April 26, 1949. R. D. BLUE ET AL 2,468,022

ELECTROLYTIC APPARATUS FOR PRODUCING MAGNESIUM

Filed Dec. 21, 1944 2 Sheets-Sheet 1

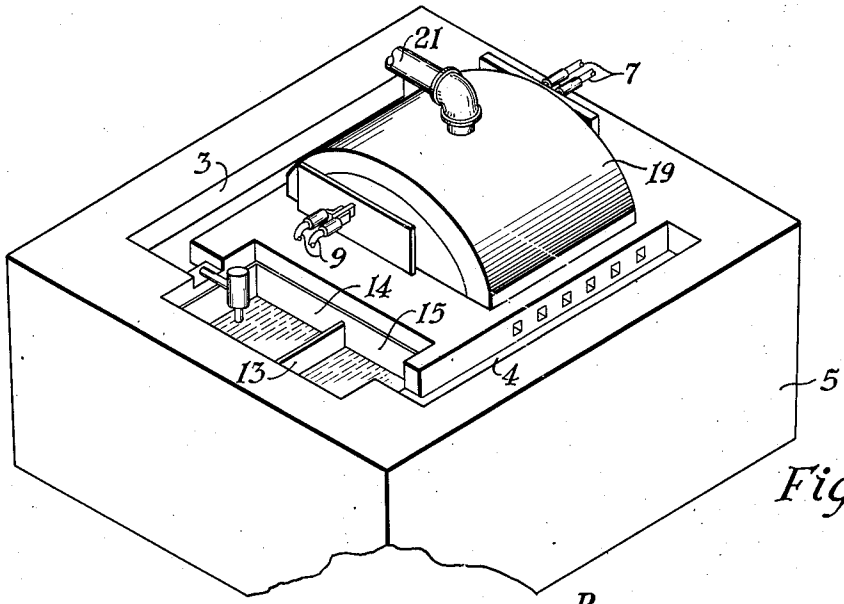


Fig. 1

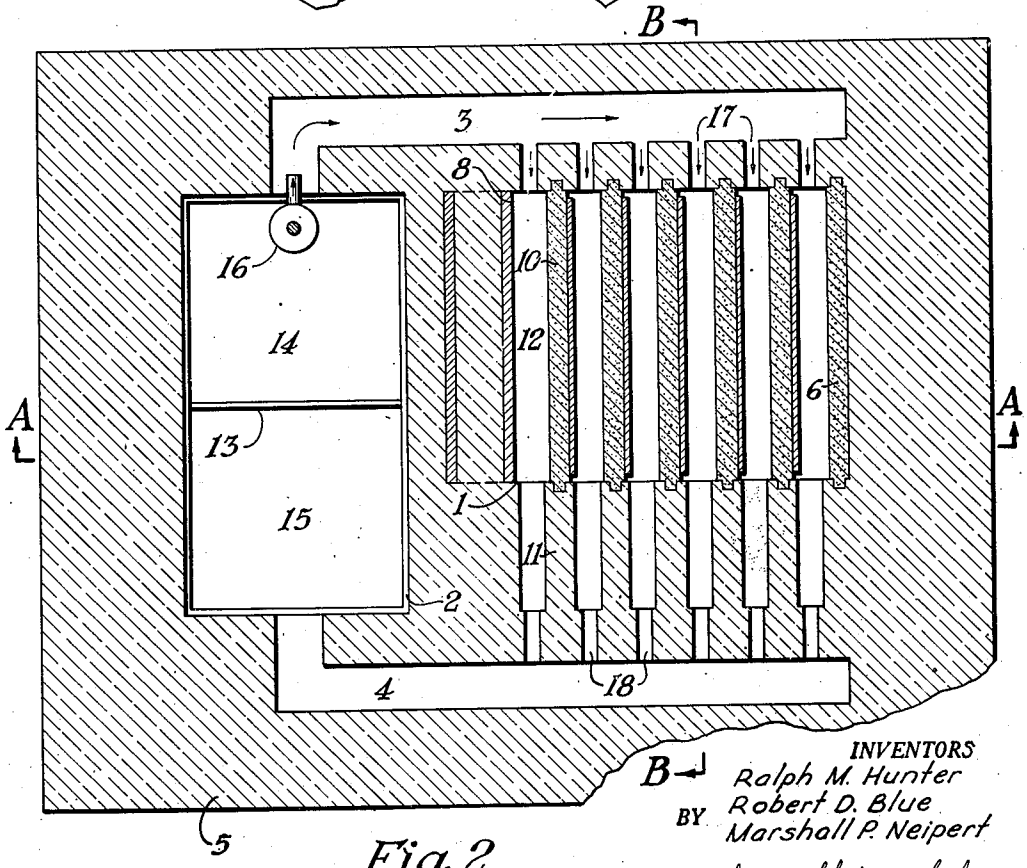


Fig. 2

INVENTORS
Ralph M. Hunter
Robert D. Blue
Marshall P. Neipert

BY Griswold & Burdick
ATTORNEYS

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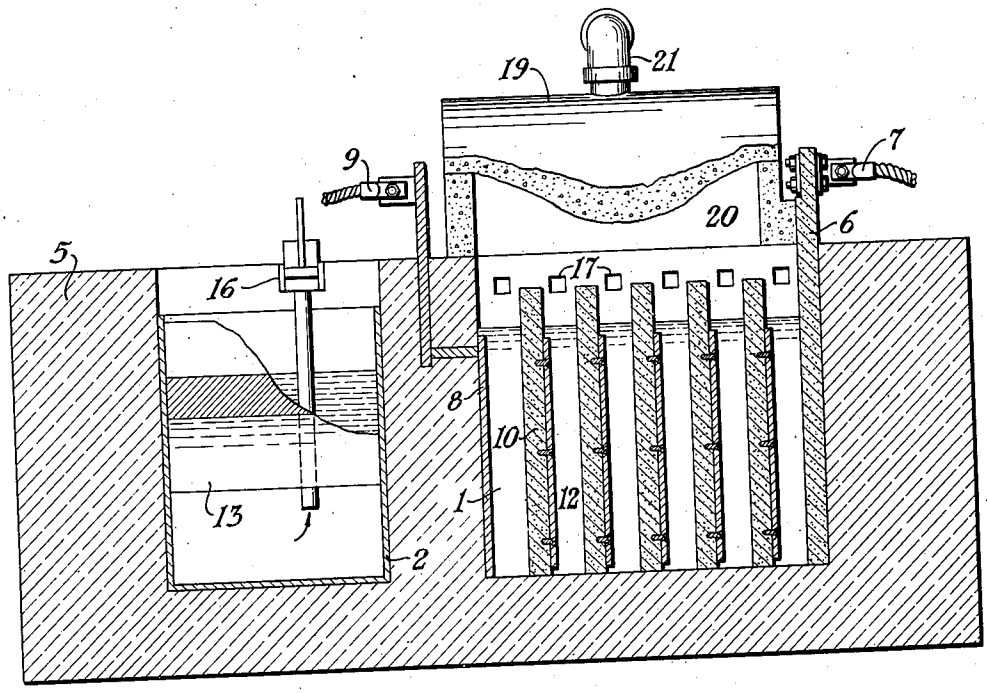


Fig. 3

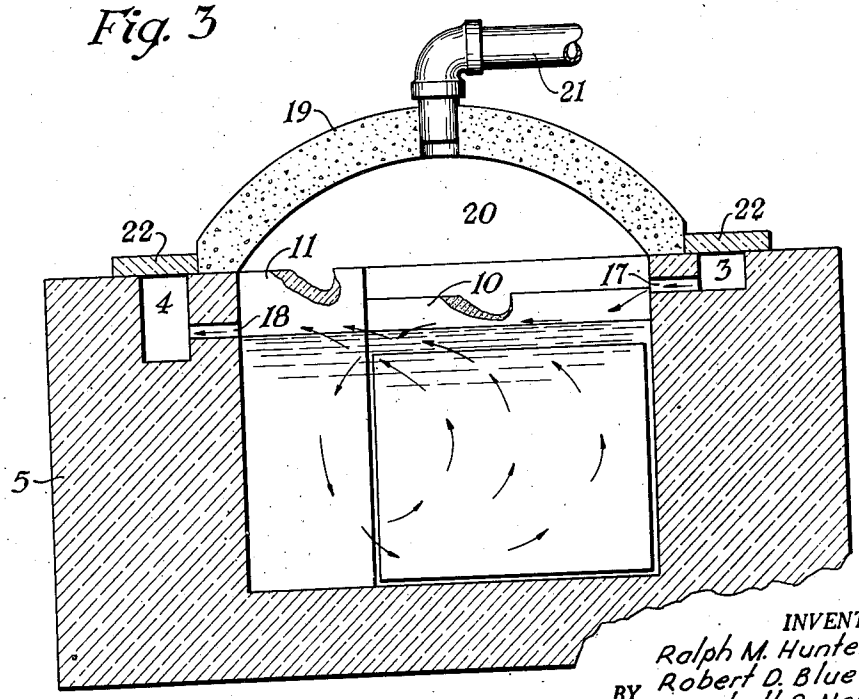


Fig. 4

INVENTORS
Ralph M. Hunter
Robert O. Blue
Marshall P. Neipert

BY Griswold & Burdick
ATTORNEYS

Patented Apr. 26, 1949 2,468,022

UNITED STATES PATENT OFFICE

2,468,022

ELECTROLYTIC APPARATUS FOR PRODUCING MAGNESIUM

Robert D. Blue, Ralph M. Hunter, and Marshall P. Neipert, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Application December 21, 1944, Serial No. 569,152

1 Claim. (Cl. 204—244)

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The present improvements relate to electrolytic cells for the production of magnesium by the electrolysis of a molten body or bath composed of magnesium chloride and chlorides of metals which are electropositive to magnesium. Examples of such other chlorides are those of sodium, potassium and calcium, as well as mixtures thereof.

The usual fused salt baths employed for the electrolysis are heavier than magnesium, hence the metal floats on the surface of the bath as it accumulates during the electrolysis. This circumstance has long caused a problem in satisfactorily separating the magnesium from the chlorine simultaneously formed by the decomposition of magnesium chloride and evolved at the surface of the bath. Various expedients have been shown in the art for separating the products of the electrolysis, which generally depend upon partitioning the space above the surface of the bath in the electrolytic cell to form separate chambers for collecting the magnesium and chlorine. The structure of such cells is further complicated by reason of the general practice of suspending the anodes from above to immerse their lower end in the bath. Such construction has given rise to a practical problem of positioning the anodes closely enough to the cathode to reduce the internal electrical resistance of the cell to a reasonable value and at the same time spacing the anodes and cathodes far enough apart to permit of a satisfactory separation of chlorine from accumulated magnesium at the surface of the bath. Another problem has been to seal the joints where the anodes enter the cell through a cover at the top, so as to prevent leakage of gas into or out of the cell. Leakage of chlorine out of the cell causes a nuisance in the cell room, while if the cell is put under suction to prevent escape of chlorine, air is drawn in and dilutes the chlorine. In cells of large capacity this problem is aggravated by the large number of anodes necessarily employed to carry the current. Each of the anodes must be connected to the source of current, and the multiplicity of current-carrying leads causes still further complication in the cell superstructure, as well as in the operation of the cell.

The invention is intended to accomplish various objects in dealing with the aforesaid problems, so as to overcome or mitigate the disadvantages or limitations of the cell structures known to the art. Among these objects are the following: (1) to obviate the necessity for a multiplicity of depending anodes, each with its separate electrical connection; (2) to insure a tighter and more permanent closure of the cell to prevent leakage of gases; (3) to simplify the internal structure of the cell and reduce the hand labor required for its operation; (4) to enable partitions within the cell, such as are now required for separating the anode and cathode products, to be dispensed with; (5) to provide a close spacing of the anode and cathode without interfering with the separation of products and their removal from the cell; (6) to secure greater accessibility of those parts of the cell in connection with which manual operations may be required during use; (7) to make feasible the construction and operation of units of greater capacity than has heretofore been considered practical in the art; (8) to reduce the power consumption per unit of product. These and other objects and advantages will be fully described in the following specification and annexed drawing.

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In said drawing:

Fig. 1 is an isometric view of an electrolytic cell according to the invention, with some cover parts removed.

Fig. 2 is a horizontal section of the apparatus shown in Fig. 1.

Fig. 3 is a longitudinal section on the line A—A of Fig. 2.

Fig. 4 is a transverse section on the line B—B of Fig. 2.

In the design of our improved electrolytic cell we have utilized the bi-polar principle, which has been adapted to the requirements for working with a fused salt electrolyte of the character in hand. Bi-polar electrolytic cells are known and extensively used in the electrolysis of aqueous solutions, such as in the production of caustic soda and chlorine by electrolysis of sodium chloride solutions, but have not hitherto been successfully applied to the electrolysis of fused salts, particularly of fused salt baths for production of magnesium.

A bi-polar arrangement of electrodes permits of close spacing of the anode and cathode surfaces, provided that suitable means are employed for limiting as far as possible the contact of the anode and cathode products, so as to prevent an excessive amount of recombination thereof. We have found that this result can be achieved to an unexpected degree by maintaining a horizontal flow of the electrolyte past the active electrode surfaces, combined with a regulated vertical circulation of the bath between the electrodes, which continuously removes the magnesium from the bath out of the zone of contact with chlorine.

The importance of these features becomes evident from a consideration of conditions existing in the space between the electrodes while the electrolysis is taking place. The chlorine evolved at the anode naturally rises in a continuous stream of bubbles, creating an upward flow of the molten bath by a gas-lift effect. Magnesium is deposited on the cathode where it forms in small globules which grow in size until torn loose by the forces acting on them. The upflow of the bath carries these detached globules to the top. This upward flow, of course, is balanced by an equal return flow. If the opposing flows occur at random within the same narrow space between the electrodes, a violent churning of the bath is caused, which hinders the rise of metal globules and intermingles the cathode and anode products to an extent that results in considerable loss of metal by recombination. On the other hand, when the return flow is diverted away from the path of the upflow so as to complete a regulated internal circuit in a vertical plane within the bath, the upward movement of the metal globules within the bath is not impeded and loss by recombination is greatly reduced. We produce such a vertical circulation by providing a neutral zone laterally adjoining the active zone of electrolysis, preferably in the direction of horizontal flow of the bath, as hereinafter more fully described.

The horizontal flow of the molten salt bath is produced by maintaining a circulation of the molten salt through the cell to sweep away the globules of metal floating on the surface of the bath. The stream of molten salt flowing from the cell and carrying the metal globules is conducted to an adjacent reservoir, in which the globules coalesce into a pool of molten metal floating on the surface of the molten salt. The molten metal is removed from the pool by skimming or other means, and the molten salt, from which the metal has separated, is recirculated to the cell. The inventory of molten salt is replenished as required by additions of magnesium chloride to maintain a suitable concentration of the latter in the bath.

For a more particular understanding of the bi-polar cell structure of the invention and the mode of operating the same, reference is made to the drawing, illustrating a preferred embodiment of the invention. Two rectangular chambers 1 and 2 (Fig. 3), separated by a wall, are interconnected at the top on both sides by conduits or troughs 3 and 4. In chamber 1 the electrolysis is carried out and in chamber 2 the separation of metal from the bath is effected, while the circulation of the bath between the chambers takes place through the connecting troughs 3 and 4. Chambers 1 and 2 may be built into a common setting 5 of brick, as shown. The inner walls and bottom of chamber ' are lined with a dense refractory brick resistant to the molten salt bath, while chamber 2 may be lined with steel plates welded at the joints. A suitable number of outer courses of brick is provided for strength and heat insulation.

At one end of chamber 1 is terminal anode 6, which is a built-up slab of graphitized carbon set in the end wall and extending upwardly above the edge to provide a clear surface for attachment of the electrical lead-in cable 7. The terminal cathode 8 of iron or steel plate is set in the opposite end wall of the chamber, and is of the same width as anode 6, but its height is such that its upper edge will be below the bath level of the cell. A connecting lead extends above

the setting to a terminal for attachment of cable 9.

Bi-polar electrodes 10 are set in alignment transversely of the chamber at spaced intervals between the terminal electrodes 6 and 8. Electrodes 10 consist of slabs of graphitized carbon having secured to the face thereof that functions as cathode an iron plate or, alternatively, an electrodeposited iron coating. An iron surface is better adapted than graphite for the electrodeposition of magnesium for the reason, well known in the art, that molten magnesium wets and adheres to an iron surface, so that during the electrolysis the magnesium forms in droplets on the face of the electrode, which grow to appreciable size before they become detached. The graphite slabs of electrodes 10 may protrude somewhat above the bath level, as shown, but the iron facings are below the surface of the bath so as not to be exposed to chlorine in the space above.

The electrodes do not occupy the full width of chamber 1. They abut on one side-wall but stop short of the opposite side-wall, and are joined to the opposite wall by panels 11 of refractory and electrically non-conducting material. Electrodes 10 and contiguous panels 11 define a plurality of parallel channels 12 running crosswise of chamber 1. The portion of these channels lying between the opposing electrode surfaces is the active zone, while that between the non-conducting panels constitutes an inactive or neutral zone, which is provided for vertical circulation of the bath within each channel, for the purpose already explained.

A partition 13 in chamber 2 divides the latter into two compartments 14 and 15 sealed off at the liquid level, leaving the lower portion of compartments 14 and 15 in open communication with each other. In compartment 14 is pump 16 adapted to lift the liquid in chamber 2 into trough or conduit 3 at a level above that of the bath. Trough 3 communicates through ports 17 with channels 12 in chamber 1, which in turn communicate through ports 18 with trough or conduit 4 leading to compartment 15, and being of sufficient depth to extend below the bath level in the chambers.

The electrolysis chamber 1 is provided with a tightly sealed arched cover 19 which defines and encloses a gas space 20. In the cover is outlet pipe 21 for removal of chlorine gas. Removable covers 22 close over the top of troughs 3 and 4, and a similar cover (not shown) closes chamber 2.

For operating the electrolytic apparatus the empty chambers, with structural parts in place excepting covers which may be removed for access, are first heated by gas torches or other means until the walls are raised to a sufficiently high temperature for admission of the charge of molten salt. The covers are then put in place and both chambers are filled to the desired level by pumping in a molten salt mixture of the composition required for the electrolyte. A typical composition contains approximately the following percentages by weight of the respective salts:

$MgCl_2$	22.0
$CaCl_2$	23.0
CaF_2	1.5
NaCl	53.5

This salt mixture has an initial freezing point of about 610° C. Simultaneously with the introduction of the molten salt the electric current is switched on, permitting the electrolysis to begin

immediately. The temperature of the bath is raised above the melting point of magnesium and thereafter maintained by the heat generated by passage of current through the bath. Circulation of the bath between the chambers is set up by pumping the molten salt from chamber 2 into trough 3, whence it flows into chamber 1 through ports 17 and overflows from the latter chamber through ports 18 into trough 4 through which it is returned to chamber 2. By continuously circulating the bath in this way and feeding magnesium chloride into compartment 14 to make up for that which is decomposed, the bath is maintained at approximately a constant composition and the level of the bath in both chambers is also held approximately constant.

Anhydrous, or a highly dehydrated, magesium chloride may be used for feeding the cell to replace material decomposed by the electrolysis. A usual form of cell feed employed in other types of magnesium cells and suitable for the present purpose consists in a granular partially dehydrated magnesium chloride prepared by an air-drying process, which contains the equivalent of from one to two mols of water of crystallization. Anhydrous magnesium chloride, either in granular or molten form, is a somewhat more advantageous, but also a more costly, type of cell feed. If desired, the operation of the present cell can be combined with the dehydration of the magnesium chloride by continuously withdrawing a portion of the cell bath from chamber 2 to a dehydrating apparatus in which partially dehydrated magnesium chloride is added to the molten salt, thereby being substantially dehydrated and fortifying the $MgCl_2$ content of the molten mixture. Such fortified molten salt is returned to the cell at a rate to maintain the liquid level therein. The latter procedure has an advantage in that it permits the final dehydration of the magnesium chloride feed to be carried out in conjunction with the cell operation but in a separate apparatus where a lower salt temperature can be maintained to reduce the amount of decomposition of the salt during the dehydration.

In the electrolysis chamber 1 the molten electrolyte flows in a continuous stream in the channels 12 between the electrodes. Each channel functions as an individual cell, one wall of which is composed of graphite and constitutes the anode, while the other wall with its iron surface is the cathode. As already shown, the electrically active walls of each channel do not extend for the entire width of the chamber but are filled out by a section or panel 11 of non-conducting material, which is advantageously, but not necessarily, at the end adjacent to the overflow outlet. Such non-conducting portion of the walls may constitute about one-fourth to one-third of the total width of the chamber. In the arrangement shown by the drawing the electrolysis takes place in each channel in the forward portion relative to the direction of flow of the bath. At the anode surface chlorine is evolved in a continuous stream of bubbles rapidly rising to the surface of the bath, where the gas escapes into the space 20 above and is removed through the gas exit pipe 21. This rising stream of gas bubbles induces an upward current of the bath within the channel in a direction normal to the overall direction of circulation of the cell bath, which current merges into the horizontal flow of the circulating bath and completes an internal circuit by a counterbalancing downward flow in

the neutral zone between the electrically inactive walls in the rearward portion of the channel, as shown by the arrows in Fig. 4. The magnesium globules, detached from the cathode, are swept upward by the rising current to the top, where they float on the bath and are carried away by the circulating stream through the outlet ports 18.

The circulating stream of electrolyte leaving the electrolysis chamber and carrying along the droplets or globules of magnesium flows through trough 4 to compartment 15 of chamber 2, where the magnesium globules collect and coalesce to form a pool of molten metal floating on the surface of the molten salt. Such accumulation of metal is removed from time to time by any convenient means, as by dipping, siphoning or pumping. The partition 13 keeps the metal in compartment 15 separate from compartment 14 where fresh salt is added to replenish the partly spent bath. Another function of chamber 2 is to serve as a settling basin for non-metallic solid substances, such as magnesium oxide, which may be suspended in the bath. Such oxide impurities are mostly derived from the dehydrated magnesium chloride fed to the cell, but may in part be formed by decomposition of magnesium chloride within the cell. It is an advantage of the mode of operation of the present apparatus that the continuous flow of electrolyte past the cathode scours the surface sufficiently to prevent for the most part the adhesion of such solid non-metallic impurities, which foul the cathode and require scraping off from time to time. The solid impurities settle to the bottom of chamber 2 as a sludge which may be removed from time to time by dipping or otherwise.

The design of the present apparatus permits the bi-polar electrodes to be spaced closely for operation at a low voltage drop between successive pairs of electrodes, which is on the order of about 5 volts. The bi-polar arrangement of electrodes has the great advantage of eliminating lead-in connections for each pair of electrodes and substituting a single terminal connection at each end of a series of bi-polar units. This results in a saving of resistance losses, which may amount to as much as 0.9 to 1.3 volts for each bi-polar unit when operated at a current sufficient to maintain the working temperature of the cell. In a large commercial installation the resultant power saving represents a significant operating economy. A suitable current density is about 2.8 to 3 amperes per square inch of electrode area. In operation a current efficiency of about 75 per cent or more is obtainable, with an energy consumption of about 7 kilowatt hours per pound of magnesium produced, calculated upon the voltage measured between the terminal electrodes.

By submerging the electrodes mostly below the surface of the bath, where they are protected from contact with chlorine or small amounts of air that may be drawn in through the few crevices of the top structure, their life is greatly increased as compared with past practice. The electrodes, of course, are fixed in place and cannot be replaced while the cell is in service. However, from our experience we are able to predict an electrode life of many months of continuous operation before there will be necessity to shut down and dismantle a cell unit for replacement of electrodes. This represents a substantial saving as compared with the operation of the cell types heretofore used commercially.

A particular advantage of the type of cell here-

in described is that it enables a single operating unit to be designed for larger capacity of output than has heretofore been practical, simply by installing a sufficient number of bi-polar electrodes. Two or more electrolysis chambers, with their series of bi-polar electrodes, may be arranged in combination with a single chamber for collecting the metal and feeding fresh salt, thereby making possible further economies in cost of operation.

In addition to the foregoing advantages, all of the working parts of the cell are easily accessible. The maintenance of the cell and the removal of metal product are not attended by any substantial exposure of the operator to extreme heat or to noxious fumes.

We claim:

In apparatus for the production of magnesium by electrolysis of a fused salt bath containing magnesium chloride, the combination of two adjacent heat-insulated chambers for containing the molten bath, one of which is an electrolysis chamber 1 and the other a metal-collecting and salt-feeding chamber 2, a terminal anode and a terminal cathode disposed transversely in said chamber 1 at opposite ends thereof, a series of vertical bi-polar electrodes disposed in alignment between said terminal electrodes transversely of the chamber and parallel to each other in spaced relation, said bi-polar electrodes extending from one side-wall of the chamber to a point short of the opposite side-wall thereof and being connected to said opposite side-wall by means of a panel composed of non-conducting material, forming channels between adjacent electrodes and co-acting panels for flow of the molten bath, a duct leading from chamber 2 to chamber 1 and communicating with the latter through ports opening into the channels between the electrodes, pump means for forwarding a

stream of the molten bath through the duct from chamber 2 to chamber 1, a return duct leading from chamber 1 to chamber 2 disposed at the opposite side of said chambers from said first duct, chamber 1 communicating with said return duct through ports in the channels between the electrodes, said chambers being connected through said ducts in a circuit through which the molten bath is circulated, means in said chamber 2 for accumulating a pool of molten magnesium floating on the molten bath therein, a cover over said chamber 1 and a gas outlet in said cover.

ROBERT D. BLUE.
RALPH M. HUNTER.
MARSHALL P. NEIPERT.

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