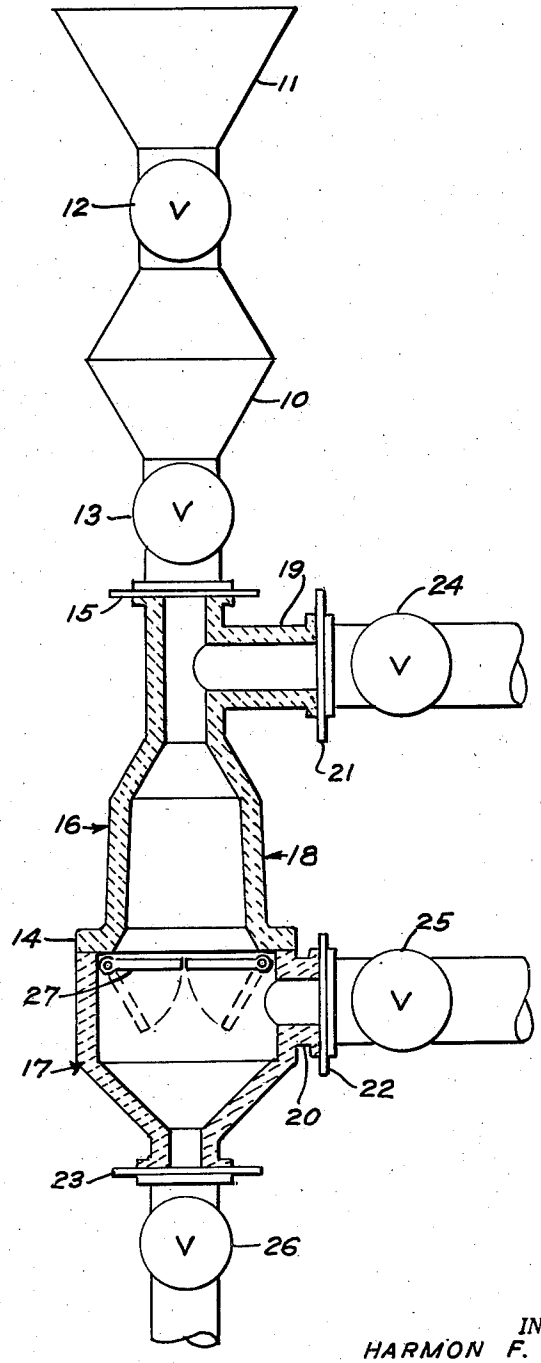
Dec. 21, 1948. H. F. FISHER 2,456,935

REFINING OF VOLATILIZABLE METALS

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Fig. 1



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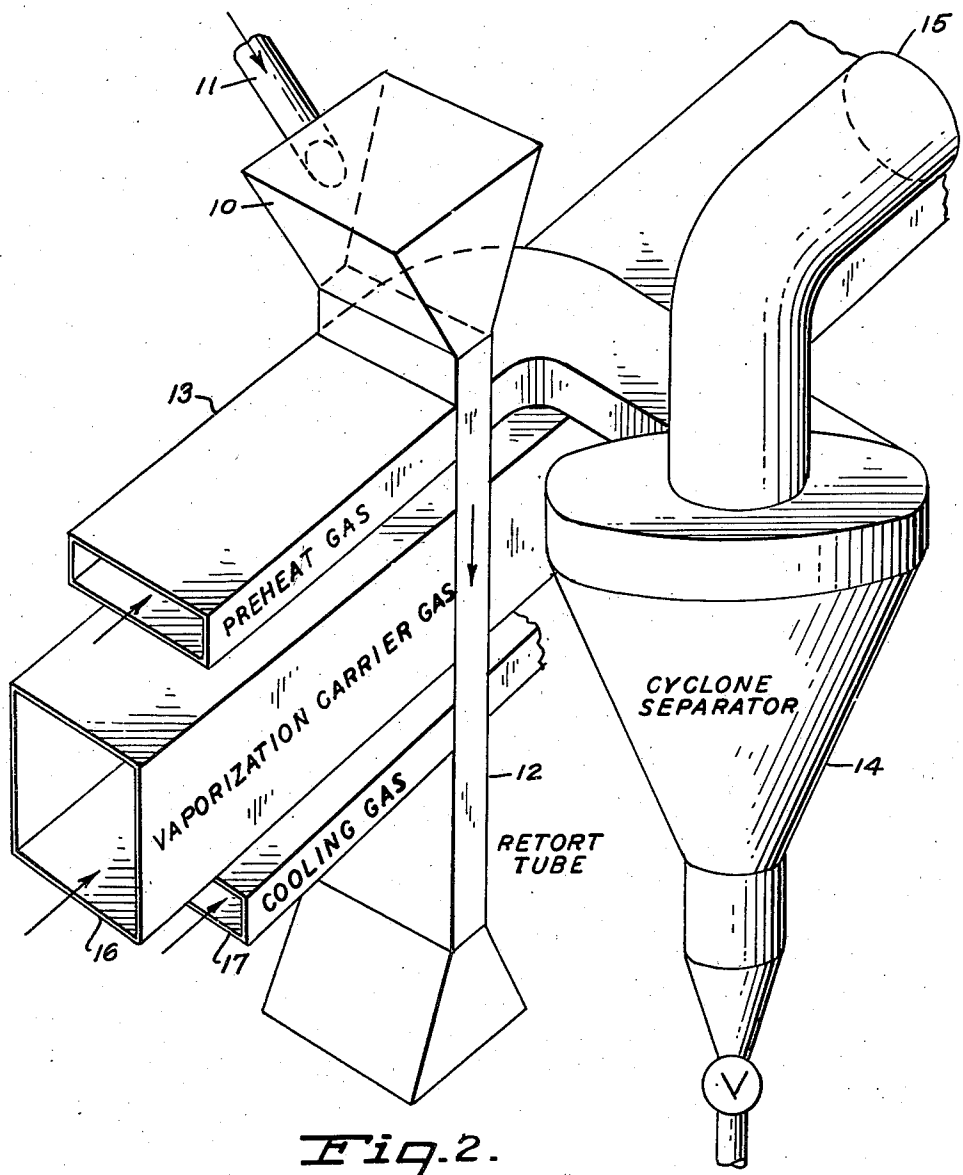


Fig. 2.

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REFINING OF VOLATILIZABLE METALS

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9 Claims. (Cl. 75—66)

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This invention relates to a method for recovering volatilizable metals from materials containing the same. More particularly, it relates to the vaporization of volatilizable metals from substantial amounts of non-volatilizable impurities by a method wherein the heat required to vaporize the metal is supplied directly to the material containing the metal by means of a carrier gas.

The invention is applicable generally to the refining of volatilizable metals such as zinc, the alkali metals, the alkaline earth metals, etc., which may be separated by vaporization from concomitant non-volatilizable impurities. For purposes of illustration, however, the invention will be described with particular reference to the treatment of magnesium. It is especially suited to the recovery of magnesium from carbothermic magnesium dust.

In the carbothermic process for the production of metallic magnesium a mixture of magnesium oxide and carbon is subjected to a temperature in the order of 2000° C. whereby magnesium and carbon monoxide are formed according to the following reaction:

$$MgO+C=Mg+CO$$

Since this reaction is reversible it is necessary to cool the magnesium and carbon monoxide to a point where they are stable in the presence of each other. This cooling or chilling operation is rapidly effected with the aid of large quantities of a chilling medium such as natural gas, liquid hydrocarbons, hydrogen, or certain of the noble gases. However, even when good chilling efficiency is achieved there is some reversion of the reaction so that the product recovered comprises a mass of about fifty per cent metallic magnesium with the remainder magnesium oxide and carbon in the ratio of about 60 to 40. There are also relatively small amounts of carbides present in addition to lesser amounts of calcium, silicon, sodium, iron and aluminum and their oxides. The material is finely divided and the individual particles range in size for the most part from several microns to a small fraction of one micron. In the industry this product is usually referred to as carbothermic magnesium dust.

The recovery of solid metallic magnesium of high purity from carbothermic magnesium dust is a very difficult problem. The dust is pyrophoric in air and must be handled in an inert atmosphere or be wet down with liquid hydrocarbons. It is not readily pelleted without the use of special equipment, and as a consequence it must be handled with considerable care and precaution.

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In the process of purifying metallic magnesium, of the type produced by the carbothermic process, the operation in the past has been to place the finely divided magnesium together with its accompanying impurities (i. e. magnesium oxide, magnesium carbide, carbon, silica, etc.) into a pelleting machine and then to feed the resulting pellets into a retort. The retort was hermetically sealed and then lowered into a pit furnace and evacuated to decrease the distillation temperature. Any volatile binders and impurities were first distilled off at a low temperature and then the temperature was raised until the magnesium metal was volatilized. Because of the evacuated interior of the retort and because of the low heat conductivity of the charge stock and the high heat capacity of the retort, the process was extremely slow. The retorts were subjected to high temperatures because of the necessity of transferring heat through the shell of the retort and thence by radiation through the poorly conducting pieces of charge stock containing the magnesium. The capital investment in heavy plant equipment was extremely high and equipment life was short because of the severe conditions imposed upon it.

It is an object of the present invention to provide a method for the distillation of volatilizable metals whereby the heat required for the distillation of the metal from the charge stock is carried directly to the charge stock by a carrier gas. An additional object is to provide a method for the distillation of metals which is rapid and efficient, and which does not require the use of expensive plant equipment or severe operating conditions that are highly destructive to plant equipment.

In practicing the present invention, a stream of carrier gas is first heated to a temperature above the boiling temperature of the volatilizable metal sought in pure form, and then the heated carrier gas is circulated through a bed of the charge stock contained in an insulated chamber or retort. Continued circulation of the hot carrier gas causes a rapid rise in the temperature of the charge stock until the boiling temperature of the volatilizable metal is approached. At these elevated temperatures the metal exhibits an appreciable vapor pressure and, in the presence of the stream of carrier gas, it vaporizes at a rapid rate. The metal vapors are conveyed by the carrier gas to a condenser where the metal is

condensed to the liquid or solid state and separated from the carrier gas. The recovered carrier gas is recycled under pressure through a suitable heating zone and fed back through the charge stock.

In the event that any dust is mixed with the charge stock pellets, fragments, or other agglomerates it may be blown out of the charge stock early in the heating cycle by several blasts of carrier gas. The dust particles picked up by the carrier gas blasts are then separated from the carrier gas by the use of cyclone filters or other suitable dust separating means.

In a modified embodiment of the present invention, a preheating step may be interposed whereby hot preheat carrier gas, which has received its heat from hot residue of a completed distillation (or from other recovery sources), is circulated through the charge stock agglomerates to heat them to a temperature somewhat below the melting point of the metal to be vaporized. As described above volatile binders—such as mineral oil, asphalt, pitch, etc.—and volatile impurities may be removed by evaporation, and dust may be removed from the charge stock agglomerates during this preheating step. After this preliminary cleaning and preheating step, the volatilizable metal is fused and vaporized with the aid of the heat supplied from hot vaporization carrier gas in the manner described above.

The adoption of the preheating carrier gas step permits a simple and economic separation of dust from the carrier gas when such separation of dust is necessary. If appreciable amounts of dust are present with the metal vapors in the carrier gas that enters the condenser, the condenser may become fouled by accumulated dust particles, and the rate of heat transfer to the cooled condensing surfaces will be decreased. In addition, the entrained dust may contaminate the recovered metal with impurities and thereby decrease its value.

Dust separators, such as filters and cyclones, employed in the process of the invention must be maintained at temperatures above the condenser temperatures. By the use of a dust collector in the primary preheat gas stream, lower temperatures may be used on the dust collector. The primary preheat gas stream which is better adapted for freeing the charge stock of dust, may be sent through the pelleted charge stock at a higher velocity than the secondary vaporization carrier gas stream, which carries metal vapors that must be condensed.

The carrier gases employed in the present process are preferably inert. Hydrogen, because of its inert character to magnesium and most of the volatilizable metals, has been found to be very satisfactory. Such inert gases as helium, and argon may also be used.

Pressures above atmospheric are conveniently used in the process, thereby minimizing the danger of air infiltration into the carrier gas system. The process may, however, be operated at pressures near or far below atmospheric pressure by using suitable precautions to prevent leakage of air into the system.

The carrier gas may be heated by any suitable means such as refractory pellets of the type contained in Royster stoves, or by electrical resistance elements, similar to Globar rods, made of silicon carbide which may be safely operated up to 2600° F. Metallic resistors may be used, provided the upper temperature limits are within the safe working range of the alloy. The heating may also be accomplished by radiant heater tubes made of high temperature alloy. These tubes are sealed off from the carrier gas in the heating furnace. Combustion of fuel within the heater tubes supplies the necessary heat.

Since all the high temperature heat required in the instant process is supplied directly to the carrier gas from within the enclosed system rather than from heat supplied to the outside walls of portions of the equipment, none of the metal walls of the equipment—such as retorts, retort shells, etc.—are at high temperatures during the operation of the process. It is, therefore, possible to line the hot gas ducts and the vaporization retorts with high temperature refractory and insulating linings such as, for example, carbon in the hottest zones, and magnesia in the low temperature zones. Thus heat losses are reduced, the need for expensive heavy plant equipment is obviated, and the metal walls and heat insulating material are not destroyed by oxidation or reduction reactions.

The carrier gas process of the invention may be operated in either batch or continuous manner. Examples of both modes of operation will be described.

Fig. 1 is a descriptive drawing of a distillation or vaporization retort which may be used in connection with a batch type operation of the invention.

A gas-sealed charging hopper 10, into which funnel 11 empties, is equipped with plug valves 12 and 13 and is mounted on top of retort 14. Between the top of retort 14 and plug valve 13 there is installed a spectacle slide valve 15.

Retort 14 is composed of a top section 16 and a bottom section 17. Both top and bottom sections of the retort are composed of joined cylindrical sections and truncated cone sections as shown in Fig. 1. The walls of section 18 of top section 16 are slightly inclined inward from the vertical and form a truncated cone rather than a cylinder. Opening into the top and bottom sections of the retort are gas inlet ducts 19 and 20, respectively. Spectacle slide valves 21, 22 and 23 are fitted to ducts 19 and 20 and to the outlet at the bottom of the retort. High temperature alloy plug cocks 24, 25, and 26 are installed adjacent to the spectacle slide valves.

The walls of the top and bottom sections 15 and 16 of the retort and of ducts 19 and 20 are composed of a steel outer shell which is lined with refractory carbon brick lining backed up with carbon black heat insulation.

Near the top of the bottom section 17 of the retort are fastened two hinged semi-circular grate bars 27. The grate bars are made of high temperature alloy and the forged hinges of the grates are oil-cooled. The spectacle slide valves 15, 21, 22, and 23 are also oil-cooled and of proper design to withstand high temperatures.

In refining magnesium in agglomerated carbothermic magnesium dust, using the apparatus of Fig. 1, the following cycle of operations may be used to advantage.

Charging

The dry pellets, fragments, or other agglomerated forms of carbothermic magnesium dust are charged into funnel 11 until it is filled. The charge is then dropped into charging hopper 10 by opening valve 12. In the hopper the charge is purged free of air with the carrier gas by passing the gas upward through the charge.

When purging is complete, valve 12 has been

closed, and grate bars 27 have been locked into horizontal position, valves 13 and 15 are opened and the charge drops into the retort (which is purged of air and contains an atmosphere of inert carrier gas) and onto the grates 27 above which a bed of charge stock is formed.

Preheating

If preheating is practiced, a preheating carrier gas stream is passed through the bed of charge stock. Valves 13, 15, 23 and 26 are closed and valves 21, 22, and 25 are opened to pass the hot gas through duct 20 up through the cold charge stock and out through duct 19. By this process the retort and charge are warmed up to a uniform temperature of about 1204° F., the melting point of magnesium. At this temperature the vapor pressure of magnesium is less than about 2 mm. of mercury and only a small amount of vaporization occurs.

During this preheating step loose dust and broken pellets are swept out of the pellet bed and into a dust separator. It is preferable, at the beginning of the preheating stage, to briefly scavenge the retort charge with a high velocity blast of carrier gas for the purpose of removing dust from the charge bed. If the charge stock contains a volatile material such as a hydrocarbon binder this material is conveniently vaporized from the charge during the preheating step.

Vaporizing

After the preheating cycle has been completed, the preheating gas stream is shut off and a stream of vaporizing carrier gas, having a higher temperature, is circulated through the retort in the same manner as described for the preheating carrier gas stream. This circulation is continued until sufficient heat is supplied to vaporize the metal in the dry pellets, fragments or other agglomerated forms. Practically the entire metal contents of the charge stock is vaporized and carried away in the hot carrier gas to a condenser (not shown) where the magnesium is recovered by condensing it to the liquid or solid state.

The temperature of the carrier gas used on magnesium charge stock should not be appreciably below 2015° F. for rapid vaporization of the metal. When the temperature of the carrier gas is appreciably below 2015° F. a much larger volume of carrier gas is necessary to vaporize a given mass of magnesium then when carrier gas having a temperature above 2015° F. is employed. Carrier gas temperatures as high as 2035 to 2050° F. are preferable for rapid rates of vaporization and have the additional advantage that smaller volumes of hot carrier gas are required. Carrier gas temperatures above 2050° F. may be used to great advantage in the process when heating elements are available to heat the carrier gas to these higher temperatures.

The rate of circulating the carrier gas is also important in connection with the speed of vaporization of the metal and the volume of carrier gas required to effect complete vaporization. The rate of gas circulation will, in turn, depend upon the depth and temperature of the charge stock as well as the size of charge stock agglomerates, radiation conditions, etc. The optimum rate of carrier gas circulation is determined experimentally for each set of conditions.

Residue cooling

After the vaporization cycle is completed, the carrier gas stream is shut off and a stream of cold carrier gas is circulated through the hot bed of residue in the retort in the same manner as described for the previous gas circulation cycles. The cold carrier gas cools the hot residue and is itself heated sufficiently to be used as a preheating carrier gas stream in another retort charged with cold agglomerated charge stock. The cold carrier gas stream is circulated until the residue bed is cooled to 1200° F. or any other desired temperature.

Discharging

After the residue and the retort have been cooled to the desired temperature the cooling gas stream is shut off, valves 21, 24, 22 and 25 are closed and valves 23 and 26 are opened to a residue receiver (not shown) which was previously purged with a blanketing gas. Hinged grate bars 27 are then lowered as shown by dotted lines in Fig. 1 and the residue drops down out of the retort into the residue receiver. The retort is then ready to be charged again as described above.

The above cycles of operations are essentially the same for the recovery of other volatilizable metals than magnesium except that different temperatures are employed.

Fig. 2 is an illustrative drawing of an apparatus which may be employed to continuously evaporate volatilizable metals in accordance with the method of the invention.

In operation with agglomerated carbothermic magnesium dust in the form of pellets, for example, the gas tight, inert gas filled surge chamber 10 is continuously charged with stock from gas locked feed bins (not shown) through pipe 11. A continuous, gradual movement of the charge stock is maintained downward in rectangular retort tube 12, which is about six times as wide as it is thick. As the charge stock moves into the zone of preheat carrier gas duct 13, it is preheated by a cross-stream of inert preheat carrier gas (having a temperature of about 1250° F.) passing through duct 13 and into cyclone separator 14. In cyclone separator 14, any dust that is picked up from the downward moving charge by the preheat carrier gas is separated from the gas, and recycled through a pelleting or agglomerating station to the feed bins. The preheat carrier gas leaving cyclone separator 14, through pipe 15, may be recirculated as cooling gas in the manner described below.

In its continuous movement through retort tube 12, the preheated charge stock next enters the zone of vaporization carrier gas duct 16, where it is contacted by a cross-current of hot inert vaporization carrier gas having a temperature of 2100 to 2150° F. or more. While passing slowly through the vaporization carrier gas cross-current at the mouth of duct 16, the charge stock is heated sufficiently to cause substantially complete vaporization of the magnesium from the stock into the stream of hot vaporization carrier gas. The magnesium is recovered from the hot vaporization carrier gas stream by passing the stream through a condenser (not shown) wherein the magnesium vapor is condensed to either the liquid or solid state.

From the mouth of duct 16, the hot residue fragments or agglomerates continuously pass to the zone at the mouth of duct 17. Here they give up a substantial portion of their heat content to a cross-current of cooling carrier gas. This cooling carrier gas may be circulated from

cyclone separator outlet pipe 15. After it is heated by the residue it may be passed into preheat carrier gas duct 13.

The cooled residue agglomerates are moved downward continuously through an adjustable discharge mechanism (not shown) and into a residue receiver (not shown) connected to the bottom of retort tube 12.

In similar batch or continuous methods of operation, other volatilizable metals such as sodium, potassium, rubidium, cesium, barium, strontium, calcium and zinc, may be recovered from carbothermic reduction dusts, and the like, and the invention is not intended to be limited to the refinement of metallic magnesium alone. However, it is particularly advantageous in recovering the latter metal since several of the difficulties encountered with magnesium are not encountered with all other readily volatilizable metals.

The process of the invention is not intended to be limited to pelleted carbothermic dust of volatilizable metals, but is applicable to the recovery of volatilizable metals from any agglomerates or fragments composed of volatilizable metals such as zinc, mercury, barium, strontium, calcium, sodium, potassium, rubidium, cesium, magnesium, cadmium, bismuth, arsenic, antimony, radium, selenium, etc., and containing non-volatilizable impurities such as carbon, metal oxides, and other inorganic compounds.

What I claim is:

1. In the method of refining a mixture of a volatilizable metal and less volatile solid impurity, wherein the mixture is heated to a temperature sufficient to vaporize the metal but insufficient to vaporize the impurity, and the metal vapor is separated from the unvaporized impurity, the improvement which comprises: supplying the heat of vaporization of the metal directly to a bed of agglomerates of said mixture by means of a preheated inert gas, by passing a stream of the hot preheated gas through said bed of the mixture at a temperature and at a rate such that the metal exerts a substantial vapor pressure, thereby vaporizing the metal from said mixture into said stream of hot inert gas at a substantial rate by virtue of the heat transferred from the hot preheated gas to the bed of the mixture; and separating the metal from the hot inert gas stream.

2. The improvement of claim 1, wherein said less volatile impurity is composed largely of the oxide of the volatilizable metal and a reducing agent capable of reducing the oxide to the metal at a high temperature, and the temperature of the mixture of inert gas and finely divided solids is well below temperatures at which substantial reduction of the oxide by the reducing agent occurs but is sufficiently high to produce substantial vaporization of the metal.

3. In the method of refining a mixture of magnesium metal and less volatile solid impurity composed largely of magnesium oxide and carbon, wherein the mixture is heated to a temperature sufficient to vaporize the metal but insufficient to vaporize the impurity, and the metal vapor is separated from the unvaporized impurity, the improvement which comprises: supplying the heat of vaporization of the metal directly to a bed of agglomerates of said mixture, by passing a stream of inert gas, preheated to a temperature within the range of about 2015° to 2050° F., through said bed of the mixture at a rate such that the metal exerts a substantial vapor pressure, thereby vaporizing the metal from said mixture into said stream of hot inert gas at a substantial rate by virtue of the heat transferred from the hot preheated gas to the bed of the mixture; and separating the metal from the hot inert gas stream.

4. The improvement of claim 3, wherein said inert gas is hydrogen.

5. The improvement of claim 3, wherein said inert gas is a noble gas.

6. The method of refining a solid mixture of volatilizable metal and less volatile impurity, which comprises establishing a cyclic flow of a gas which is inert with respect to the metal, heating the gas during the course of its flow to a temperature at which the metal exerts a substantial vapor pressure but below the temperatures of substantial vaporization of said impurity, passing a stream of the hot inert gas, after it has been thus preheated, through a bed of agglomerates of said mixture at such a rate to effect substantial heat transfer from the gas to the solids and to effect substantial vaporization of the metal from the solid mixture, then condensing metal vapor from the inert gas and recycling the inert gas.

7. The method of claim 6, wherein the volatilizable metal is an alkali metal.

8. The method of claim 6, wherein the volatilizable metal is an alkaline earth metal.

9. The method of claim 6, wherein the volatilizable metal is zinc.

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The following references are of record in the file of this patent:

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