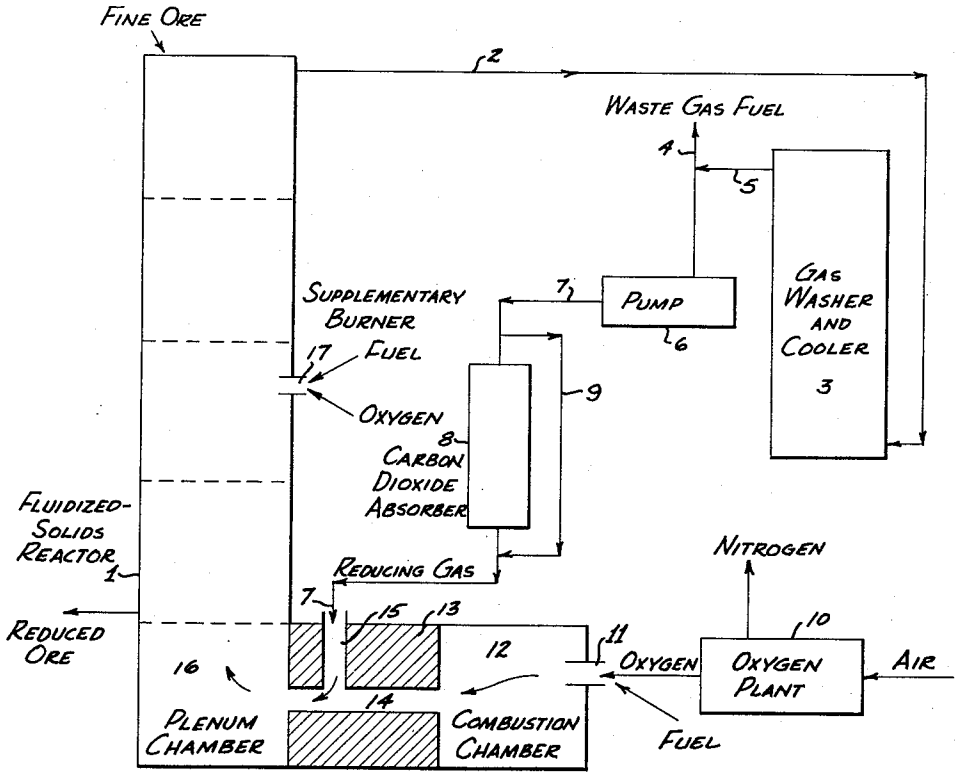
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METHOD OF REDUCING FINE IRON ORE IN A FLUIDIZED-SOLIDS REACTOR

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METHOD OF REDUCING FINE IRON ORE IN A FLUIDIZED-SOLIDS REACTOR

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This invention relates to the reduction of fine iron ores to finely divided iron by means of reducing gases under heat, where the finely divided iron ore is fluidized in the presence of the reducing gas. Various procedures for this purpose have hitherto been suggested, including procedures in which the reducing gases are maintained in a circulating condition in a closed system which includes the reactor or fluidizing apparatus. The gases circulating in the closed system have to be continuously renewed as to their reducing potential. This is accomplished in part by treatment of the gases within the closed system; but it also requires the introduction of fresh gas from an outside source.

In the operation of a fluidized-solids reactor for reducing iron ore, it is customary to prepare the processing gas from natural gas in various ways, as by steam-methane reforming, or partial combustion with oxygen, followed by catalytic gas shifting and carbon dioxide removal, so as to obtain gases of the desired compositions. Natural gas cannot be used for reduction without pretreatment; and any method of reforming the gas results in the production of substantial quantities of moisture-vapor. Moist gases tend to be oxidizing rather than reducing; and therefore a gas drier must be provided outside the closed recirculatory system. The reforming of the gases is for the purpose of stepping up their reducing potential, usually by increasing their free hydrogen content, although the carbon monoxide content is also frequently increased. But it will be evident that prior proposals have required, in addition to the gas drier, a gas shifter or reformer, and usually a carbon dioxide remover, outside the closed recirculatory system. Since these pieces of apparatus have usually been duplicated inside the closed system, it will be evident that the installation becomes cumbersome and expensive.

It is an object of the invention to provide a method and apparatus requiring a minimum of gas-treating devices outside the closed recirculatory system.

It is an object of the invention also to simplify the requirements for gas-treating apparatus within the closed system, by eliminating the need for a gas shifter, and if desired, the need for a gas heater or a carbon dioxide remover.

When natural gas or other gaseous fuel is cracked or otherwise fitted for reducing use by partial combustion with air, considerable quantities of nitrogen dilute the active gases and form a load on the system. The efficiency of reduction is cut down; and the cost of heating and cooling neutral gases becomes an added expense. It is an object of the invention to provide a method of fitting natural gas or other gaseous fuels for reducing use while avoiding the accumulation and treatment of inert gases.

It is an object of the invention to provide a system in which sensible heat from the cracking or reforming of processing gases is directly applied to the heating of the gases to reducing temperature.

These and other objects of the invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications are accomplished by that procedure and in that apparatus

of which an exemplary embodiment will now be described. Reference is made to the accompanying drawings in which:

The drawing is a diagrammatic showing of the apparatus which is employed in practicing the invention.

Briefly, in the practice of the invention, gaseous fuel is prepared for use as processing gas by partial combustion with oxygen at or adjacent to the fluidized-solids reactor. It will be understood that any mobile fuel may be used such as gas, oil, or pulverized coal. Examples of gas are natural gas, essentially methane, and other gases such as ethane, propane, butane and the like, providing they are available in sufficient quantity at a low enough price. Oil can be any fuel oil. Coal can be of any type which after pulverization can be burned with equipment commonly used for this purpose as in steam power plants.

Natural gas is widely available and in some sections of the country is less expensive compared to other local fuels. For simplicity, natural gas will be used in describing examples given in this disclosure but it is understood that other mobile fuel can be used.

Natural gas can be subjected to partial combustion with oxygen to yield products consisting essentially of hydrogen and carbon monoxide with lesser amounts of carbon dioxide, water vapor and methane. In order to accomplish this, the gas/oxygen ratio must be kept high during combustion as will be understood by the skilled worker. For example, with a natural gas consisting essentially of methane, the gas/oxygen ratio may be in the range of 1.2 to 1.8, with the specific ratio actually used, within this range, depending on other procedures employed in the operation.

The partial combustion generates flame temperatures between 2000° F. and 3500° F. depending on the ratio used. The flame temperature is inversely proportional to the gas oxygen ratio. The combustion chamber temperature is, of course, lower than the flame temperature and is dependent on construction, size, and quantity of gas used per unit time on a specific size of chamber.

These temperatures are too high for the direct treatment of finely divided ores, since in most instances sticking or sintering would be encountered. Also, the products of combustion contain too high a percentage of water vapor and carbon dioxide to be an efficient reducing medium. For instance, the analysis of the combustion products for two ratios would be about as follows as indicated by actual combustion tests.

Analysis of Combustion Products

Case	G/O	H_2	CO	CO_2	H_2O	CH_4	O/S	C/S	Reducing Potential
I	1.26	50	30	3	15	1	.237	.156	.063
II	1.65	55	28	4	7	5	.190	.166	.120

O/S=oxygen fraction.
C/S=carbon fraction.

The O/S and C/S fractions are the coordinates of a point on the Gurry diagram. The vertical distance from this point to the 1400° F. line is taken as a relative measure of the reducing potential. The Gurry diagram is widely accepted in the field of gas chemistry and is to be found in Transactions A.I.M.E., vol. 188, April 1950, page 685, FIGURE 7.

The reducing power of these gases can be increased by quenching with cold water to remove the moisture but this would sacrifice their sensible heat which it is desired to use to heat the iron ore. Consequently, instead of subjecting the products of combustion to a drying operating, the present invention contemplates that they be immediately mixed with cool dry reducing gases from

the recirculation system. This accomplishes several things. First, the cool gases from the closed system lower the temperature of the combustion products to a range of about 1500–1700° F. which is a temperature range favorable for introduction into a fluidized bed for heating and reducing iron ore. Second, the dilution of the products of combustion with the drier recirculated gas lowers the effective water content of the mixed gases so they have a higher reducing potential. The following table gives examples of three cases:

Case A—CO_2 not removed from recirculated gas.
Case B—CO_2 removed from recirculated gas.
Case C—CO_2 removed and recirculated gas heated to 600° F.

In each case the amount of recirculated gas is the quantity which after mixing with the combustion gas will give a temperature of 1600° F. entering the reducer.

Analysis of Gas After Mixing

Case	G/O Ratio	Percent Recirc. Gas	H_2	CO	CO_2	H_2O	CH_4	O/S	C/S	Reducing Potential
A	1.65	26	53	29	6	5	7	.195	.180	.131
B	1.27	49	57	26	2	8	7	.160	.150	.133
C	1.27	60	59	25	1	7	8	.146	.147	.145

The Gurry diagram shows that the gas in case A has reducing power essentially equal to that of the gas in case B where the recirculated gas was scrubbed to remove CO_2.

Such gases are suitable for the reduction of finely divided iron ores and the excess heat generated in the flame is directly used to reheat the recirculated gases making it unnecessary to include a reheater in the closed system. If, of course, the recirculated gas were heated as in case C, the reducing power would be increased. But the purpose here is to show that it should be possible to operate the process without heating the recirculated gas.

The burning of the gaseous fuel with oxygen insures the absence from the processing gases of inert gases such as nitrogen from the air. As will be shown later, such quantities of inert or non-reducing gases as may be contained in or derived from the gaseous fuel do not tend to accumulate in the system. The burning of the fuel with oxygen, moreover, insures a high temperature of the flame, at which temperature the products of combustion will be low in methane and in carbon dioxide.

Referring now to the drawing, the numeral **1** indicates a fluidized-solids reactor having four stages or platforms. This is exemplary merely of fluidizing devices which can be employed. Instead of a single four-stage unit, a plurality of single stage fluidizers, either in parallel or in series, may be employed; and under some circumstances devices acting on the cyclone separator principle are likewise available. The point is that the processing gases shall be brought into intimate contact with the finely divided iron ore, while both are at the proper temperature for reduction, in a suitable reactor. It will be understood that the reactor will be provided with means for the introduction of the iron ore in finely divided condition, and means for the withdrawal of the reduced material. Normally, separators are employed in connection with fluidized-solids reactors for the purpose of separating and returning fines. These last mentioned elements have not been illustrated since they are well known in the art.

The top gases from the reactor are carried through a conduit **2** to a gas washer and cooler **3**. In the system of this invention, gases will be bled out of the closed recirculatory system in an amount equal to the amount of fresh gases introduced. If the withdrawn gases can be used elsewhere at high temperature this may be done ahead of the washer and cooler **3**. If not, it may be done following the washer and cooler; and an outlet for gases has been indicated at **4**. The gases bled out of the system contain combustible values, and hence are of use elsewhere for heating, for the generation of steam, for the protection of reduced material taken out of the reactor, and the like.

The gas washer and cooler **3** may take various forms which do not constitute a limitation on the invention. Usually and preferably it is in the form of a gas washer in which the cooling medium is water. It will be understood that the washer and cooler is also a drying device since the lowering of the temperature of the gases will result in the condensation of moisture therefrom. In the exemplary procedure the gases may enter the cooler and washer **3** at a temperature of 400°–1000° F. and a moisture content of 10–20%, and leave it at a temperature of 60°–70° F. and a moisture content of about 1%.

The washer and cooler are shown connected by a conduit **5** to a pump **6**; and it is one of the advantages of the system of this invention that the reduction can be carried on under pressure so that its efficiency is increased. The pressures normally employed in the closed recirculatory system are 25 p.s.i. to 100 p.s.i.

The pump **6** sends the processing gases back to the reactor through a conduit **7**. If desired a carbon dioxide absorber **8** may be connected in this conduit and provided with a valved bypass **9**. It will be understood that the removal of carbon dioxide will increase the reducing potential of the processing gases; but because of the characteristics of the process a carbon dioxide absorber is not necessary. Thus in the exemplary procedure 1 volume of recirculated gas containing about 11% CO_2 will be mixed with 3 volumes of fresh combustion gases, containing about 4% CO_2, formed by the partial combustion of the gaseous fuel as shown in the aforementioned case II, to give a mixed gas in the reactor containing about 6% CO_2, which is tolerable at the temperatures set forth above. The carbon dioxide absorber if used may be of the known type using monoethanolamine, which will be regenerated.

The use of oxygen for the partial combustion implies the availability of a source of this gas. Usually the oxygen will be produced in an air reduction plant which is indicated at **10** in the figure. The gases bled off at **4** may if desired provided some of the power required in the oxygen plant.

A burner is indicated at **11** fed with oxygen and the gaseous fuel, e.g. methane in the proper proportions as previously set forth. The flame from the burner is formed in a combustion chamber **12** which is separated from the reactor **1** by a refractory partition **13** having a central passageway **14** and a branch passageway **15** to which the conduit **7** is connected. A mixture of the recirculated processing gas and the products of combustion is thus effected before the gases enter the reactor **1**; and it is desirable to provided a plenum chamber **16** at the base of the reactor for gas distribution and homogenization. Thus the gaseous mixture contacting the ore in the reactor will be of the proper composition and at the correct temperature for efficient reduction.

The iron ore may be finely divided oxide of iron from any source. There are differences in iron ores having to do with their content of silica or other diluents. The reduced products of the iron ores differ also in accordance with the nature of the source. Some reduced iron ores respond readily to magnetic separation, while others do not. The reduced materials withdrawn from the reactor **1** will normally be protected by reducing gases (which may be some portion of the gases withdrawn at **4**), until they have cooled to below the reoxidation temperature. Magnetic separation may be practiced, if feasible, on the cooled product. The cooled reduced material may be briquetted, and will usually be melted in a suitable type of furnace such as an electric-arc furnace. These matters are well known in the art and form no limitation

upon the present invention, nor have they been illustrated.

However, it does not constitute a departure from the principles of this invention to employ finely divided oxides or ores in admixture with other substances, if desired. A flux such as limestone may be added to the ores before introduction into the reactor. The iron particles formed by the reduction of some ores exhibit a greater tendency toward sticking together during reduction than do the reduced products of other ores. Fluxes are not generally effective in inhibiting sticking or sintering during fluidization; but finely divided carbon is effective for this purpose. Some carbon will be produced by the cracking of the gaseous fuel; and in the process of this invention sticking may be obviated by controlling the amount of carbon entrained in or formed from the reducing gases by varying the ratio of gas to oxygen in the partial combustion step. It will be understood that carbon is produced also by the decomposition of two carbon monoxide molecules to form free carbon and a carbon dioxide molecule. This reaction tends to be more rapid at temperatures lower than the temperatures preferred for the reducing gases in the process of this invention; but the amount of carbon present with the iron in the reactor can be controlled also by a control of temperature and by control of the presence of carbon monoxide in the gases.

If desired, and for the purpose of boosting the temperature of the ore and the gases in the upper part of a tall reactor, use may be made of a supplementary burner indicated at **17** in the figure, at which the gaseous fuel is burned with oxygen in the general ratios set forth above. In some instances the burner **17** may feed its flame directly into the reactor or the arrangement shown and described for the lower burner may be employed at the position **17**, including the introduction and admixture of processing gases from the closed recirculatory system.

The entire foregoing description is intended to be taken as an example of the practice of the invention in the best forms known to the inventors.

Modifications may be made in the invention without departing from the spirit of it. The invention having been described in certain exemplary embodiments, what is claimed as new and desired to be secured by Letters Patent is:

1. In a process of reducing finely divided iron ore by fluidized-solids reduction, the steps of:

(*a*) reducing fluidized finely divided iron ore by means of a reducing gaseous mixture at elevated temperature,

(*b*) withdrawing and introducing into a circulatory system all of the gases derived from said reduction step,

(*c*) subjecting said withdrawn gases in said circulatory system to cooling for the lowering of the moisture content of said gases, whereby to increase their reducing potential,

(*d*) bleeding out of said closed system an amount of the said withdrawn gases therein substantially equal to the amount of gases produced by the combustion of fuel as hereinafter set forth,

(*e*) burning a mobile fuel with oxygen in the substantial absence of inert gases so as to produce products of combustion consisting essentially of carbon monoxide, carbon dioxide, hydrogen and moisture, said products of combustion as formed being at a temperature of substantially 2000° to substantially 3500° F.,

(*f*) mixing the cooled and dried gases in said circulating system with said products of combustion in such quantity as to form said gaseous mixture having a temperature of substantially 1500° to 1700° F., said gaseous mixture having a diminished moisture content as respects said products of combustion and having strongly reducing characteristics at said temperatures, and

(*g*) employing the said gaseous mixture so formed in the said fluidized-solids reduction step.

2. The process claimed in claim 1 including the step of removing carbon dioxide from the withdrawn gases in the circulatory system.

3. The process claimed in claim 1 wherein the products of combustion and the circulated gases are mixed outside the zone in which the reduction step takes place.

4. The process claimed in claim 3 including the step of burning an additional quantity of hydrocarbon gas with oxygen and introducing the products of combustion thereof into another portion of the zone in which the reduction takes place.

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