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REDUCTION OF METAL OXIDES

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Fig. 1.

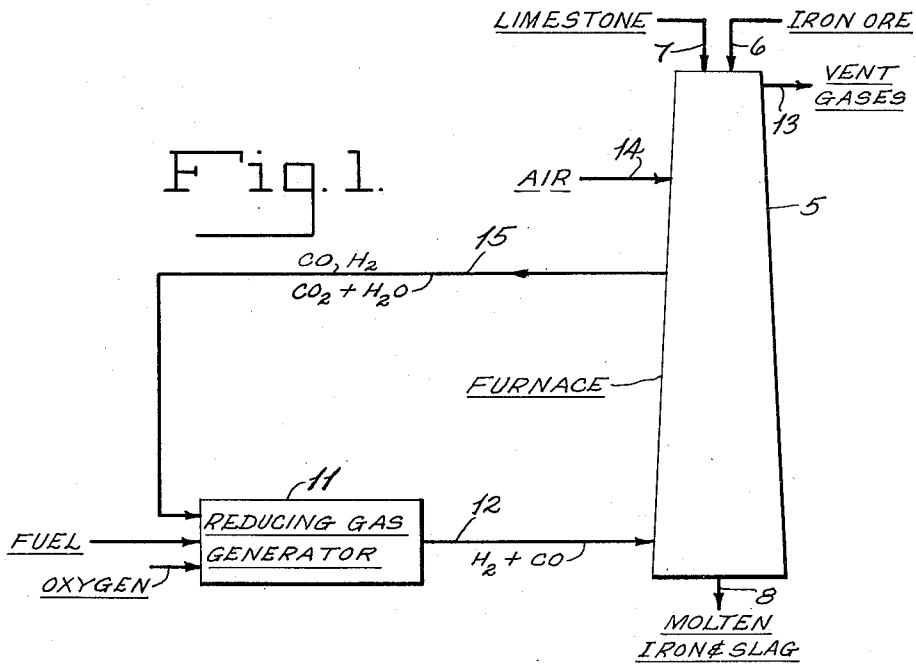
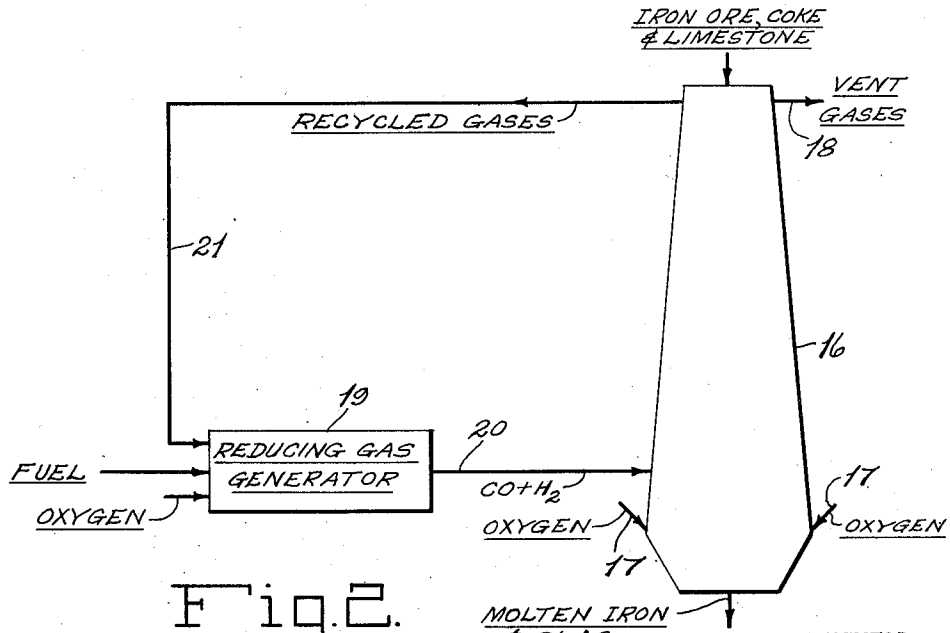


Fig. 2.



INVENTORS
F. BURTON SELLERS
PETER L. PAULL
BY
Daniel Shuyler
J. H. Graham
ATTORNEYS

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REDUCTION OF METAL OXIDES

Frederick Burton Sellers, Tarrytown, N. Y., and Peter L. Paull, Norwalk, Conn., assignors to Texaco Development Corporation, New York, N. Y., a corporation of Delaware

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4 Claims. (Cl. 75—41)

This invention relates to a process of reduction of a metal oxide with carbon monoxide and hydrogen. In one of its more specific aspects, this invention relates to a process for the production of metallic iron or pig iron by the reduction of an iron oxide, particularly iron ore, with carbon monoxide and hydrogen.

In the process of the present invention a reducible metal oxide in lump form is contacted with a mixture of carbon monoxide and hydrogen at a temperature sufficient to cause reduction of the metal oxide to metal and fusion of the resulting metal. The reduction of the solid metal oxide to molten metal takes place in a reduction furnace in which a downwardly moving bed of the metal oxide is maintained. The metal oxide is charged to the top of the bed and the molten metal drawn from the bottom. A reducing gas is introduced near the bottom of the bed and passed upward countercurrent to the flow of the metal oxide. The reducing gas is generated from any suitable fuel by reaction with oxygen. Among the suitable fuels are included hydrocarbon gases, oil, oil shale, coke and any of the various grades of coal, including lignite, anthracite and bituminous coal.

The present invention is particularly suited to the production of pig iron from iron ore. In the production of pig iron in a conventional blast furnace, coke and fluxing agents, generally limestone, are added to the furnace with the ore. Air is introduced at the base of the blast furnace, to consume the coke and generate carbon monoxide which, in turn, reduces the ore. The process of the present invention differs from conventional blast furnace operations in that at least a portion of the reducing gas required in the furnace is generated in a separate gas generator; in many cases it is desirable to generate all of the reducing gases in the gas generator.

By the process of this invention, part or all of the coke required for conventional blast furnace operations may be eliminated. This represents a tremendous practical advantage, as a number of sources of high grade iron ore are situated at a great distance from a source of coking coal. The production of pig iron may now be made independent of coking coals.

A number of processes for the generation of carbon monoxide and hydrogen from various fuels are known. In the process of this invention the carbon monoxide and hydrogen are generated by partial combustion of the fuel with an oxygen-containing gas. While air may be used as the oxygen-containing gas, relatively pure oxygen is preferred. Steam is preferably used in combination with the oxygen for all of the fuels except gaseous hydrocarbons. The reducing gas generator is operated at a temperature within the range of from about 2,000° F. to about 3,000° F., preferably at a temperature above about 2,200° F. and sufficient to insure that the metal and slag are in molten form. In the production of pig iron, a reducing gas temperature of about 2,400° F. is about the minimum temperature required when all of

the reducing gas is generated outside the ore reduction furnace.

A flow-type gas generator is preferably used for the generation of reducing gas for the process of this invention. The flow-type generator is characterized by the reaction of the fuel in an unpacked reactor in the absence of catalyst. When solid fuel is used, the fuel particles are suspended in the gaseous reactants and the gasification reaction takes place with the solid particles suspended in reactants and gaseous reaction products. For most successful operation of a generator of this type for the production of carbon monoxide and hydrogen, the temperature throughout the generator must be maintained at a temperature above about 2,000° F. The temperature may be as high as 3,000° F., although generally it is undesirable to maintain the temperature at this level because most refractory lining materials rapidly deteriorate at temperatures of 3,000° F. and above. Practical considerations, particularly apparatus limitations, usually limit the operating temperature to 2,600° F. to 2,800° F.

Suitable metal oxides which may be treated in this process include the oxides of iron, copper, vanadium, nickel, chromium, manganese and titanium.

In accordance with a specific embodiment of the present invention, iron oxide is reduced to metallic iron in a cylindrical shaft similar to a conventional blast furnace. Carbon monoxide and hydrogen generated in a separate reducing gas generator by partial combustion of fuel with oxygen is introduced at a temperature above about 2,400° F., into the lower part of the shaft. These gases ascend countercurrent to the descending bed of iron oxide, reducing the iron oxide to molten metallic iron.

Unless pure iron oxide is used, it is generally desirable to add a fluxing agent mixed with the iron oxide to produce a fluid slag at the base of the shaft. A flux is useful to reduce the fusion temperature of the slag and to render it more fluid. Fluxing agents are known in the blast furnace art. Limestone is generally suitable as flux for iron ores, although it may be desirable in some instances, to add fluorspar, silica, alumina, or magnesia to increase the quantity or fluidity of the slag. The kind and amount of flux required may be determined from the composition of iron ore as is known in the blast furnace art. In general, the most satisfactory fusion is obtained when the sum of the lime and magnesia in the feed material is approximately equal in weight to the sum of the alumina and silica. The lime or magnesia may be added in the form of the carbonates, but should be converted to equivalent quantities of the oxide in determining the quantity of flux required.

When a solid fuel is used in the gas generator, a fluxing material may be added to the gas generator to lower the fusion temperature and insure a molten fluid ash. The requirements for a satisfactory flux may be determined from the composition of the ash, following the foregoing rule for fluxing ore. With most coals, limestone is a satisfactory fluxing material. Generally, it is desirable to discard the slag from the generator; if desired, however, the molten fluid ash from the generator may be discharged directly into the ore reduction shaft together with the hot gases.

The reducing shaft may be operated at atmospheric pressure or at an elevated pressure. An elevated pressure is desirable in that it increases the capacity of the apparatus by speeding up the reactions involved in the reduction of the metal oxide. The gas generator preferably is operated at an elevated pressure above about 100 p. s. i. g. and preferably at a pressure of at least 100 p. s. i. higher than the pressure in the reducing shaft.

The reduction of the metal oxide may be carried out with carbon monoxide or hydrogen or mixtures of car-

bon monoxide and hydrogen in almost any desired portion.

It has previously been mentioned that when the metal oxide is an iron oxide or iron ore, it is preferable to operate the furnace at a temperature on the order of 2,500° F. or higher in order that both the iron and slag may be withdrawn in molten form as in conventional blast furnace operations. The temperature at the base of the shaft may sometimes exceed the temperature in the generator. This higher temperature in the shaft may result due to the reaction between the gas and the iron oxide.

In another embodiment of the invention, reducing gas is supplied to a conventional type blast furnace. The blast furnace is charged in the usual manner with iron ore, coke and limestone, but with less than the usual amount of coke. Air, or preferably oxygen, is supplied to the blast furnace in the usual manner, but in less than the usual amount. Since the amount of coke fed to the blast furnace is less than the usual amount, less oxygen is required for reaction with the coke. The deficiency in the quantity of reducing gas resulting from reduction of quantity of coke charged to the furnace is made up by supplying hydrogen and carbon monoxide from a separate gas generator. This operation permits a reduction in the coke requirements for blast furnace operations and permits application of the present invention to existing installations of blast furnaces.

In some instances it may be desirable to charge ceramic pieces, for example, pieces of refractory brick, to the furnace to make up for the omission of coke, to provide support for the charge in the reactor and permit free flow of the gas upwardly through the charge. This has the disadvantage of requiring fusion of the brick or, alternatively, batchwise operation of the furnace.

An object of this invention is to provide an improved process for the reduction of a metal oxide with carbon monoxide and hydrogen. A further object is to provide a process for the production of pig iron from iron oxide wherein the iron oxide is reduced with gas from an external source. A still further object is to provide an improved process for the operation of blast furnaces to reduce the requirements for high grade metallurgical coke. Other objects and advantages of the invention will be apparent from the following detailed description of the invention and the accompanying drawings.

Figure 1 of the drawings illustrates diagrammatically one embodiment of the invention as applied to the production of pig iron from iron ore. Figure 2 illustrates diagrammatically the application of the process of this invention to blast furnace operation.

With reference to the drawing, the numeral **5** designates a shaft filled with iron ore in which the ore is reduced to the molten metal. The ore is preferably reduced in apparatus in the form of a tall vertical column or shaft slightly larger in diameter at the bottom than at the top. Iron ore and limestone are introduced as charge to the upper end of the shaft as indicated in the drawing by lines **6** and **7**, respectively. Molten iron and slag are tapped off the bottom of the shaft as indicated by line **8**.

Reducing gas is generated in a gas generator **11**, in which fuel and oxygen are combined to produce a mixture of carbon monoxide and hydrogen. In this example, the generator is operated at a temperature of about 2,600° F. The resulting stream of hydrogen and carbon monoxide is passed without cooling through line **12**, directly into the lower portion of the shaft. The temperature at which the gas generator is operated is preferably the maximum temperature which may be tolerated in the generator wtihout unnecessarily shortening the life of its refractory lining.

As the reducing gas from line **12** passes up through the shaft it is contacted by the iron oxide and limestone slowly descending through the shaft. In the lower portion of the furnace, the iron oxide is substantially completely reduced to metallic iron. Oxygen given up by the iron oxide during its reduction converts the carbon monoxide and hydrogen ascending through the shaft to carbon dioxide and steam. Only a part of the ascending gas stream is oxidized, so that some carbon monoxide and hydrogen is still present in the upper portion of the shaft. Gases are vented from the upper part of the shaft through line **13**. These gases contain considerable quantities of heat which may be used for the generation of steam.

Air or oxygen may be introduced into the upper portion of the furnace through line **14**, for combustion of the unreacted carbon monoxide and hydrogen. Burning these gases in the upper part of the furnace preheats the incoming charge of iron ore and limestone. It is generally desirable to recirculate gas from an intermediate point in the shaft to the gas generator. This is indicated in the drawings by line **15**. The recycle stream may range as high as about 70 percent of the gases ascending through the shaft.

Sulphur may be removed from the reducing gas before it is introduced to the shaft. Sulphur removal may be effected by passing the hot reducing gas stream over iron or limestone. In the process of the invention it is preferable to pass the gas through a bed of limestone, or calcium oxide, for sulphur removal. The calcium oxide may be subsequently charged to the shaft with the ore and the sulphur removed therefrom by burning with the air or oxygen introduced through line **14**. Removal of sulphur from the reducing gas is desirable when the fuel supplied to the synthesis gas generator contains an appreciable amount of sulphur, such as, for example, coal, oil shale, sour natural gas, or a sour hydrocarbon oil.

Figure 2 of the drawings illustrates the application of the principles of my invention to the production of pig iron in a conventional blast furnace. A blast furnace **16** is charged with a mixture of iron ore, coke, and a fluxing material, for example, limestone. In accordance with this invention, less than the usual amount of coke is used which, in turn, reduces the limestone requirements. Thus the charge to the furnace is richer in iron ore than is the charge to the conventional blast furnace. Molten iron and slag are tapped from the lower portion of the blast furnace in the usual manner. Air or other oxygen-containing gas, preferably relatively pure oxygen, is introduced to the blast furnace through the usual tuyeres **17**. Gases are vented from the upper end of the furnace through line **18**.

A stream of reducing gas, comprising carbon monoxide, is generated in a reducing gas generator **19** by partial combustion of a carbon-containing fuel with an oxygen-containing gas, preferably relatively pure oxygen. These gases are introduced through line **20** into the blast furnace at an intermediate point, above the point of introduction of air. A part of the gases may be recycled from the upper portion of the blast furnace through line **21** to the reducing gas generator. These gases contain carbon dioxide and water vapor resulting from oxidation of hydrogen and carbon monoxide with oxygen given up by the ore. In the reducing gas generator, the carbon dioxide and water vapor are again converted to carbon monoxide and hydrogen.

It will be evident that, by supplying an auxiliary stream of reducing gas from an external generator to the blast furnace, economies are realized due to the savings of high grade coke. When the limestone charged to the shaft has been previously used for removing sulphur from the gases from the reducing gas generator, the sulphur may be eliminated from the limestone by introducing air or oxygen to the furnace as previously described. This converts the sulphur associated with the limestone or iron ore to sulphur dioxide which is discharged from the shaft with the vent gases.

Example 1

Iron ore containing 63 weight percent iron is reduced

in a shaft using a limestone containing about 95 percent calcium carbonate as a flux. Ore is charged at the rate of 4.25 tons per hour, mixed with about 1,200 pounds of limestone. The ore is reduced with a stream of carbon monoxide and hydrogen from a separate gas generator, the operation of which is described more fully hereinafter.

The furnace is operated at a pressure of about 200 pounds per square inch gauge and with a hearth temperature (botton of shaft) of 2,700° F. The furnace produces about 2.7 tons of pig iron per hour containing about 99 weight percent metallic iron and only about 0.01 weight percent sulphur. Molten iron and slag are tapped from the base of the furnace as in conventional blast furnace operations.

Hot reducing gas is produced in a flow-type coal-fired gas generator. A dispersion of powdered coal in steam is reacted with commercially pure oxygen in an unpacked reaction zone containing no catalyst or packing. Bituminous coal having the following proximate analysis is used.

	Weight percent
Moisture	4.3
Volatile matter	39.7
Fixed carbon	46.7
Ash	9.3

The coal contains about 0.4 weight percent sulphur.

Commercial oxygen obtained by air rectification and analyzing about 95.3 volume percent oxygen is supplied to the generator. Approximately one ton of coal per hour is fed to the generator, together with about 110 pounds of steam and 20,000 standard cubic feet of oxygen. The oxygen, steam and coal are preheated to a temperature of about 1,000° F. The resulting generator temperature is about 2,700° F. The hot gas from the generator is passed without preliminary treatment directly to the ore reduction furnace.

A stream of gas is withdrawn from an intermediate point in the ore reduction shaft and recycled to the generator. This gas contains about 24 volume percent water vapor and has the following approximate analysis on a dry basis.

	Volume percent
Hydrogen	10.5
Carbon monoxide	40.8
Carbon dioxide	45.8
Nitrogen	2.9

The recycle gas stream amounts to about 138,000 cubic feet per hour.

The gas from the generator has the following approximate analysis on a dry basis.

	Volume percent
Hydrogen	14.8
Carbon monoxide	56.9
Carbon dioxide	25.5
Nitrogen	2.8

About 204,000 S. C. F. H. of gas, containing about 20 volume percent water vapor, is passed from the generator into the ore reduction furnace.

Ash containing about 18.5 weight percent carbon is drawn from the generator in molten condition.

About 7,000 standard cubic feet per hour of air is introduced to the shaft above the point from which the recycle stream is withdrawn to burn the remaining gases in the shaft and preheat the incoming ore and limestone.

Example 2

Iron ore containing 63 weight percent iron is mixed with coke and with limestone containing 97 weight percent calcium carbonate. The mixture is charged into a conventional type blast furnace in the following proportions:

	Lbs./hr.
Iron ore	6000
Limestone	965
Coke	1950

86,700 S. C. F. H. of air is supplied to the blast furnace through tuyeres in conventional manner.

Above the level of the air tuyeres, additional reducing gas is introduced into the furnace from a gas generator of the type shown in U. S. Patent 2,582,938 to duBois Eastman and Leon P. Gaucher. San Ardo crude oil is fed to the generator with steam and commercial oxygen in the following proportions:

Oil	lbs./hr.	747
Steam	lbs./hr.	211
Oxygen	S. C. F. H.	8030

The oil and steam are preheated to 730° F.; high purity oxygen is supplied at ambient temperature.

The reducing gas has the following composition:

	Volume percent
Hydrogen	46.0
Carbon monoxide	44.8
Carbon dioxide	2.7
Nitrogen	0.7
Methane	1.2
Hydrogen sulfide	0.5
Water	4.1

The temperature of the gas generator is about 2,600° F. The reducing gas is introduced into the blast furnace at the rate of 37,950 S. C. F. H. The gases are introduced above the tuyeres and below the point at which the temperature of the furnace is below 2,000° F.

A pressure of 350 pounds per square inch gauge is maintained in the gas generator. The pressure at the inlet to the blast furnace is in the range of 5 to 40 p. s. i. g. Pressure reduction between the generator and the blast furnace inlet takes place across an Alundum sleeve 0.6 inch inside diameter.

Iron and slag are tapped from the furnace in conventional manner at the rate of 3,785 pounds of iron and 1,310 pounds of slag per hour.

By way of comparison, reduction of the iron ore by conventional blast furnace operation to produce the same amount of pig iron requires 3,070 pounds of coke and a considerable increase in limestone.

Operation of the gas generator at a pressure considerably higher than the pressure in the blast furnace, e. g., 100 to 500 p. s. i. higher than the blast furnace pressure, is an important feature of our invention. The difference in pressure between the gas generator and the blast furnace produces a high velocity jet of reducing gas at its point of introduction to the blast furnace. This insures deep penetration of the blast of reducing gas into the ore bed. A deLaval type nozzle (a convergent-divergent nozzle) may be used to impart maximum velocity to the jet of reducing gas. The velocity of the stream of reducing gas at the point of pressure reduction is preferably in excess of about 1,000 feet per second.

We have found that an auxiliary reducing gas suitable for use in a blast furnace may be produced by partial oxidation of a carbonaceous fuel at a temperature of 2,000 to 3,000° F., preferably at a temperature of 2,400 to 2,800° F. We have also found that a satisfactory reducing gas stream may be prepared by reacting a hydrocarbon fuel oil with substantially pure oxygen and with from about 20 to about 40 weight percent steam based on the weight of the oil. The resulting reducing gas contains from about 2 to about 8 percent steam and from about 1 to 4 percent carbon dioxide by volume. It is preferable to maintain the water content of the reducing gas stream within the range of 2 to 4 percent by volume.

This application is a continuation-in-part of our application Serial No. 264,158, filed December 29, 1951, now abandoned.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a process for the reduction of iron oxide to molten metallic iron wherein iron oxide admixed with coke and a fluxing material is contacted in an elongated vertical reduction zone with an upwardly flowing stream of reducing gas comprising carbon monoxide whereby the iron oxide is reduced to molten iron, and an oxygen-containing gas is introduced into the lower portion of said reduction zone whereby coke is converted to carbon monoxide, the improvement which comprises generating an auxiliary stream of reducing gas comprising carbon monoxide and hydrogen containing not more than 8 percent steam and not more than 4 percent carbon dioxide by volume by reaction of a hydrocarbon fuel oil with an oxygen-containing gas and from about 20 to about 40 weight percent steam based on the weight of said oil at a temperature within the range of from about 2,000° F. to about 3,000° F. in a separate gas generation zone, and introducing said auxiliary stream of reducing gas substantially at said

reaction temperature directly into said reduction zone at a point above the point of introduction of said oxygen-containing gas to the reduction zone.

2. A process as defined in claim 1 wherein said auxiliary stream of reducing gas is generated at a pressure at least 100 p. s. i. higher than the pressure in said reduction zone and said stream of gas passed through a zone of restricted cross-sectional area imparting a velocity in excess of 1,000 feet per second to said stream.

3. A process as defined in claim 1 wherein said auxiliary stream of reducing gas contains not more than 4 percent steam by volume.

4. A process as defined in claim 1 wherein said oxygen-containing gas is substantially pure oxygen.

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