23

May 31, 1938. F. HANSGIRG 2,118,973

REFINING OF METALS

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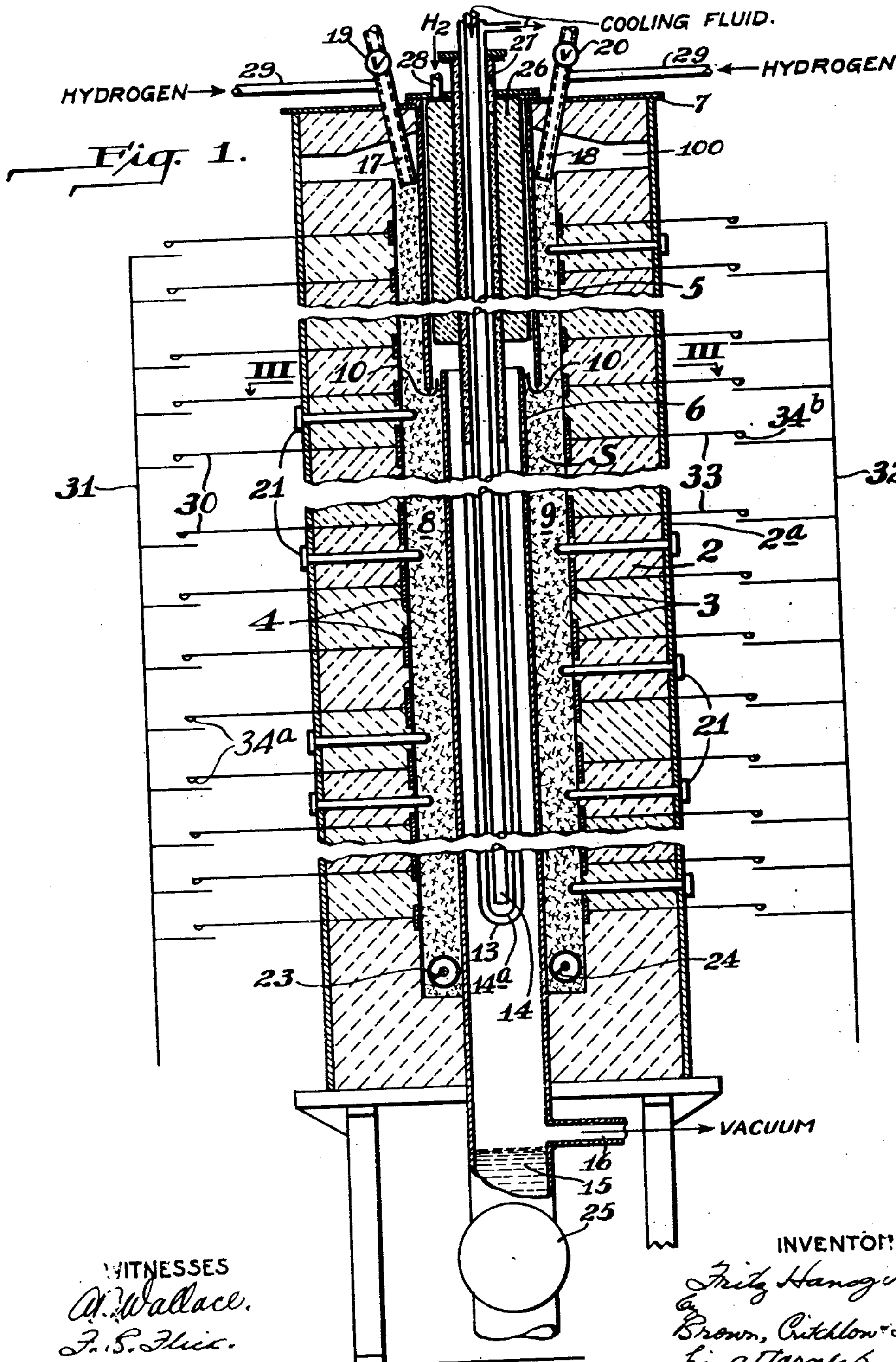
Fig. 1.



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13. ELECTRIC FURNACES.

23

Cross Reference

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REFINING OF METALS

Filed Dec. 21, 1934 2 Sheets-Sheet 2

Fig. 2.

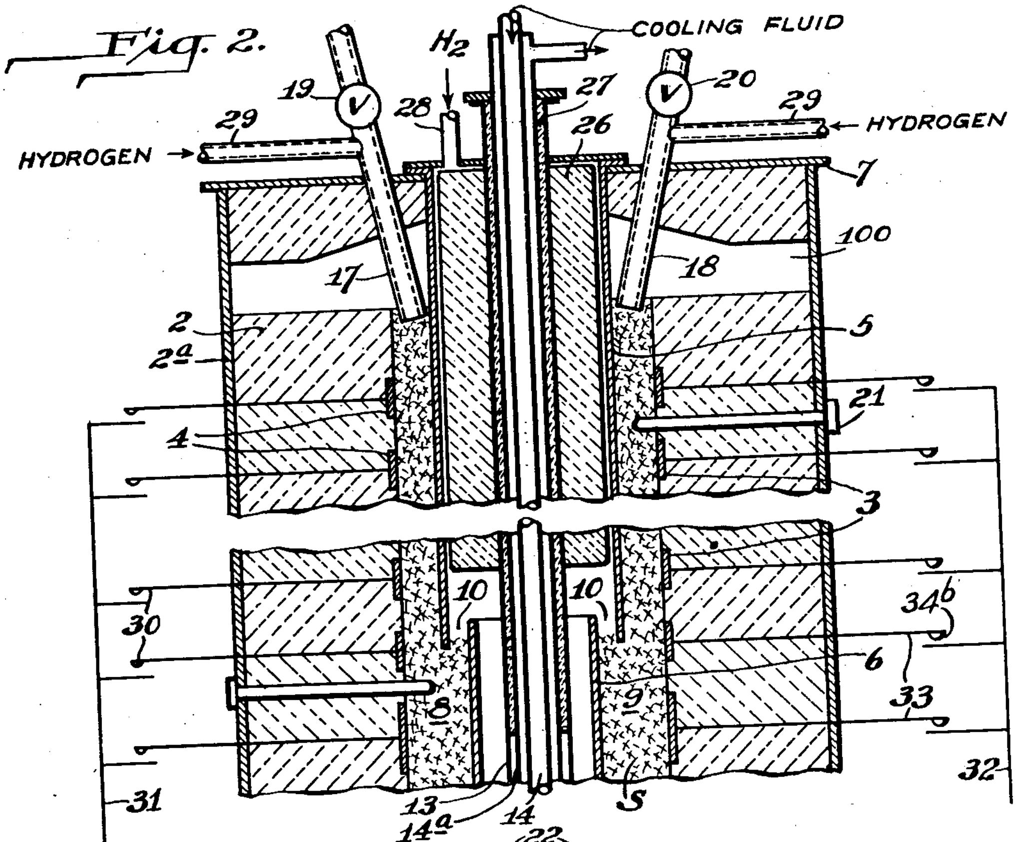
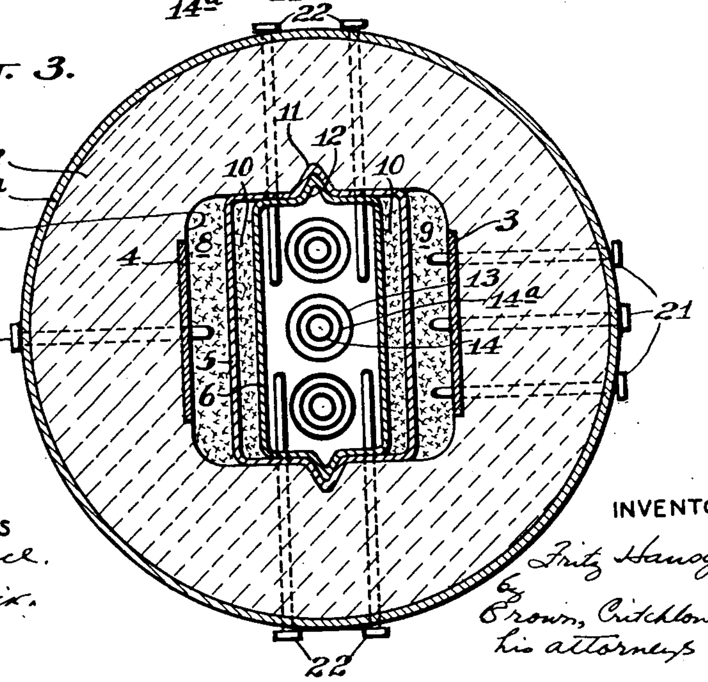


Fig. 3.



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Patented May 31, 1938 2,118,973

UNITED STATES PATENT OFFICE

2,118,973

REFINING OF METALS

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Application December 21, 1934, Serial No. 758,622

3 Claims. (Cl. 13—8)

This invention relates to the distillation or sublimation of impure metals, particularly for refining metals in finely divided form.

The invention is applicable generally to the treatment of metals and materials containing metals susceptible of evaporation, e. g. distillation, especially those produced in finely divided form, such as magnesium and zinc. For purposes of illustration, however, it will be described with particular reference to the treatment of magnesium, to which it is especially suited.

It has been proposed heretofore to refine such metal-containing materials by converting them to granular form and heating the granular material, to effect distillation or sublimation, by passing an electric current therethrough. Such procedures have not become commercially practical because of disadvantages that have inhered in them as previously proposed. The granulation may be accomplished, according to prior suggestions, by mixing the powdered metal-containing material with conductors and semi-conductors of the electric current, which in the case of magnesium might be carbon and magnesium oxide, and adding to the mixture a bonding agent, suitably a carbonizing binder, such as hydrocarbon oils. The mixture is subjected to heat to cause evaporation of hydrocarbon oil and to form a granular solid mass in which the pulverulent materials are bonded by a coked residue which is formed in volatilization of the hydrocarbon oils.

Although by using such granular material as a current conductor it is possible to develop the amount of heat necessary for vaporization of the magnesium to accomplish distillation or sublimation, this has not been commercially realizable previously. One reason is that such materials have the disadvantage that their conductivity changes materially with the temperature, that is to say, that the conductivity decreases with increasing temperature. Also, as the magnesium, or other metal such as zinc, which is contained in the material is distilled away, the conductivity decreases further. This in combination with the types of furnace suggested previously has acted detrimentally.

For instance, if such a material is subjected to heating by current conduction in a shaft furnace of circular cross section, such as that recommended by Nathusius for the reduction of zinc ores, the use of segmental electrodes is unavoidable and this entails variations in current conduction in consequence of the differences in distance between the curved segmental electrodes. This causes the granular material, which moves downwardly in the shaft, to be heated to varying degrees. Through decrease of the resistance the hotter spots are then favored, which causes further stronger heating, so that undesirable overheating occurs in the charge at a few spots. Care must be taken in the evaporation of magnesium if a pure product is to be obtained, and such variations in heating lead to disturbances in the process and through local melting phenomena may even cause complete interference with operation.

According to the recommendations of Nathusius six segmental electrodes are positioned in three horizontal planes in the shaft, the electrodes being connected to the six poles of a noncoupled three-phase current system. Through this it should follow that the current not only flows horizontally across the direction of movement of the granular material, but also diagonally, and so lead to the greatest possible uniformity of heating. But this arrangement can not overcome the difficulties pictured hereinabove.

In the previously proposed zinc distillation apparatus the vapors pass from the shaft-like distillation chamber to the outside and are condensed in a separate condenser. Such a procedure is not practicable for the distillation of magnesium, particularly under vacuum, because the magnesium in consequence of its low specific gravity per unit of volume possesses an intrinsically small heat of vaporization, which is liberated as heat of condensation in the condensation step. Through working in vacuum the resultant dilution causes the heat of condensation per unit volume of magnesium vapor to be significally smaller, amounting, for example, in the case of distillation under a vacuum of 40 millimeters, to only about 1/50th of the heat of condensation per unit of volume of zinc vapor when distilled under atmospheric pressure.

In order to accomplish the liquefaction of such a dilute metal vapor in a condenser with the greatest possible freedom from loss it is necessary to cool the vapors extremely slowly in a large surfaced condenser. But since the vapors to be condensed carry a relatively small amount of heat per unit of volume, the condenser must be heated from the outside for condensation of the magnesium vapors in vacuum, in order to obtain that temperature which is necessary to condense the metal vapor to liquid without loss. This procedure requires a certain energy input in order to bring the condenser to the correct initial temperature.

It is among the objects of the invention to provide a method of distilling or subliming metal of the general type just referred to, in which the granular material containing the metal is heated by passage of an electric current, which provides for uniformly heating the distillation stock through its cross section, which avoids or minimizes the foregoing and other disadvantages, is readily and easily controllable, provides operating economies, and permits commercial and economical application of the general principle involved.

A further object is to provide an apparatus for practicing the method embodied in the invention, which is compact, relatively inexpensive, easily operated and controlled, and possesses the advantages which characterize the method.

Among still others, another and special object is to provide an apparatus in which the metal vapors are received and condensed in a condenser embodied in the distillation apparatus, whereby to avoid the foregoing named disadvantages in condensation, especially of magnesium vapor, and to afford maximum heat economy and yield of purified metal.

The invention will be described in connection with the accompanying drawings, which represent its preferred embodiment. Fig. 1 is a longitudinal vertical section through the furnace; Fig. 2 a view similar to Fig. 1 showing the upper part of the furnace to an enlarged scale; and Fig. 3 a cross section taken on line III—III, Fig. 1.

The invention is practiced in connection with granular stock. If the material is not in such form it is granulated, advantageously by mixing it with carbon, with or without another conductor or semi-conductor, and a suitable binder. For example, powdered magnesium is mixed with granular carbon or granular magnesium oxide, or both, to provide bulking agents capable of conducting electric current, at least to some extent. To the mixture is added a binder, suitably a material which carbonizes when heated, of which the hydrocarbon oils constitute the preferred example. Enough oil is added to produce a paste. The mixture is heated to expel the excess oil and cause bonding. If heated en masse the coked product is broken up to form granules of suitable size.

In accordance with the invention the granular stock is passed through a distillation chamber of substantially rectangular cross section. For instance it is passed downwardly through a vertical shaft of square cross section in which it is heated. Electric current is passed through the stock in a direction transverse to the direction of movement of the stock. To this end the current flows through the stock in zones from one face of the shaft to the opposed face, and in accordance with the invention this is accomplished by the use of flat, or plate-like, electrodes disposed in opposed pairs at opposite surfaces of the shaft, the pairs being spaced longitudinally of the shaft. This avoids the disadvantages attendant upon the use of segmental electrodes, for with the plate electrodes of this invention the electrodes of an opposed pair are uniformly spaced at all points, thus providing a condition ideal for uniform flow of current through the column of material which moves through the shaft.

The electrodes are not connected vertically, and being disposed in horizontal zones there are provided current conducting zones alternating with current-free zones. All of the electrode plates on each side are supplied with current at the same potential, the current being supplied to the individual pairs of plates which, as just noted, are not connected vertically. In the apparatus provided by the invention means are provided for passing current to or cutting it from the individual pairs of opposed electrode plates, according to need. The provision of conditions for uniform current flow in a given zone, and of means for cutting current into or from the separate zones makes it possible to control the heating and avoid irregularities thereof, since the flow in any zone is uniform and further heat in any region can be supplied or avoided by switching appropriate pairs of plates into or out of the circuit.

In order that the magnesium vapor liberated in the distillation need not be passed to a condenser situated outside of the shaft furnace, the invention provides for condensation of the vapor in the furnace structure. To this end the vapor is passed into a condenser which suitably divides the shaft into two vertical halves. Preferably this is accomplished by suspending from the top of the distillation shaft and centrally therein a tubular metallic member of substantially rectangular section. The section of this member is less than that of the shaft to provide a passage on each of two sides for the distillation stock, and it extends to a region of the furnace at which there is attained a temperature which lies above the boiling point of the metal. From the bottom of the shaft there projects upwardly within the lower end of the tubular member a similar tubular member but of lesser cross section, whereby the juncture of the two tubes provides a slot-like opening into the interior of the condenser. The distillation stock flows on opposite sides of the condensing chamber thus formed and at the juncture of the two tubes it forms a natural slope through which the metal vapor evolved from the granular material escapes into the inner condenser chamber.

In the centrally arranged condenser chamber one, two or more tubes, closed at their lower ends, project from above downwardly to a zone at which the temperature in the condensing chamber is above the condensation point of magnesium or above that of the particular metal being distilled. These tubes are cooled from within by circulation of a cooling fluid to bring the surface of the cooling tubes to such a temperature that the metal, such as magnesium, vapor is condensed to liquid thereon and drips off at the lower end of the tubes. Most suitably the condenser tube wall is indirectly cooled, as described hereinafter, for example.

The lower tubular member projects in gas-tight manner downwardly through the bottom of the shaft and its outer portion is filled with oil into which the magnesium drips, in the manner described in my application Serial No. 722,278, filed April 25, 1934, and in the manner there described is recovered in granular form.

Having reference now to the drawings, the apparatus shown comprises a distillation shaft 1 formed, for example, between refractory walls 2 enclosed within a mantle 2*a*. This shaft is of substantially rectangular section, as seen in Fig. 3, and of substantially uniform aperture throughout. An expansion space 100 may be provided in the refractory wall if desired. Granular distillation stock S is passed downwardly through the shaft, and electric current is passed across the stock in a plurality of zones transverse to the movement of the stock between a plurality of electrode plates 3 and 4 disposed in opposed pairs at two opposite faces of the shaft. The disposition of the pairs of electrode plates is such that the current zones alternate with zones in which no current is passed. To avoid current scattering the electrode plates may be somewhat shorter than the face of the shaft, as seen in Fig. 3.

The vapor liberated from the distillation stock is condensed in a condensing chamber formed of rectangular tubular metallic members 5 and 6 disposed centrally in distillation shaft 1. Member 5 is suspended from a gas-tight shaft cover 7 and it extends down to a region in which the stock reaches a temperature above the boiling point of magnesium. As seen in Fig. 3, one dimension of member 5 is such that two of its faces contact two opposed faces of shaft 1, its other dimension being such that there are provided two channels 8 and 9 for the stock 3 to flow downwardly along opposite sides of the condenser structure. Member 6 projects upwardly through the bottom of shaft 1 into the lower end of member 5. Member 6 is wide enough to contact the inside of the walls of member 5 which lie against the shaft, but its depth is less than that of member 5, as seen in Fig. 3. Thus the opening in distillation channels 8 and 9 increases at the juncture of the two condenser elements, forming a slope in the distillation stock through which the metal vapors evolved from the stock escape through the slot-like openings 10 into the interior of the condenser.

Most suitably members 5 and 6 are provided with interengaging longitudinal outstruck noses 11 and 12, respectively, noses 11 being disposed in complementary grooves formed in shaft 1. This construction fixes the position of the condenser members in the shaft and permits the two members to move relative to one another and the shaft as they expand or contract longitudinally.

Mounted within the condensing chamber are a plurality of tubes 13 closed at their lower ends and cooled interiorly by a suitable cooling fluid, such as water, oil or air, circulated therethrough. Advantageously the construction is such that the condenser tubes are cooled indirectly. In the embodiment shown the cooling fluid is introduced through a tube 14 mounted within another tube 14*a*, closed at its lower end, which is disposed coaxially within condenser tube 13. The cooling fluid thus is introduced through tube 14 and is withdrawn from the top of tube 14*a*, whereby the transfer of heat from the wall of condenser tube 13 to the cooling fluid circulated in tubes 14 and 14*a* takes place principally by radiation. The construction may be such that tubes 14 and 14*a* are movable vertically in tube 13 to vary the cooling effect in that manner. The cooling may be controlled also by the character of cooling fluid used, its initial temperature, and the rate of flow through the condenser.

The tubes 13 are cooled to such an extent that magnesium vapor entering through slots 10 is condensed to liquid. The lower end of tubular member 6 projects, in gas-tight connection, through the bottom of the furnace and contains a body of oil 15 into which the liquid magnesium drips from the ends of tubes 13. The solid granules of magnesium which collect in the oil are removed periodically through a lock chamber indicated schematically at 25.

The system may be evacuated, if desired, through a pipe 16. Granular distillation stock is supplied continuously to channels 8 and 9 through pipes 17 and 18 provided, respectively, with lock valves, or chambers, indicated schematically at 19 and 20, to maintain the system under vacuum where used, and to prevent escape of metal vapor.

Pyrometers 21 extend through the refractory walls 2 into channels 8 and 9, and pyrometers 22 project into the condensing chamber, for measuring the temperatures and controlling the distillation and condensation conditions. While the pyrometers are shown at certain levels in the distillation and condensing shafts, and also disposed at various positions laterally thereof (Fig. 3), it will be understood that more or fewer pyrometers may be used, and that their positions are more dependent on the conditions prevailing and the control desired.

The granular distillation residue which reaches the bottom of the shaft is removed by screw conveyors 23 and 24 whose outlets are suitably sealed to prevent entry of air into and escape of metal vapor from the apparatus. The granular solid pure magnesium which collects in oil 15 is removed at intervals through a lock chamber indicated schematically at 25.

To avoid escape of the magnesium vapor the cooler upper portion of the condensing chamber and the upper ends of tubes 13 and 14*a* are surrounded by heat insulated inserts 26 and 27, of slag wool for example, which extend so far downwardly that a temperature zone is obtained which always lies above the condensation point of the metal.

Hydrogen is introduced from a pipe 28 into the space between the heat insulated insert 26 and the wall of tube 5 to avoid a penetration of the magnesium vapors upwardly into this portion of the apparatus. Similarly the two feed conduits 19 and 20 are provided with connections 29 for the introduction of hydrogen, to provide a flow of gas which drives any metal vapor escaping into the upper part of the shaft through the opening 10 into the inner condenser chamber. Hydrogen can likewise be introduced through screws 23 and 24 in order to drive the vapors evolved in the lower part of the shaft in the direction of opening 10, where they pass into the centrally arranged condensation chamber.

It will be understood that the entire furnace is of gas-tight construction to avoid loss of metal vapor or ingress of air.

In the practice of the invention using the apparatus just described granular stock is fed continuously to the top of the shaft, flows downwardly, is heated by current flowing across the column to a temperature such that the metal, magnesium in this case, is vaporized, the vapors pass into the condenser, which is regulated to convert them to liquid, and the residue from the distillation is carried away by the screw conveyors. For a definite velocity of flow of the granular material the temperature of the stock in the separate horizontal zones is so regulated by switching current to and from the individual opposed pairs of plates that the desired temperature in the zone concerned is reached. Through this procedure of distributing the electrical energy input in horizontal separated streams, which can be alternatively cut in and out, it is possible to attain the desired temperature for the granular material in every portion of the shaft, and without energy loss through rheostatic resistances.

Various modes of accomplishing this are available in the art. By way of example, Fig. 1 shows all of the conductor plates 4 on one side of the furnace connected by leads 30, each provided with a switch 34a to a common bus 31 connected to one pole of a suitable generator, either A. C. or D. C. On the other side of the furnace current is supplied by a bus 32 connected to the other pole of the generator, but on this side each of the conductor plates 3 is connected to the bus 32 by a lead 33 containing a switch 34b, so that by operation of switches 34a and 34b current may be supplied to or cut off from any of the individual pairs of opposed plates according to need. The switches may be operated by hand upon observation of the readings of the pyrometers, or they may be operated automatically from pyrometers 21 by means, such as relays, known in the art.

The two channels formed on opposite sides of the condenser chamber being filled with granular distillation stock, the current flows from the electrode plates through the granular material in one channel, e. g., 8, to the centrally disposed metallic condenser elements 5 and 6, through the metal walls thereof to the other side and from here through the granular material in the other channel, i. e., 9, to the electrode plates on the opposite side of the shaft. By this means the centrally arranged condenser, into which the magnesium vapor escapes, serves simultaneously as a central electrode and also upon two sides is surrounded by hot granular material heated to the distillation temperature, so that there is obtained a supplementary heating for the centrally disposed condenser space.

Through the invention it is possible to provide a shaft furnace with a double shaft and a centrally disposed condensation chamber, to apply as a distillation apparatus for granular material containing magnesium or other metal, whereby through the process of the zone-like distribution of the current conduction and the periodic operation of the current introduction to the various zones the granular material containing magnesium is heated exactly to the temperatures which are necessary to evaporate the magnesium without the possibility of overheating of the granular material. This flexibility in temperature control is of great importance, particularly in connection with magnesium powder which has been produced by electrothermic reduction of magnesium oxide with carbon, for the preparation of granular material which is to serve for distillation, to avoid overheating the material in the distillation.

The magnesium powder prepared according to my Patent No. 1,884,993 commonly contains, in consequence of the reoxidation which can not be wholly avoided, a certain proportion of carbon and magnesium oxide, but for the provision of a solid granular residue after distillation there is added further carbon and magnesia.

Likewise it contains in consequence of the high reduction temperature which prevails, also other constituents of magnesite, such as iron, silicon, calcium and aluminum in the form of free metals or their carbides. If such material is heated over the boiling point of magnesium under the conditions of vacuum prevailing, the carbon content of the charge may cause a reduction process to occur which causes formation of carbon monoxide, which latter in the condensation prevents the separation of liquid magnesium. Also the accompanying impurities, such as calcium and silicon, can simultaneously evaporate and contaminate the condensed magnesium and render it less useful. It is therefore of outstanding significance that the distillation process of this invention can be so carried on that in the heating of the granular material at no point is a temperature such as to produce these effects, say 950° C., reached or essentially exceeded. In the use of a corresponding vacuum this temperature can be essentially lower.

The arrangement of the central condensation chamber permits the magnesium vapor to be conducted the shortest distance for condensation and the hot granular charge of material to be distilled serves simultaneously for heating the centrally arranged condensation shaft.

Since the resistance of the granular material used for distillation decreases with increasing temperature, while on the other hand, however, the use of the same voltage in all of the heating zones possesses a certain advantage, the application of a two-step distillation shaft is advantageous since in the upper part of the shaft the current path is shorter than in the lower part, where the resistance of the material is lowered.

A regulation of the temperature relations can also be introduced by variation of the width of the conductor strips in the separate heating zones, as also by the separation of the zones free from current which alternate with the current-carrying zones.

A further feature of importance which accrues from the invention is the provision of an apparatus in which the unbalanced pressure forces created in the use of vacuum are applied to the cold, or relatively cold, outer portion of the furnace, such as its mantle, instead of to heated metallic parts as has been the case with prior distillation apparatus. Thus, the condenser is mounted within the distillation chamber so that for all practical purposes both sides of the condenser are exposed to substantially the same pressure. The mantle, top and bottom members, and all connections and other elements are so associated as to form a gas-tight casing enclosing the furnace shaft and other parts, wherefore the casing receives the stresses due to the vacuum in the furnace. But in the construction provided by this invention the shaft mantle is not highly heated, so that the mantle and its associated parts are fully able to withstand the stresses created by the vacuum in the furnace, in contrast with furnaces in which such unbalanced forces must be taken up by more or less highly heated metallic elements. Thus the refractory masonry serves to form the rectangular distillation shaft and also to insulate the charge in the shaft against loss of heat by radiation while keeping the outer gas-tight casing cool to resist the unbalanced forces set up by the vacuum within the furnace.

The method disclosed herein is disclosed and claimed in a copending application, Serial No. 48,540, filed by me on November 6, 1935, as a division hereof.

According to the provisions of the patent statutes, I have explained the principle and operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. An apparatus for distilling metal from material containing it, comprising a vertical distillation shaft of rectangular section of substantially

uniform area, means for feeding material into the top of said shaft and for removing residue from the bottom of the said shaft, a plurality of electrodes disposed in horizontally opposed pairs at opposed vertical faces of said shaft, a bus bar connecting the electrodes on one of said faces with one pole of a source of current, and another bus bar connecting the electrodes on the other of said faces with the other pole of said source of current, for conveying current in horizontally separated streams through the shaft, and a condensing chamber comprising a metallic tube of substantially rectangular section extending downwardly from the top of said distillation shaft centrally therein, a second metallic tube of substantially the same width but of lesser depth than said first-named tube extending upwardly from the bottom of the distillation shaft into the lower end of said first-named tube, and cooling means disposed within said tubes.

2. An apparatus according to claim 1, with means for switching current into and from the individual horizontally opposed pairs of plate electrodes.

3. An apparatus for distilling metal from material containing it, comprising a vertical distillation shaft of a rectangular section of substantially uniform area, means for feeding material into the top of said shaft and for removing residue from the bottom of the said shaft, a plurality of electrodes disposed in horizontally opposed pairs at opposed vertical faces of said shaft, a bus bar connecting the electrodes on one of said faces with one pole of a source of current, and another bus bar connecting the electrodes on the other of said faces with the other pole of said source of current, for conveying current in horizontally separated streams through the shaft, means for switching current into and from the individual horizontally opposed pairs of plate electrodes, and a condensing chamber comprising a metallic tube of substantially the same width as said shaft but of a depth less than that of the shaft section extending downwardly from the top of said distillation shaft, a second metallic tube of substantially the same width but of lesser depth than said first-named tube extending upwardly from the bottom of the distillation shaft into the lower end of said first-named tube, said condenser dividing the shaft vertically into two parallel distillation conduits, and cooling means disposed within said tubes.

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