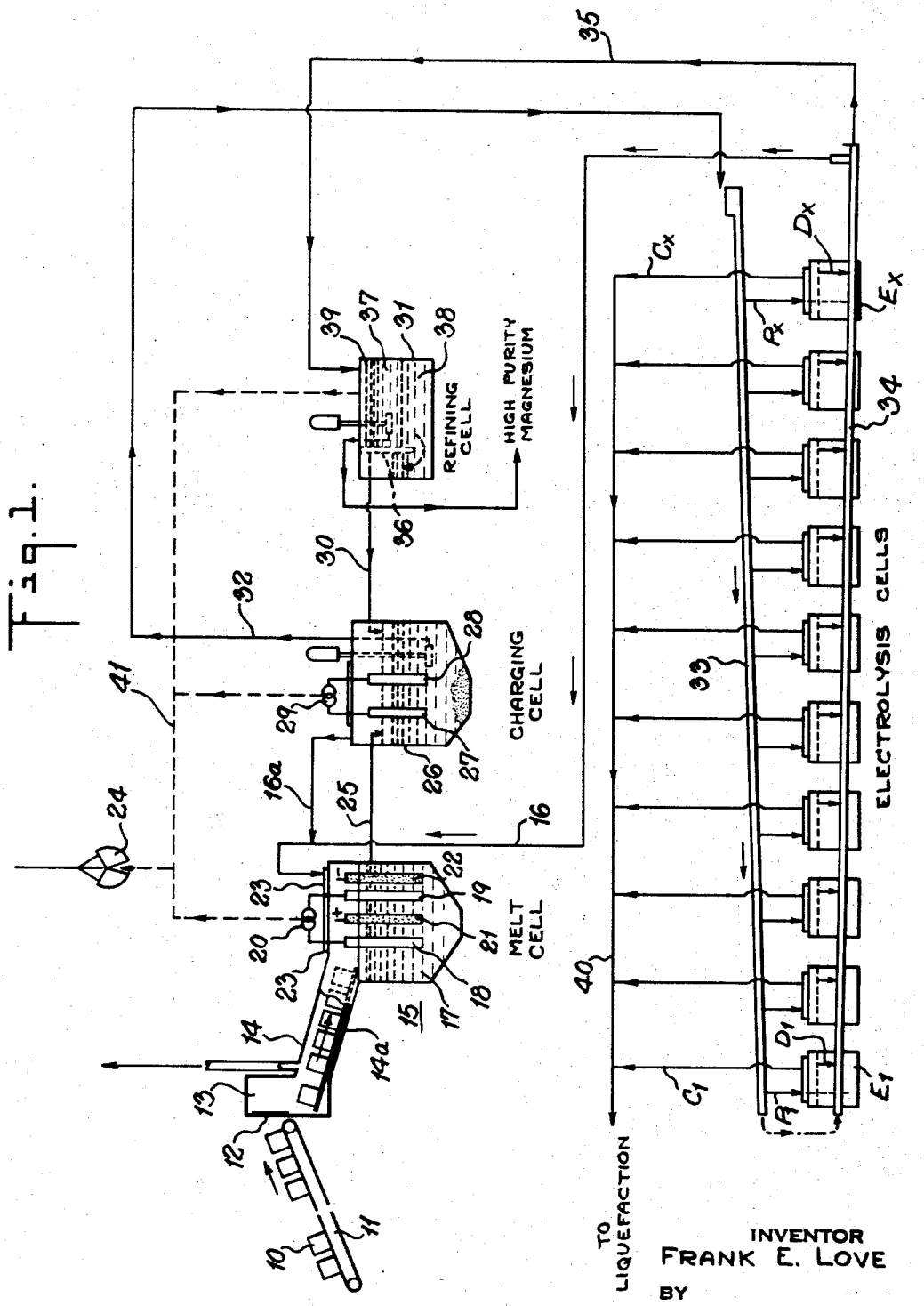
Dec. 24, 1968 F. E. LOVE 3,418,223

CONTINUOUS PROCESS FOR PRODUCING MAGNESIUM METAL FROM MAGNESIUM CHLORIDE INCLUDING FUSED BATH ELECTROLYSIS

Filed June 8, 1966 4 Sheets-Sheet 1

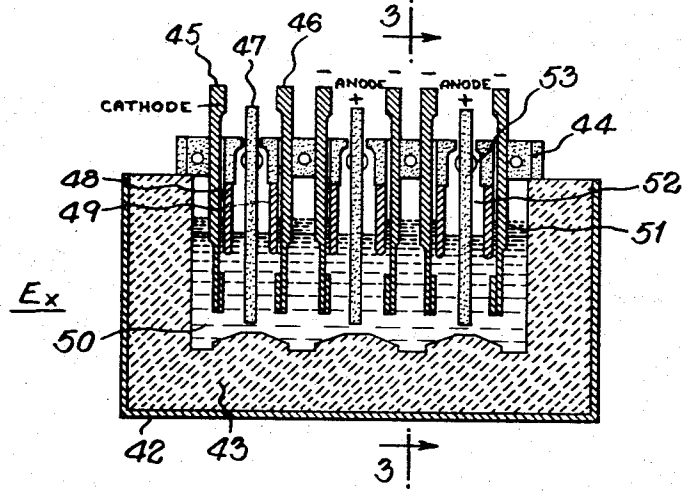
Fig. 1.



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Fig. 2.



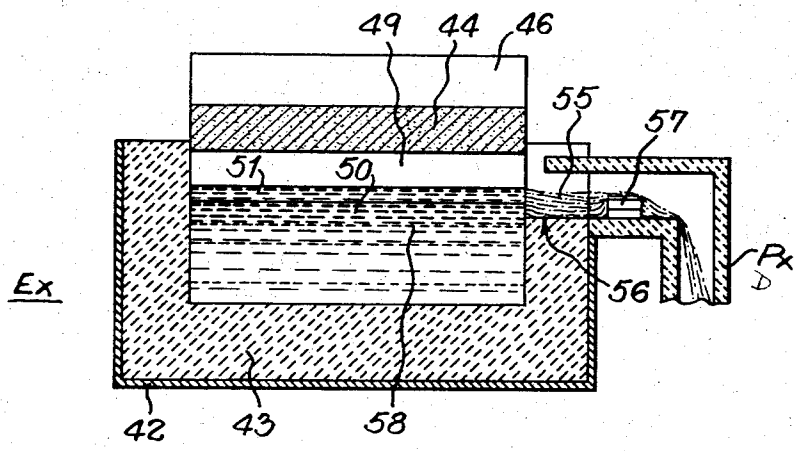


Fig. 3.

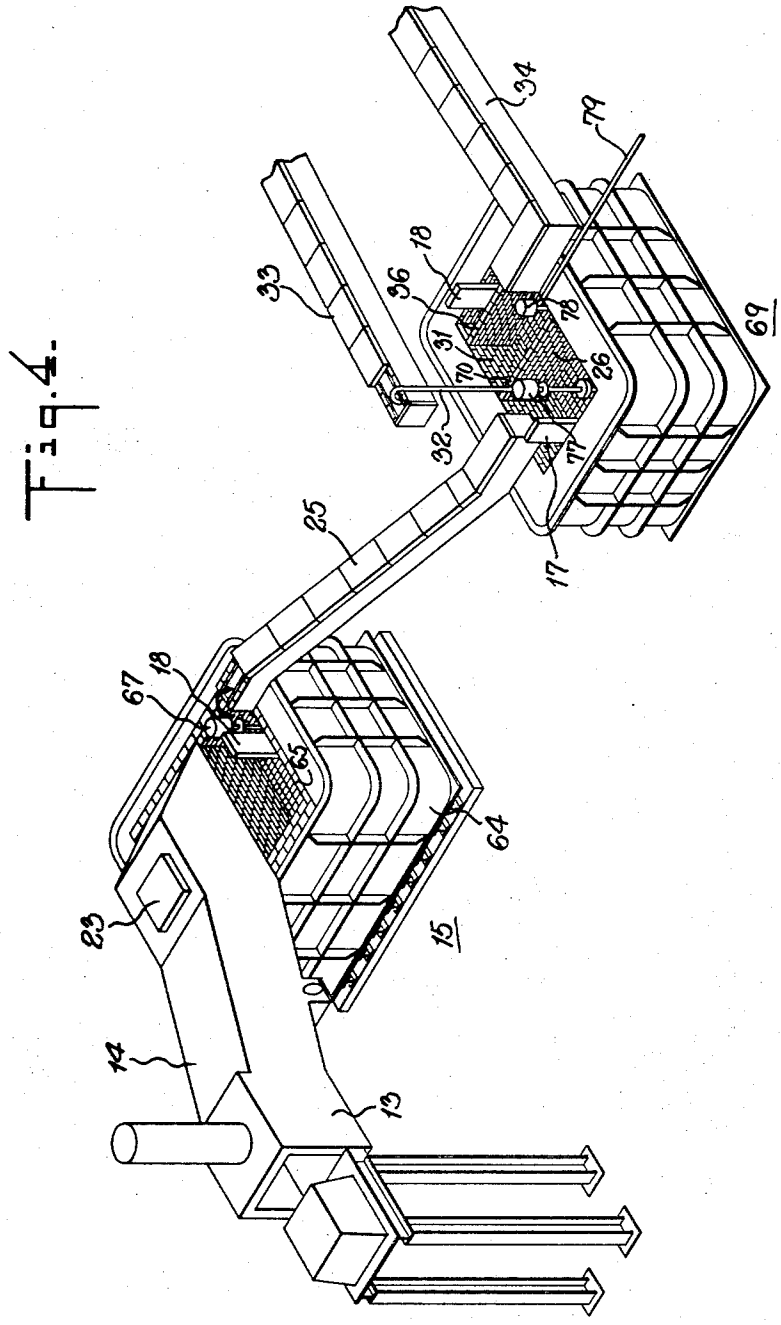
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Fig. 4.



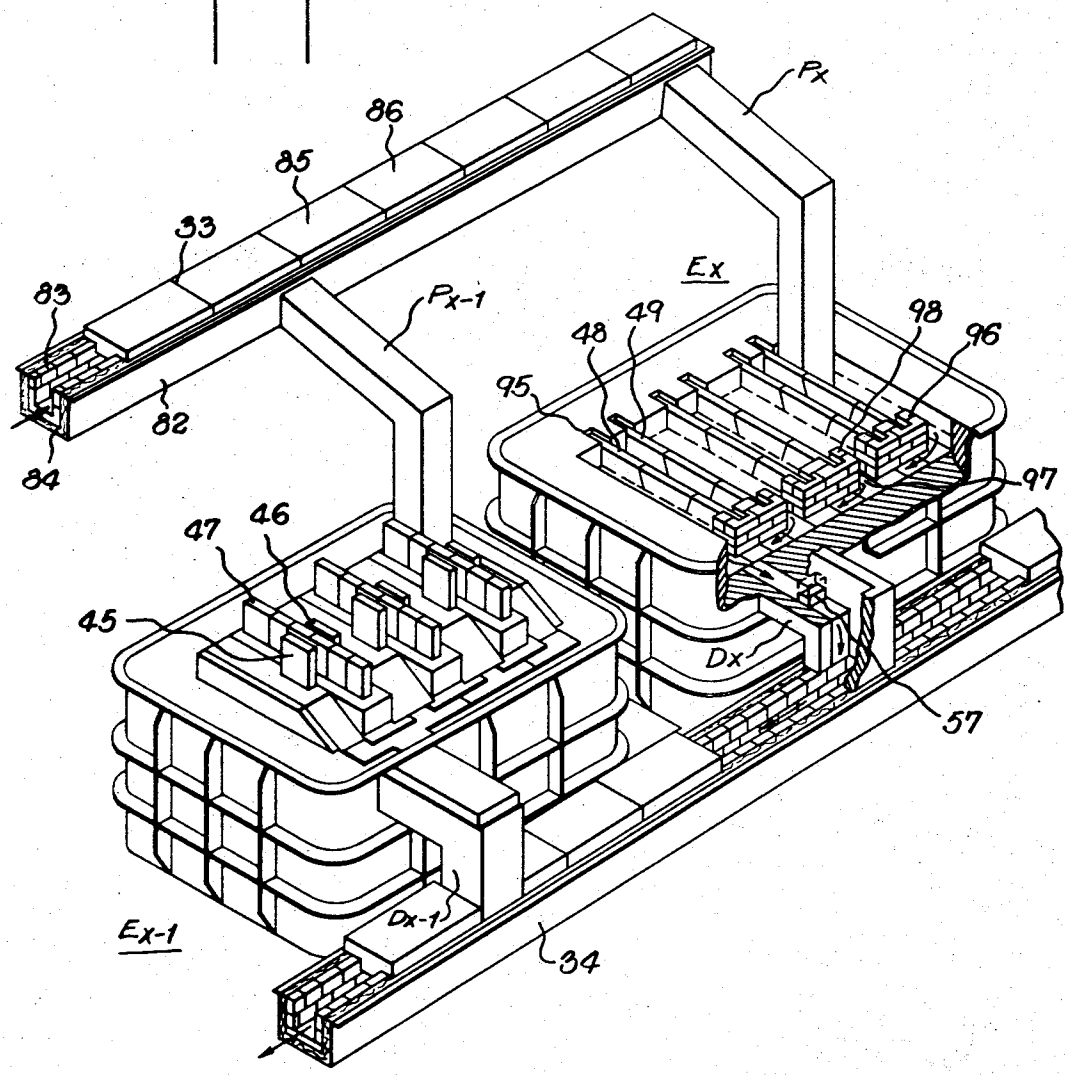
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Fig. 5.



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CONTINUOUS PROCESS FOR PRODUCING MAGNESIUM METAL FROM MAGNESIUM CHLORIDE INCLUDING FUSED BATH ELECTROLYSIS

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7 Claims. (Cl. 204—70)

This invention pertains to a continuous process for large-scale, quantity-production of high purity magnesium metal and chlorine by electrolysis of substantially anhydrous magnesium chloride.

The production of magnesium metal by electrolysis of magnesium chloride as presently practiced commercially, is generally carried out as a batch-type operation in a series of electrolytic cells, into each of which a mixture of metal chloride salts, such as the chloride salts of sodium, potassium, calcium and magnesium, in appropriate proportions, is initially charged, usually in a molten state, and subjected to electrolysis by passage of direct current between spaced anode and cathode electrodes dipping into the bath. The resulting electrolysis of the bath breaks dwon the magnesium chloride into magnesium metal and chlorine gas, which pass to the cathode and anode electrodes, respectively, for separate removal and recovery. The chlorine gas is continuously drawn off through ducts penetrating the cell covers, while the molten magnesium metal is manually taken off at intervals. Usually the salt bath employed is denser than the molten magnesium which accordingly rises to the bath surface and floats thereon for periodic removal as by manual ladling.

Accordingly production as thus commercially practiced involves operating a large number of individual cells which function independently of one another, each of which has different operating characteristics from the others and which must therefore be independently tended by workmen who must periodically take off the accumulated magnesium metal and sludge from each cell. Also the melts must be individually analyzed and refurbished with magnesium chloride, and also occasionally with other of the salts comprising the bath make-up, to maintain the relative proportions of each within required operating limits. In addition, adjustments of the cell electrodes must be made to control the cell operating temperature. Operation of a large bank of such cells, therefore, involves high labor and maintenance, and requires rigid scheduling of charging and of metal and sludge removal, generally referred to as metalling and smutting. In addition the work on the cells thus required reduces the efficiency of operation and the quality of both the magnesium and chlorine products. Also where high humidity exists in the plant, the periodic opening of the cells for charging, metalling and smutting, decreases the cell efficiency and increases the problems of handling the magnesium chloride in both the solid and molten states.

In accordance with the present invention these objectionable features of present commercial practices are eliminated, basically by a continuous process employing enclosed equipment wherein a large number of cells are operated as a unit in a continuous and automatic manner.

In the accompanying drawings:

FIG. 1 is a flow sheet illustrative of the process of the invention with the essential equipment components shown more or less diagrammatically; while

FIG. 2 is an enlarged longitudinal sectional elevation, and FIG. 3 is a transverse section at 3—3 of FIG. 2, of one of the electrolysis cells of the FIG. 1 showing, and

illustrating the structural details and performance thereof under operating conditions.

FIGS. 4 and 5 are perspecitve views with parts removed to show the interior constructions of an apparatus for practicing the invention on a commercial scale, FIG. 5 being a continuaiton of the FIG. 4 apparatus.

Referring to FIG. 1, solid blocks **10** substantially anhydrous magnesium chloride, such as cast or pressed blocks thereof, are fed upwardly over a conveyor **11**, and introduced thence through a double-door assembly **12**, into an enclosed preheating chamber **13**, and delivered thence onto a downwardly-inclined chute **14***a*, along which the blocks **10** slide into a melt cell **15**. An extension **14** of the preheating chamber enclosure houses the chute **14***a* and the opening into the melt cell **15** as shown. Into this housing is also fed HCl-containing hot gases over pipelines **16**, **16***a*, collected from the electrolysis cell cathode compartments, launders, charging and refining cells, as hereinafter explained. These gases remove some of the surface moisture from the magnesium chloride and tend to reduce decomposition thereof.

The magnesium chloried blocks are melted in the melt cell **15**, to form a molten bath **17** thereof, by electrical resistance heating provided by spaced electrodes, as at **18**, **19**, extending into the bath and energized from an alternating current suorce **20** for heating the salt without decomposition. In addition, spaced carbon electrodes, **21**, **22**, extend into the bath and are energized from a low voltage, direct current source of up to two volts or so for the purpose of decomposing oxygen-bearing compounds in the salt and converting the decomposed oxide to carbon monoxide gas evolved as such. The housing **14** is provided above the melt cell with an opening, closed by a removable cover **23**, for sludge collection and removal, employing for such purposes a suitable device, such as a clam shell **24**, back hoe, etc.

A feeder launder **25**, extends from a level near the top of the melt cell into a charging cell **26**, whereby the molten $MgCl_2$ overflows from the melt cell into the charging cell. The launder **25** is heated or suitably thermally insulated to prevent solidification of the molten salt in passing from the melt cell into the charging cell. Alternatively, the molten salt in the melt cell may be pumped or tapped intermittently over the launder **25** into the charging cell. The salt in the charging cell is heated by spaced electrodes **27**, **28**, energized from an A.C. source **29**, to maintain the salt in molten condition in the charging cell.

The charging cell **26** receives over a conduit **30** from a refining cell **31**, a circulating flow of cell melt cycled thereto from a series of electrolysis cells as hereinafter explained. This cell melt has been stripped in the refining cell of molten magnesium metal resulting from the electrolysis and also is deficient in magnesium chloride due to the electrolysis. The molten magnesium chloride from the melt cell **15** is added to this circulating cell melt at a controlled rate in the charging cell **26**, and in such proportion as to maintain a specified magnesium chloride content in the melt of the charging cell. Conventional controls on the A.C. heating circuits for the melt and charging cells, control the temperature of the circulating melt and also the feed rate of solid magnesium chloride into the melt cell.

The thus recharged cell melt, at controlled temperature, is pumped over a conduit **32** and into an enclosed and thermally insulated, inclined feeder launder **33** extending along and above a row of electrolysis cells, as at E_1–E_x, inc. Thermally insulated conduits, as at P_1–P_x, inc., extend downwardly from the feeder launder **33** into the cells E_1–E_x, inc., respectively, and to a level below the surface level of the molten salt bath of each, for feeding the molten salt into these cells. Either intermittent or

continuous feeding may be employed. Intermittent feeding has the advantages that a smaller quantity of circulating melt is required and there is elimination of the possibility of electrical shorting between the cells. Also the molten magnesium will be carried out of the cells more cleanly than otherwise, and by overflow therefrom as hereinafter described.

The cell melt is fed into the cells E_1–E_x, inc., under the surface of the molten bath therein via the conduits P_1–P_x, inc., and the displaced melt overflows out of the cathode compartments thereof together with the molten magnesium metal produced, into an overflow launder **34** via overflow conduits D_1–D_x, inc., extending from the cells, respectively. The level of molten salt in each cell E_1–E_x, inc., is maintained by a weir disposed in its associated overflow conduit, and, as semi-walls of the electrolysis cell fail, the cell level can be raised by adding bricks to the overflow weir, as explained below.

The overflow launder **34** is of opposite inclination to the feeder launder **33**, and extends along the cells E_1–E_x, inc. The overflow from all electrolysis cells is thus collected in overflow launder **34**, and conveyed thence over a conduit **35** into the refining cell **31**. This cell is divided into two compartments by a deep semi-wall **36**, so that the molten magnesium metal will float, as at **37**, above the cell melt **38**, in the first compartment thereof disposed on the right-hand side of the semi-wall **36**. The cell melt **38** flows under the semi-wall **36** and overflows to the charging cell **26** over the interconnecting conduit **30**. A permanent stiff-flux cover **39** is maintained on the surface of the molten metal **37**, and the refined molten magnesium metal is pumped intermittently to casting or alloying. The refining cell bath is electrically heated in the same manner as cells **15** and **26**, but also can be cooled by a heat-exchanger (not shown) which normally will be operated to cool the molten magnesium metal to optimum casting temperature. The chlorine gas evolved from the electrolysis cells, is conveyed over conduits C_1–C_x, inc., extending from the respective cells to a manifold **40**, which conveys the same to a liquefaction unit, or alternatively to a point for use as gaseous chlorine. Sludge collection and removal from cells **26** and **31** is accomplished in the same manner as for cell **15**, as indicated by the dotted lines **41**.

Referring now to FIGS. 2 and 3, the electrolysis cell E_x shown, and which is representative of the construction and operation of each of the cells E_1–E_x, inc., comprises a steel tank **42**, lined with thermal insulating refractory brick **43**. The top of the cell is made up of a number of precast shapes, as at **44**, which rest on the main cell structure (not shown), and which support a series of spaced pairs of cathodes, as at **45**, **46**, and interposed anodes, as at **47**. Interposed between each anode **47** and its associated pair of cathodes **45**, **46**, are a pair of semi-walls, as at **48**, **49**, for directing the chlorine and molten magnesium metal as freed from the molten salt bath **50**, to the anodes and cathodes, respectively. The molten magnesium rises to the surface of the fused salt bath and floats thereon in the cathode compartments, as at **51**, from whence it is continuously discharged as explained below. The chlorine gas rises into the spaces, as at **52**, between the anodes and the semi-walls which dip into the bath as shown, and is drawn-off, through outlet ports, as at **53**, provided in the sidewalls of the precast shapes in which the anodes are mounted. The outlet ports **53** are connected to the conduit C_x, FIG. 1. The anodes **47** are made of graphite blocks, while the cathodes **45**, **46**, are steel casting, shaped to provide large parallel surfaces on opposite sides, respectively, of the interposed anode.

Referring to FIG. 3, the steel tank **42** and brick lining **43**, are cut off along the tank sidewall, as at **55**, **56**, to permit the molten magnesium metal **51** and a portion of the fused salt **50** to overflow, as at **55**, through the outlet duct D_x and over a brickwork weir **57** mounted therein as shown. It will be observed from FIG. 3, that the top of the weir **57** is disposed above the lower edges of the semi-walls, the latter as indicated at **58**, in order not to interfere with the function of the semi-walls in directing the chlorine gas and molten magnesium metal as formed, to the cell anodes and cathodes, respectively. During extended operation, as the semi-walls fail and break away in part along their lower edges, the level of overflow over the weir **57** may be compensatively raised by the addition of bricks thereto.

The electrolyte salt bath **50** of the cell E_x is preferably of the composition described in my copending application Ser. No. 448,852, filed Apr. 21, 1965, now abandoned, and consisting of about 5–25% magnesium chloride, 5–55% lithium chloride, and the balance chlorides of one or more of calcium, potassium, and sodium, preferably in minimum amounts of about 5% each by weight of the total. A preferred bath is that consisting of about 50% LiCl, 5% NaCl, 10% KCl, 20% $CaCl_2$ and 15% $MgCl_2$. This bath is characterized by a density exceeding that of the molten magnesium, such that the magnesium metal as formed will rise to the surface of the bath and float thereon while the sludge being of greater density than the bath will sink to the bottom of the cell for automatic separation of the two. Also this bath by reason of its high lithium chloride content has much higher electrical conductivity and hence much lower ohmic resistance per unit volume than has heretofore been employed for the electrolytic production of magnesium metal in a bath of the density aforesaid insofar as I am aware.

Reference will now be had to FIGS. 4 and 5, wherein like elements are similarly designated as in FIGS. 1–3, inc. In this embodiment for practicing the invention on a commercial scale, the melt cell **15**, comprises a reinforced outer steel housing **64**, lined with refractory brick as at **65**, the top of the chamber housing being removed to show the interior construction, and one of the resistance heating electrodes for converting the magnesium chloride to the molten state being shown at **18**.

A pump **67**, pumps the molten $MgCl_2$ into the upper end of the enclosed feed launder **25**, extending from the top of the melt cell **15** thence downwardly into a combined charging and refining cell unit **69**, the top of cell unit **69** being also removed to show the interior construction. The cell unit **69** is divided into two compartments by a refractory brick semi-wall **70**, which divides it into the charging cell **26** on the left of the partition, and the refining cell **31** on the right. The refining cell is provided with a semi-wall **36**, as in FIG. 1. Resistance heating electrodes, A.C. energized, are shown at **17**, **18**. A pump **77** pumps the molten magnesium chloride from the charging cell **26**, upwardly over pipeline **32**, and into the upper end of the feed launder **33**, continuation of which is shown at **33** in FIG. 4. The overflow launder from the electrolysis cells is shown at **34** in FIG. 3, as a continuation of the like-numbered component of FIG. 4. As shown in FIG. 3, this overflow launder feeds into the refining cell **31**, on the right-hand side of the semi-wall **36** as in FIG. 1. The molten magnesium metal is pumped from the refining cell, by means of pump **78**, and delivered over a discharge line **79**.

Referring to FIG. 5, the feed and overflow launders **33**, **34**, are of generally similar construction so that only one need be described in detail. Thus the feed launder **33**, comprises an outer sheet metal trough-like casing **82**, and an inner refractory brick lining **83**, between which and the casing is interposed, a layer of thermal insulating material, such as glass wool, as at **84**. The resulting trough-like construction is covered by means of a series of removable thermal insulating blocks, as at **85**, **86**, of shallow T shaped cross-section, to seat into the trough of the basal assembly. From the feed launder **33**, the cell launders as at P_x–**1**, P_x, extend downwardly to the associated cells E_x–**1**, E_x.

Electrolysis cell E_x–**1** is shown with the cover and top assembly in place, while for cell E_x, these components are

removed. Referring to cell E_x–**1**, the cathode electrodes are shown as at **45**, **46**, and the interposed anode electrodes, as at **47**. The cell overflow conduits D_x–**1**, D_x, extend from the cells E_x–**1**, E_x, respectively, to the overflow launder **34** as shown.

Referring to cell E_x, the semi-walls are shown at **48**, **49**, seated at opposite ends in slots of brickwork, as at **95**, **96**. The molten magnesium metal produced in the cell flows outwardly between slots as at **97**, of contiguous brickwork supports, **96**, **98**, and thence over the weir **57**, in conduit D_x, and thence into the overflow launder **34**. The operation of the FIGS. 4 and 5 embodiment is the same as that above described with reference to FIGS. 1–3, inc.

The circulating cell melt system of the invention has the following improved characteristics as compared to prior art practices: All cells operate on the same melt composition. Individual cells operate at constant cell levels. Little if any variation in temperature occurs between cells since the melt is continuously blended. Little if any operating work is done on the cells. Magnesium is removed from the cells as formed, so that the chance of burning or recombination is minimized. Since little if any operating work is done on the cells, the cathode compartments can be sealed. Magnesium is removed from the electrolysis cells, as it is formed, and is conveyed thence to the refining cell in a closed conduit while being washed with cell melt, and is settled in the refining cell under a flux cover with good temperature regulation.

What is claimed is:

1. The method for continuous production of magnesium metal and chlorine gas from magnesium chloride, which comprises: progressively feeding substantially anhydrous magnesium chloride salt into a melt cell and fusing therein to a molten state, discharging said molten salt into a charging cell for admixture with a molten metal chloride salt containing a salt of at least one other metal, feeding the molten salt admixture from said charging cell thence into a feeder manifold and thence distributively into a series of electrolysis cells having overflow outlets for establishing and maintaining molten baths of said salt admixture therein, electrolyzing said magnesium chloride constituent therein into molten magnesium metal and chlorine gas, withdrawing said gas as formed from said cells into a collecting conduit, and separately withdrawing as overflow from said cells and into a collector manifold, said molten metal as formed together with a portion of the molten salt of each said cell, delivering the contents of said collector manifold into a refining cell and separating said molten metal from said fused salt therein, and recycling the magnesium chloride depleted molten salt from said refining cell into said charging cell for admixture with additional molten magnesium chloride salt supplied from said melt cell.

2. The method according to claim **1** wherein the salt in each of said melting, charging and refining cells is heated without decomposition by passage of an alternating current therethrough.

3. The method according to claim **1** wherein oxidic compounds in the salt charged into said melting cell are decomposed and the oxygen content eliminated in gaseous state by passage through said salt of direct current between spaced carbon electrodes contacting said salt.

4. The method according to claim **1** wherein the molten salt admixture fed to said electrolysis cells has a density exceeding that of molten magnesium metal, for floating the released molten magnesium metal thereon.

5. The method according to claim **1** wherein said molten salt admixture is gravity-fed from said feeder manifold into said electrolysis cells and is gravity-fed from said electrolysis cells into said collector manifold.

6. The method according to claim **1** wherein the molten salt admixture fed to said electrolysis cells consists of about 5–25% of magnesium chloride, 5–55% of lithium chloride by weight of the total, the balance being chloride salts of one or more of calcium, potassium and sodium, and wherein said molten salt admixture has a density exceeding that of molten magnesium metal.

7. The method according to claim **1** wherein said molten salt admixture fed to said electrolysis cells consists substantially of about 50% lithium chloride, 5% sodium chloride, 10% potassium chloride, 20% calcium chloride, and 15% magnesium chloride, each by weight of the total.

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U.S. Cl. X.R.

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