United States Patent [19]

Svensson

[11] **3,929,463**

[45] **Dec. 30, 1975**

[54] **METHOD OF CARRYING OUT ENDOTHERMIC METALLURGICAL REDUCTION PROCESSES WITH THE AID OF A CONTINUOUSLY OPERATING MECHANICAL KILN**

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[22] Filed: **Jan. 4, 1974**

[21] Appl. No.: **430,620**

[30] **Foreign Application Priority Data**

Jan. 9, 1973 Sweden 73002404

Jan. 9, 1973 Sweden 73002412

[52] **U.S. Cl.** **75/37;** 75/72; 75/63; 75/82; 75/89; 75/90; 241/23; 241/26; 266/18; 432/93

[51] **Int. Cl.**[2] **C21B 13/00; C22B** 15/00; C22B 23/00

[58] **Field of Search** .... 75/72, 63, 89, 90 R, 82, 75/37; 266/18, 37; 241/18, 22, 23, 26; 432/93, 247

[56] **References Cited**

UNITED STATES PATENTS

799,189	9/1905	Reynolds	75/37
987,850	3/1911	Braddock	241/18
2,132,149	10/1938	Edwin	75/89
2,235,154	3/1941	Jones	75/37
2,462,900	3/1949	Riott	75/90 R
3,113,859	12/1963	Moklebust	75/90 R
3,206,300	9/1965	Udy et al.	75/90 R

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[57] **ABSTRACT**

Continuous endothermic reduction of oxidic compounds of nickel is carried out in a space inaccessible to air and at a rate of speed below critical speed, the reactants being subjected to mechanical work generating the heat required for the reaction.

A kiln for carrying out endothermic reduction processes comprises a sturdy external shell, a heat-insulating layer covering the interior surface of the shell, and an innermost layer or lining of heat-resistant, abrasion-resistant and corrosion-resistant material covering the insulating layer. The kiln further comprises inlet means and outlet means which are provided with sealing means preventing entrance of air into the kiln.

6 Claims, 4 Drawing Figures

FIG. 1

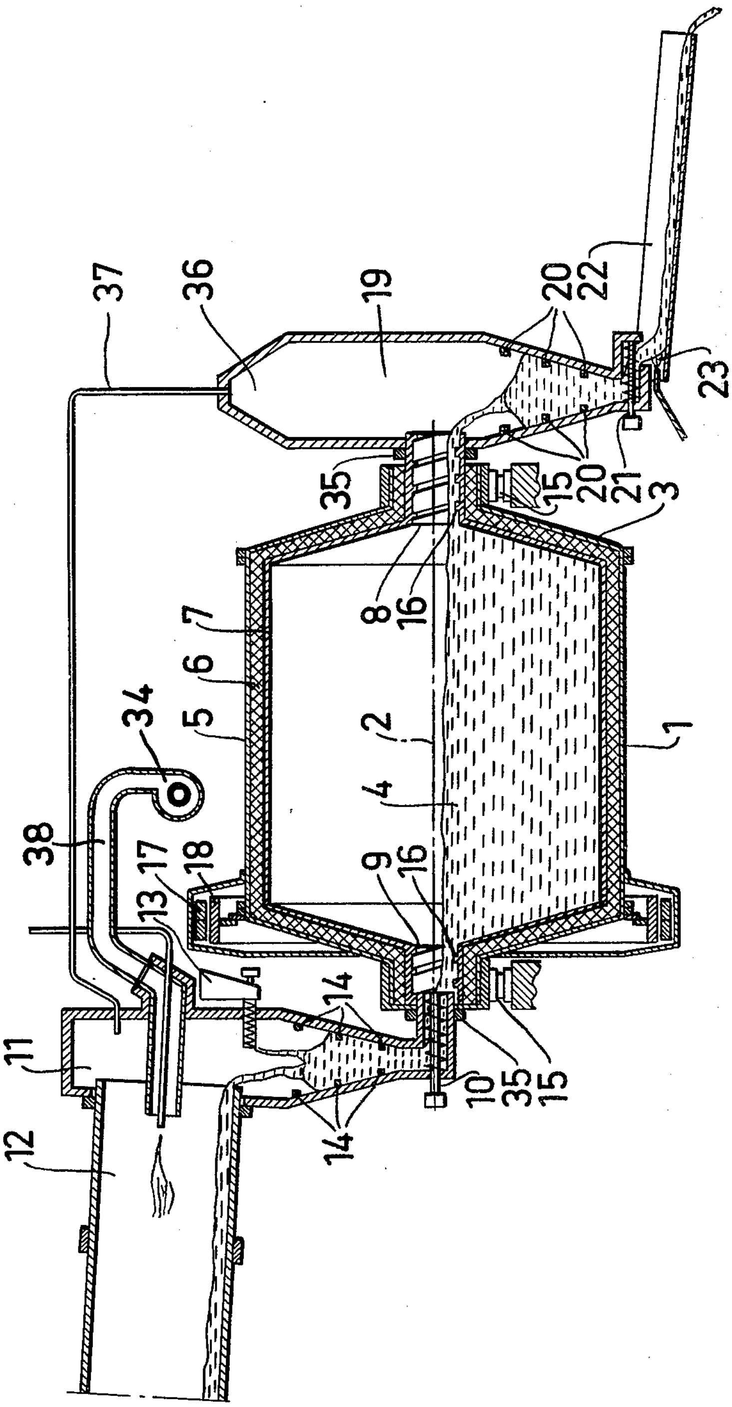

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FIG. 2

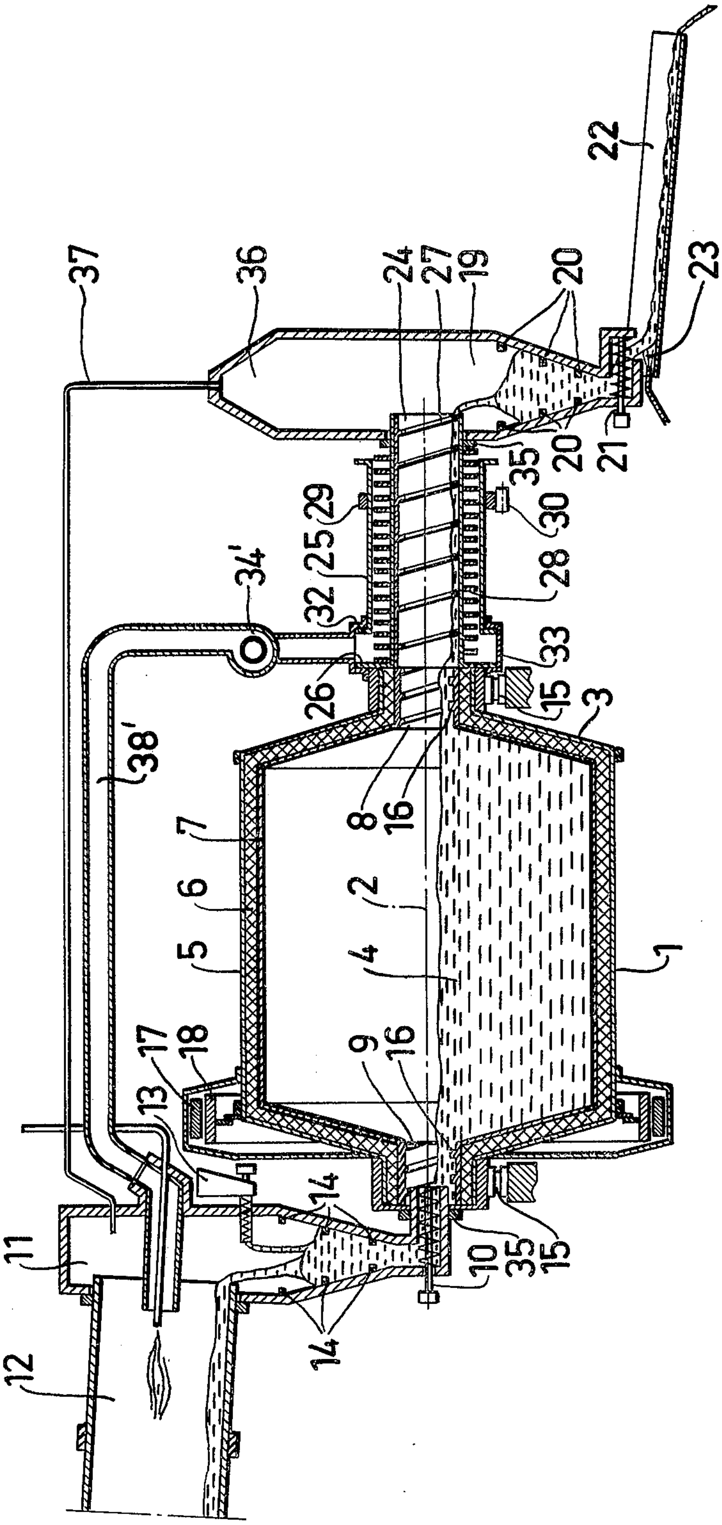
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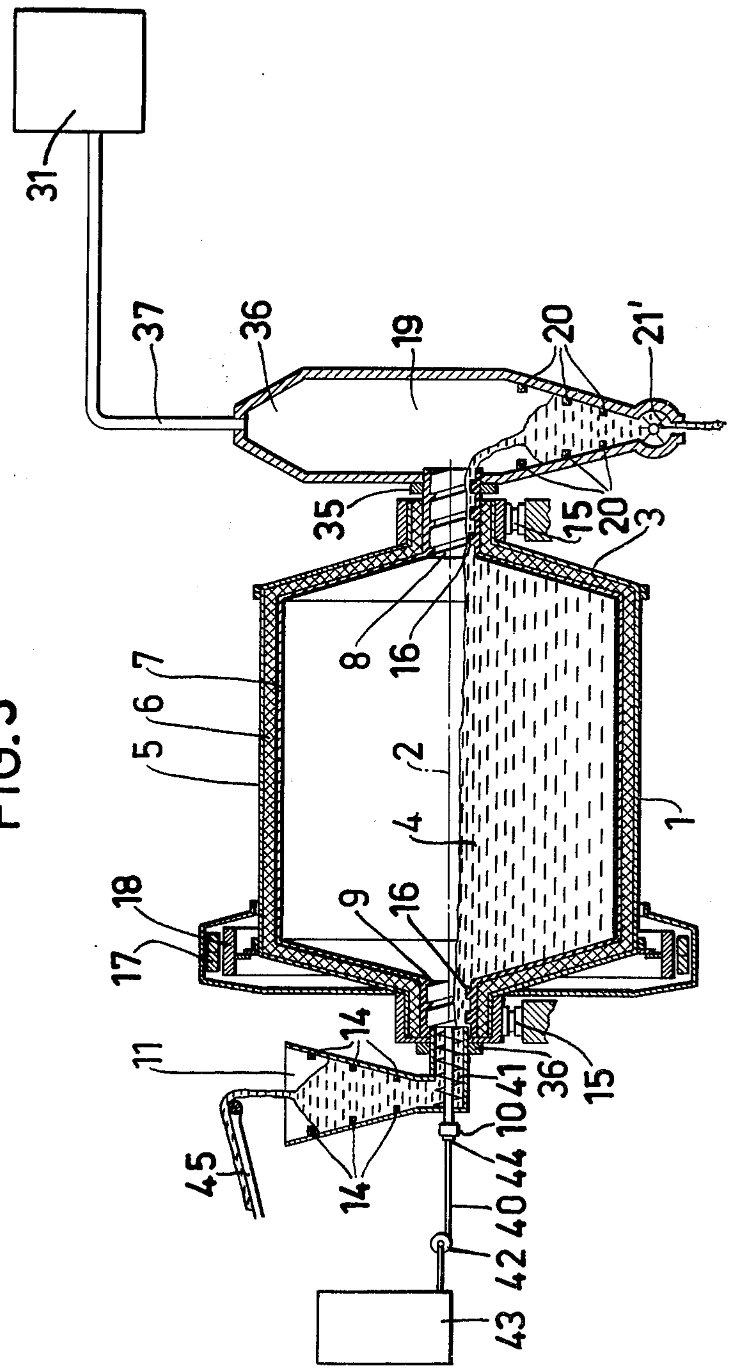
FIG. 3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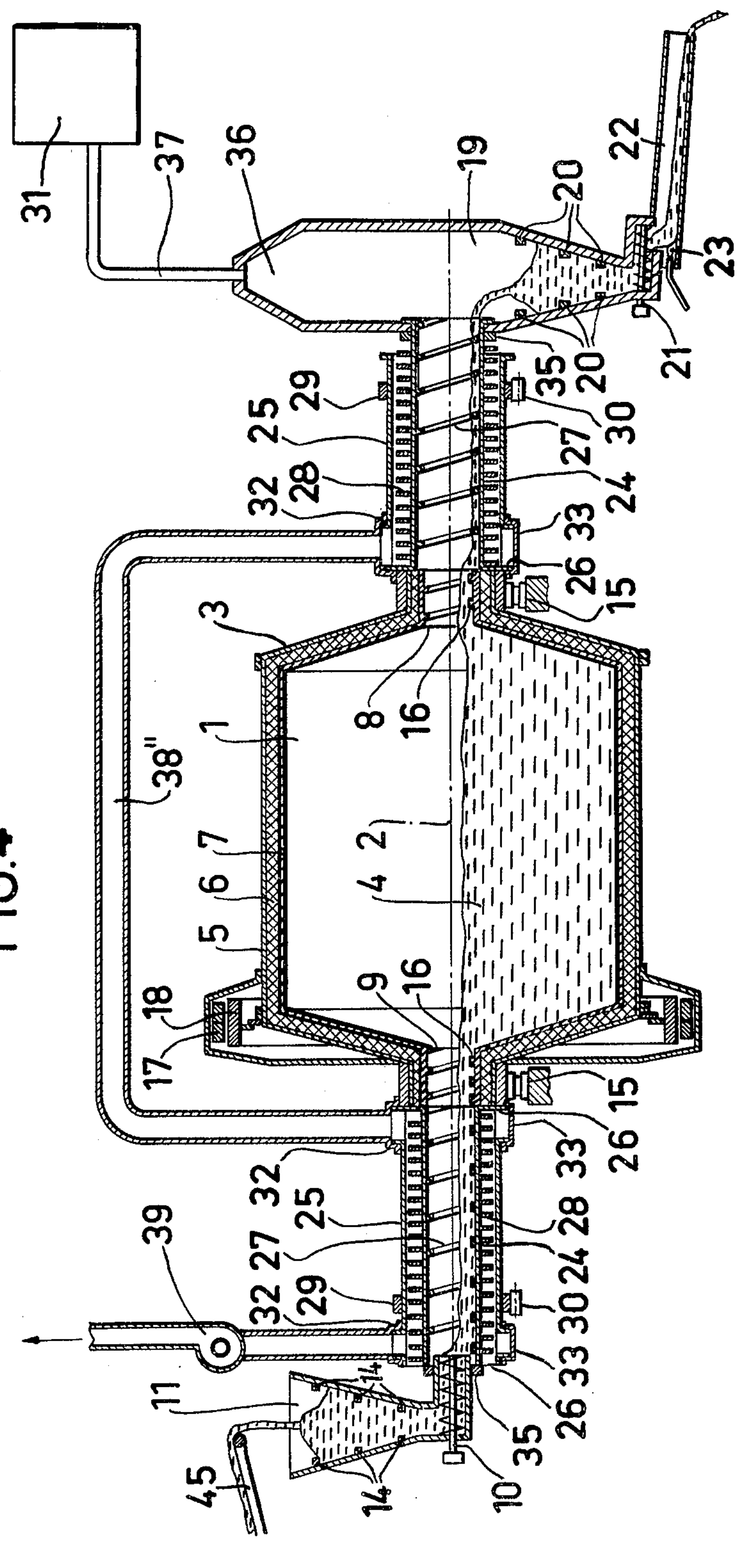
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FIG.4

METHOD OF CARRYING OUT ENDOTHERMIC METALLURGICAL REDUCTION PROCESSES WITH THE AID OF A CONTINUOUSLY OPERATING MECHANICAL KILN

This invention relates to a method of carrying out heat-absorbing processes, and in particular metallurgical reduction processes with the aid of a continuously operating mechanical kiln. The invention renders possible continuous operation for a variety of processes that at present can be carried out in a continuous manner only with great difficulty, e.g. endothermic reduction reactions, for example between solid carbonaceous reducing agents and solid oxides.

The method, therefore, is well adapted for the industrial implementation of the so-called segregation process, by means of which copper and nickel compounds are reduced without smelting from their oxide ores in the form of metallic particles of such a size, that they can be separated from the gangues by means of flotation, or in the case of nickel, also by magnetic separation. The method according to the invention is particularly suitable for use at the segregation of garnierite nickel ore.

Laboratory experiments have shown that the segregation method can be applied to the extraction of nickel from oxide ores. These experiments have proved that by mixing nickel oxide ores with $CaCl_2 \cdot 2H_2O$ and coke, all in a finely dispersed form, and then heating the mixture in a nitrogen atmosphere to approximately 1000°C and keeping the mixture at that temperature for a suitable period of time, the nickel and a small amount of iron segregate in the form of particles, which then can be separated from the gangues by flotation or magnetic separation.

No method, however, applicable on an industrial scale was developed. One of the difficulties encountered in the industrial implementation of the segregation process is that of maintaining a suitable atmopshere in the kiln. The process seems to work best when the atmosphere consists only of those gases evolved in the process itself.

The problem of implementing the segregation process on an industrial scale has been solved in the TORCO-process for segregating copper ore by first preheating the ore to a sufficiently high temperature and then introducing it together with the reagents into a special furnace, in which the process takes place without further addition of heat. This process is not suitable for nickel ore, because it would require preheating to 1200°–1300°C. However, it was found that preheating the ore to temperatures above 900°C lowers the nickel yield at the segregation to an extent increasing with the preheating temperature exceeding 900°C. Irrespective of this fact, it is entirely impossible to preheat garnierite ore to 1200°–1300°C because the ore then undergoes pronounced sintering as soon as the temperature exceeds 1150°C.

The present invention has as its object to render it possible to utilize the segregation process for nickel ores on an industrial scale under optimum conditions, particularly with regard to the kiln atmosphere, while at the same time enabling the ore to be broken down to a very high degree of fineness. This disintegration of the ore is necessary to permit separation of the ferronickel particles from the gangues by mechanical means.

This object is achieved in that the reaction is carried out in a manner known per se without permitting air to enter and at a speed below the critical speed, and that the kiln charge is held isolated from the ambient so that the mechanical work applied to the kiln charge by the rotary movement of the kiln generates the heat required for the reaction process. A kiln for carrying out the method according to the invention is characterized in that the kiln chamber and heads consist of a sturdy shell with a heat-insulating layer on its inside, which layer is covered with a lining being heat-resistant, abrasion-resistant and corrosion-resistant to the reaction gases, and that the introduction and discharge means are provided with sealing means to prevent air to enter the kiln chamber.

Provided that the ore is calcined at 700°–900°C and then without cooling fed into the mechanical rotary kiln, together with the necessary reagents, a power input of 200–300 kWh per ton of calcined ore must normally be calculated for carrying out the segregation process. This is half the quantity of energy required to melt the hot calcined ore in an electric furnace and produce ferro-nickel in the process now commonly used for processing garnierite ores.

Examples of different procedures for carrying out the method according to the invention are shown in the drawings, in which

FIG. 1 shows an embodiment of the charge when being fed to the mechanical kiln first being preheated and possibly calcinated in another kiln.

FIG. 2 shows a similar embodiment, but in this case the material leaving the mechanical kiln is cooled with air in a recuperative heat exchanger. The preheated air is then used as combustion air in the first kiln.

FIG. 3 shows an embodiment where the material being fed is processed in the mechanical kiln without preheating.

FIG. 4 shows an embodiment when preheating is accomplished with the aid of heat exchangers on both the charge and discharge sides. On the discharge side, the material preheats the air which subsequently is used for preheating the material being fed to the kiln.

In all Figures, one and the same embodiment of the mechanical kiln is shown which is provided with various auxiliary means for realizing the idea of the invention. Details being common in the different Figures shown have been given the same designations.

As can be seen from the Figures, the kiln has the form of a straight cylinder **1**, with a horizontal axis **2** and slightly conical heads **3**. The kiln is slightly less than half-filled with ore and grinding media **4**. The charge is heated by the rotation of the kiln about its horizontal axis.

The kiln walls consist of a sturdy steel shell **5**, inside of which a thermal insulation layer **6** is provided, and inside of said layer a heat-resistant lining **7** offers high resistance to mechanical abrasion and also good resistance to the other conditions prevailing within the kiln. Said lining may, for example, be of fused cast alumina or silicon carbide. Each end of the kiln has a centrally positioned trunnion, which are provided with a centrally positioned circular opening **8, 9,** one of which (**8**) is somewhat larger than the other (**9**). The kiln in its remaining parts is entirely sealed. The solid materials used in the reaction are charged through the smaller opening **9**, and the solid reaction products are discharged through the larger opening **8**. When one of the reaction components is a gas, it may be advantageous under certain circumstances to introduce it through the larger opening **8** and discharge it through the smaller opening **9.** In this way, the incoming gas, along with any gas evolved in the kiln, will flow countercurrently to the solid materials. Even when no gaseous reactants are fed into the kiln, it may be useful to discharge the evolved gases through the smaller opening **9.**

A suitable way of feeding the solids into the kiln is to use a screw conveyor **10** from a bin **11,** in which the charge mixture is stored.

FIGS. **1** and **2** illustrate procedures adapted for the segregation of garnierite nickel ores, which apart from containing at least 20% water as surface moisture also include at least 10% chemically bound water. This moisture is removed by calcining the ore — preferably after partial drying, screening and crushing in advance — at a temperature of 700°–900°C whereupon it is transferred in heated state to the mechanical kiln, together with the necessary reagents.

In FIGS. **1** and **2,** thus, it is assumed that the ore is first preheated in a kiln **12,** from which the material falls into the bin **11.** The kiln **12** is supplied with heated air by a fan **34** through a pipe **38.** The screw conveyor **10** can advantageously be provided with a water-cooled shaft. Also other components, such as coal and calcium chloride used in the nickel segregation process, which are preferably added after preheating the ore, can be fed to the bin **11** from a separate bin **13.**

In FIG. **3** it is assumed that a liquid component is also introduced into the kiln via a pipe **40** passing through the hollow shaft **41** of the screw conveyor. The liquid is pumped from a storage tank **43** by means of a pump **42.** The pipe **40** is sealed to the shaft by means of a gland **44.** In the event that gases introduced and/or evolved in the process should be discharged through the inlet opening **9,** this can be effected in principle in the same manner as when feeding in liquids, i.e. through the hollow shaft **41** of the screw conveyor.

The bin **11** in FIGS. **3** and **4** is supplied with material by a belt conveyor **45.** The level in the bin **11** is monitored by level gauges **14,** e.g. of the gamma radiation type.

Appropriate supports for the kiln **1** are so-called hydrostatic bearings **15** at the inlet and outlet trunnions. The bearing trunnions, like the rest of the kiln, are provided with a heat-insulating layer enclosing a lining of heat- and abrasion-resistant material. The bearings are cooled by the circulating oil carrying the trunnion. In order to facilitate transport of material through the trunnions, the inside of the lining can be designed as a more or less continuous screw thread **16** within the trunnions.

As is shown in FIGS. **1, 3** and **4,** the discharge trunnion of the kiln can open directly into a bin **19.** The bin is entirely sealed, except for a gas outlet **37.** A waste gas cleaner and collector connected to the outlet **37** is designated by **31.** The material level is monitored and controlled by level gauges **20,** e.g. of the gamma radiation type. Discharge from the bin can be performed by a feeder **21** of the cell or screw type.

The hot material in the bin on the discharge side of the kiln can be taken out of the bin e.g. by means of a screw feeder or a cell feeder **21.** In those cases where it is important to protect the hot material from oxidation, it is advisable to allow the material fall down into a chute **22.** As soon as the material begins to fall, it meets a wide jet of water **23** aimed in chute direction. The quantity of water used is controlled so as to cool the material rapidly to below 100°C without evolving troublesome amounts of steam. When so required, by the temperature of the material being discharged, both the outside of the bin and the shaft and housing of the screw feeder can be designed for water cooling.

The volume of the exhaust gases from the kiln is generally small. However, the bin **19** for discharged material may well be equipped with a dust chamber **36,** in which the greater part of the dust accompanying the gases is allowed to settle. In the event that the kiln gases are discharged through the inlet opening **9,** a corresponding device should also be placed there as well.

According to another way of working with the method as shown in FIGS. **2** and **4,** the material is cooled indirectly before reaching the bin, and the heat so obtained is utilized to preheat the combustion air for a preceding preheating kiln (FIG. **1**) or to preheat the material being fed to the kiln (FIG. **4**). Both cooling and preheating as in FIG. **4** can be effected with drums having inner and outer shells **24** and **25,** respectively, of heat-resistant material. The inner shells are attached to the inlet and outlet trunnions, respectively, by a flange **26.** The inner shells **24** have internal screws **27,** which convey the material forward as the drum rotates. In the space between the concentric shells **24, 25** of the drums a helical steel fin **28** is provided, the short sides of which are rigidly connected to the shells **24, 25,** or at least form a seal with the shell surface. A steel tire **29** is located near the end of the outer drum shell farthest from the kiln. The steel tire is carried by rollers **30.** The outer shell does not extend all the way to the ends of the inner shell, but terminates somewhat short of them. A fixed spiral-shaped housing **33** forms a seal with the flanges **26, 32** on the inlet end of the cooling drum and on both the inlet and outlet ends of the preheating drum in FIG. **4.** In FIG. **2** the firstmentioned housing is connected to a fan **34'**, which blows the preheated air through a pipe **38'** into the preheating furnace **12** where it is used as combustion air. In FIG. **4** the same housing is connected via a pipe **38''** to the corresponding housing **33** on the outlet end of the preheating drum. The housing of the inlet end of this drum is connected to another fan **39.** Both fans **34, 39** draw air from the discharge end of the cooling drum to its inlet end through the helical space formed by the steel fin **28** and the two shells **24, 25.** In FIG. **4** the preheated air is drawn via the pipe **38''** through the preheating drum and is cooled before it passes the fan **39.**

Both at the inlet and outlet ends of the kiln there are seals **35,** which prevent the air from entering the kiln or coming into contact with the hot reaction products. Since the material in the bins **11, 19** at both ends of the kiln is kept above a pre-set level, the kiln gases are prevented from escaping and air from entering the kiln through the feeders **10, 21.** The gas evolving in the kiln is discharged through a gas outlet in which the pressure is kept at such a level that substantially the same pressure is maintained in the reduction kiln as in the surrounding atmosphere.

The kiln may be driven in several ways. One way, which offers technical and economical advantages, is to drive the kiln by means of one or, in the case of higher power ratings, two gear rings mounted at the feed and/or discharge heads on the same flange, which connects the head to the shell. Transmission of power to the gear rings is achieved in the usual manner by a pinion, reduction gear and motor.

Instead of mounting the gear rings on the heads, they can also be mounted on the bearing trunnions outside the bearings. With such an arrangement, the gear ring diameter does not impost any limitation on the kiln diameter.

A radically different method of driving the kiln is to drive it directly by means of a low-frequency synchronous electric motor, the stator **17** of which is wrapped around the kiln shell and the rotor **18** is attached to the shell as shown in FIGS. **1, 2, 3** and **4.** In this case it would also be conceivable to fit the motor to the kiln trunnion. This form of direct drive is especially interesting for very high power ratings. It also has the advantage that the speed of rotation can be varied. By controlling the speed of rotation, the amount of energy per ton of material passing through the kiln can be controlled at a constant feed. This is not possible with the previously described drive method unless special drive motors are applied.

To enable cooling of the kiln at shutdowns, maintenance or inspections, it is necessary to be able to drive the kiln at a low speed, ranging from a tenth to a hundredth of the normal speed. If the kiln is then fed with normal amounts of material that have not been preheated, the kiln will be cooled relatively rapidly. This can be achieved with established techniques at whatever driving arrangements.

The kiln rotates at a speed which is lower than the so-called critical speed, above which the charge closest to the kiln wall ceases to move relative to the wall.

At speeds lower than the critical speed the charge will be agitated vigorously by the rotation of the kiln. By selecting sufficiently large length and diameter for the kiln, and by providing the kiln walls with sufficient insulation, it is possible to generate the heat necessary for the process solely by the movement of the reaction mixture inside the kiln. At the same time, the tumbling action of the rotating kiln assures effective mixing and mechanical disintegration (comminution) of the charge. Both these factors are favourable to the progress of the chemical reaction.

Considering that the density of the reaction mixture generally is low, it is often advisable to charge the kiln with a certain amount of foreign grinding media. These should be resistant to the atmopshere inside the kiln, and also be made from as heavy a material as possible as the power consumption of the kiln and thereby also the heat generation in the charge increases with the density of the charge. Power consumption also increases with the quantity of grinding media used up to a point where the kiln is filled to 50% of its volume with grinding media. Since the holding time of the reaction mixture in the kiln decreases as the quantity of grinding media is increased, and this reduction in holding time can have a negative effect on the reaction, it is usually best to use a grinding media load which is lower than 50% of the kiln volume. Even a relatively small quantity of heavy grinding media greatly increases the power rating of the kiln, since the power rating increases in proportion to the product of the charge weight and the distance between the axis of rotation of the kiln and the centre of gravity of the charge, and since heavy grinding media tend to take up a position far from the axis of rotation. A suitable grinding medium for the nickel segregation process is the ferronickel produced, for example, by melting and casting the ferronickel powder obtained in the segregation process, since it will be stable in the corrosive atmosphere prevailing within the kiln. Another feasible material is alumina. If a grinding medium is used, it is favourable to crush the ore as much as possible as this will enable smaller grinding media to be used, which will result in less wear on the kiln lining.

The use of the invention, though having been described in relation to the segregation process, is by no means restricted to this process. It can also be applied advantageously to carrying out a great number of other reactions. Examples of such reactions are:

$$Fe_2O_3 + 3\,C = 2\,Fe + 3\,CO\uparrow \qquad (1)$$

$$CuO + C = Cu + CO\uparrow \qquad (2)$$

$$NiO + C = Ni + CO\uparrow \qquad (3)$$

$$ZnO + C = Zn\uparrow + CO\uparrow \qquad (4)$$

The reactions in the formulas (1), (2) and (3) take place at temperatures, at which no melting of the charge normally occurs. In reaction (4) zinc is given off in gaseous form in the known manner, although no melting of the charge need occur in this case, either.

The invention also renders it possible to reduce most of the iron content in titaniferous magnetite and ilmenite in the form of magnetic powder, which can then be separated magnetically. The non-magnetic residue can then be used for the production of titanium oxide, and possibly even vanadium oxide as well, in a more economical way than with the original material. To attain iron particles of sufficient size, it is known that certain additives such as borax, sodium carbonate, fluorspar, phosphorus and sulphur have a beneficial effect.

Furthermore, the new method offers a solution to one of the most serious pollution problems currently facing us since it enables copper, nickel, zinc, iron and other metals to be extracted directly from their sulphide concentrates while simultaneously binding the sulphur as calcium sulphide. Examples of such reactions are:

$$CuFeS_2 + 2\,CaO + 2\,C = Cu + Fe + 2\,CaS + 2\,CO\uparrow \qquad (5)$$

$$NiS + CaO + C = Ni + CaS + CO\uparrow \qquad (6)$$

$$FeS + CaO + C = Fe + CaS + CO\uparrow \qquad (7)$$

$$ZnS + CaO + C = Zn\uparrow + CaS + CO\uparrow \qquad (8)$$

CaS can then be used together with NaCl, CO_2, water and air to produce Na_2CO_3, S and $CaCl_2$ in accordance with the process described in the U.S. Bureau of Mines Report of Investigation 6928.

Examples of other reactions in which the procedure can offer tangible advantages are:

$$FeS_2 = FeS + S\uparrow \qquad (9)$$

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl\uparrow \qquad (10)$$

$$Al_2O_3 \,.\, 2\,SiO_2 \,.\, 2\,H_2O + 4(NH_4)_2SO_4 = 2(NH_4)Al(SO_4)_2 + 2\,SiO_2 + 6\,NH_3\uparrow + 5\,H_2O\uparrow \qquad (11)$$

In reactions (9) to (11) it is of utmost importance to be able to collect the gaseous products in an as pure and concentrated form as possible. This has proved to be impossible with currently used kiln designs, but is readily accomplished with the kiln described in this invention.

What I claim is:

1. In a continuous method of effecting an endothermic metallurgical reduction reaction in the reactor space of a rotatable mechanical kiln as reaction vessel, in which the reaction materials at ambient temperature or in a preheated state are continuously charged into the reaction space and the resulting reaction mixture continuously discharged from the kiln, the improvement which comprises causing the charged kiln to rotate at lower than the speed at which the charge closest to the kiln wall ceases to move relative to the wall, whereby the charge is continuously isolated from air whilst being cascaded on itself and thereby autogeneously disintegrated and heated without any other heating to a temperature at which reaction is effected.

2. A method as defined in claim 1, characterized in that the material being charged and discharged is utilized for preventing air from entering the reaction process.

3. A method as defined in claim 1, characterized in that to the kiln charge are added heavy grinding media to a volume, which is half of that volume being available for the kiln charge movement.

4. A method as defined in claim 1, characterized in that the major part of the hot discharge products obtained from the reaction process is cooled, and that the heat so recovered is used to preheat the material being fed to the kiln.

5. A method as defined in claim 1, characterized in that possible gaseous reaction components and/or gases evolving at the reaction are caused to flow in the same direction as the solid reaction components passing through the mechanical kiln.

6. A method as defined in claim 1, characterized in that possible gaseous reaction components and/or gases evolving at the reaction are caused to flow countercurrent to the solid reaction components passing through the mechanical kiln.

* * * * *