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**FLUIDIZED ORE REDUCTION WITH BASIC
NITROGENOUS ADDITIVES TO PREVENT
BOGGING**

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ABSTRACT OF THE DISCLOSURE

Fluidized beds of reduced iron ore particles tend to defluidize or bog at high temperatures due to the particles sticking together. This tendency can be inhibited by providing in the fluid beds certain basic nitrogenous compounds such as ammonia. This disclosure is especially pertinent to multi-stage fluidized iron ore reduction processes.

This invention relates to the production of sponge iron by reaction of oxidic iron ores by contact with reducing gases. In particular, it relates to an improved iron ore reduction process wherein fluidized iron ores are metallized by direct contact with hydrogen, carbon monoxide, or mixtures of these and other gases.

The production of sponge iron by reduction of oxidic iron ores, i.e., ores containing or consisting essentially of oxides of iron, in beds fluidized by upwardly flowing gases, at temperatures ranging generally from about 1000° F. to about 1800° F., is well known to the art. Moreover, such processes wherein the fluidized beds are staged as separate reduction zones, and the zones operated at the same or different elevated temperatures generally within this given range are also known.

In a typical staged fluidized iron ore reduction process, iron oxides are, e.g., provided: in a first fluidized bed wherein the oxides are reduced from the ferric state to magnetic oxide of iron; in a second fluidized bed wherein magnetic oxide of iron is reduced to ferrous oxide; and in a third zone wherein ferrous oxide is reduced to metallic iron. The separate stages may be operated at the same or different elevated temperatures, and one of a plurality of ferric reduction zones or ferrous reduction zones may be provided. A burning zone wherein the reducing gas, e.g., hydrogen, is burned with an oxygen-containing gas, e.g., air, may be provided or the burning zone may be combined with a ferric reduction zone to provide heat for the reaction.

In all such processes it is desired to have sufficiently high temperature to achieve maximum reduction, and to achieve such reduction smoothly and efficiently. One would expect to achieve maximum reduction by increasing the temperature of the reaction, and for the reaction to proceed at a faster rate with increasing temperature. However, high temperatures can produce bogging or, if the temperature becomes sufficiently high, sintering of the ore.

Bogging is a phenomenon manifested by a "stickiness" occurring at the surfaces of the individual solids iron ore particles. It is postulated, and fairly well supported, that the surfaces of the individual ore particles become covered, in whole or in part depending on temperature, with crystalline forms of iron. These crystalline forms, microscopic in character, take on the appearance of nodules or "whiskers" extending outwardly from the individual particles. The microscopic appearance of the individual ore particles with projecting deposits or nodular growths, in fact, is not too different from that of certain forms of vegetable or plant leaves which contain potassium oxalate

or calcium carbonate growths. Because of these claw-like projections, or reactive spots, the particles tend to attach one to another upon contact so that individual iron ore particles cling or weld together to form aggregates or agglomerates. Such phenomenon militates against proper fluidization of the particles and hence bogging, or loss of fluidization of the bed occurs. This phenomenon is not unlike sintering of the particles in its effect, but differs from sintering inasmuch as the latter is caused by an actual melting of the reduced iron upon the surfaces of the particles, this causing the individual particles to cling or fuse one with another to also produce agglomeration.

Bogging is a very undesirable phenomenon and the tendency of an ore to bog increases with metallization and with increasing temperature, especially as the degree of metallization increases. High temperatures ranging just below that which will produce sintering—i.e., about 1800° F.—are desired, however, inasmuch as more efficient reduction and faster rate of reaction are achieved. This, then, presents a dilemma for, on the one hand, the higher temperature the more acute the tendency toward bogging and, on the other hand, the lower the temperature the less the efficiency of the process. With certain ores, e.g., Carol Lake ore, the tendency to bog at elevated temperature is especially severe, and for this reason it is difficult to treat this and some other ores in a fluidized iron ore reduction process.

The present invention has for its primary objective a solution of the problem of bogging. In particular, its objective is to provide the art with a simplified, new and novel fluidized iron ore reduction process wherein bogging is inhibited and, in some cases, completely eliminated so that more elevated temperatures can be used and the process operated more effectively for longer periods. A specific object is to provide an improved process wherein the tendency toward bogging is inhibited or eliminated in the several stages of a fluidized iron ore reduction process wherein oxidic iron ores are treated with a reducing gas, or gases, to successively reduce the iron oxides to lower stages of oxidation; and finally to metallic iron. An even more specific object relates to such process providing a series of staged reaction zones wherein a significant portion of hydrogen is used as the reducing gas.

These and other objects are achieved in accordance with the present invention which contemplates the use of a novel class of agents or additives added to, injected within, or otherwise mixed or contacted with fluidized oxidic iron ore in a reduction process, which even in very minor or minute concentrations, inhibit or prevent bogging of the particulate ore. It has thus been found that small quantities of basic nitrogenous compounds, including ammonia, or mixtures thereof, can be directly added or injected into a fluidized iron ore reduction bed, or admixed with the reducing gas, to inhibit and in some instances to entirely prevent bogging.

The reasons for the effectiveness of these added agents in inhibiting or preventing bogging are not fully understood. While applicants do not desire to be bound by any theory of mechanism, it is believed that the novel additives of this invention chemically react with, alter, or otherwise poison the nodular growths or active sites on the surface of the individual iron ore particles which form as temperature is increased. Because of this poisoning effect, the normal tendency of the particles to stick or bridge together upon physical contact one particle with another is inhibited or eliminated.

While concentrations as low as about 200 parts per million parts by volume, based on the amount of reducing gas fed into the process, will inhibit bogging to some extent, it is generally preferable to employ concentrations ranging from about 0.5 to about 5.0 percent, based on

the volume of the reducing gas. Greater concentrations can be used if desired but, except in the instance of very stubborn ores, such amounts of additives are not required. In most instances it is found suitable to employ concentrations ranging from about 0.5 to about 1.5 percent of the additive, based on the volume of reducing gas.

Additives suitable for use in accordance with the present invention, whether added to the process ab initio or generated in situ, are the basic nitrogenous compounds and preferably those characterized as a substituted ammonia compound and represented by compounds of the structural formula



wherein R_1 , R_2 and R_3 are the same or different and can be hydrogen or a hydrocarbon radical, such as alkyl, alkenyl, alkynyl, aryl, aralkyl, and the like, and N is the chemical symbol for nitrogen. Preferably, the hydrocarbon radical contains no more than about 10 carbon atoms, and more preferably not more than about 6 carbon atoms. Exemplary of such compounds are dimethylamine, divinylamine, tripropylamine, isoamylamine, aniline, o-toluidine and mesidine. Especially preferred of such compounds are those wherein two or more hydrogen atoms are directly affixed to the nitrogen atom, such as ammonia, n-decylamine, allylamine, benzylamine, and 1-naphthalenemethylamine.

Polyamines are also suitable. These are illustrated, for example, by 1,4-diaminobutane, o-phenylenediamine, 1,4-anthradiamine, 1,2,4-benzenetriamine, 3,3'-biphenyldiamine; and including as well, heterocyclic amine compounds and amino derivatives of heterocyclic compounds such as 2-aminopyrrole, pyridine, piperidine, 2,6-diaminopyridine, 1-aminoacridine and the like. The alkinol amines are also useful, exemplary of which are 2-aminoethanol, diethanolamine, trimethanolamine and the like. Quaternary ammonium hydroxides, illustrative of which are such tetralkylammonium hydroxides as tetramethylammonium hydroxide, tetrabutylammonium hydroxide, and the like are also suitable. Ammonium hydroxide is likewise useful. Mixtures of such compounds with other substances or with each other are suitable. Many commercial mixtures and naturally occurring materials which provide these compounds—e.g., shale or shale oil—can also be added, preferably after pulverization where solids are used, to the process to generate the desired compounds in situ.

An outstanding compound because of its availability, readily usable form and the effectiveness thereof in extremely small concentrations is ammonia gas. Suitably, it is added by admixture in volume of from about 0.5 to 1.5 with the reducing gas, and then fed directly into the ferrous reducing zone, or zones.

In a particularly preferred embodiment according to this invention, oxidic ores or iron oxides solids particles are contacted with upwardly flowing hydrogen-containing gases and a plurality of staged zones are provided. The zones contain fluidized beds operated at varying temperatures and the ore is at different stages of reduction. Also, the reducing gas in contact with the beds is at a different stage of oxidation within the zones. There is provided, in accordance with such embodiment, one or more ferric reduction zones operated at temperatures ranging from about 1000° F. to about 1800° F. and one or more ferrous reduction zones operated at temperatures ranging from about 1300° F. to about 1500° F. The basic nitrogenous compounds are added to the ferrous reduction wherein the bogging tendency is particularly acute.

The following nonlimiting examples and pertinent demonstrations bring out the more salient features and provide a better understanding of the invention.

A large quantity of raw Carol Lake ore is pulverized in a ball mill, to a mesh size ranging from 28 to 325, and

divided into several like portions. This ore is one well known as possessing a severe tendency to bog.

A portion of the ore is charged into a fluidized iron ore reactor or reduction process wherein is provided a series of four staged fluidized zones, two ferric reduction zones and two ferrous reduction zones. The ore is fluidized by an upwardly flowing gas initially sixty percent hydrogen and forty percent nitrogen. The gas flows from a zone containing an iron ore at a lower level of oxidation to the next higher level of oxidation, i.e., from the bottom to the top of the reactor. In the top ferric zone the partially oxidized gas is burned with air to provide heat to the various reduction stages and the reduced ore moves from the top to the bottom of the reactor from one stage of reduction to the next. The ferric reduction stages, wherein ferric oxides are reduced essentially to magnetic oxides or iron, are operated at 1300° F. as were the ferrous reduction stages wherein the ferrous oxide is reduced, in the final stage, to provide 94 percent metallization.

Pursuant to operating at such conditions, the ferrous reduction beds show signs of bogging within about ten minutes and are severely and totally bogged in only twenty minutes of continuous operation.

Example I

The foregoing demonstration is repeated in precise detail employing a second portion of the ore except in this instance one percent of ammonia gas, based on the volume of the gas feed, is added to and continuously charged into the two ferrous reduction zones. At the end of an eighty-one minute period, there is only slight evidence of a tendency toward bogging. The beds appear normal and the process functions normally prior to this time in every way. The improvement was thus at least a 700 percent improvement over the foregoing demonstration, and clearly evidences the advantages of the present process.

Example II

When Example I is repeated with another portion of ore at a temperature of 1400° F. and ammonia added in three percent concentration, there is yet no bogging or tendency toward bogging at the end of a significantly longer period.

Example III

When the conditions of operation of the process of Example II are repeated and the same amount of ammonium hydroxide is injected into the process, there is again little evidence of bogging at the end of the period.

Examples IV-IX

When Example I is repeated except that isopropylamine, tert-butylamine, m-toluidine; and, methanolamine, triethanolamine, ethylenediamine, respectively, are successively added to the process in 0.5, 1.5, 3.0, and 5.0 percent concentrations, significant benefits are also obtained. The tendency to bog is considerably reduced and operating time is significantly extended in each instance.

It is apparent that certain modifications and changes can be made in the present process without departing the spirit and scope of the invention. The key and novel feature of the invention is the use of small and minor portions of basic nitrogenous compounds directly added to, injected within, premixed, or otherwise physically admixed with the reducing gases in contact with oxidic iron ores which are subjected to reduction in a fluidized process.

Such basic nitrogenous compounds in contact with the fluidized ore at the time of reduction provided benefits, whether added ab initio or generated in situ from an added material itself capable of providing such compounds.

Having described the invention, what is claimed is:

1. In a process for the production of sponge iron from oxidic iron ores wherein the iron ore in particulate form

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is fed into the process and fluidized within a bed and reduced by a stream of reducing gas at temperatures ranging from about 1000° F. to about 1800° F., the improvement comprising feeding a basic nitrogenous compound with the reducing gas in quantities sufficient to inhibit bogging of the ore.

2. The process of claim 1 wherein the compound is fed in quantities ranging from about 0.5 to about 5.0 percent, based on the volume of reducing gas.

3. The process of claim 1 wherein the compound is fed in quantities ranging from about 0.5 to about 1.5 percent, based on the volume of reducing gas.

4. In a process for the production of sponge iron from oxidic iron ores wherein the iron ore in particulate form is fed into the process and fluidized within a bed and reduced by a stream of reducing gas at temperatures ranging from about 1000° F. to about 1800° F., the improvement comprising providing within the reducing gas in contact with the fluidized bed a basic nitrogenous compound represented by the structural formula



wherein R_1 , R_2 and R_3 are members selected from hydrogen and hydrocarbon radicals containing up to about ten carbon atoms, said basic nitrogenous compound being provided in an amount sufficient to inhibit bogging of the ore.

5. The process of claim 4 wherein the temperature ranges from about 1300° F. to about 1600° F., and the basic nitrogenous compound is ammonia.

6. In a process for the production of sponge iron from oxidic iron ores wherein the iron ore in particulate form is fed into the process and fluidized by a stream of gas within a series of staged zones containing fluidized beds, including a ferric reduction zone and a ferrous reduction zone, and reduced at elevated temperatures ranging from about 1000° F. to about 1800° F., the improvement comprising feeding a basic nitrogenous compound directly into a fluidized ferrous reduction zone in concentrations sufficient to inhibit bogging.

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7. The process of claim 6 wherein the basic nitrogenous compound fed to the ferrous reduction zone is in concentrations ranging from about 0.5 to about 5.0 percent, based on the volume of the reducing gas.

8. In a process for the production of sponge iron from oxidic iron ores wherein the iron ore in particulate form is fed into the process and fluidized by a stream of gas within a series of staged zones containing fluidized beds, including a ferric reduction zone and a ferrous reduction zone, and reduced at elevated temperatures ranging from 1000° F. to about 1800° F., the improvement comprising providing within the reducing gas of a fluidized ferrous reduction zone a basic nitrogenous compound represented by the structural formula



wherein R_1 , R_2 and R_3 are members selected from hydrogen and hydrocarbon radicals containing up to about ten carbon atoms, said basic nitrogenous compound being provided in an amount sufficient to inhibit bogging.

9. The process of claim 8 wherein the temperature of the fluidized ferrous reduction zone ranges from about 1300° F. to about 1600° F., and the basic nitrogenous compound is ammonia.

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