline earth fluorides based on the weight of the electrolyte. The preferred range for the fluoride fraction is from 0.25 to 0.75 percent by weight of the electrolyte. For example, if the fluoride added is CaF_2, then, since the fluoride (F) fraction of CaF_2 comprises about 48.7 percent of CaF_2, the recommended addition of CaF_2 is about 0.5 percent to 1.5 percent by weight of the electrolyte. The fluoride facilities coalescence of the liberated magnesium and settling of it into a single body of molten metal.

During the electrolysis a small amount of non-metallic insoluble matter called "sludge" may accumulate at the bottom of the cell below the coalesced magnesium. Such sludge may be removed either by a dipper as in the case of the produced metal or by removal through the valve assembly **13**. Desludging operations are necessary after protracted operation.

The following examples illustrate the practice of the invention but in no sense restrict its scope or application.

Example 1

A cell similar to that illustrated in Figures 1 and 2 of the drawing was heated by means of a gas flame to a temperature between 700° and 750° C. and 600 lb. of dry LiCl salt were placed therein. The LiCl melted. Thereafter 60 lb. of substantially anhydrous $MgCl_2$ were added to form the electrolyte and 7 lb. of CaF_2 were added as a coalescing agent. The resulting percentage composition was about 89 percent LiCl, 10 percent $MgCl_2$ and 1 percent CaF_2. A D.C. potential was applied across anode **12** and cathode **3** thus starting the electrolysis. Concentrated chlorine gas evolved through outlet pipe **11**. Substantially pure Mg formed at cathode **3** and began to settle and collect into body **19**. The run continued for 30 days (720 hours) at an average current flow of 1462 amp. which was a current density of 10.2 amp. per sq. in. of anode cross-section. The cell voltage was constant at 4.5 volts. Mg metal was periodically removed from the bottom of the cell by means of a dipper. During cell operation, 984 pounds of magnesium were produced. This output corresponds to a current efficiency of 91 percent calculated according to the formula:

$$\frac{\text{Wt. of Mg produced}}{\text{Wt. of Mg possible}} \times 100$$

=percent efficiency according to Faraday's law

The conductivity of the electrolyte was about 6 mhos per cc. The kwh. of power consumed per lb. of Mg produced was found to be 4.81 as calculated by the following formula:

$$\text{Kwh./lb. of Mg produced} = \frac{\text{amp.} \times \text{volts} \times \text{hours}}{1000 \times \text{lb. of Mg produced}}$$

The effluent gas passing out through outlet pipe **11** analyzed between 85 and 95 percent chlorine. The operation proceeded smoothly and was easily controlled. Good coalescence of the Mg took place and no difficulty was encountered in removing the Mg metal from the electrolyte. The amount of sludge formed was small. The sludge was easily removed from the cell during operation without interrupting the process and without appreciable loss of Mg or electrolyte. Very low anode graphite consumption was experienced, there being only 0.006 lb. of anode consumed per pound of Mg produced. Such low graphite consumption rate made frequent anode to cathode spacing adjustments unnecessary.

Example 2

In this example, a modified cell similar to the cell shown in Figures 3 and 4 was used. The cell was charged with 500 lb. of anhydrous LiCl. A gas flame was lowered through port **9** and played directly on the salt crystals until a temperature of 750° was obtained. A.C. was then passed between electrodes **19** to maintain the temperature at about 750° C. 50 pounds of anhydrous $MgCl_2$ were added to form the electrolyte and 5 lb. of CaF_2 to serve as a coalescent agent. D.C. was then passed between anode **12** and cathode **21** to effect electrolysis. The amperage was 739 amp. The current density was 7.4 amp. per sq. in. of cross-section of the anode. Chlorine gas evolved through outlet pipe **11** and molten Mg formed at the cathode. The anode to cathode spacing was maintained at 1 inch. This close spacing was made possible by the smooth operation of the cell due to the particularly suitable density of the electrolyte which was about 1.48 g. per cc. The density differential between the electrolyte and the molten Mg was about .087 g. per cc.

The chlorine concentration of the effluent gas was 90 to 100 percent. The voltage was 3.4 volts. 161.5 pounds of magnesium were obtained during 10 days of operation. This is a current cathode efficiency of 90.4 percent and a power efficiency of 71.7 percent calculated according to the following formula:

$$\frac{\text{Decomposition voltage of } MgCl_2}{\text{cell voltage}} \times \text{percent cathode efficiency} = \text{percent power efficiency}$$

A decomposition voltage for $MgCl_2$ of 2.7 volts was used for this calculation.

As in Example 1, the cell operated very smoothly, and the Mg coalesced readily into a molten pool at the bot-

tom of the cell. The molten Mg was easily removed; frequent spacing of anode to cathode was unnecessary and sludge formation was small.

Example 3

To further evaluate coalescing agents for the molten Mg, 7265 g. of LiCl, 1235 g. of $MgCl_2$, and 285 g. of LiF were added to a cell similar to that shown in Figures 1 and 2. The cell and contents were heated to 700° C. by means of a gas flame. A D.C. of 250 amp. was passed between anode 12 and cathode 3. The average cell voltage was 5.0 volts. The run continued for 18 hours. $MgCl_2$ was added during the run at approximately every 0.5 hour to replenish that which had been electrolyzed. The Mg coalesced readily into a molten pool at the bottom of the cell. 2408 g. of Mg were removed without difficulty at the end of the run.

Example 4

In this example no coalescing agent was used. A salt mixture of 13,592 g. of LiCl and 1510 g. of $MgCl_2$ were heated to 765° C. in a cell similar to that shown in Figures 3 and 4 following substantially the same procedure as that set out in Example 2. Electrolysis was effected by passing a D.C. of 200 amp. between anode 12 and cathode 21. The cell voltage was 4.9 volts. Chlorine evolved through outlet 11 and molten Mg formed at cathode 21. Coalescence was somewhat inferior to that of the previous examples. The Mg, substantially free from electrolyte and sludge, was dipped from the cell. The cathode current efficiency was 62.5 percent.

The run was repeated twice with 1 percent CaF_2 present as a coalescent agent. Coalescence was improved but the cathode current efficiencies were but little different, being 65.4 percent and 61.7 percent in the successive repeat runs.

A number of advantages over known electrolytes and methods of their use may be realized by practicing the present invention. They may be readily observed by comparing the results of the above examples of the invention to those obtained in the production of Mg from fused salts containing $MgCl_2$ in current practice. Among the more salient advantages of the present invention are:

(1) Decreased power consumption. In electrolytic cells currently in general use, the power consumed per pound of Mg produced is about 8 kilowatt-hours whereas the power consumed in the present invention is 4.5 to 5 kilowatt-hours per pound of Mg produced. The savings represented by such reduced power consumption are clearly appreciable.

(2) Higher conductivity. The conductivity of electrolytes currently in general use is about 2.25 mhos per cc. whereas the conductivity of the electrolyte of the invention is about 6.0 mhos per cc.

(3) Higher power efficiency. The power efficiency of cells currently in general use is about 30 to 35 percent whereas the power efficiency of the present invention can be higher than 70 percent.

(4) High strength chlorine without penalizing power consumption. The utilization of this electrolyte makes it possible to produce and anode gas containing chlorine at a concentration approaching 100 percent without the increase in power consumption incurred by the use of curtains or other mechanical means of separation of the electrode products.

(5) Simplified cell design. Although the design of the cells shown in the drawing forms no part of this invention, a reference to the drawing shows a relatively simple cell when contrasted to those currently in general use. The reason is that extensive precautions are necessary in cells in current use to prevent recombination of the chlorine and molten Mg because the Mg rises to the surface and is removed therefrom. In the present invention, the Mg, since it sinks to the cell bottom, is separated from the chlorine by the main body of the electrolyte.

(6) Less loss of Mg by burning. Molten Mg when exposed to the atmosphere as in current practices tends to burn accompanied by a loss of metal and presenting a hazard to safety. In accordance with the invention, the Mg sinks to the bottom of the cell and is separated from the atmosphere during electrolysis.

(7) Ease of metal collection. The density relationships between the metal and electrolyte allows the metal to be collected below the electrolyte where it is protected from oxidation. This allows large quantities of metal to be accumulated in the cell over long periods of time without adverse effects. The metal can be produced, stored in the cell and removed from the cell, by the use of suction or a siphon, without coming into contact with air, oxygen, chlorine, or other contaminating substances associated with the operation.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. The method of producing magnesium and high purity chlorine which consists of electrolyzing at a temperature above the melting point of magnesium a molten salt bath consisting of from 5 to 38 percent by weight of magnesium chloride the balance consisting of lithium chloride, said salt bath having a density at least 0.034 gram per cc. less than the density of molten magnesium at a temperature of between 660° and 900° C.

2. The method according to claim 1 wherein the molten salt bath contains from 0.25 to 0.75 percent by weight of the fluoride (F) portion of a fluoride selected from the group consisting of the alkali and alkaline earth metal fluorides.

3. The method according to claim 2 wherein the fluoride is calcium fluoride.

4. The method of claim 2 wherein the fluoride is lithium fluoride.

5. The method of claim 2 wherein the fluoride is magnesium fluoride.

6. An electrolytic bath consisting of from 5 to 38 percent by weight of magnesium chloride, from 0.25 to 0.75 percent by weight of the fluoride (F) portion of a fluoride selected from the group consisting of the alkali and alkaline earth metals, and the balance of lithium chloride.

7. The electrolytic bath of claim 6 wherein the fluoride is calcium fluoride.

8. The electrolytic bath of claim 6 wherein the fluoride is lithium fluoride.

9. The electrolytic bath of claim 6 wherein the fluoride is magnesium fluoride.

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