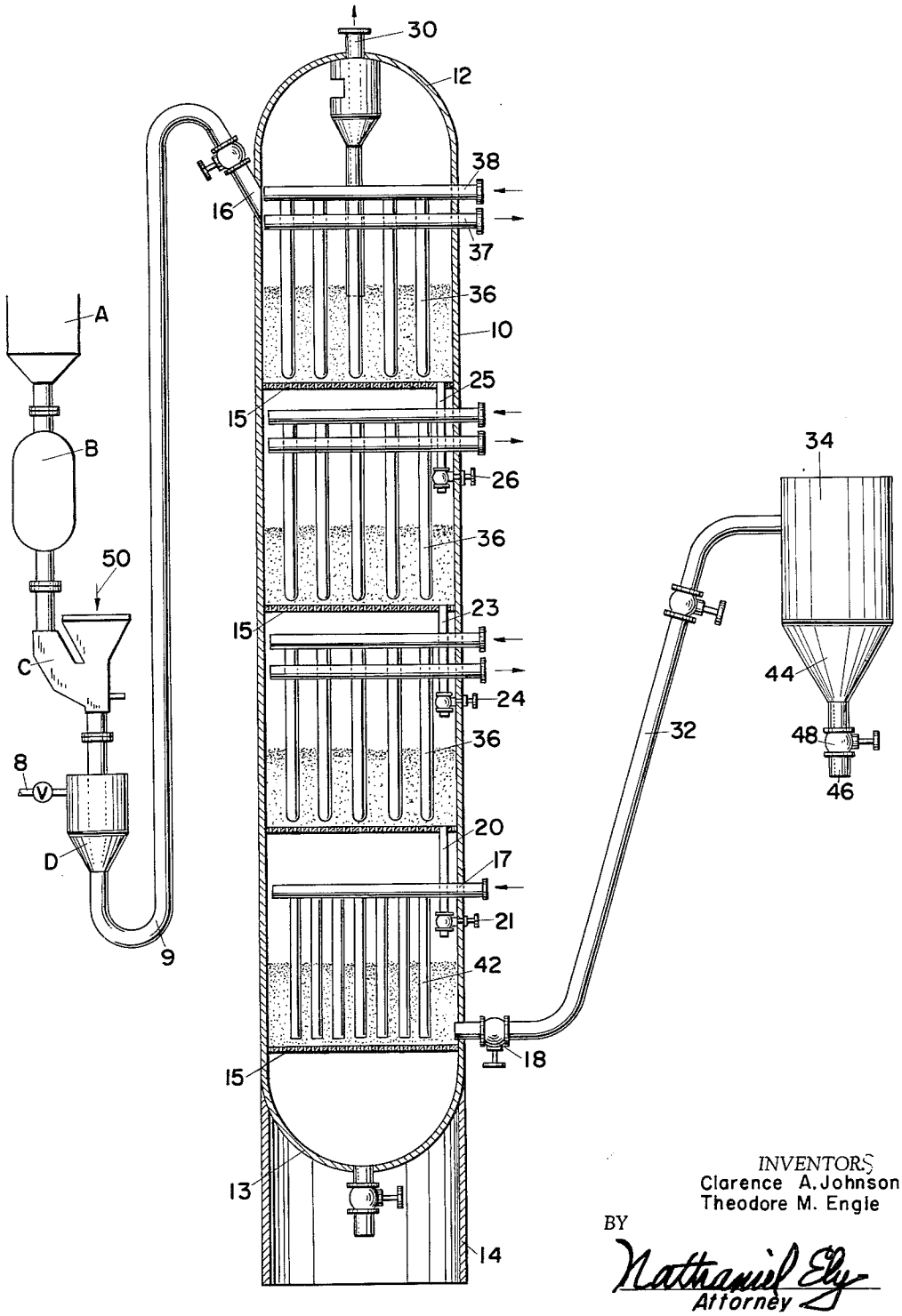
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DIRECT REDUCTION OF METALLIC ORES

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DIRECT REDUCTION OF METALLIC ORES

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This invention relates to improvements in the production of metallic oxides and more specifically to an improved process of reducing iron oxide by the direct reduction at temperatures less than fusion with a reducing gas such as hydrogen. It is a continuation-in-part of our copending application, Serial No. 201,123, filed June 8, 1962, now abandoned.

In the patents to Keith et al., 2,900,246, and Keith, 2,995,426, it has been pointed out that iron ore can be effectively reduced by passing relatively pure hydrogen upwardly through a bed of ore at a gas velocity such as to fluidize the bed. Preferred operating conditions are set forth in such patents and they are usually characterized by temperatures in the range of about 700° F. to 1000° F. and pressures in the order of 200 to 600 p.s.i.g. Hydrogen purity is expressed in average molecular weight in the range of about 3 to 7.5 and provision is made for the control of the water vapor content of the recycle gas.

Considerable experience has been had with operations as set forth in the foregoing patents and semi-commercial size units have been under continuous operation for extended periods of time. Furthermore, these operations have been carried out on various ores in the usual category of hematite and magnetite.

More recently, however, unexpected interference with smooth operations were noted not only in the evidence of plating in the transfer lines but there was evidence of plugging of valves, apparently due to a stickiness, and there was an increased pressure drop across the respective fluidized bed distributor plates. This materially interfered with continuity of operations and in several cases required a complete shut-down for cleaning of the plant.

On a further study of the different operating conditions which tended to develop these interferences with uniformity of operations, it was noted that they frequently, and almost invariably resulted when a mill scale was being reduced. As this is a commonly available supply of iron oxide and its reduction thus of economic importance, considerable study was given to the problem of avoiding this plating, sticking and increased pressure drop and also to the problem of eliminating these conditions after they had started.

Our invention is thus addressed to the reduction of metallic oxides by direct gaseous fluidized contact to render the process generally applicable to various ores and to maintain uniform operating conditions.

A further object of our invention is to provide an improved process for the direct reduction of mill scale with hydrogen in a fluidized bed at superatmospheric pressure and temperatures below fusion.

A more specific object of our invention is to add carbon to the feed material to a ball mill, rod mill or other grinding equipment when grinding iron bearing material such as mill scale, hematite or magnetite ore to eliminate, suppress and minimize stickiness of this powder when reduced at temperatures in the range of 600–1000° F.

Further objects and advantages of our invention will appear from the following description of a preferred form of embodiment thereof when taken with the attached drawing illustrative thereof and which represents in part a schematic flow diagram and in part a central vertical action through a reducer.

The novel feature of our invention is the addition of carbon to the metallic oxide in a highly dispersed form to become a surface coating. It is found that this carbon, which may be in the form of graphite, coal (anthracite or bituminous), charcoal, coke, or other substances containing a high percentage of carbon, is particularly helpful with low carbon containing materials such as mill scale, and is also helpful even with the other iron oxides such as hematite or magnetite.

In a commercial operation, the iron ore is collected in a hopper A from which it passes through drier B into a pulverizing mill C. Usually these are of gravity feed character and inasmuch as the reactor is operated at relatively high pressure, the charge is periodically pressurized by a suitable gas entering line 8 to the charge hopper or pressure chamber D. The ore is thus discharged through transfer line 9 to reducer 10. It will be understood that this equipment heretofore mentioned is commonly available and is only schematically shown, valves and other controls being omitted but commonly provided.

The reducer 10 as generally shown is preferably a cylindrical tower having a hemispherical top 12 and bottom 13, the bottom being supported on a cylindrical extension 14. This extension or skirt 14 is usually provided with access openings, not shown, and is of sufficient height to give the desired head room under the bottom 13.

The reducer 10 is divided into a plurality of sections or beds, or reaction zones, which are established by the horizontal partitions 15 of which four are shown in this instance. Generally, there are at least three and they serve to receive and hold the metallic oxides which may be introduced to the top bed through inlet 16.

In reducer 10, in each of the several beds, the finely divided metal oxide (iron oxide) is intimately contacted and reacted with a high purity hydrogen at temperatures in the range of about 700° to 1000° F., preferably about 850° to 950° F., and at pressures in the range of about 200 to 600 p.s.i.g. (pounds per square inch gauge), preferably about 350 to 450 p.s.i.g. For the purpose of this invention, high purity hydrogen containing only small amounts of such gas as carbon monoxide and dioxide, methane, nitrogen and water vapors; more specifically, the high purity hydrogen used in the process of this invention generally has a composite average molecular weight in the range of about 3 to 7.5, preferably less than about 5.5. Since hydrogen has a molecular weight of 2 and the aforesaid admixed gases have molecular weights varying from 16 to 44, it is obvious that the quantities of the admixed gases must be kept small to hold the composite average molecular weight below the upper limit of 7.5. Furthermore, the moisture content must be kept below the range of 0.5% by volume to 3.0% by volume as set forth in the aforesaid Keith et al., Patent 2,900,246.

To effect the intimate contact between the finely divided iron oxide and the reducing hydrogen in accordance with this invention, the iron oxide is maintained as a layer or bed, usually not exceeding about 10 feet in depth, while the pressurized high-purity hydrogen is passed upwardly therethrough at a rate sufficient to mobilize the particles. For the usual particle sizes and densities of the iron oxide treated by this invention, the reducing gas will generally have a superficial linear velocity of the order of 0.5 to 2.0 feet per second while contacting the mass of iron oxide.

By operating at pressures in the range of 200–600 p.s.i.g., the moisture content of the reaction gases withdrawn at 30 is rapidly reduced to less than 0.4% by volume by cooling gases to a temperature of 100° F. or lower with water at temperatures available in most localities. While not shown herein, it is contemplated that

such gases will be recycled as described in Keith et al., Patent 2,900,246 provided, of course, that a certain proportion of the gases will be vented or discarded to prevent the content of methane and nitrogen from building up to an extent that the mixed recycle and make-up gases have a composite average molecular weight exceeding 7.5.

For the purpose of this invention, the reducing gas is shown as entering the bottom chamber through tubes **42** from inlet **17** by which the gas is preheated and distributed as described in the Stotler Patent 2,805,144.

After sufficient reduction is completed in the lowermost bed, the solids discharge out of the bottom through valve **18** and transfer line **32** to storage hopper **34**. This, in turn, permits dumping the next ore bed above through downcomer **20** by opening the valve **21**.

The hopper **34** is conveniently provided with a cone shaped bottom **44** and discharge conduit **46** which may be provided with a valve **48**.

In turn, the next above bed can be discharged through the downcomer **23** by opening valve **24** and similarly the next bed may then pass by gravity downwardly by downcomer **25** when valve **26** is open. Thereafter fresh feed is introduced to the top bed through the inlet **16**.

While a full explanation and understanding of the particular reaction is not essential for the understanding of this invention, it is found desirable as set forth in the aforementioned patent, 2,995,426 to provide heat exchange or vertical baffle surfaces in the respective zones to establish and maintain suitable fluidity. It is usually found desirable to make these baffles of a heat exchange or tubular type, the upper bed being provided with series of U-tubes **38** supported from headers **37** and **38** for the passage of heat exchange material which may be liquid or, as preferred, the hydrogen gas which is to be used as the reducing medium. In a similar manner, the lower beds may be suitably provided with similar heat exchangers or tubes **42** each of which is provided with suitable headers.

In accordance with our invention, we find that the addition of carbon, particularly to mill scale having less than 2 weight percent carbon, not only prevents plugging of the orifices in the fluid bed distributor plates and avoids plating and fouling of the reactor internals, as well as plating and ultimate plugging of the transport lines but tends to remove plating and plugging if there has become a tendency of the parts to become coated or plated. The amount of carbon to be added is preferably in the range of 0.15% to 3.0% to give the fines a superficial carbon content of at least 0.2 weight percent and not to exceed about 3.0 weight percent, when operating at temperatures in the range of 600° to 1400° F. Generally, it is unnecessary to add carbon in excess of 0.35 weight percent. This is particularly advantageous under pressure operations in two or more beds and it is irrespective of the gas velocities through the bed. Generally, the velocity of gas through the bed is in the range of 0.5 to 2.0 feet/second, and the velocities in the transfer lines frequently run in the range of 3 to 30 feet/second. Temperatures in the reactor are usually maintained in the range of 700° F. to 1100° F. and generally below 1400° F.

As an example of operation, a three bed reducer was operated at a temperature of 750° F. and at a pressure of 350 to 400 p.s.i.g. with mill scale containing less than 0.1 weight percent of carbon. This was dried at temperatures within the range of 800° to 1000° F. and was charged to the reducer. The pressure drop across the grid plates from top to bottom was measured at 20, 20, and 13 inches of water respectively.

It was found that as soon as the temperature in the reducer reached 700° F. the material defluidized.

Graphite was added at **50** to the ball mill C on a batch basis at the rate of 0.3 weight percent and it was found that the grid plate pressure drops dropped substantially. Whereas after operation without carbon, the pressure drop had increased from 20 to 40 inches of water on the top plate; from 20 to 40 inches of water in the intermediate plate, and from 13 to 15 inches of water on the bottom plate, the pressure drop after adding carbon was then measured at a maximum of 27, 40, and 15 inches of water respectively and no defluidization was noted.

The addition of carbon is considered to be a surface function and is to be limited to an amount less than contemplated in prior disclosures where carbon was added to control the steel product. Other forms of carbon can be used including the spray of residual oils at temperatures which cause coking. It is considered, however, that graphite is the most satisfactory for the desired purpose.

Our invention applies to any fluidizable grind of iron oxide (iron ore) which, without the addition of the carbon, would lose its fluidizability due to heating, reduction, or other chemical or physical change. Generally, we find it most effective with fines smaller than 200 micron average size with a typical grind as follows:

All through	20 mesh (Tyler).
Approximately 40%	20–100 mesh.
Approximately 25%	100–200 mesh.
Approximately 35%	Smaller than 200 mesh.

In view of the various modifications of the invention which will occur to those skilled in the art only such limitations should be imposed as are indicated by the appended claims.

We claim:

1. A method of directly reducing metallic oxide fines of the class of mill scale, hematite, and magnetite ore which fines contain less than 0.1 weight percent carbon, and which fines are smaller than 200 micron average size and tend to adhere one to the other when reduced with a hydrogen rich gas at temperatures above 600° F. and pressures in the range of 200 to 600 p.s.i.g., which comprises mixing said fines with a carbonaceous material selected from the group consisting of graphite, coal, charcoal and coke to give the fines a superficial surface coating of carbon whereby the carbon content of the fines is at least 0.15 weight percent and not to exceed 3.0 weight percent, introducing said coated fines into a reaction zone maintained at a temperature in the range of 700 to 1400° F., and passing a reducing gas of high purity hydrogen upwardly through the fines at a velocity to maintain the fines in a mobilized condition and to establish direct contact of the reducing gas with the fines, and thereafter removing the reduced material from the reaction zone.

2. The method of reducing iron oxide fines as claimed in claim **1** wherein the fines are reduced in a series of vertical beds through which the reducing gas passes upwardly at gas velocities in the order of 0.5 to 2.0 feet per second, and said carbonaceous material is graphite.

3. The method of reducing iron oxide fines of smaller than 100 micron size and of the class of mill scale having less than 2 weight percent of carbon which comprises adding to said iron oxide a carbonaceous material adapted to contact with the ore particles to form a coating of carbon and passing said carbon coated ore through a reaction zone in the presence of a hydrogen containing gas of an average molecular weight of 7.5 and under a temperature of at least 600° F. and at a pressure of at least 200 p.s.i.g. at a velocity to maintain the iron oxide particles in a fluidized condition and separately removing the reduced iron oxide and the gaseous products of contact from the reaction zone.

No references cited.

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