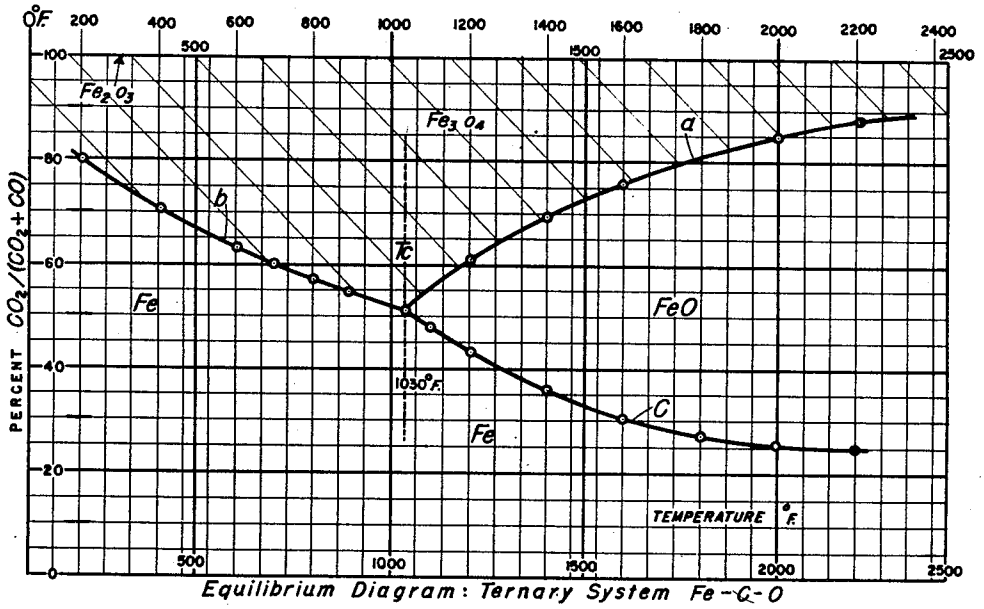
Nov. 7, 1950 P. H. ROYSTER 2,528,552

PROCESS FOR MAGNETICALLY ROASTING HEMATITIC ORE AND ORE MATERIALS

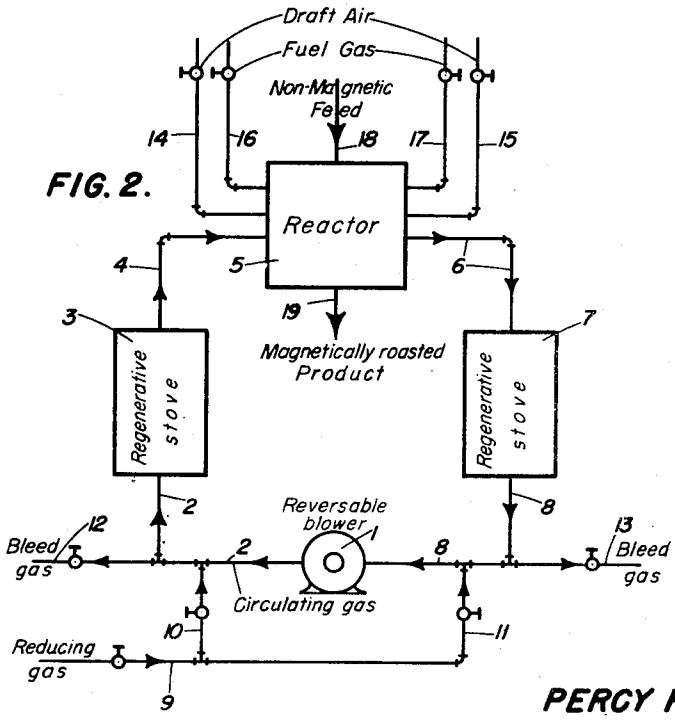
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FIG. 1.



Equilibrium Diagram: Ternary System Fe-C-O

FIG. 2.



INVENTOR.

PERCY H. ROYSTER

BY

Pierce, Scheffler & Parker

his Attorneys.

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PROCESS FOR MAGNETICALLY ROASTING HEMATITIC ORE AND ORE MATERIALS

Percy H. Royster, Chevy Chase, Md., assignor to Pickands Mather & Co., Cleveland, Ohio, a co-partnership

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4 Claims. (Cl. 75—1)

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This invention relates to the art of beneficiating low grade iron ores and other ferruginous materials, and is particularly concerned with an improved process of and apparatus for converting to magnetite an ore material's relatively non-magnetic oxide of iron (e. g., Fe_2O_3) content incident to the upgrading of the so-treated ore material by magnetic separation of the magnetite content thereof from gangue minerals and other relatively non-magnetic components of said ore material.

According to the present invention, magnetic roasting is effected by forcing a gas containing CO_2 and CO but no free oxygen through a mass of ferruginous ore material whose iron content consists largely of ferric oxide, said mass being maintained at an elevated reactive temperature and said gas being in thermodynamic equilibrium, at the temperature of operation, with Fe_3O_4 only. That is to say, the gas is of such composition that, at the temperature of operation, it is reducing with respect to Fe_2O_3 but is oxidizing with respect to FeO and Fe. Under these conditions, Fe_2O_3 of the ore material is reduced to Fe_3O_4 and substantially all of the CO initially present in the gas is converted to CO_2.

For reasons of economy, the process is made cyclical, whereby after each passage of the gas through the mass of heated ore material a small portion of the gas (substantially equal in volume to the enriching addition about to be described) is wasted to atmosphere, the remainder of the gas is enriched by the addition thereto of a reducing gas, whose major reducing component is CO, in an amount sufficient to re-establish the initial CO/CO_2 ratio, and the resulting re-constituted gas is again forced through the mass of heated ore material.

In the cases of some ferruginous ore material, the heat released by the exothermic reaction:

$$3Fe_2O_3+CO=2Fe_3O_4+CO_2$$

may be sufficient to maintain the ore material at the elevated temperature desirable for effecting the reduction. In other cases the exothermic heat is not sufficient, and it is necessary to supply heat to the ore material undergoing treatment.

The process may be carried out in any one of a variety of specific forms of apparatus, which forms substantially fall into two general categories, viz.: (1) a pair of substantially vertical, insulated, stoves communicating with each other through a functionally central insulated combustion chamber (i. e., "side-by-side" arrangements), with means for maintaining in each stove a

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gravitationally descending column of the ore material and means for passing the reducing gas serially through one column, the central combustion chamber and the other column; and (2) "straight line" arrangements wherein the pair of stoves are disposed one above the other and the charge gravitationally descends from the upper into the lower through a relatively constricted connector and wherein means are provided for continuously passing a current of the gas upwardly through the charge in the lower stove, thence to the functionally central combustion chamber, and thence upwardly through the charge in the upper stove.

The invention will now be described in greater particularity and with reference to the accompanying drawing, in which:

Fig. 1 is an equilibrium diagram in the ternary system Fe—C—O; and

Fig. 2 is a diagrammatic representation of a system of apparatus operable in the carrying out of the process of the present invention.

At temperatures above 1030° F. (T_c, critical temperature for the stability of FeO), magnetite is the equilibrium form of iron oxide in the presence of the oxides of carbon when the ratio of CO_2-to-CO lies above curve *a*. Successful magnetic roasting can be achieved at any temperature above 1030° F. when the gas complies with this restriction. No FeO can be produced, regardless of length of time of exposure, the intimacy of contact, the character of the ore, the presence or absence of inert gas (e. g., N_2), or the amount of gas per unit of ore. Prior attempts to prevent "over-reduction" (i. e., conversion to non-magnetic FeO), have been made by using a limited amount of reducing agent, curtailing reaction time, limiting intimacy of contact, and otherwise.

It is observed that Fe_2O_3 does not appear in Fig. 1. There is no equilibrium amount of Fe_2O_3 in the presence of more than the merest trace of CO (e. g., CO_2-to-CO ratio of 1000 to 10,000).

The ordinate 100% at the top of Fig. 1 is the boundary of the Fe_2O_3 area, which is too microscopic to be drawn.

At temperatures below 1030° F., FeO is unstable. Over-reduction at such lower temperature presents an even more serious difficulty. Over-reduction in this temperature range produces metallic iron, which is more than twice as magnetic as is magnetite, but nine times as much CO is required to convert Fe_2O_3 to Fe as is required to convert an equal weight of iron from Fe_2O_3 to Fe_3O_4.

In the diagrammatic representation, Fig. 2, is

shown a re-entrant circuit involving in closed series a reversing blower 1, main 2, regenerative stove 3, main 4, reactor 5, main 6, regenerative stove 7 and main 8. A conduit 9 communicates between a source (not shown) of reducing gas under pressure and mains 2 and 8 through valved branch conduits 10 and 11, respectively, whereby to introduce reducing gas into one and alternately into the other of said mains. Main 2 is provided with a valved branch conduit 12 for bleeding gas from the system, and main 8 is provided with a valved branch conduit 13 having similar function. Reactor 5, as shown, is provided with two valved draft air conduits 14 and 15 and with two valved fuel gas conduits 16 and 17. Reactor 5 also is provided with means 18 for introducing non-magnetic feed thereinto without material concurrent passage of gas into or out of the reactor, and with means 19 for removing magnetically roasted product therefrom without material concurrent passage of gas into or out of the reactor.

In the operation of the process I feed an iron ore, originally largely non-magnetic, into reactor 5. This part of the apparatus may be of any conventional type, e. g., a multiple hearth furnace (of the Herreschoff, Wedge or McDougall type), a rotary kiln such as is employed in the lime and cement industries, or a vertical shaft furnace of the conventional counter-current type. In some instances I recommend using a heating furnace positioned above a cooling furnace, such as is described in my copending application Serial No. 605,861. In particular, I prefer to employ a bank of two or more vertical furnaces in which batch charges of ore are used, and in which the ore is maintained immobile during the reaction, as is described in my copending application Serial No. 602,988, filed July 3, 1945, of which latter the present application is a continuation-in-part.

In order to achieve magnetic roasting, it is necessary only that the reactor be constructed in a fashion to permit adequate chemical contact between the reactive gas and the ore to be roasted.

In actual practice only two reducing chemical compounds are of practical interest, viz., CO and H_2. For the reducing gas to be admitted through conduit 9, Fig. 2, into the system I contemplate employing blast furnace gas or other industrial gas containing CO as the essential active reducing agent, without or with incidental H_2. When operating near an iron ore mine, I prefer using gas produced by gasifying a solid carbonaceous fuel in a slagging type gas producer as described in my copending application Serial No. 690,547, filed August 14, 1946, such as the typical slagging type gas producer gas having the approximate analysis:

	Per cent		Per cent
CO_2	0.42	H_2	1.39
CO	34.60	N_2	63.59

The fuel gas introduced through 16 or 17 may well be identical with the reducing gas admitted through conduit 9, although more frequently hydrocarbons, e. g., natural gas and fuel oil, are cheaper per unit of heat than are gases high in CO.

In operating my process with the apparatus indicated diagrammatically in Fig. 2, I feed the raw ore material into reactor 5 either continuously or intermittently at a suitable rate, I remove through 19 equivalent amounts of treated ore material, and by means of reversing blower 1 I force a stream of re-cycled "carrier" gas to recirculate through the re-entrant circuit 2, 3, 4, 5, 6, 7, 8, and 2, traversing in sequence stove 3, reactor 5, and stove 7. At the beginning of the operation described, stove 3 has been preheated in prior operation to roasting temperature T which latter may be from 600° to 2000° F. or higher. The selected roasting temperature depends upon the character of the ore, its composition and the structure of reactor 5. With hard, dense lump ore, relatively impermeable to gas, I recommend using the maximum temperature practical (avoiding any serious fusion of the roasted product) in order to realize a rapid rate of reduction. With porous, soft ores of the Mesabi type, it is convenient to operate at temperatures below 1600° and even below 1000° F. Wherever rapid diffusion of the reactive gas obtains, extremely low temperatures are permissible, e. g., as low as 500–600° F.

The recirculating gas, before entrance into stove 3, is chemically enhanced by the introduction of a carefully controlled amount of reducing gas admitted through open valved conduit 10 and commingled with recycled gas flowing through conduit 2.

The amount of reducing gas introduced is carefully proportioned with respect to the pounds of iron fed into reactor 5. In order to convert 1 pound of iron initially in the form of Fe_2O_3 into Fe_3O_4, 1.12 cu. ft. of CO (dry basis, 60° F., 29.92 in. Hg.) is converted into CO_2. I therefore may limit the amount of CO introduced through 10 to a figure a little in excess of this, in order to achieve a reasonable approach to efficiency in the utilization of my reducing gas. All of the CO in excess of this 1.12 figure will be discharged unused and wasted. In actual practice, with many ores, I have found that I may use much less than 1.12 cu. ft. of CO per 1 pound of iron, with close approach to 100% in efficiency of gas utilization. It is true that the conversion of hematite to magnetite in such cases falls short of completion, but the magnetic properties of the finished product are sufficiently intense to permit highly satisfactory magnetic separation. With close-grained ores loosely bound with contaminating gangue material, I have found that as little as 0.6–0.7 cu. ft. per lb. Fe yields a product which permits a clean separation in a magnetic cobber. Because of the cost of reducing gas I seldom carry the magnetic roasting beyond the degree necessary to realize desired separation.

The conversion of Fe_2O_3 to Fe_3O_4 by CO-reduction is quite exothermic, generating a substantial amount of heat and causing a rise of several hundred degrees F. in the ore mass undergoing reduction. This heat is generated at the point of reduction and must be transported with the gas stream through the ore mass, whether with a stationary bed (batch operation) or in a counter-current furnace with a moving bed. I therefore prefer to adjust the amount of gas traversing reactor 5 to total from 5 to 15 cu. ft./lb. ore. This requirement is directed to providing sufficient heat capacity to control the thermal conditions in the ore mass. With a thermally inefficient reactor, such as a rotary kiln, little intimacy in heat exchange is possible, and total gas volumes as high as 20–30 cu. ft./lb. ore are frequently required.

In a large scale apparatus, where several thousand tons of ore are treated each day, and when the raw feed is low in moisture, I have found that the exothermic heat generated by the reduction is or may be sufficient to maintain the apparatus

at desired roasting temperature and to compensate for heat lost through the insulated walls and for the heat carried away by the discharged ore and by the gas discharging from stove 7. In many cases, however, it is necessary to provide additional heat to the apparatus. This is done by introducing a fuel through conduit 16 and draft air through conduit 14. When supplementary heat is required, I carefully adjust the proportions of fuel and draft air respectively to realize "perfect combustion"—i. e., the amount of O_2 in the draft air is controlled to the stoichiometric amount required for complete combustion of the combustibles in the fuel, to limit the products of combustion to the four compounds CO_2, H_2O, SO_2 and N_2, with no remanent excess of O_2, H_2 or CO. It is difficult to specify the amount of fuel gas required to maintain the desired thermal conditions, since this heat requirement depends so largely on the type of furnace used, its construction and the efficiency of heat transfer, as well as the efficiency of the two stoves 3 and 7. When using properly designed Royster pebble stoves as the regenerators and with a reactor of the type described in the parent application, as little as 800–1200 cu. ft./min. of slagging type gas producer gas (application Serial No. 690,547, referred to above) is sufficient. The worst case which can be encountered is when stoves 3 and 7 are of the conventional checkerwork design and reactor 5 is of the conventional rotary kiln or multiple hearth type. In such case the quantities of fuel and draft air may well exceed the volume of recycled gas. Since, therefore, the composition of the recycled gas exiting from stove 7 consists almost exclusively of N_2, CO_2 and H_2O, as does the gaseous product of fuel combustion from fuel and draft air, the relative amounts of recycled gas and of combustion gas have little effect upon the gas composition or upon the chemical control of the process.

Care in control need be exercised primarily only with respect to proportioning the ratio of fuel gas (conduit 16) and draft air (conduit 14). The second operating control is made in proportioning the volume of recycled gas (conduit 2) to the reducing gas (conduit 10), in order to provide concurrently the necessary volume of CO required for magnetic roasting of the Fe_2O_3 in the raw ore feed and to proportion the heat capacity of the total gas to the heat capacity of the ore.

It is obvious that reducing gas experiences no change in volume when reacting with iron ore, since the volume of CO_2 and H_2O is identical with the volume of CO and H_2 oxidized. When supplementary heat is not required a volume of gas discharging from stove 7 is bled to waste, through bleed line 13, equal in volume to the reducing gas admitted through conduit 10. When supplementary heat is introduced by burning fuel gas and draft air, the amount of bled gas is increased in amount equal to the volume of the products of this fuel combustion.

The operation as described above is termed "direct flow." In its course, heat is extracted from stove 3 and added to stove 7. When the temperature of the gas discharging from stove 3 into conduit 4 falls too low, and when the temperature of the gas exhausting from stove 7 into conduit 8 rises to an unacceptable level, the direction of flow of blower 1 is reversed, and the recycled gas is forced to traverse the circuit 1, 8, 7, 6, 5, 4, 3, 2, and 1. In that event, reducing gas is introduced through conduit 11 and bled gas is exhausted through conduit 12. Draft and fuel gas concurrently are introduced through 15 and 17 respectively, and conduits 14 and 16 are closed. This operation is termed "reverse flow." Continued operation is effected by alternating direct and reverse flows in conventional manner.

I claim:

1. Process of magnetically roasting a ferruginous ore material whose iron content occurs mostly in the ferric state whereby to convert at least the major portion of the ferric oxide content thereof to magnetite, which comprises repeatedly circulating a stream of mixed non-oxidizing gas through a reentrant circuit containing a mass of the ore material at an elevated temperature between 500° F. and the liquidus point of the ore material, the mixed gas consisting essentially of nitrogen, CO_2, H_2O and CO, the ratio of CO_2 to the sum of the CO_2 and CO in said mixed gas being maintained at a value above the line *"b a"* in the equilibrium diagram for the ternary system Fe—C—O represented in Fig. 1 of the accompanying drawing; after each passage through said mass of ore material reconstituting the original composition and volume of the mixed gas by discarding a minor fraction of the mixed gas and adding to the residue a like amount of a gas containing nitrogen and CO_2 and being rich in CO, the amount of CO so added being from about 0.6 to a little in excess of 1.12 cu. ft. of CO per each 1 pound of Fe content in the ore material treated; heating the mixed gas, prior to each passage thereof through said mass of ore material to a temperature between 500° F. and the liquidus point of the ore material; and maintaining the mass of ore material at a temperature between 500° F. and the liquidus point of the ore material by heat transferred thereto from said heated mixed gas, the volume of the mixed gas being adjusted, between 5 and 30 cu. ft. per each 1 pound of the ore material treated, to have a heat capacity sufficient to insure that the mass of ore material is heated to such elevated temperature.

2. Process defined in claim 1, in which the ore material is heated to a temperature between 1030° F. and the liquidus point thereof during the countercurrent passage of mixed gas through the column of ore material.

3. Process defined in claim 1, in which the volume of the mixed gas is maintained at between 5 and 15 cu. ft. per 1 pound of ore material treated.

4. Process defined in claim 1, in which the ore material is contained as two columns in a pair of generally vertical furnace chambers communicating at their upper ends and is maintained substantially immobile in said furnace chambers during the passage therethrough of the reducing gas.

PERCY H. ROYSTER.

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