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Mueller et al.

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[54] **ORE PRETREATMENT PROCESS**

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[63] Continuation of Ser. No. 111,680, Feb. 1, 1971, abandoned.

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[51] **Int. Cl.**[2] **C22B 1/11**

[58] **Field of Search** ..... 75/6, 101 R, 121

[56] **References Cited**

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[57] **ABSTRACT**

A process is provided for lowering the sulfur and phosphorus content of a particulate oxidic iron ore which renders the ore more suitable for use in direct ore reduction processes. By pretreating the ore with an aqueous solution of an inorganic base, preferably at slightly elevated temperatures, the sulfur and phosphorus levels in the ore are lowered to a desirable range.

10 Claims, No Drawings

ORE PRETREATMENT PROCESS

This is a continuation, of application Ser. No. 111,680, filed Feb. 1, 1971 now abandoned.

BACKGROUND OF THE INVENTION

Modern steelmaking processes utilize furnace feed consisting of a sintered or pelleted oxidic iron ore product that had undergone extensive benefication and preparation. Pretreatment of the ore has been necessitated by the relative scarcity of high grade ore. Thus, numerous processes are known in the art for improving the chemical and physical characteristics of iron ores to make them more desirable feed for iron and steelmaking processes.

In direct iron ore reduction processes, for example, the iron ore is crushed and then concentrated prior to being reduced. Conventional concentrating methods include washing, jigging, flotation processing and magnetic processing.

After concentrating the oxidic iron ore the concentrate contains generally of the order of about 90 to about 95% iron oxide with the balance of the feed material being predominantly the gangue constituents. Such a typical feed material, however, also contains up to about 0.5% phosphorus and 0.3% sulfur.

Sulfur and phosphorus are undesirable contaminants in iron ores and particularly in prereduced iron-bearing materials. Consequently, several techniques have been developed to lower the sulfur and phosphorus content of prereduced iron-bearing materials.

In preparing sponge iron in a rotary kiln, for example, it has been suggested to add various alkaline earth compounds to the rotary kiln along with the coal and ore in order to produce a low sulfur sponge iron.

It is also known to roast ores at temperatures above about 800°C. with alkali metal hydroxides, carbonates, bicarbonates and mixtures of these compounds in order to lower the sulfur and phosphorus content of the ore.

In fluid bed processes an oxidic iron ore concentrate that has been crushed and sized for fluidization is heated at temperatures ranging from about 750°C. to 800°C. in an oxidizing atmosphere. Under these conditions, sulfur present in the ore is oxidized to sulfur dioxide.

As will be readily appreciated by one skilled in the art, these processes for lowering the sulfur and phosphorus content of particulate oxidic iron ore concentrate require a relatively high level of capital investment. Consequently, there is great demand for new, improved and economical processes for lowering the sulfur and phosphorus content of ore concentrates to be directly reduced to highly metallized materials.

SUMMARY OF THE INVENTION

According to the present invention, a method for lowering the sulfur and phosphorus content in particulate oxidic iron ore is provided which is surprisingly effective and relatively simple. The subject process comprises washing an oxidic iron ore concentrate with an aqueous solution in an inorganic base and thereafter washing the ore with water.

In a particularly preferred embodiment of the present invention, particulate oxidic iron ore concentrate is washed with an aqueous solution of an inorganic base selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates and mixtures thereof. The ore is washed at temperatures ranging from ambient temperature up to about 100°C.

In one embodiment of the present invention the inorganic base is mixed with the particulate oxidic iron ore and the mixture is heated to a temperature up to about 300°C. After heating, the mixture is washed with water thereby solubilizing and removing sulfur and phosphorus from the ore.

DETAILED DESCRIPTION OF THE INVENTION

The surprising effectiveness and simplicity of this process for lowering the content of sulfur and phosphorus in particulate oxidic iron ores will be readily understood from the discussion and examples which follow.

Commercially available particulate oxidic iron ore concentrates containing up to about 0.5 wt. % phosphorus and 0.3 wt. % sulfur, can be treated according to the present invention for use in direct ore reduction processes. Such conventional particulate oxidic iron ores include specular hematites, earthy hematites, limonite and the like.

Typically, such commercially available iron ore contains up to about 95 wt. % iron oxides. The ore also contains as already stated, up to about 0.3 wt. % sulfur and 0.5 wt. % phosphorus. Gangue constitutes the balance of the ore.

In a preferred embodiment of the present invention, the ore received is ground and sized for fluidization in a direct reduction process. Grinding and sizing of iron ores is accomplished by well known techniques. For example, grinding can be achieved by subjecting the ore to ball milling, gyratory grinding, rod milling or hammer milling and the like. Sizing of the ore is accomplished generally by screening.

Ore sizes generally employed in fluidized iron ore reduction processes have particles having an average size of about 100 microns to 400 microns or about 65 mesh; preferably the average particle size is 450 microns to about 300 microns and more preferably, the average particle size is from about 175 microns to about 250 microns.

After the ore is ground and sized for fluidization in direct ore reduction process, the ore is washed in accordance with the present invention. Specifically, the particulate oxidic iron ore is washed in an aqueous solution of an inorganic base. Generally, the base employed is one which will form a soluble salt with the phosphorus and sulfur present in the ore. Preferably, the base is selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates and mixtures of these materials. The preferred basic compound employed in the present process is sodium carbonate.

Generally, at least 0.1 part of base and up to about 1.5 parts by weight of base is used per part by weight iron ore. In the practice of the present invention, it is preferred to use a ratio of base to iron ore ranging from about 0.5 to 1.0.

In one mode of practicing the present invention the requisite amount of inorganic base is mixed with the particulate oxidic iron ore and the mixture is heated to temperatures up to about 300°C. Although higher temperatures may be employed, increasingly higher temperatures are economically less desirable. Consequently, the mixture of inorganic base and oxidic iron ore may be heated up to about 650°C. but preferably the mixture is heated in the range of from about 250°C. to about 350°C. Heating need not be for any extensive time period. Typically, heating for 60 minutes is suffi-

cient and the cycle from ambient to a given elevated temperature can be adjusted to provide the equivalent of 60 minutes at about 300°C. After the mixture is heated to the specified temperature range, the heated mixture is washed with water thoroughly. Typically, about 2000 wt. % water based on the total mixture of ore and base is sufficient to lower the phosphorus and sulfur content of the ore and at the same time to remove any other soluble sodium salts. Preferably, water is employed in an amount ranging from about 500 wt. % to about 5000 wt. % with from about 1000 wt. % to 2000 wt. % being more preferred.

In another mode of practicing the present invention, the inorganic base is dissolved in water to provide an aqueous solution having a concentration of about 10 wt. %. Generally, the concentration of the aqueous basic solution is in the range of 1 wt. % to 40 wt. %, with 5 wt. % to 20 wt. % being preferred. This solution can then be mixed with the particulate oxidic iron ore in an amount sufficient to provide the base to ore ratios specified previously. After mixing the particulate oxidic iron ore with the aqueous basic solution, the solution can be drawn off or otherwise filtered and any residual salts may be removed from the ore by washing with an additional quantity of water.

When washing the ore with an aqueous basic solution slightly elevated temperatures may be employed to more effectively lower the sulfur and phosphorus content of the ore. Thus, the ore is washed with aqueous solution at temperatures ranging generally up to about 100°C. Preferably, the ore is washed at a temperature ranging from about 20°C. to about 100°C. with about 70°C. to about 90°C. being more preferred.

After the ore has been washed with aqueous base and rinsed with water, the ore can be dried for subsequent processing. If the ore is going to be utilized in a fluid bed process, for example, drying can generally be accomplished by heating the ore to about 65°C. up to about 175°C. Selection of the proper time and temperature for drying the ore, of course, will depend upon the allowable water content of the ore. Generally, for fluid bed operations, after drying the bed will contain less than 4 wt. % water, and preferably less than 2% water. Drying and even preheating the ore can be accomplished for example, by contacting the ore with fluid reducing gases from the direct reduction process.

Following examples illustrate the techniques and advantages of treating a particulate oxidic iron ore concentrate in accordance with the present invention.

EXAMPLE 1

The ore used in this test consisted of an earthy hematite from Brazil. The ore contained 95% iron as iron oxides, 0.16 wt. % phosphorus and 0.052 wt. % sulfur. The average particle size of the ore was 14 to 325 mesh. The ore was washed at about 70°C. with a sufficient amount of 10% sodium carbonate solution to provide approximately 1 part of base per part of ore. Subsequently, the aqueous phase was separated from the ore and the ore was rinsed with water. Analysis showed that washing the ore with sodium carbonate solution resulted in a decrease in the phosphorus level in the ore to 0.05 wt. %, the sulfur level in the ore was decreased to 0.015 wt. %.

EXAMPLE 2

The procedure of Example 1 was applied except that the temperature of the wash was about 95°C. Under these conditions, the phosphorus level of the ore was lowered to 0.04 wt. % and the sulfur level was lowered to 0.013 wt. %.

EXAMPLE 3

This example shows that the wash is even effective at relatively low temperatures for lowering the phosphorus content of the ore. Thus, following the procedure of Example 1, the ore was washed at about 20°C. with the aqueous sodium carbonate solution. The result was that the phosphorus level had been lowered to 0.13 wt. % and sulfur level was lowered to 0.02 wt. %.

EXAMPLE 4

As a further illustration of the effectiveness of the instant process in lowering the sulfur content of oxidic iron ores the procedure of Example 2 was followed using several ores of different origin. The results are given in Table I below.

TABLE I

Sulfur Removal From Iron Ores

Ore Type	Origin	Original Sulfur Content Wt.%	Base: Ore Ratio	Sulfur in Product Wt.%
Hematite-limonite	Venezuela	0.052	1:1	0.01
Earthy hematite	Australia	0.037	1:1	0.015
Goethite hematite	Australia	0.097	1:1	0.043

EXAMPLE 5

A sample of an earthy hematite oxidic iron ore from Brazil was mixed with an equal part by weight of sodium carbonate and subsequently roasted at about 300°C. for one hour. After roasting, the ore mixture was washed with about 20 times its weight in water, and then analyzed to determine the sulfur and phosphorus content of the so treated ore. The phosphorus, by this technique, has been lowered from 0.16 wt. % to 0.07 wt. % and the sulfur has been lowered from 0.053 wt. % to 0.015 wt. %.

While the process of the present invention has been described in terms of preparing a feed material for a fluidized iron ore reduction process which contains below 0.2 wt. % sulfur, and below 0.10 wt. % phosphorus, it can be readily appreciated by those skilled in the art that the process is equally adaptable for preparing ore concentrates for other direct ore reduction processes.

What is claimed is:

1. A method of pretreating a gangue-containing particulate oxidic iron ore to lower the sulfur and phosphorus in the ore which comprises washing a particulate oxidic iron ore consisting essentially of iron oxides and gangue with an aqueous solution of an inorganic base and thereafter washing the ore with water.

2. The method of claim **1** wherein the inorganic base is selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates and mixtures thereof.

3. The method of claim **2** wherein the alkali metal is sodium.

4. The method of claim **1** wherein said ore is washed with said solution at a temperature in the range of about 20°C. to about 100°C.

5. The method of claim 1 wherein said inorganic base is sodium carbonate.

6. The method of claim 1 wherein at least 0.1 part by weight of base is used per part by weight of ore.

7. The method of claim 1 wherein about 1.0 part by weight of base per part by weight of ore is used.

8. A process for lowering sulfur and phosphorus in particulate oxidic iron ores comprising:

mixing an inorganic base with an oxidic iron ore consisting essentially of iron oxides and gangue in the ratio of about 0.1 to about 1.5 parts of base by weight per part of iron ore;

heating the mixture up to about 300°C.; and

washing the heated mixture with water.

9. The process of claim 8 wherein the base is selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates and mixtures thereof.

10. The process of claim 8 wherein the inorganic base is sodium carbonate; about 1.0 parts of base per part of ore is used; and the mixture is heated to about 300°C. for about 60 minutes.

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