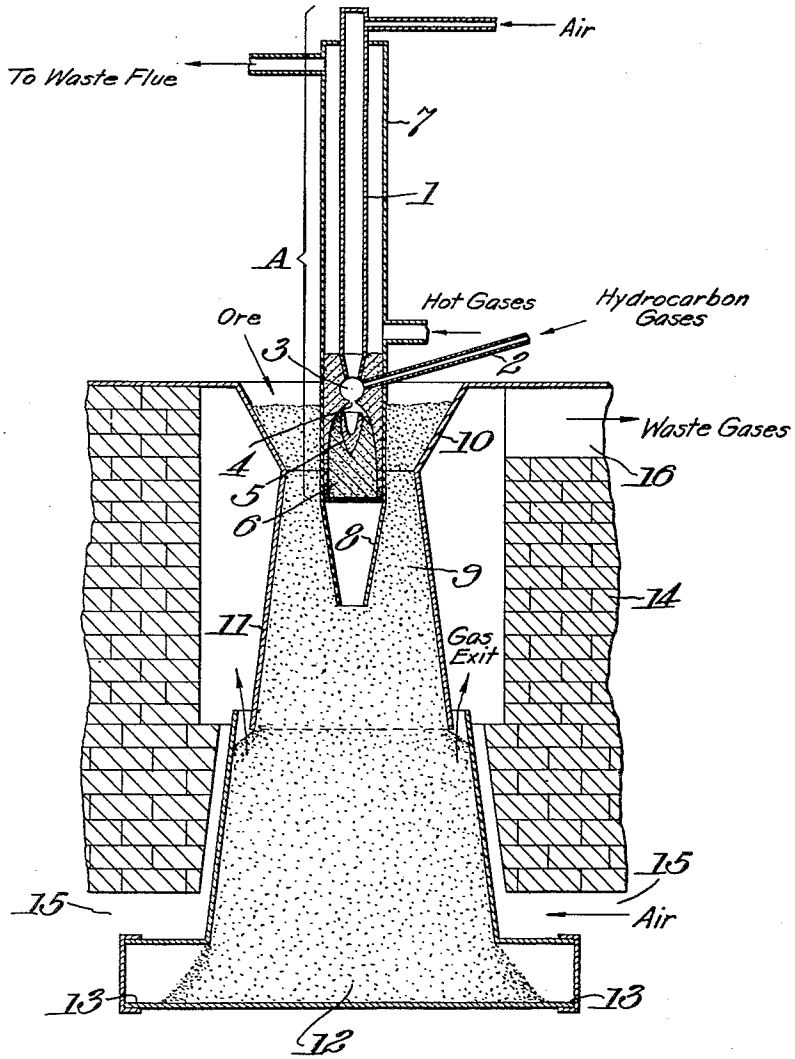
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ORE REDUCTION PROCESS

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ORE REDUCTION PROCESS

Application filed May 7, 1932. Serial No. 609,966.

This invention relates to a process of continuously utilizing hydrocarbon gases, methane or natural gas, for reducing ores.

My process is especially adapted to the reduction of ores of base metals which are reducible wholly or in part only by supplying heat from external sources due to the endothermic requirements of the reduction. It is moreover particularly adapted to the reduction of base metal ores containing such quantities of metalloidal materials, as sulphur or phosphorus, as to be unsmeltable by ordinary methods. An example of such an ore is the so-called pyrite cinder or residue from plants where iron pyrites are burned for the sulphur content. Such materials often contain from 50 to 60% metallic iron as oxides, and must therefore be considered as potential iron ores. In the past it has been impractical to smelt such materials because ordinary methods do not remove the residual sulphur, which may vary from 0.5 to 2.0% even in the best pyrite burning practice. The ordinary reduction of such ore would produce iron containing from 1 to 4% of sulphur, thus rendering it unfit for use without further expensive and difficult purification.

My process may also be used advantageously for other base metal ores having similar requirements, such as those of manganese, chromium, zinc, and many others of the moderately strongly basic metals.

In the prior art, attempts have been made to utilize the well known desulphurizing action of hydrocarbon gases in the treatment of ores and materials of the type referred to. Some workers have attempted to replace part of the solid fuel used in blast furnace operation by hydrocarbon gases, both for the sake of saving the locally more expensive solid reductant, and for the sake of the desulphurizing and cleansing action of hydrocarbons on the metal.

It has been the general experience that such procedure has been ineffective, because most of the hydrocarbon gases passed through the furnace unutilized, due to the chemical inertness of methane and other hydrocarbons.

Further it was found that the cleansing action of methane or other hydrocarbon gases in removing sulphur, phosphorus, or other metalloids, was less effective at higher temperatures and in particular when the metal or ore was fused.

The cleansing action of methane or hydrocarbon gases in removing suplhur has been shown to be due largely to the hydrogen produced by thermal decomposition of the hydrocarbon at high temperatures. In the case of iron, the most efficient temperatures for desulphurizing are from 750 to 1050° C. Desulphurizing produces H_2S as gaseous product. Below 750° the rate of desulphurizing is slow, but above 1050 H_2S is itself dissociated largely into sulphur vapor and hydrogen, which tends to reverse the cleansing action.

It has further been found that when methane or other hydrocarbon gases were used directly to reduce oxide ores, the process became more highly heat absorbing because of the necessity of supplying the heat of decomposition of the hydrocarbon. Other troubles arose from the harmful formation of elementary carbon, due to thermal dissociation of the hydrocarbon gases, which tended to clog the ore column being reduced.

Other workers have attempted to supply the necessary heat for reduction by admitting some air with the hydrocarbon gases. This results in increased concentration of carbon dioxide and water vapor, which slows up, or may completely prevent, reduction.

Still others have attempted to secure the removal of metalloidal impurities along with reduction by using water gas, consisting essentially of mixtures of carbon monoxide and hydrogen, for reduction. These methods have not found practical use for the following reasons:

1. The water gas has in the past been necessarily made by discontinuous or intermittent processes, usually from solid carbonaceous fuels and steam, with intermittent blasting with air to supply the necessary heat of the gas manufacturing process.

2. The necessary heat for the reduction process, using water gas or similar reducing mixed gases, has had in the past to be

supplied by admixture of air, by preheating, or by recirculation, or by heating through retort walls. The admixture of air in the reducing furnace here again acts deleteriously on the reduction by producing high CO_2 and H_2O concentrations. Preheating to sufficient degree to supply the thermal requirements of reduction necessitates the use of such high temperatures that local overheating of the ore occurs, and as indicated above, the desulphurizing or cleansing action suffers, and the metal or ore may be undesirably melted. Recirculation involves expensive pumping costs and the loss of heat because no mechanical means are available for pumping gases at such high temperatures. Heating through retort walls is notoriously inefficient from a thermal viewpoint, and again may cause local overheating of the furnace charge.

The manner in which I overcome these difficulties and utilize the highest economic and scavenging effects of hydrocarbon gases is as follows:

In my process I first preheat air to a temperature of at least 800° C.

I then intimately mix this preheated air with hydrocarbon gases, methane or natural gases, under such conditions that no combustion or flame ensues. The specific manner in which this may be done is set forth in my copending application, Serial No. 609,965, filed concurrently herewith.

After intimate mixture is obtained I pass the mixed gases through a catalytic mass in such a way as to avoid flame. A chemical reaction ensues which generates heat and at the same time causes the methane or hydrocarbons and air to be continuously converted to a mixture of hydrogen, nitrogen, and carbon monoxide at a temperature from 150° to 250° higher in temperature than the preheated air.

I submerge said catalytic converter in an ore mass, or lead the gases from it through a heat insulating duct directly into or over an ore mass.

The principal novel features of my process are as follows:

1. Use of preheated air with hydrocarbon gases. Ordinarily this procedure would result in a flame or combustion, and deleteriously affect the reducing power of the mixture. I avoid this in the manner specified in my copending application.

2. The continuous catalytic conversion of the air-hydrocarbon mixture to a reducing gas, with the setting free of utilizable heat, and without permitting the presence of appreciable quantities of CO_2 and H_2O. The amount of CO_2 and H_2O in the reducing gas is less than 1% of each.

3. The maintenance of suitable temperature conditions in the reducing part of the furnace to ensure the utilization of the scavenging effect of hydrogen gas.

4. Ensuring an adequate heat carrying capacity for continuous operation without recirculation by maintaining a nitrogen content of the reducing gas of approximately 40% or more by volume. The maintenance of this nitrogen content enables sufficient heat to be supplied to the reduction without excessive thermal gradients which would fuse the charge, render it impervious, and prevent desulphurization.

5. Utilizing the heat generated by the catalytic conversion of air-hydrocarbon mixtures for endothermic ore reductions by carrying out such catalytic conversion in or adjacent to an ore mass.

The invention is illustrated by the following example of a method of making sponge iron from pyrite cinder which is described in connection with the accompanying drawing which is a diagrammatic vertical section of apparatus suitable for the execution of the process. It is to be understood that my invention is not limited to this specific apparatus or to the specific procedure or conditions described hereinafter excepting as required by the claims.

Referring to the drawing the A marks the assembly, which is more fully described in my copending application, in which preheated air at a temperature of at least about 800° C. and gaseous hydrocarbon are mixed and subjected to catalytic reaction without flame to yield a gas mixture consisting essentially of hydrogen, carbon monoxid and nitrogen, substantially free of carbon dioxid and water vapor and at a temperature in the neighborhood of 1000° C. or higher. For completeness it is noted that 1 is the air supply pipe and 2 is the hydrocarbon gas supply pipe both nozzled into the mixing chamber 3 from which the mixture flows through orifice 4 against the refractory deflector 5 and then downwardly through the catalytic mass 6 of e. g. porous crystalline alumina impregnated with nickel salts or nickel oxid. Pipe 1 is surrounded by the jacket 7 through which hot gases are passed for preheating the air supply. The outlet of the gas forming device A discharges into the short conduit 8 of truncated cone shape, made of suitable refractory material such as 10-gauge sheet chrome-nickel steel. Conduit 8 and the lower end of the device A are submerged in the ore column in the reducing chamber 9. The reducing chamber also may be made of sheet chrome-nickel steel and is shaped so that the wall 10 at the upper end diverges upwardly to facilitate the feeding of ore and the wall 11 at the lower end diverges downwardly to facilitate the flow of the ore. The lower edge of wall 11 fits loosely into the upper end of the cooling and collecting chamber 12 which is provided at its bottom with

outlets 13—13. The reducing chamber 9 and collecting chamber 12 are surrounded by the brick wall 14 so shaped and spaced therefrom as to permit flow of air from the inlets 15—15 therefor upwardly in contact with the walls of the chambers 9 and 12 and out through the outlet opening 16.

In operation the device A is operated in the manner briefly described above and more fully described in my companion application, and ore is fed into the hopper shaped upper end of the reducing chamber 9. The position of the outlet end of the conduit 8 is adjusted so that about 2/7 of the gas discharged therefrom passes upwardly through the ore while the remainder, 5/7, flows downwardly and out through the space between the walls of chambers 9 and 12. In the upper part of the reducing chamber the principal reactions are the reduction of Fe_2O_3 to Fe_3O_4 and FeO with the oxidation of the CO and H of the gases to CO_2 and H_2O. In the lower part of the chamber the reduction of the ore is completed to sponge iron with only a partial utilization of the reducing capacity of the gases. The temperature in the chamber 9 ranges from about 750° C. at the top to about 1000° C. at the bottom. Since the gas leaving the chamber 9 at the bottom still contains considerable amounts of CO and H, it burns with the air passing up between the brick wall 14 and the wall 11 of the chamber 9, and thus serves to, to some extent, retard loss of heat from the chamber 9. The heat within the chamber 9 ordinarily is higher than that of the surrounding atmosphere within the brick wall 14.

A typical ore charge consists of pyrite cinder of the following composition:

	Per cent
Fe_2O_3 calculated as Fe	54
CuO	0.2
S	0.6
As	0.2
Zn	0.1
Insoluble	20

When the hydrocarbon gas used in the process is natural gas containing about 85% methane and 13% ethane about 16,000 to 25,000 cubic feet thereof and about 56,000 to 87,000 cubic feet of air are consumed per ton of iron produced. The sponge iron product contains about 70 to 71% of metallic iron, less than 1% of iron as oxid, 0.3 to 0.4% of copper, less than 0.005% of sulphur, less than 0.002% of arsenic, a trace of zinc and 1 to 2% of carbon. The balance is unreducible material which may readily be separated from the iron by magnetic means.

The sponge iron after the separation of non-magnetic material is valuable as a foundry iron, for the manufacture of steel, and as a chemical or metallurgical precipitant. It is a true sponge iron and may be briquetted by simple pressing without a binder. It is highly porous. It will be noted from the low sulphur and arsenic content of the product that the process is highly effective in the removal of metalloidal materials.

A specific example of the method of preparing the highly heated reducing gas consisting essentially of hydrogen, carbon monoxid and nitrogen and being substantially free of carbon dioxid and water vapor for use in the above described process is as follows:

Hydrocarbon gas and preheated air enter the chamber 3 through pipes 2 and 1, the air being preheated to a temperature of 800–1000° C. by hot combustion gases or flame entering as indicated near the bottom of pipe 7 and passing upwardly in contact with the pipe 1 to the flue. The nozzle ends of pipes 1 and 2 are made of such size that they deliver the gas and air into the chamber 3 in proper proportion and at a velocity exceeding the flame propagation rate. The gas and air streams impinging in the chamber 3 are efficiently mixed and the mixing is made more complete by the passage of the mixture through the orifice 4, and its movement into and out of the cavity of the deflector 5 and over its upper edge downwardly into the catalytic mass. The size of the chamber 3, orifice 4, the cavity in the deflector 5 and the passageway between the upper edge of the deflector 5 and the wall of cavity containing the catalytic mass 6 and between the outer wall of the deflector 5 and the adjacent wall of said cavity are such that the flow of the gases exceeds the flame propagation rate until the gases reach a point about half way down the outer wall of the deflector 5 in the catalytic mass. Under these conditions it is found that reaction zones and zones of concentration of heat do not occur, there is no local overheating and destruction of the catalytic mass and other parts of the apparatus, and secondary reactions converting any carbon dioxide and water resulting from the primary reaction into carbon monoxide and hydrogen, are completed.

The following specific conditions of operation are illustrative. The pipe 1 is made of 10 gauge alloy steel 2 inches in diameter and 5 feet long, nozzled at one end to an orifice ½ inch in diameter. The pipe 2 is of the same material and ¾″ diameter, but nozzled to a ⅜ inch orifice. The chamber 3 is 1½ inches in diameter and the orifice 4 is ¼ inch in diameter. The cavity containing the catalytic mass 6 to 7 inches long and 6 inches in diameter. The deflector thimble 5 is 3½ inches long, 1¼ inches maximum internal diameter and 2¼ inches maximum external diameter. The catalyst is crystalline alumina of 4 to 10 mesh size impregnated with nickel. Air is delivered into the chamber 3 at 900° C. and at the rate of 100 liters per minute and natural gas is delivered at the rate of 35 liters per minute, both gas and air

under a gauge pressure of about 2 pounds per square inch. The gas passing out through the conduit 8 is at a temperature of 1050–1100° C. The analysis of the natural gas used is:

	Per cent
Methane (CH_4)	86.85
Ethane (C_2H_6)	7.86
Propane (C_3H_8)	3.87
Higher paraffine hydrocarbons	1.47

The gas produced is of the following composition:

	Per cent
Methane (CH_4)	0.5
Carbon dioxide (CO_2)	0.9
Water (H_2O)	0.9
Carbon monoxide (CO)	19.3
Hydrogen (H_2)	36.4
Nitrogen	41.9

I claim:

1. In the process for the reduction of oxygen containing metal compounds and ores by contacting the same at a temperature of from 750° to 1050° C. with a gas mixture containing carbon monoxid, carbon dioxid, hydrogen, water vapor and nitrogen, produced by reacting a hydrocarbon with an oxygen containing gas, the improvement which consists in limiting the contents of both carbon dioxid and water vapor in said gas mixture to less than 1% and providing a nitrogen content in the gas mixture of at least 40%.

2. In the process as defined in claim 1, contacting the gas mixture with the oxygen containing metal compound or ore under substantially complete exclusion of oxygen containing gas and combustion products.

3. In the process as defined in claim 1, limiting the hydrocarbon content of the gas mixture to less than 1%.

In testimony whereof, I affix my signature.

CHARLES G. MAIER.