Jan. 29, 1946. B. G. HUNT ET AL 2,393,686

ELECTROLYTIC PRODUCTION OF MAGNESIUM

Filed Feb. 6, 1942

Fig. 1,

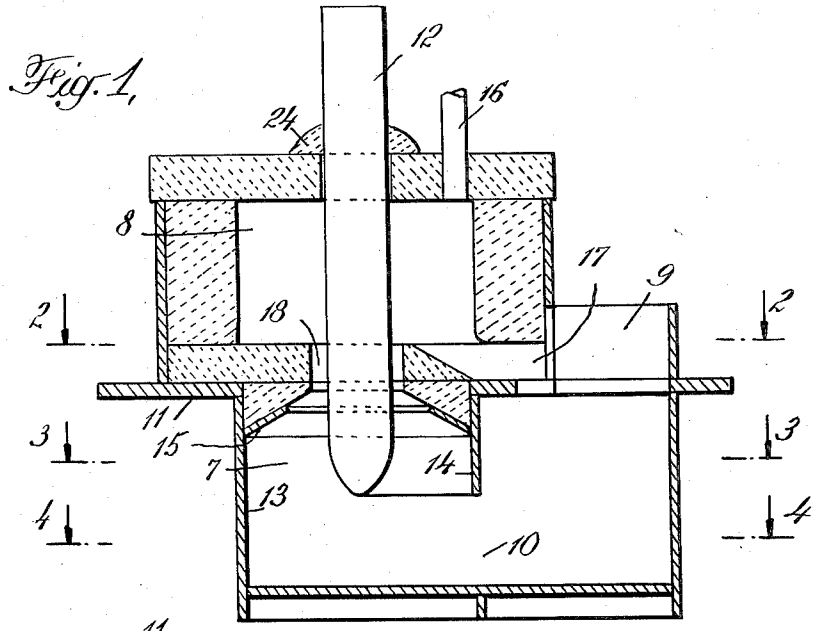


Fig. 2,

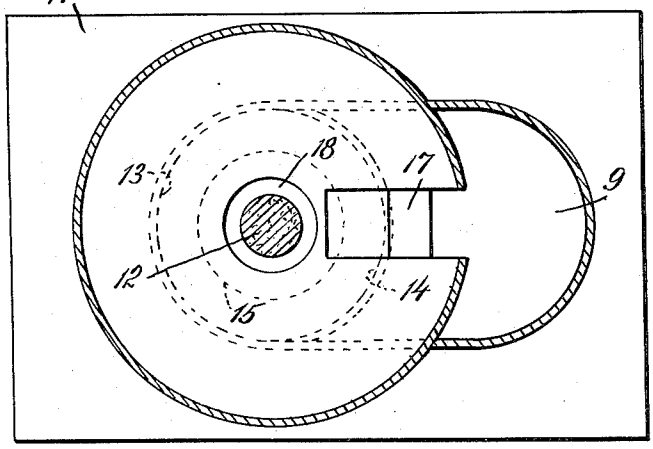


Fig. 3,

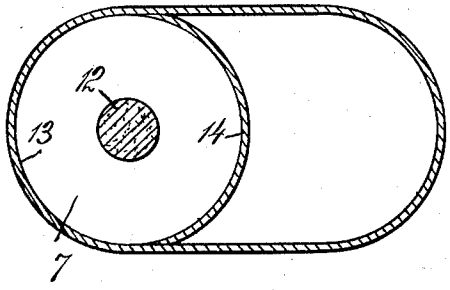
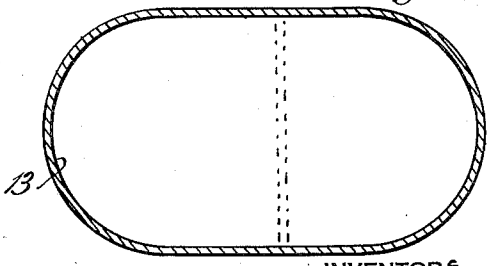


Fig. 4,



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ELECTROLYTIC PRODUCTION OF MAGNESIUM

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Application February 6, 1942, Serial No. 429,730

4 Claims. (Cl. 204—70)

Our invention relates to improvements in the electrolysis of chloride fusions heavier than magnesium and comprising magnesium chloride to produce magnesium metal and chlorine. Our invention includes improvements in the electrolysis of such fused electrolytes and in the construction of cells for carrying out the electrolysis.

Magnesium and chlorine are liberated by the electrolysis of such fused electrolytes comprising magnesium chloride. Hitherto it has been regarded as essential to effect a prompt separation of liberated chlorine and magnesium within the region of electrolysis in order to avoid recombination of these elements. Such recombination would of course destroy the work intended to be done by the electrolysis to the extent that it occurred, with corresponding losses in efficiency in a number of aspects, and must therefore be kept at a minimum. In general, this separation of the liberated chlorine and magnesium has been effected by interposing a refractory baffle or curtain between the cathode and anode in the cell in the upper part of the region of electrolysis to trap the magnesium liberated at the cathode on one side and to permit the chlorine to escape on the other side, between the baffle and the anode at which the chlorine is liberated. Cells embodying this accepted principle of design suffer a number of disadvantages, but prior to our invention no other way of effecting satisfactory recoveries of the magnesium and chlorine liberated by the electrolysis has been devised.

The nature of the problem can be illustrated by summary reference to some of the difficulties involved in the construction and operation of this general type of cell. The interposition of a baffle between the anode and the cathode necessarily increases the distance between them with a consequent increase in the voltage required for operation and corresponding increase in power consumption per unit of metal produced. This increase in the distance between the anode and the cathode also increases the size of the cell required, per unit of capacity, which not only increases the cost of cell construction but also involves a cumulative power loss following from the increased heat losses from a larger cell. The refractory used in the construction of the baffle or curtain must withstand the action of the chloride fusion and the hot liberated chlorine and must maintain its mechanical and electrical properties notwithstanding such exposure. Where the baffle or curtain is suspended, as in conventional construction, extreme strength, extreme resistance to breakage and extreme resistance to erosion are required of the refractory. Further, since the baffle or curtain lies in part between the cathode and the anode, electrolysis tends to take place through the refractory with consequent impregnation of the refractory with metal followed by rapid deterioration of the refractory. Also, to the extent that the refractory becomes conducting in this manner, magnesium tends to be liberated between the baffle and the anode and thus the original purpose of the baffle is defeated. The resulting problem with respect to refractories is one of the more serious problems involved in the construction of cells for this electrolysis.

Contrary to the view generally accepted, the prompt separation of liberated magnesium and chlorine within the region of electrolysis is not essential under all conditions of operation. The liberated chlorine and the liberated metal can be maintained as a composite mixture, both present but separately dispersed in the fused electrolyte, for sufficient time to permit their removal from the region of electrolysis as such a mixture for subsequent separation and recovery of the chlorine and the magnesium without substantial recombination. Perhaps the fused electrolyte, as an external phase surrounding the separately dispersed liquid particles or globules of magnesium and gaseous particles of chlorine, is sufficient chemical insulation, while the dispersion particularly of the chlorine, is maintained, to inhibit recombination. But whatever the explanation may be, the fact that substantial recombination does not occur for some time in such composite mixtures of liberated magnesium and chlorine in the fused electrolyte is more important. In these composite mixtures, the dispersion with respect to chlorine is, usually, fairly uniform and intimate but, as we will explain, the dispersion with respect to magnesium may be quite irregular and the size of the particles or globules may vary widely. We have applied this discovery in our process and apparatus, our present invention, to overcome the disadvantages of the general type of cell previously used by removing the magnesium and chlorine from the region of electrolysis as a composite mixture in the fused electrolyte without attempting any separation of the magnesium and chlorine within the region of electrolysis.

The electrolytic cell of our invention comprises a cell chamber, a superposed chlorine collection chamber communicating with the electrolysis chamber through an aperture in the floor of the chlorine collection chamber, a cathode surface in the electrolysis chamber arranged beneath and around that aperture confining to that aperture the upward flow of electrolyte and of chlorine and magnesium liberated by electrolysis from the electrolysis chamber to the collection chamber, an anode depending through the chlorine collection chamber and the aperture into the electrolysis chamber and co-operating with the cathode surfaces to form an annular electrolysis channel, a magnesium collection chamber laterally disposed with respect to the electrolysis channel and the

chlorine collection chamber, a passage between the lower parts of the electrolysis channel and the magnesium collection chamber, and a port opening from beneath the normal electrolyte level in the chlorine collection chamber into the magnesium collection chamber. In operation, the magnesium and chlorine are removed from the region of electrolysis as a composite mixture in the fused electrolyte and the chlorine and magnesium are separated from that dispersion outside of the region of electrolysis. Circulation of the fused electrolyte from the electrolysis channel successively through the chlorine collection chamber and the magnesium collection chamber and back to the electrolysis channel is maintained by the gas lift action of the chlorine liberated at the anode assisted by the thermosiphonic action resulting from the liberation of heat in the region of electrolysis. No separation of liberated magnesium and chlorine is attempted within the region of electrolysis and consequently no refractory baffle or curtain between the anode and the cathode is required. As the fused electrolyte rises through the aperture, in the free space around the anode, from the electrolysis channel into the chlorine collection chamber, it spreads radially over the floor of the chlorine collection chamber and, with the resulting reduction in velocity, a liquid level being maintained in the chlorine collection chamber, gaseous chlorine separates from the electrolyte. The magnesium present is carried, by the circulating electrolyte, on into the magnesium collection chamber where it separates. The discharge of liberated magnesium from the electrolysis channel may be fairly regular but in some cases, apparently with electrolytes of high purity, the liberated magnesium tends to wet the cathode and thus to accumulate in masses there which are carried off by the circulating electrolyte as relatively large globules at more or less irregular intervals. We thus provide a special process and apparatus for carrying out this electrolysis which has a number of important advantages.

The cell, and the operation of the cell, illustrated in the accompanying drawing, will exemplify our invention. In the drawing, Fig. 1 is an elevation in section of a cell embodying our invention, Fig. 2 is a plan in section on line 2—2 of Fig. 1, Fig. 3 is a plan in section on line 3—3 of Fig. 1 and Fig. 4 is a plan in section on line 4—4 of Fig. 1. The accompanying drawing is substantially to scale of a cell in which the anode illustrated is about 4 inches in diameter.

The cell illustrated in Figs. 1 to 4, inclusive, comprises an electrolysis chamber 7, a chlorine collection chamber 8 and a magnesium collection chamber 9. The lower part of the magnesium collection chamber communicates with the lower part of the electrolysis chamber through the passage 10. The electrolysis chamber and the magnesium collection chamber are with advantage constructed of steel plate as illustrated. The chlorine collection chamber 8, lined with refractories as illustrated, is superposed upon the electrolysis chamber from which it is separated by a steel plate 11, an annular baffle 15 and the refractories forming the floor of the chlorine collection chamber. The anode 12, a conventional graphite rod, extends through the chlorine collection chamber and an aperture 18 in the floor of the chlorine collection chamber 8 into the electrolysis chamber 7. The cathode surface comprises the inner surface of the metal walls of the electrolysis chamber indicated at 13 and 14, and the inner surface of the annular baffle 15 to be described. The aperture 18 is restricted in area as compared with the horizontal area of the electrolysis chamber, as defined by the cathode surface, to accelerate the flow of fused electrolyte through this aperture into the chlorine collection chamber thus to assist in the maintenance of the dispersion of magnesium and chlorine in the composite mixture formed in the electrolysis chamber. The refractories forming the floor of the chlorine collection chamber 8 are not suspended but are supported from below by the plate 11 and the annular baffle 15, advantageously made of steel and welded to the walls of the electrolysis chamber. These refractories overhang the inner edge of the baffle 15, which, as illustrated, extends but a limited distance toward the anode to avoid excessively energetic cathodic action at its inner edge. Chlorine separated in the chamber 8 is recovered through connection 16. The port 17 in the wall of the chlorine collection chamber forms a passageway that connects the lower part of the chlorine collection chamber with the magnesium collection chamber. This passageway opens into the chlorine collection chamber from beneath the normal electrolyte level therein, thereby serving as a liquid outlet while the lower edge of the top of this passageway, being positioned below the normal electrolyte level, forms a gas seal with the electrolyte. The opening in the roof of the chlorine collection chamber 8 through which the anode 12 enters is sealed with fire clay 24 or other appropriate compound.

In operation, the cell illustrated in Figs. 1 to 4 is charged with fused electrolyte to a level submerging the port 17, and current is passed between the anode and the cathode to liberate magnesium and chlorine in the electrolysis chamber 7. Circulation of the electrolyte is maintained as previously described, the electrolyte from the electrolysis chamber containing the liberated magnesium and chlorine as a composite mixture rising through the aperture 18 around the anode into the chlorine collection chamber 8. Anhydrous magnesium chloride is introduced through the chamber 9 as required to maintain the electrolyte level. As the electrolyte leaves the aperture 18, it spreads radially over the floor of the chlorine collection chamber and gaseous chlorine separates from the electrolyte therein as previously described. The level in the magnesium collection chamber 9 being lower than that in the chlorine collection chamber 8, due to the circulation of the electrolyte, the electrolyte and the magnesium it carries are rapidly discharged from the chlorine collection chamber into the magnesium collection chamber through the port 17. There the rate of flow of the circulating electrolyte is reduced and the magnesium, separating as floating molten magnesium, collects as a relatively deep pool in the upper part of the magnesium collection chamber. The fused electrolyte then returns through the passage 10 to the electrolysis chamber.

For example, a cell constructed as illustrated in Fig. 1 was charged with 200 pounds of a chloride fusion consisting of about 60% $MgCl_2$, 39% NaCl and 1% $CaCl_2$. Current was passed between the anode and the cathode under an impressed potential of from 6 to 14 volts depending upon the temperature to be maintained in the fusion, these temperatures ranging from about 670°–780° C. We estimated the rate of flow of the dispersion rising through the aperture above the elec-

trolysis chamber to be of the order of one or more feet per second. Additional anhydrous magnesium chloride was supplied as required to maintain the level of the electrolyte by introduction into the magnesium collection chamber. Recoveries of magnesium metal at rates exceeding ½ to ⅔ pound per hour were secured with the current efficiencies exceeding 70%–80%.

In the cell illustrated, the refractories forming the floor of the chlorine collection chamber, and in contact with the fused electrolyte, are supported from below, materially reducing the mechanical burdens imposed upon the refractories and requiring, in construction of the cell, only simple refractory shapes. In the cell illustrated there is no refractory within the region of electrolysis between the anode and the cathode surface and there is no refractory within this region closer to the anode than is the cathode curface. Electrolytic degradation of refractories is thus avoided.

In referring to chloride fusions, we intend to include generally salt fusions, comprising magnesium chloride heavier than magnesium and liberating magnesium and chlorine when subjected to electrolysis. Such fusions may contain chlorides other than magnesium and may contain salts other than chlorides. The various additions made to control properties of the fusion such as density, viscosity and melting point are generally useful in our process and apparatus as in conventional practice.

While the cell illustrated, and more particularly described, embodies but a single anode, our invention is equally useful in unitary cells embodying a plurality of anodes in either a single electrolysis chamber or a corresponding plurality of electrolysis chambers.

The withdrawal of the liberated magnesium and chlorine from the electrolysis chamber as a composite mixture in fused electrolyte, characteristic of our invention, is applied in our process and apparatus to secure a number of important advantages. The problems presented with respect to refractories, in the construction and operation of such electrolytic cells, are either avoided or substantially ameliorated. Since anode and cathode surfaces can be brought into proximity impossible in cells of conventional construction, the cells can be made smaller per unit of capacity thus to secure several advantages. The smaller size of the cells, coupled with their simplicity, reduces construction costs, less space is required and less copper is required in busbars to deliver the current for electrolysis to the cells. Smaller cells for a given metal producing capacity also reduce heat losses and consequently power consumption. The proximity of the anode and cathode surfaces further reduces the voltage required to effect the electrolysis, by reducing the resistance of the fused electrolyte between the anode and cathode surfaces, which makes possible important power savings. The rapid circulation of electrolyte within the cell promotes the maintenance of uniform temperatures throughout the cell and thus promotes ease and uniformity of operation. The liberated magnesium can be collected in a relatively deep pool, promoting the recovery of metal of high purity. The cell is well adapted to the production and recovery of chlorine in high concentration.

We claim:

1. In the electrolysis of chloride fusions heavier than magnesium in a diaphragmless cell to produce magnesium and chlorine, the improvement which comprises flowing the electrolyte through the electrolysis zone at a rate sufficient to remove essentially all of the magnesium and chlorine from the region of electrolysis as a composite mixture in the fused electrolyte and separating in the order named the chlorine and the magnesium from that mixture outside of the region of electrolysis.

2. In the electrolysis of chloride fusions heavier than magnesium in a diaphragmless cell to produce magnesium and chlorine, the improvement which comprises flowing the electrolyte through the electrolysis zone at a rate sufficient to remove essentially all of the magnesium and chlorine from the region of electrolysis as a composite mixture in the fused electrolyte, successively separating in the order named the chlorine and the magnesium from that mixture outside of the region of electrolysis and returning the fused electrolyte to the region of electrolysis.

3. In the electrolysis of chloride fusions heavier than magnesium in a diaphragmless cell to produce magnesium and chlorine, the improvement which comprises circulating the fused electrolyte upwardly from the region of electrolysis to and through a chlorine collection chamber, thence laterally to and through a magnesium collection chamber and thence back to the region of electrolysis, removing the magnesium and chlorine from the region of electrolysis as a composite mixture in the fused electrolyte, maintaining an electrolyte level in the chlorine collection chamber whereby gaseous chlorine is separated from the electrolyte therein, maintaining a substantially lower electrolyte level in the magnesium collection chamber whereby the electrolyte and magnesium carried by the electrolyte are rapidly and continuously discharged from the chlorine collection chamber to the magnesium collection chamber, reducing the rate of flow of the electrolyte in the magnesium collection chamber whereby floating molten magnesium is separated from the electrolyte therein, and returning the fused electrolyte from the magnesium collection chamber to the region of electrolysis.

4. In a diaphragmless cell for the electrolysis of chloride fusions heavier than magnesium to produce magnesium and chlorine, the combination comprising a generally vertical electrolysis channel defined by confining walls comprising separated anode and cathode surfaces, a superposed chlorine collection chamber, said electrolysis channel communicating at its upper end with the chlorine collection chamber only, whereby all electrolyte, magnesium and chlorine discharged from the upper end of the electrolysis channel will be required to enter the chlorine collection chamber, means forming a metal collecting well laterally disposed with respect to the electrolysis channel and to the chlorine collection chamber, the walls of the chlorine collection chamber being shaped to provide a passageway extending between the chlorine collection chamber and the metal collecting well with the lower edge of the top of said passageway being positioned below the normal electrolyte level forming a gas seal with the electrolyte, and means forming a passage extending between the lower part of the metal collecting well and the lower part of the electrolysis channel.

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