

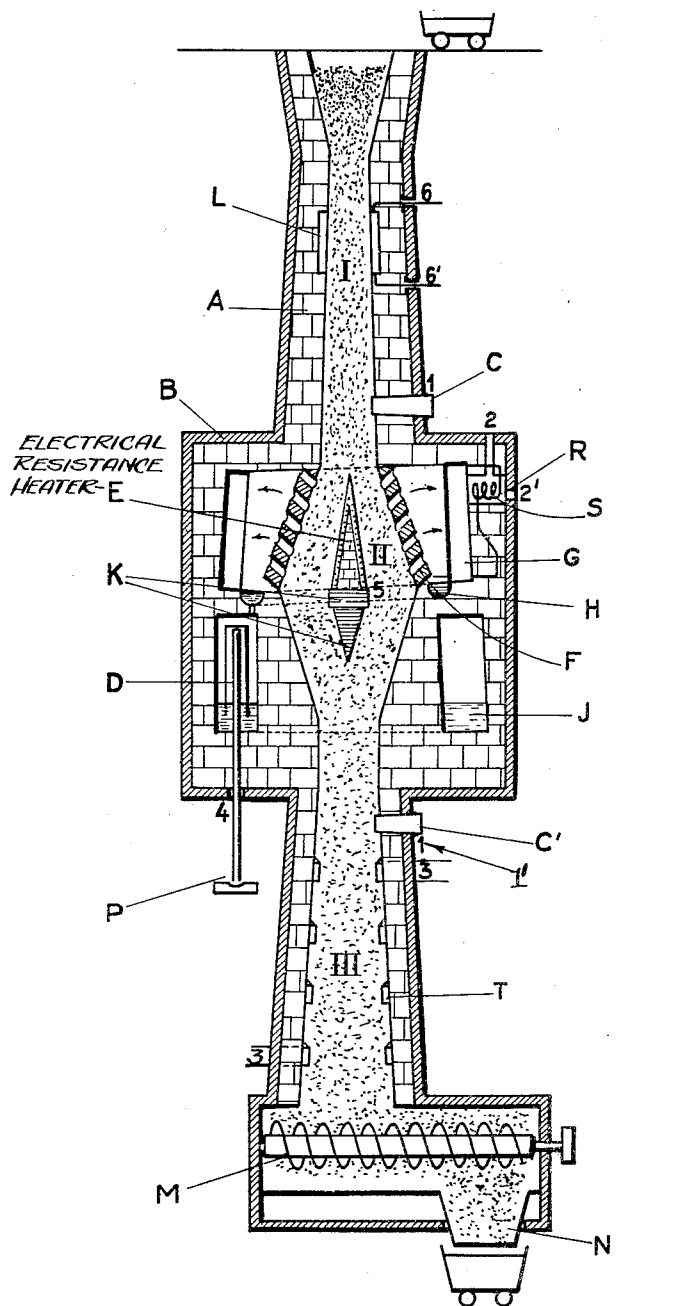
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APPARATUS FOR PRODUCTION OF VOLATILIZABLE METALS

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APPARATUS FOR PRODUCTION OF
VOLATILIZABLE METALS

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The present invention relates to apparatus for extracting certain volatile metals and in particular magnesium from their oxidized ores, and for magnesium in particular from magnesite or dolomite, further for obtaining the metal so extracted in the liquid state so that it can be cast immediately into ingots, and lastly for achieving these results in a continuous manner. The extraction is effected by reduction according to the well-known chemical action, by means of reducers which, in the case of magnesium, may be for example silicon or ferro-silicon.

Such apparatus has already been proposed in its main essentials in my pending patent application Serial No. 762,755, filed July 22, 1947 (now abandoned).

The present invention has for its main object the provision of an improved apparatus operating with a pulverulent mixture of the ore and reducer, preliminarily ground to suitable size and mixed together, but not briquetted or agglomerated, this apparatus giving for a predetermined reaction temperature, on the one hand the metal in gaseous state with a definite vapor tension, and on the other hand residues not volatilized at that temperature, which residues can thus be readily separated from the gaseous metal. The gaseous metal is brought to the liquid state by cooling the said gaseous metal to a definite temperature, thus causing condensation of the metal, according to the known rules of distillation. The liquid metal can be collected by simple gravity flow at a place where there is maintained the temperature necessary for the persistence of the liquid state, the metal being tapped off from that place and cast in the ordinary conditions.

A further object of the invention is to provide continuously operating apparatus of this character in which the reducing reaction, the distillation and the storage of the liquid metal are effected, in a medium such that neither the metallic vapor nor the liquid metal run the risk of being oxidized or nitrified at any point or at any time. This medium may be provided by a substantial vacuum or by an inert gas such as hydrogen or helium.

In view of the fact that the distilling operation normally causes a movement of the metallic gas towards the cooled condensation region, it is not necessary to set up mechanically a current for conveying this metallic gas.

In order to fulfil these various conditions, it is desirable to provide a high temperature for the reaction; it has been found that in the case of magnesium extracted from dolomite reduced by

ferro-silicon containing 75% of silicon, at a temperature approximating to 1400° C., the normal tension of the metallic gas produced was about 140 mm. of mercury. For the condensation, the cooling must be such that the gas is only liquefied and not solidified; it has been found that in the case of magnesium, at a temperature of 700° C., the normal state of the metal was liquid with a vapor tension not exceeding a few mm. of mercury. This difference of pressure (between 140 mm. and say 10 mm.) of about 130 mm., causes the desired movement of the metallic vapor towards the condensation chamber.

For securing the desired medium free from ordinary atmospheric gases (oxygen and nitrogen), it has been found that it is possible to employ columns of finely powdered material for establishing blockages substantially proof against passage of the gases, and thus isolating the metal from the ordinary atmosphere, both at the time of its production in gaseous state during the reducing reaction, and in the course of its condensation to liquid state and its storage. The height of these columns depends naturally upon the character of the pulverulent materials and their fineness, as well as upon the shape of the columns; there has been determined as a function of these parameters the minimum height necessary for the case of magnesium contained in a mixture of powdered dolomite and ferro-silicon, the dolomite employed having a particle size of 1 to 10 μ , and the ferro-silicon a size of 10 to 100 μ .

Profiting from these determinations, knowing also that pulverulent mixtures lose almost the whole of their entrained atmospheric gases and humidity, as well as their adsorbed atmospheric gases and humidity, at a temperature not exceeding 750° C., and lastly knowing that for powdered dolomite or magnesite, at a temperature of the order of 800° C., their decarbonation is complete under a pressure of 760 mm. of mercury, another object of the present invention is to provide apparatus adapted to produce in continuous operation certain volatile metals and in particular magnesium in the liquid state ready to be cast into ingots.

The invention will now be described in a more precise manner, with particular reference to the accompanying diagrammatic drawing, which refers to an example of a furnace for treating mixtures of dolomite and ferro-silicon for the production of magnesium.

The drawing is a section of such a furnace, showing the three zones, I being the charging

zone, II the reducing, condensing and storage zone, and III the discharging zone, and showing also the complete lay-out according to the invention, without provision for movement of inert gas.

The apparatus illustrated comprises an elongated vertical column allowing the passage into a first heated zone I (known as the charging and preheating zone) materials containing the oxidized metal and its reducer, in which zone there are eliminated the entrained, occluded and adsorbed gases and moisture, as well as the carbon dioxide gas which may be present from an incomplete preliminary decarbonation of these materials, all these gases expanded under the effect of the increase of temperature rising to the free surface at the top opening of the column, as through a liquid. The materials continuing their downward movement reach the strongly heated reaction zone II (known as the reducing, condensing and storage zone), where there is produced and evolved the metallic vapor resulting from the reduction. In this position, the metallic vapor is absolutely protected from any oxidizing action by the blockage effect of the pulverulent column composed of the materials themselves, which isolates the vapor from the external atmosphere. The metallic vapor, of which the tension in the particular case of magnesium is 140 mm. if the temperature is 1400° C., becomes forced towards a condenser connected integrally with the reaction zone and consisting of a steel casing which is maintained at a temperature in the vicinity of 700° C. by the circulation in the interior of the casing of a bath of molten tin itself maintained at that temperature by a method which will be described in more detail hereinafter. As already stated, the metallic vapor evolved in the reaction zone under a tension which is about 140 mm. for magnesium, travels of itself towards the outer wall of the casing having a temperature of 700° C., on which it will condense. There is provided at the height of the reaction zone, a free space clear of the reacting materials, in such a way that the metallic vapor evolved will only have to traverse, as a maximum, in order to reach the condensing surface, the small thickness of the column of pulverulent material which is itself in downward movement.

The residual materials, already deprived of their metallic content, continue their movement through a lower column occupying the zone III (known as the discharging zone) the length of which is determined like that of the upper or charging zone I, so as to produce tightness against atmospheric gases which might tend to enter at the base of the column. During the descent of the residues, a device for recovery of their latent heat may be brought into action with the double object of avoiding losses of heat and lowering their temperature as quickly as possible.

The metallic vapors condensed on the wall surface of the condenser casing flow down that surface and are collected in a semi-cylindrical gutter provided at the lower edge of the surface. This gutter has a slope which allows the liquid metal to be collected from the lowest point of the gutter into a receiver itself maintained by thermal insulation at a temperature higher than the melting point of the metal, namely for magnesium above or in the vicinity of 650° C., from which receiver it is discharged very simply by siphon effect, which allows of maintaining absolute tightness of the vacuum affecting the move-

ment and reaction regions for the treated materials.

The metallic condenser casing is formed of welded iron or steel plates. The interior is filled with tin, at a temperature of 700° C., which is well above its melting point. This tin arrives through an iron pipe at the bottom of the casing and leaves through another iron pipe at the top. Having regard to the thermal expansibility of tin, there will thus be a movement of the liquid bath by thermo-siphon effect at a speed determined by the temperature to which it is cooled. The flow and return pipes are continued externally of the condenser casing by a gilled tube coil itself immersed in a large iron casing through which there is circulated a cooling fluid, which may be water, steam or air. The speed of circulation of this fluid in the casing is controllable to allow of maintaining the temperature of the casing at such a value that the tin circulating through the coil gives up to the cooling fluid the heat units abstracted in the condenser casing. Thus by regulation of the speed of circulation of the cooling fluid it is possible to regulate the temperature of the tin in the condenser and thus to maintain the temperature of the walls of the condenser casing at 700° C. in a very simple manner.

It is to be noted that over the whole distance travelled by the particles forming the mass of the materials under treatment, from the head of the charging column or zone I down to the foot of the discharge column or zone III, these particles are constantly rubbing against one another, which is a circumstance favorable to the evolution of the occluded, adsorbed and entrained gases, and moreover allows for evenly distributed heating of the particles, specially in the reducing zone.

The furnace illustrated is formed by a non-homogeneous structure A made of brickwork, enclosed in a metallic sheathing B made of edge-welded plates, having external connections at only six points, viz. at 1 and 1' for the passage of a bar C or C' transmitting a supersonic wave of relatively low frequency (1½ to 2 kilocycles per second) intended to facilitate the descent of the charges at the base of the preheating zone I and at the top of the discharging zone III; at 2 and 2' for the admission of a current of fluid intended for the cooling of the condensing liquid; at 3 for the circulation of water for the recovery of latent heat from the residues; at 4 for the outlet of the liquid magnesium extraction siphon D; at 5, transversely, in the seating of a beam supporting a dihedral heating element E, for the lead-in and lead-out of the heating current; and at 6 and 6' for the heating of the preheating element L.

In this brickwork structure A there are provided an upper shaft or flue for the descent of the charges in zone I, a heating chamber in zone II with seatings for the condensing and storage apparatus, and the pipes necessary for the movement of the liquid metal, and a lower shaft or flue for the discharge of residues in zone III.

The brickwork must be highly refractory in the strongly heated parts and thermally insulating in the parts which are in contact with the metallic sheathing; it is therefore formed in each zone or region by a superposition of heavy refractory bricks in the interior, these bricks being made of magnesia not affected by vapors of magnesium in particular, and of outer bricks of increasingly lighter weight and more porous nature

until they make contact with the metallic sheathing.

The heating chamber is constituted by the space inside a widened out portion of the brickwork, masked on the side towards the interior of the furnace by a curtain of refractory bricks F interrupted by staggered openings and sloping upwards. Through these multiple openings the magnesium vapor can easily reach the inner surface of the condenser casing G on which it liquefies, trickling down into the gutter H placed at the bottom of that surface, and flowing by gravity to the reservoir J, from which the liquid metal is tapped off in order to be cast into ingots at P. The casing G is filled with tin which circulates through a coil S immersed in the cooling fluid contained in the casing R. The widened-out portion or heating chamber is traversed from one side to the other by a beam K, made of long stiff slabs of fused and molded magnesia, set firmly in the brickwork but without rigid joints, so as to be able to play laterally in their seating in the brickwork.

This beam supports the element E, which is of very acutely pointed dihedral shape, made of wide and smooth molded plates of fused magnesia, having their outer surfaces polished so as not to oppose any resistance to the sliding of the particles of reacting materials which pass down over them. At its lower part, the supporting beam K is fashioned to a more obtuse dihedral shape serving as a guide for the movement of the descending pulverulent material.

The plates of the dihedral element E are heated internally by an electric current flowing through metallic resistances placed in recesses made beforehand in the thickness of these plates, the resistances being such that they are not affected by their contact with magnesia at temperatures of about 1400° C. at which the operation is carried out. It is easy to determine the amounts of current which are necessary for developing and maintaining the desired temperature on the surface of the plates of the dihedral element; it will be remembered on this point that the reaction of the reduction of magnesia by silicon is slightly exothermic, and account will be taken of that circumstance in calculating the amounts of electrical energy required.

Account will also be taken of the variation of electrical conductivity of magnesia, which is a function of its temperature, increasing at first and then diminishing when the temperature of 1400° C. is reached. In fact magnesia then behaves like a high-resistance conductor and becomes heated by the current. The electrical connections of the heating conductors with the external supply are ensured by baths of molten metal which afford perfect tightness of the whole electrical heating circuit.

The preheating device L may be provided by an insulated heating ring sunk in the brickwork of the shaft or flue in which the charges descend, the ring being made up in the same manner as the plates of the dihedral element E described above.

The descent of the charges may be held up either by the formation of blocks due to the establishment of bridges in the charging and preheating zone or in the discharging zone, or by initial agglomeration of the particles after reaction due to the formation of silicates fusible at the reaction temperature. In both cases the freedom of each particle in the charge will be greatly increased by a vibratory movement tra-

versing the mass of the charge and being transmitted to the same. This vibration may be caused mechanically by the emission of a supersonic flux produced by a magnetostriction emitter of which the vibrating bar will be welded to the main sheathing and will therefore not prevent its gas-tightness. Two of these emitter groups are shown provided, one C near the base of the charging zone, the other C' at the top of the discharging zone. Calculation of the relations of the frequency and intensity of vibration with the size of the particles will allow of bringing the parameters to their optimum value. For the same object, the charging and discharging columns in the zones I and III may present a slight widening out downwards.

Thermo-electric couples (not shown) allow of observing constantly and recording the temperatures developed:

(1) in the preheating column at the level of the heating ring L.

(2) at the outer surface of the dihedral heating element E.

(3) at the surface of the condenser casing G turned towards the reaction column.

(4) in the coil S for cooling the tin from the condenser casing.

(5) at the top of the discharging column or zone III.

(6) at the base of this same column.

The charging of the materials to be treated takes place freely at the top of the charging column. The discharging of the spent materials takes place at the base by the operation of a horizontal worm conveyor M which delivers into a hopper N open at its base for the removal of the residues. A device for the recovery of the latent heat of these residues is provided at T.

Modifications can naturally be applied to the apparatus described and illustrated without departing from the scope of the invention.

What I claim is:

1. Apparatus for continuous production of a volatilizable metal by chemical reduction of an ore of said metal, comprising a vertical shaft furnace including three superposed zones, means for charging into the uppermost zone a pulverulent mixture of said ore and a reducer, means for heating said uppermost zone to preheat said mixture for elimination of entrained gases, the middle zone of said furnace being widened out in relation to the uppermost zone, means for strongly heating said middle zone to cause reaction of said ore and reducer, with volatilization of the metal evolved by said reaction, the heating means of said middle zone comprising an electrical resistance element of acutely upwardly pointed dihedral shape with smooth outer surfaces located interiorly of the descending mixture, an apertured curtain of refractory material surrounding said descending mixture and heating means of said middle zone, an annular condenser surrounding said curtain for cooling the metal volatilized by the reaction in said middle zone to condense it to liquid state, said volatilized metal having access to said condenser by passage transversely through the descending mixture and through the apertures of said curtain, an annular gutter below said condenser for collecting the condensed liquid metal, a receiver for liquid metal collected by said gutter, a siphon discharging liquid metal from said receiver, and means for discharging unvolatilized residues descending through the lowermost zone.

2. Apparatus for continuous production of a

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volatilizable metal by chemical reduction of an ore of said metal, comprising a vertical shaft furnace including three superposed zones, the uppermost zone having at least part of its internal surface widening out slightly in the downward direction, the middle zone having the upper part of its internal surface widening out considerably in the downward direction and the lower part of its internal surface narrowing considerably in the downward direction, and the lowermost zone having at least part of its internal surface widening out slightly in the downward direction, means for heating said uppermost zone to preheat a pulverulent mixture of said ore and a reducer charged into the top of said zone, heating means located within the widened upper portion of said middle zone, said last-mentioned means strongly heating said mixture within said upper portion to cause reaction of said ore and reducer, with volatilization of the metal evolved by said reaction, said last-mentioned means comprising an electrical resistance element of acutely upwardly pointed dihedral shape with smooth outer surfaces, an apertured curtain of refractory material forming a way for said upper portion of said middle zone and surrounding the descending mixture, an annular condenser exterior to said wall-forming curtain, the metal volatilized by said reaction having access to said condenser by passage transversely through the descending mixture and through the apertures of said curtain, means for collecting the liquid metal condensed from said volatilized metal, and means for separately discharging unvolatilized residues descending through the lowermost zone.

3. Apparatus for continuous production of a volatilizable metal by chemical reduction of an ore of said metal, comprising a vertical shaft furnace including three superposed zones, the middle zone being widened out to provide internally a heating chamber for a pulverulent mixture of said ore and a reducer descending

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through the uppermost zone, heating means located within said chamber for heating said mixture to the temperature of reaction, an apertured curtain of refractory material forming a downwardly divergent conical wall for said chamber, the apertures in said curtain sloping upwardly from the interior so as to remain substantially unobstructed by the descending mixture, a condenser on the external side of said wall-forming curtain, the metal volatilized by said reaction having access to said condenser transversely through the descending mixture and through the substantially unobstructed apertures of said curtain, means for collecting the liquid metal condensed from said volatilized metal, a storage reservoir enclosed in said furnace and receiving the liquid metal from said collecting means, means for recovering heat from the unvolatilized residues descending through the lowermost zone, and means for discharging said residues at the base of said lowermost zone, the height of said uppermost and lowermost zones being sufficient to exclude atmospheric gases from said heating chamber by the close-packing of the particles of mixture and residues therein.

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