

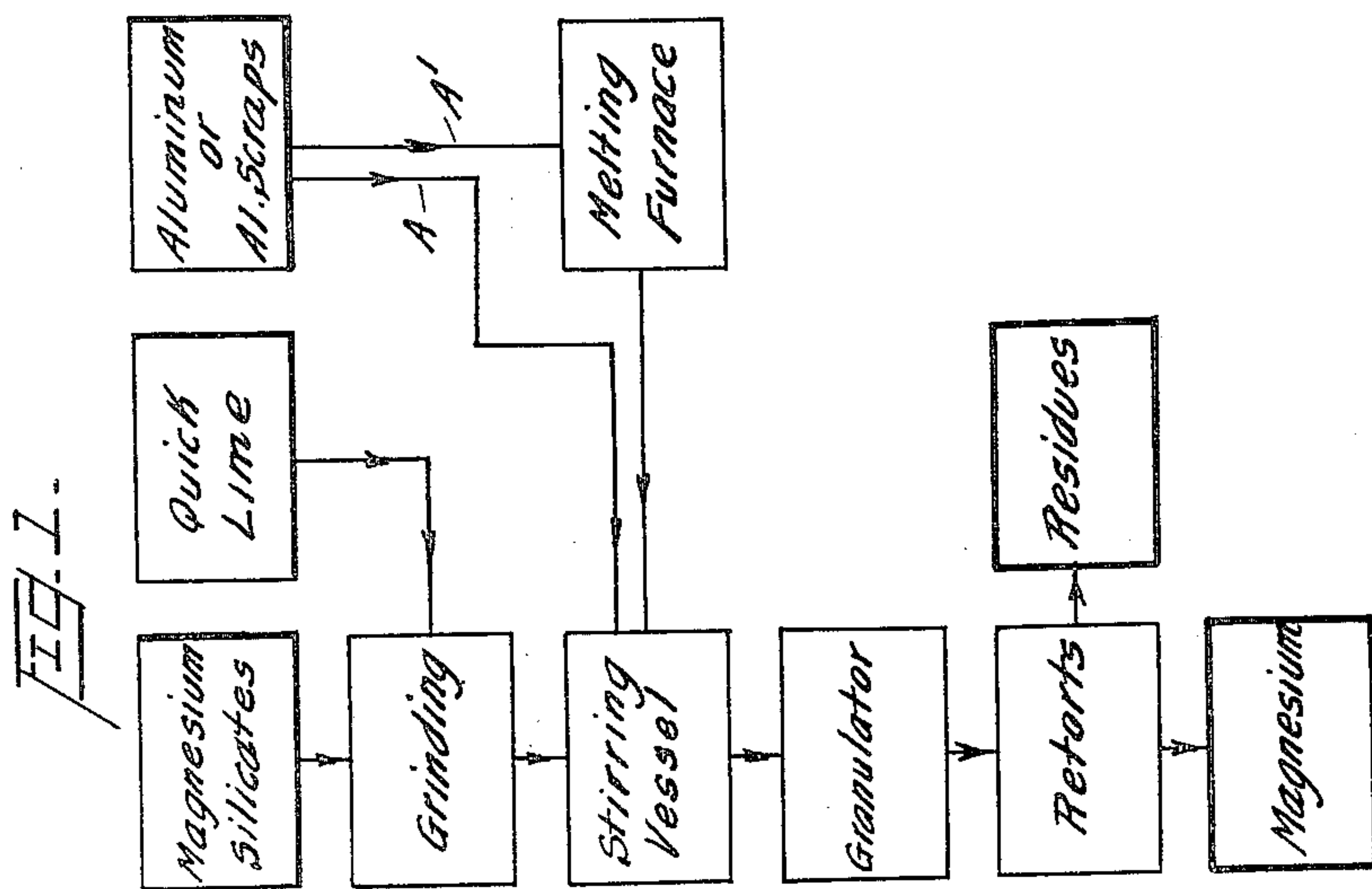
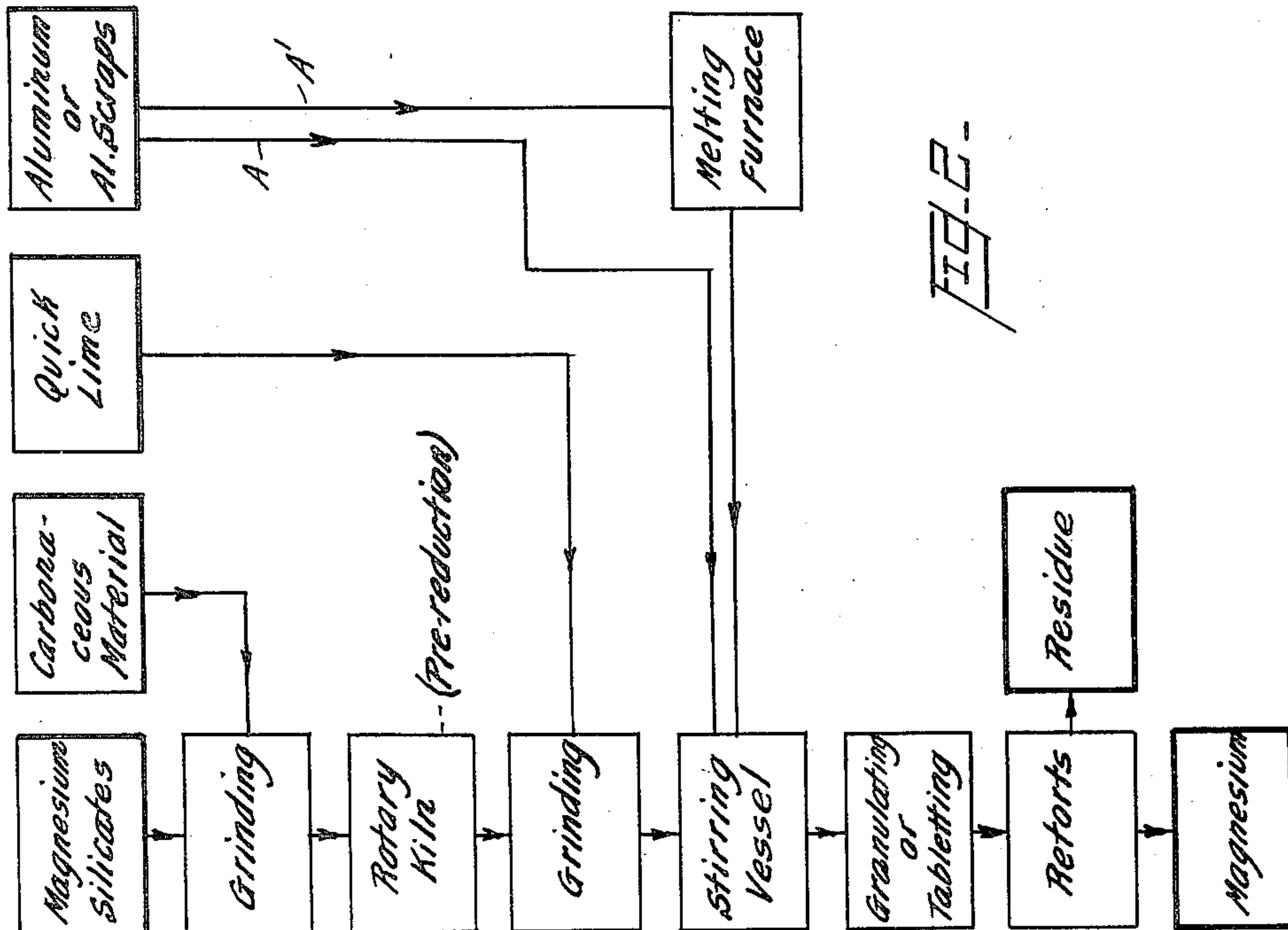
Oct. 31, 1950

F. J. HANSGIRG  
PRODUCTION OF MAGNESIUM

2,527,722

Filed May 27, 1946

2 Sheets-Sheet 1



Inventor

F. J. Hansgirk

By Watson, Cole, Grindle & Watson  
Attorneys

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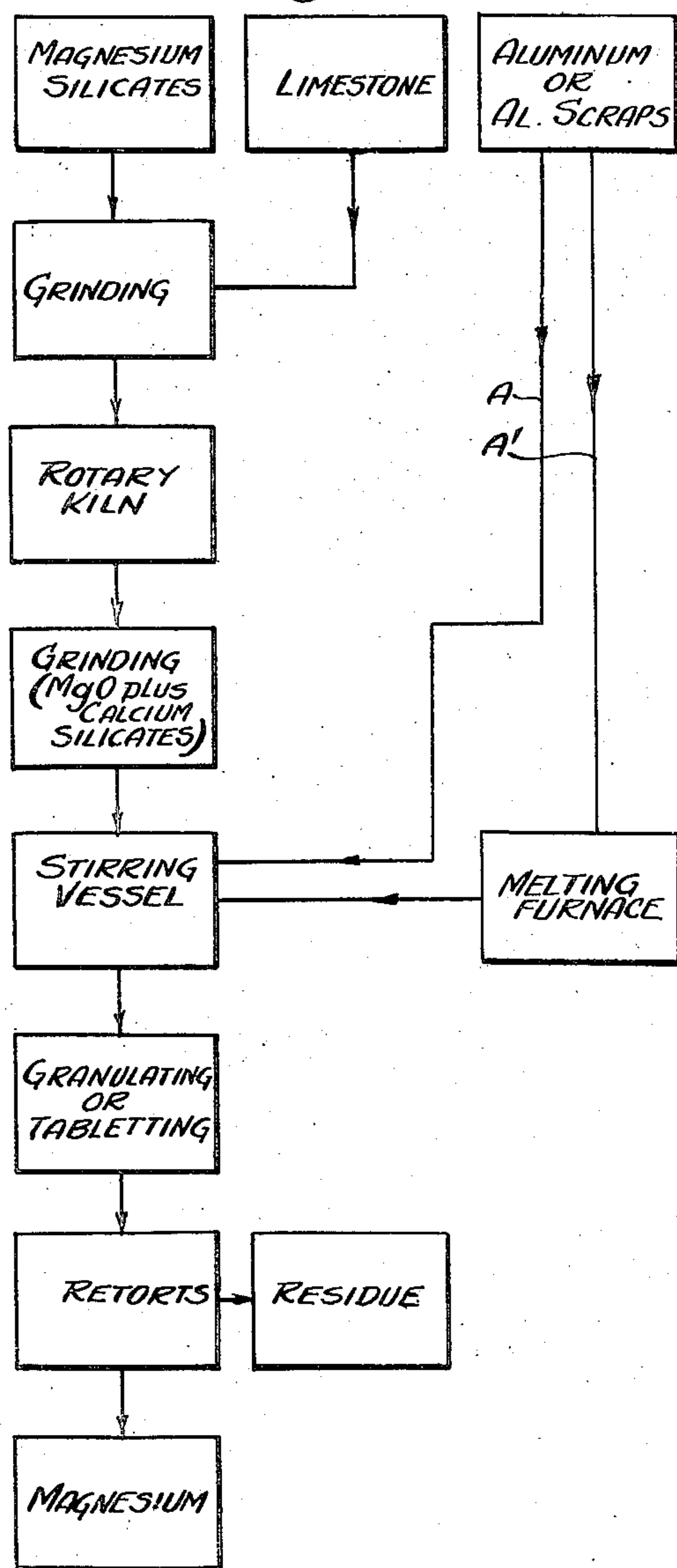
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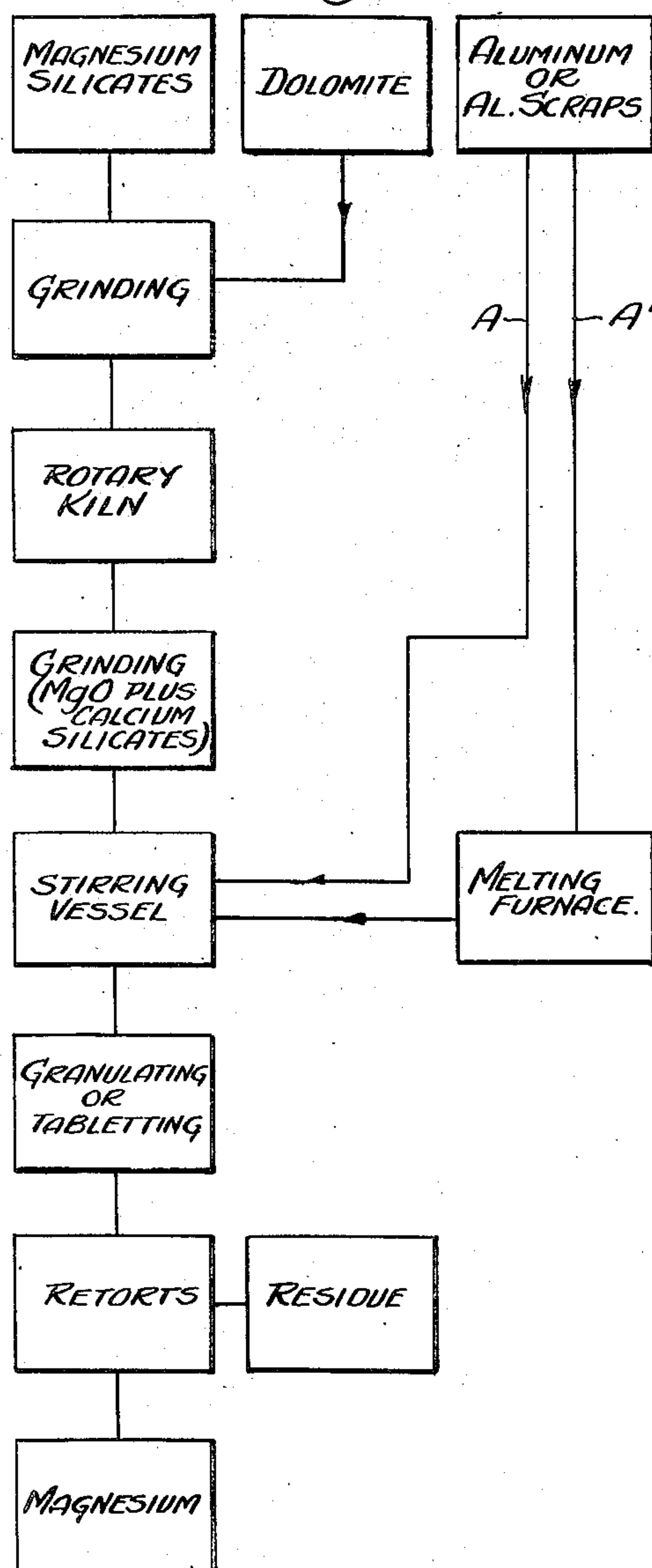
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2 Sheets-Sheet 2

*Fig. 3.*



*Fig. 3a.*



Inventor

*Fritz J. Hansgirk*

*By Watson, Cole, Grindler & Watson*  
Attorneys



## UNITED STATES PATENT OFFICE

2,527,722

## PRODUCTION OF MAGNESIUM

Fritz J. Hansgig, Black Mountain, N. C., assignor  
to North Carolina Magnesium Development  
Corporation, Asheville, N. C., a corporation of  
North Carolina

Application May 27, 1946, Serial No. 672,531

4 Claims. (Cl. 75—67)

1

This invention relates to the production of metallic magnesium, and has for its general object the provision of novel processes for recovering the metal by reduction from magnesium silicates and related materials.

In my United States Patents Nos. 2,372,571 and 2,379,576, I have described processes for producing metallic magnesium from magnesium silicates either by reduction with calcium carbide or by processes involving a pre-reduction step consisting of reducing the silica contained in the magnesium silicates to silicon by the use of carbon, and this without attacking the magnesium oxide in any considerable degree. These processes also include the subsequent step of employing the silicon thus formed as a reducing agent to effect the evaporation of magnesium vapors from the materials at elevated temperatures and in vacuum.

The present invention contemplates a process in which aluminum is employed as a reducing agent in connection with magnesium silicates. It has already been proposed to use aluminum as a reducing agent for magnesium oxide either alone or in combination with metallic silicon or even alloys of aluminum and silicon containing iron. In all of these prior processes, either the aluminum, the aluminum and silicon, or the aluminum and ferro-silicon alloys are crushed and ground to a fine powder, and such powder is admixed with the magnesium oxide and the mixture briquetted. Magnesium is evaporated from the briquets at elevated temperatures and either at atmospheric pressure or in vacuum. In general, such processes are not economical since aluminum is a quite expensive material and the processes of bringing the aluminum and the aluminum alloys into a powdered condition adds additional expense.

The present invention, in its preferred embodiment contemplates the reduction of magnesium silicates, which presents different problems from those encountered in the reduction of magnesium oxides. Another feature of novelty of the invention is the preforming of calcium silicates and magnesium silicates and magnesium oxide in the magnesium silicate ore, before the aluminum is added, and then effecting the main reduction.

Another novel feature of the invention is the effective combination of reduction by aluminum with the pre-reduction with carbon as described as a preliminary step in my Patent No. 2,379,576; but in this case the amount of carbon

2

used is below that which would be necessary to reduce all of the silica.

Within the broad scope of the present invention, the aluminum may be introduced in solid or liquid form and mixed with the powdered ore either by stirring vigorously or by injection into a suspension of the powdered ore in an air or gas stream.

When solid aluminum is used it is intended to be in the same form as described in my co-pending application, Serial No. 672,812, filed May 28, 1946.

Other objects and features of novelty will be apparent from the following specification when read in connection with the accompanying drawings in which certain embodiments of the invention are illustrated and diagrammed, by way of example.

In the drawings,  
Figure 1 is a flow chart illustrating a process in which the magnesium silicate ore is ground with lime and then the molten aluminum stirred in;

Figure 2 is a flow chart showing the steps in a modified process involving a pre-reduction phase;

Figure 3 is a flow chart outlining a process in which the lime and the silicates are treated at elevated temperatures in a rotary kiln to form mixtures of magnesium oxide and calcium silicate, before the injection of the aluminum; and

Figure 3A is a flow chart describing a process in which olivines or other magnesium silicates, and dolomite are treated together.

In one process within the scope of the present invention, the ores used are magnesium silicates, for example, olivine, serpentine, or similar materials. These silicates are ground to a fine powder of 200 mesh or less, and this powder is heated to a temperature slightly above the melting point of aluminum, but below the temperature at which the aluminum starts to react upon the charge. Into this powder, the necessary amount of aluminum is charged either in solid or liquid form, and the whole mass is stirred vigorously in order to coat the particles of the mineral powder thoroughly with a thin layer of aluminum.

After this coating process is completed, the mass is charged into a rotating drum where it is cooled below the melting point of aluminum and the resulting granulated mass is discharged from the end of the drum. This granulated mass of material is then charged hot into a retort and pure magnesium vapor is evolved at elevated

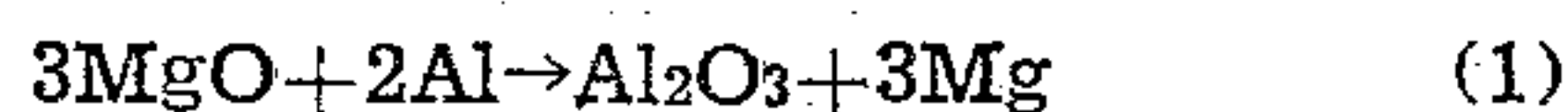


3

temperatures and under vacuum conditions, the vapors being condensed in the usual well known manner. As a residue, an aluminum silicate is formed.

The above process becomes particularly economical if scrap aluminum is used as the reducing agent. The great consumption of aluminum during the war, and also after the war, has resulted in a huge supply of scrap aluminum, which is very difficult to use again as primary aluminum alloy. A great amount of labor is necessary in order to separate the aluminum from other metals such as steel, copper, zinc, and magnesium. Those skilled in the art know that the composition of aluminum alloys must be carefully controlled if they are to show valuable mechanical properties. Therefore secondary aluminum as recovered from scrap is a very inferior material for structural or industrial use, if the selection of the scrap has not been made very carefully. For use in magnesium reduction as in the present invention, aluminum scrap even in an impure form can be used without any adverse influences on the operation of the process, so that any tedious selection of material can be avoided. Any scrap metal available on the market can be directly used in this method.

The reduction of magnesium oxide with aluminum proceeds according to the equation,



But in the present case in which magnesium silicates are used, which generally contain magnesium oxide and silica in the ratio of between  $2\text{MgOSiO}_2$  to  $\text{MgOSiO}_2$  and it is then necessary to balance the equation in such a way that certain aluminum silicates are formed as residues. For example, if olivines low in iron are taken as a starting material, then the reaction proceeds according to the equation,



In this case the ratio of alumina to silica in the residue is 2:3. Such aluminum silicates have a very high melting point and at the reaction temperature and in vacuum, all partners of the reaction remain in the solid state.

The yields can be greatly improved if lime is added to the mixture, since in this case, ternary compounds of alumina, silica, and calcium oxide are formed. By the addition of lime, it is possible to lower the melting point of the residue to temperatures of between  $1300^\circ\text{C}$ . and  $1400^\circ\text{C}$ ., which means that at the reaction temperature of between  $1000^\circ\text{C}$ . and  $1200^\circ\text{C}$ ., there already occurs some sintering between the alumina, silica, and lime. This sintering process has two advantages, first the granulated mass formed during the first step of the process, in which finely ground magnesium silicates are treated with molten aluminum shrinks during the evaporation of the magnesium; and second, the granular mass becomes so much more dense which insures the reaction going to completion, and greatly promotes the evolution of pure dust-free magnesium vapors.

In connection with the processes now being described, reference is made to the chart in Figure 1 of the drawings. In this figure and in Figures 2 and 3, the reference characters A and A' represent alternative paths pursued, depending upon whether the aluminum is mixed in in molten form or not.

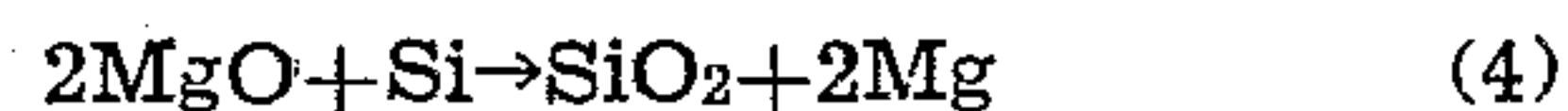
However, the formation of a residue of a lower melting point, is not the only reason for the ad-

4

dition of the lime. If magnesium silicates are heated with aluminum it is not possible to prevent giving rise to a side reaction. Silicon dioxide ( $\text{SiO}_2$ ) reacts with aluminum according to the equation,



This silicon can later react with the magnesium oxide according to the equation,



It is of no consequence to the reduction capacity of the added aluminum, in the ultimate result, if the aluminum first reduces the silica to silicon, and this silicon (or ferrosilicon if iron is present) later reacts with magnesium vapors. But the reaction between magnesium oxide and silicon remains incomplete if the necessary amount of lime is not added. To what extent the aluminum reacts directly with magnesium oxide according to Equation 2, or indirectly according to Equations 3 and 4 depends upon the temperature of the reaction. When added to magnesium silicates, aluminum already starts to react with considerable speed at a temperature of  $850^\circ\text{C}$ ., and at such temperature about half reacts directly with the magnesium oxide contained in the silicates. The other half is used up by the silica to form silicon or ferrosilicon and silicon monoxide.

It is therefore possible to conduct the reduction of magnesium silicates with aluminum in two steps. First, at a temperature of between  $850^\circ\text{C}$ . and  $950^\circ\text{C}$ ., about half of the magnesium contained in the ore can be recovered. Then the temperature has to be raised to from  $1100^\circ\text{C}$ . to  $1150^\circ\text{C}$ . at which the other half of the magnesium contained in the ore is recovered. But the second half of the magnesium, based on the reduction with silicon according to Equation 4, can only be recovered with a high yield, if lime is present. In this two-step process, initially the necessary amount of aluminum is added to the magnesium silicates to reduce the magnesium oxide in the silicates without an addition of lime. This mass is then charged into retorts and about fifty per cent of the magnesium contained in the silicate is recovered at a temperature of between  $850^\circ\text{C}$ . and  $950^\circ\text{C}$ . To the residue from this reaction, the necessary amount of lime is added, and in the second step, the other half of the magnesium is recovered at temperatures from between  $1050^\circ\text{C}$ . and  $1150^\circ\text{C}$ .

The recovery factor in each separation is about eleven per cent magnesium from the charge, which is similar to the results of the ferrosilicon-dolomite reduction. The great advantage in this case, resides in the fact that in about half of the plant the retorts can be operated at from  $850^\circ\text{C}$ . to  $900^\circ\text{C}$ . which greatly prolongs the life of the retorts.

It is also possible to carry on the process in one step, by immediately adding the necessary amount of lime to the mixture of magnesium silicates and aluminum, and to carry on the reduction at from  $1050^\circ\text{C}$ . to  $1150^\circ\text{C}$ ., and recover the magnesium simultaneously from both reduction reactions.

I have found that, in reducing magnesium silicates with aluminum, it is of great advantage to put the magnesium silicates through a pre-reduction step; and this comprises another embodiment of the invention. In this connection, reference is made to the flow chart in Figure 2 of the drawings. Olivines and serpentines con-



tain iron oxide and water in varying amounts and both these compounds would react with aluminum and diminish the reducing agent available for the magnesium oxide reduction. Consequently, according to a preferred embodiment of the invention, olivines or serpentines are mixed with carbonaceous material in a quantity sufficient to reduce all of the iron oxide and the water to metallic iron and hydrogen and carbon monoxide, respectively. To this pre-reduced ore, the molten aluminum is then admixed as previously described.

It is also possible to combine the reduction by aluminum with the reduction by silicon described in my Patent Number 2,379,576. However, unlike the procedure in the patented process, the magnesium silicates are first treated with less carbon than is necessary to produce the amount of silicon needed for the reduction of the total magnesium oxide content of the magnesium silicates. In this case the pre-reduction step can be carried out at a lower temperature, and the amount of magnesium oxide which is attacked during the pre-reduction step is reduced practically to zero. Such pre-reduction material, consisting of magnesium oxide, unreacted silica, and ferrosilicon is then treated with aluminum to form a reaction mixture in which the silicon and the aluminum together act as reducing agents, at the same time forming a residue again consisting of silica and alumina.

For the purpose of obtaining a better reaction, calcined lime may be added. Also, in pursuing this combined method, the charge should preferably be composed in such a way that in the residue the ratio of alumina to silica to lime falls between the ratios 2:3:3 and 2:3:6.

If the pre-reduction of magnesium silicates with carbonaceous material is carried on with such amounts of carbon that an incomplete reduction of the silica takes place, the carbon is reacted completely and the pre-reduced material does not contain any more free carbon. This is of great advantage, as in the later reduction reaction when the magnesium vapors are liberated in vacuum, a side reaction between any surplus carbon and the silica formed can be avoided.

Silica under the conditions of high vacuum and temperatures between 1100° C. and 1150° C. in reacting with carbon evolves carbon monoxide along with the magnesium vapors, and this interferes with the proper crystallization of the condensed magnesium. Therefore, the combined processes afford a great improvement in the quality of the condensed magnesium, by first reducing the magnesium silicates with carbon to partly provide the necessary silicon for the magnesium reduction, and later adding aluminum in such amounts as to furnish enough reducing agent to reduce the total magnesium oxide content of the charge.

As in all reductions of magnesium silicates, in case silicon and ferrosilicon are formed, it is necessary to produce as a final end product of reaction (in addition to the magnesium) calcium silicates, either  $\text{CaSiO}_3$  or  $\text{Ca}_2\text{SiO}_4$ . By certain of the methods provided by the present invention, it is possible to treat magnesium silicates with lime or dolomite at elevated temperatures to break up the magnesium silicates and to form mixtures of magnesium oxide and calcium silicate, and then add the reducing agent. See the flow charts in Figures 3 and 3A of the drawings.

In carrying out this process, the magnesium silicates are ground together with quicklime,

limestone, or dolomite (either raw stone or calcined) to a powdered mixture, and charged into a rotary kiln. In case raw limestone or raw dolomite is used, they should preferably be added in the form of a wet slurry. At the same time carbonaceous material may be added to reduce the iron and other heavy oxides contained in the magnesium silicates.

The mixture is heated to a temperature of approximately 1650° C., at which temperature the calcium oxide formed by driving out the carbon dioxide from the limestone or dolomite, reacts with the magnesium silicate to form calcium silicate and free magnesium oxide. The use of dolomite is especially economical as additional magnesium oxide is introduced into the mixture so that in the latter retort process the specific recovery of magnesium from the reaction mixture is very considerably improved.

To such preformed magnesium silicate, at temperatures just above the melting point of aluminum but below the temperature at which the aluminum starts to react upon the charge, the necessary amount of aluminum or scrap aluminum is thoroughly distributed throughout the mass of ore as described before. The granulated mass is then charged into retorts, and at elevated temperatures and under high vacuum, the magnesium is recovered in the vapor state.

The following examples illustrate the procedures described above in connection with the present invention.

(1) As the starting material, an olivine containing 48%  $\text{MgO}$ , 8.5%  $\text{FeO}$ , and 43%  $\text{SiO}_2$ , is used. One hundred parts of this olivine material are treated with three parts of carbonaceous material containing 85% fixed carbon, as a pre-reduction step. To one hundred parts of the pre-reduced material and forty parts of calcined lime, twenty-five parts of aluminum are added and thoroughly mixed and granulated at a temperature of from 670° C. to 680° C. The granulated mass is then charged in the conventional way into a retort, and the magnesium evaporated under high vacuum at temperatures from between 1050° C. and 1150° C. From this mixture, twenty-five parts of metallic magnesium are produced, and a residue formed wherein the ratio of alumina to silica to lime corresponds to about 2:3:4.

(2) To one hundred parts of olivine pre-treated as described in Example 1, from twenty-five to twenty-seven parts of aluminum scrap are added and the mass intimately mixed at a temperature of from 670° C. to 680° C. The mass is granulated and charged into retorts and treated under high vacuum at a temperature of from 850° C. to 950° C. About twelve to thirteen parts of magnesium are recovered. The residue is ground and mixed with forty parts of calcined lime, tabletted and charged into retorts maintained at from 1050° C. to 1150° C., and an additional twelve to thirteen parts of magnesium recovered.

(3) One hundred parts of olivine of the above mentioned composition are ground, mixed, or tabletted with fifteen parts of carbonaceous material containing 85% fixed carbon. This material is subjected to pre-reduction at a temperature of between 1400° C. and 1600° C., the optimum temperature range being from 1500° C. to 1620° C. The silica in the olivine is partly reduced to ferrosilicon. To one hundred parts of this pre-reduced material, sixteen parts of aluminum are added together with forty-five parts of lime. The material is granulated at temperatures of



between 670° C. and 680° C., briquetted and charged in the usual way into retorts which are heated to temperatures of between 1050° C. and 1150° C. under high vacuum conditions. Magnesium vapors are evolved and condensed, and the recovery is between twenty-five to thirty parts magnesium.

(4) One hundred parts of olivine and from one hundred forty-five to one hundred fifty parts of limestone are ground together to form an intimate mixture, and such mixture is charged into a rotary kiln and brought to a temperature of between 1500° C. and 1650° C. The granular mass so produced is again ground and twenty-five parts of aluminum added, the mass being intimately mixed at temperatures of from 670° C. to 680° C. The mixture is granulated and charged into retorts and treated at high vacuum and at a temperature of between 850° C. and 1150° C., giving a recovery of from twenty-six to twenty-seven parts of metallic magnesium.

(5) One hundred parts of olivine and from two hundred sixty to two hundred seventy parts of dolomite are ground together to form an intimate mixture, and such mixture is charged into a rotary kiln and brought to a temperature of between 1500° C. and 1650° C. The granular mass so produced is again ground and fifty-five parts of aluminum added, the mass being intimately mixed at a temperature between 670° C. and 680° C. The mixture is granulated or briquetted, charged into retorts, and treated under high vacuum at a temperature of between 850° C. and 1150° C., giving a recovery of from fifty-eight to sixty parts of metallic magnesium. It will be noted that the relative recovery from the charge in this case rises to between 20% and 21% magnesium, as against 13% to 15% of magnesium in the case of the addition of lime alone.

It was also found that all of the reactions described above under Examples 1 to 5 inclusive, can be accelerated and the yield improved if there is added to the reaction mixture from between 1% to 10% of calcium fluoride or aluminum fluoride.

Various changes and modifications may be made in the embodiments of the invention illustrated and described herein without departing from the scope of the invention as defined by the following claims.

It will be understood that when magnesium silicate is mentioned in the claims, the compound referred to may include magnesium silicate in a relatively pure form or an ore containing various amounts of iron oxide and other heavy metal oxides and the like.

Also, the term "aluminum" as used in the claims in defining the chief reducing agent, may designate either pure aluminum or aluminum alloys such as may be found in the wide varieties of aluminum scrap now on the market.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A process for producing metallic magnesium from magnesium silicate, which comprises grinding together a quantity of magnesium silicate and dolomite, heating the resulting mixture at a temperature of from about 1400° C. to about 1650° C., grinding the mass thus produced and then mixing in a quantity of aluminum of larger than granular size and thicker than foil, at a temperature just above the melting point of aluminum but below the temperature at which the aluminum starts to react upon the charge, then heating the resulting mixture in a retort under high vacuum and at a temperature of from about 850° C. to about 1150° C. to evaporate metallic magnesium therefrom.

2. A process for producing metallic magnesium from magnesium silicate, which comprises grinding together a quantity of magnesium silicate and a lime-supplying material, heating the resulting mixture at a temperature of from about 1400° C. to about 1500° C., grinding the mass thus produced and then mixing in a quantity of aluminum of larger than granular size and thicker than foil, at a temperature just above the melting point of aluminum but below the temperature at which the aluminum starts to react upon the charge, then heating the resulting mixture in a retort under high vacuum and at a temperature of from about 850° C. to about 1150° C. to evaporate metallic magnesium therefrom.

3. The process according to claim 2 in which the lime-supplying material is calcined lime itself.

4. The process according to claim 2, in which the lime-supplying material is limestone.

FRITZ J. HANSGIRG.

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