

Dec. 11, 1945.

E. E. ENSIGN ET AL

2,390,698

MAGNESIUM RETORT

Filed Aug. 12, 1942

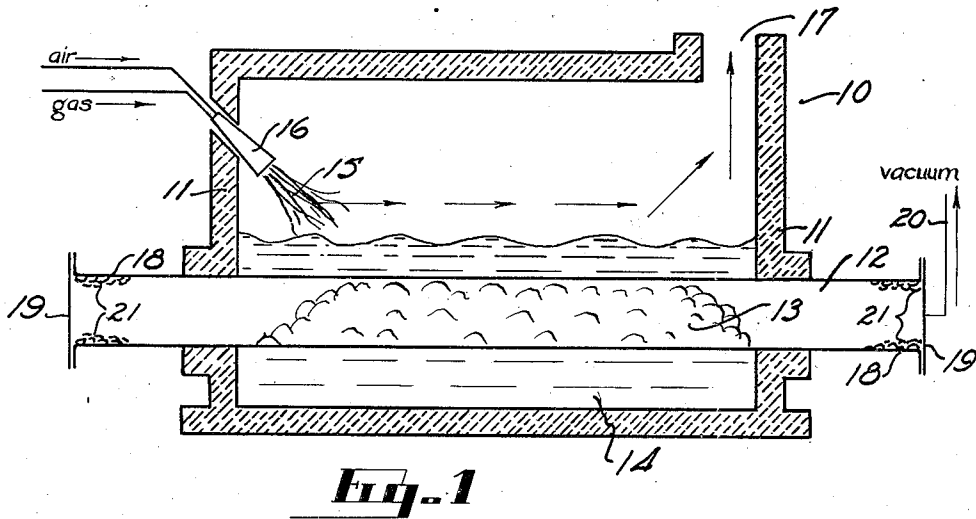
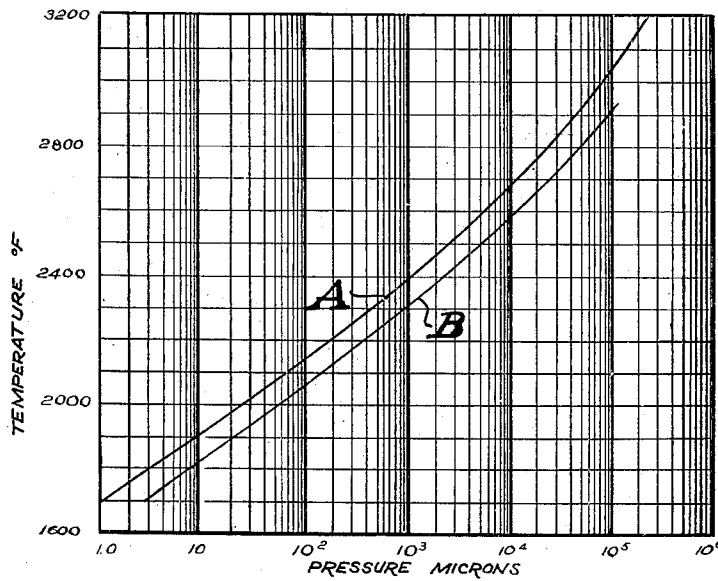
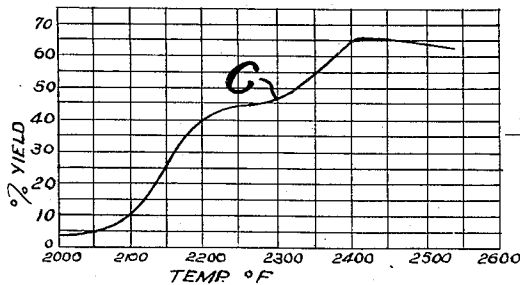


**Fig. 2**

**Fig. 3**

*E. E. Ensign*  
*F. G. Shank*

INVENTORS

BY *Edwin C. McRae*  
*R. G. Harris*  
Attorneys.

## UNITED STATES PATENT OFFICE

2,390,698

## MAGNESIUM RETORT

Elbert E. Ensign, Ypsilanti, and Frank G. Shaub,  
 Detroit, Mich., assignors to Ford Motor Com-  
 pany, Dearborn, Mich., a corporation of Dela-  
 ware

Application August 12, 1942, Serial No. 454,580

5 Claims. (Cl. 266—19)

This invention relates to furnaces or retorts for the production or refining of metals at high temperatures and low pressures, with particular reference to furnaces for the reduction of magnesium ores at high temperatures and low pressures.

The object of this invention is to provide a furnace including a metal retort in which the reduction of magnesium under vacuum can be efficiently and economically performed. Another object of this invention is to provide a method by which retorts of ingot iron or other substantially pure iron normally readily oxidizable in furnace atmospheres may be used and their superior high-temperature strength characteristics utilized. Another object is to devise a furnace in which metal retorts may be maintained at uniform high temperatures without failure occurring from thermal strains, oxidation or loss of strength due to the temperatures prevailing.

The process of producing magnesium directly by the reduction of its ores under subatmospheric pressures has been greatly hampered by a lack of suitable equipment. The reduction of ores, such as magnesium oxide or dolomite, either by carbon or silicon, necessitates the use of temperatures well above 2,000 degrees F. However, present-day techniques have been unable to produce metals suitable for use in retorts able to withstand such temperatures under subatmospheric pressures for the length of time required in the reduction process.

Nichrome alloys so far seem to have the best combined heat and oxidation-resisting properties but even these deteriorate and collapse on continuous heating at temperatures ranging above 2,100 degrees F. in a comparatively short time. In fact the life of a retort at 2,400 degrees F. is rarely more than several hours. Since the practical, direct reduction of magnesium is limited only by the restrictions imposed by available retort materials, the importance of this invention may readily be realized. The advantages, too, are directly reflected in the cost of operation of the process, in which, heretofore, retort cost has been a major item.

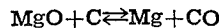
With these and other objects in view, the invention consists of the arrangement, construction and combination of the various parts of the improved device and the steps of the method disclosed, as described in the specification, claimed in the claims, and illustrated in the accompanying drawing in which:

Figure 1 is a diagrammatic view of a molten bath furnace, following this invention.

Figure 2 is a temperature-pressure chart computed for the reduction of magnesium oxide by carbon under vacuum, but illustrative, generally, of the thermal reduction process.

Figure 3 is a curve that shows the actual temperature and yield relationship in the reduction of magnesium oxide by ferrosilicon under pressures in the range 50–150 microns.

At this point, reference is made to Figure 2, which shows the computed temperature-pressure equilibrium equation obtained in the magnesium oxide carbon reaction in which



although it will be subject to variation when other substances such as  $\text{N}_2$ ,  $\text{H}_2$  or  $\text{CO}_2$  are present. Of course, specific values will differ when other materials are used in the presence of other gases, but the general conditions remain the same and the curves may be taken as indicative, generally, of the thermal reduction process. Curve A shows the equilibrium condition and is expressed in partial pressure of magnesium vapor against temperature. It may be shown that the partial pressure of the carbon monoxide must equal the vapor pressure of Mg, and accordingly curve B represents the permissive total pressure obtained in the system for equilibrium conditions if no other gases are present.

Therefore, at all points above the curve B, it will be seen that at least some magnesium will be disassociated and present as a gas. Moreover, it is seen that if magnesium vapors are to be had at very low temperatures, pressure must be extremely low—that is, in order to obtain magnesium vapors at 2,000 degrees F., pressures not to exceed 20 microns must be maintained. Thus far, in commercial production, it has been very difficult to maintain these low pressures and practical operation, therefore, must be carried on at temperatures well above the minimum range. However, it is apparent that if retort equipment could stand higher temperatures, say around 2,400 degrees F., the present-day, low-pressure equipment would be more than adequate. In this invention, the reduction of magnesium ores at temperatures of about 2,400 degrees F. is accomplished and the life of the retort actually lengthened which makes this type of extraction economically and practically feasible.

The curve in Figure 3 shows the percentage yield against temperature relationship in the reduction of a dolomitic ore by ferrosilicon.

curve shows that with each increment in temperature the actual yield expressed in percentage of the yield theoretically obtainable correspondingly increases. Increase in temperature is not directly reflected in a proportional increase in yield, since the curve is not a straight line although the exact reason is not yet clear. The yield is approximately constant and the curve follows a plateau between 2,000 and 2,100 degrees F., but the next increase of 100 degrees in temperature shows a sharp rise in yield. Again, between 2,200 and 2,300 degrees the yield is constant but then rises sharply within the next 100 degrees and again levels off to another plateau. Curve C was obtained by running numerous tests on a briquetted, dolomitic, ferrosilicon mixture and varying the temperatures while maintaining the pressure relatively constant at from 50-150 microns.

These theoretical considerations clearly show the necessity for operation at temperatures in excess of 2,100 degrees F. and pressures not to exceed 100 microns. Other data, not detailed here, show that yield is also a function of time of reaction which may vary from two to seventy-two hours. Equating these, it will be observed that the conditions for maximum yield are mutually antagonistic to the conditions for retort life which requires temperatures not to exceed 2,000 degrees F. at the stated vacuum and minimum time of exposure to high temperature. Other considerations such as chemical deterioration of the retort metal and physical deformation due to unequal heating or intermittent operation must be considered as well. All these factors must be reconciled if a proper retort is to be obtained. Experience has shown that present constructions employing a tubular or other shaped retort heated externally by flame or radiation or internally by resistance means or any of the other variations proposed will not suffice.

Referring to Figure 1, the retort constructed according to this invention is shown schematically. Essentially this consists of a furnace 10 having at least its lower portion constructed of fluid-tight refractory material. Extending through opposite walls 11 of the furnace is a metallic tubular retort 12 preferably made of a substantially pure iron, such as ingot iron, to avoid eutectic combinations which would lessen high-temperature strengths in which is placed the charge indicated as 13. The retort 12 is submerged in a molten bath 14 of a material which remains molten in the reaction range as, for example, sodium silicate, barium chloride or calcium chloride which are fluid between 1,900 and 2,800 degrees F. The bath 14 is shown as heated directly by a gas flame 15 which is directed on it by a jet 16 which may be of the type used in glass furnaces. However, other means of heating the bath may be employed such as submerged glow bars, regenerative or recuperative furnaces, electrical conduction through the bath or other commonly used industrial heat sources. A stack 17 is provided to remove the products of combustion from the chamber of the furnace.

It will be noted that the retort 12 has ends 18 extending a considerable distance outside of the walls 11 and these are tightly sealed by covers 19. A vacuum connection 20 is provided on at least one end 18 (it may be applied to both) and means 22 to admit nitrogen or other inert substance when the tube is open. The ends 18 are normally cool and the gaseous magnesium formed by the thermal reaction of the charge

13 flows to these end surfaces and condenses thereon in the form of reguline magnesium 21. As a practical matter, if the walls 11 are of appreciable thickness, the retort 12 need not make close contact with them. The bath material will flow through any aperture at that point but will freeze as the wall temperature lowers adjacent the outer surface, forming an efficient seal. This may be aided by providing a slightly elongated sleeve in the wall and fitting the retort in it with a moderate clearance.

In operation, the bath 14 is brought to the desired temperature of from 2,200 to 2,500 degrees F. The covers 19 are removed to permit the placing of the charge 13, replaced, and the interior of the retort evacuated. Obviously, the molten bath has a high specific heat so that the retort is not appreciably lowered in temperature by the introduction of the charge. Moreover, the fluid has uniform contact with the entire portion of the retort inside the furnace; and as the fluid temperature is substantially uniform throughout or, under most extreme conditions, has a uniform gradient, so will be the temperature to which the retort is exposed. Finally, the contact between a fluid and metal is far superior from the standpoint of heat transfer to the gas-metal obtaining in prior furnaces.

It will therefore be found that due to the uniformity of heating condition and speed of heat transfer, the time of reaction is considerably reduced. Further, the same uniformity of temperature coupled with the uniformity of pressure exerted on the retort by the fluid in which it is immersed increases the effective retort life markedly. Still another advantage is that the protective character of the bath permits the use of ingot iron as a retort material which is less expensive and has a higher melting point and better heat-strength characteristics than any of the alloys previously used, but which could not withstand the usual furnace atmosphere. This is not limited to high-purity iron, however, for the usual retort metals may be used if desired with greatly improved life attributable mainly to the fluid immersion.

While sodium silicate has been found very suitable as a bath, salts and other stable materials in the desired range may be used. Whatever may be the thermal insulating qualities of these materials in the solid state, they are found to be very good heat conductors when fluid. In using the silicate bath, the high temperature appears to reduce the sodium content leaving a silica having a much higher melting point. This can be controlled and the fluidity maintained by addition of a sodium compound such as sodium carbonate or a like related material. The depth of the bath should be adequate, of course, to cover the retort and the volume should be sufficient to provide the heat content necessary for the maintenance of substantially uniform temperatures throughout the bath. The bath should be substantially pure—or at least should not include substances such as sulphur or phosphorus which might react with the retort metal forming an eutectic having a lower melting point with consequent deterioration of the retort under heat. By using substantially pure iron having, as example, the following composition:

|    |       |                     |
|----|-------|---------------------|
| C  | ----- | .01%                |
| P  | ----- | .005%               |
| S  | ----- | .025%               |
| Mn | ----- | .015                |
| FE | ----- | Substantial balance |

and heating the retort made therefrom in the medium of a molten bath, the reasonable life expectancy of the retort will be measured in months. Experiments with the best heat-resistant alloys available in the conventional furnace show, at best, a useful life of 15 to 20 days. And this saving is actually accompanied by a reduction in reaction time.

A further advantage is that the weight of tube and charge may be proportioned to the volumetric displacement in the bath so that the tube and charge, in effect, float in it. Thus, at the high reaction temperature obtaining, the tube may float in the bath and be free from structural supporting stresses. On the other hand, at unloading and loading the temperatures are somewhat lower and the strength of the retort material correspondingly higher so that it will better withstand the flotation forces.

Another advantage is that provision may be made to protect the interior of the tube as well. Thus, while the interior is under vacuum during the reaction and hence will not oxidize, during loading and unloading it is open to the atmosphere and, of course, still at very high temperatures. To deal with this condition, the interior of the tube may be coated with a thin nonoxidizable coating of nichrome or the like, or it may be given one of a number of other available surface treatments which will retard oxidation. As an alternative, an inert atmosphere such as nitrogen may be maintained in the tube when it is opened to reduce oxidation.

It is believed that the foregoing clearly shows the advantages inherent in this method and apparatus. Longer life from retorts made of less costly materials, greatly reduced operating time, increased safety, larger yields—these and others are the advantages which accrue.

Some changes may be made in the arrangement, construction and combination of the several parts comprising the improved device without departing from the spirit of the invention, and it is the intention to cover by the claims such changes as may reasonably be included within the scope thereof.

The invention claimed is:

1. In a reaction furnace, an enclosure, a metal retort tube supported within said enclosure and having a portion extending therefrom, a bath in said enclosure submerging said tube, said bath comprising molten sodium silicate, and means to

heat said bath to the reaction temperature, said tube being formed of substantially pure iron.

2. In a reaction furnace, an enclosure having oppositely disposed walls and constructed of refractory materials, a tubular retort formed of substantially pure iron normally readily oxidizable at the reaction temperatures supported on said walls extending through said enclosure and having a portion extending therefrom, said portion in said enclosure serving as a reaction chamber, said extending portion serving as a condensing chamber for the product of said reaction; a closure at the end of said retort, means to evacuate the interior of said retort, a bath in said enclosure in contact with the reaction portion of said retort and comprising molten sodium silicate substantially nonreactive with said retort material, and means to control oxidation of the interior of the retort by establishing a nitrogen atmosphere therein operable when said closure is removed.

3. The method of prolonging the effective life of substantially pure iron retorts subjected to reaction conditions which include low-internal pressures and temperatures in excess of 2,000 degrees Fahrenheit which comprises the steps of submerging said retort in a bath of molten sodium silicate, heating said bath to the reaction temperature, the volumetric displacement of said retort being proportioned to the weight of said retort and the included charge to minimize the structural stresses on said retort.

4. The method of surface protection of substantially pure iron tube retorts which are characterized by high strengths at temperatures in excess of 2,000 degrees Fahrenheit and low resistance to surface oxidation in oxidizing atmospheres at such temperatures which comprises the steps of submerging the exteriors of said tubes into molten sodium silicate, heating said sodium silicate to the desired temperature, and periodically treating said bath to prevent the formation of higher melting point silicas.

5. The method of protecting the inner and outer surfaces of substantially pure iron tubular retorts under high temperature, which comprises the steps of maintaining molten sodium silicate on the exterior of the tube and a nonoxidizing gaseous atmosphere in the interior of said tube.

ELBERT E. ENSIGN.  
FRANK G. SHAUB.