June 29, 1965 M. HAUCKE ETAL **3,192,037**

DESULFURIZATION METHOD

Filed Oct. 3, 1963 3 Sheets-Sheet 1

FIG. 1

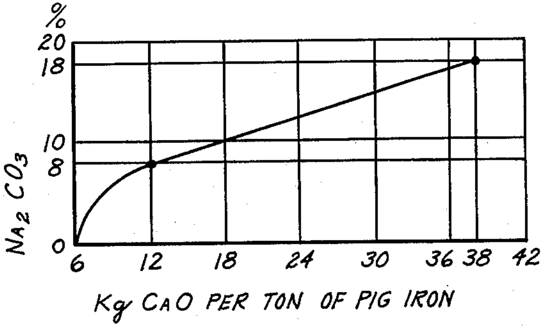
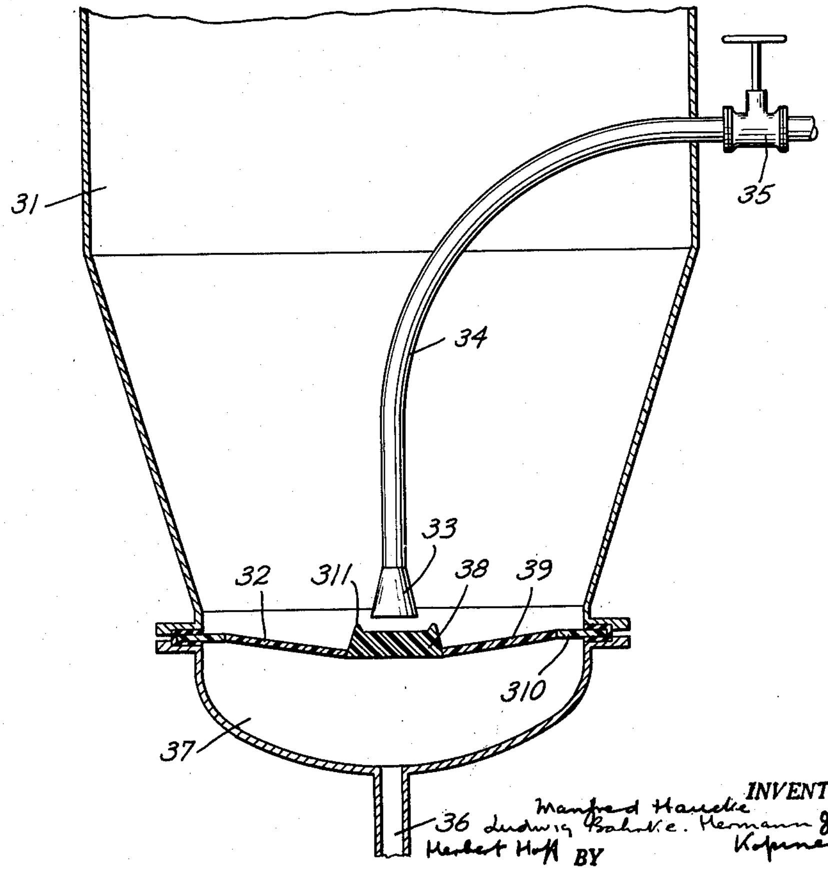


FIG. 3



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DESULFURIZATION METHOD

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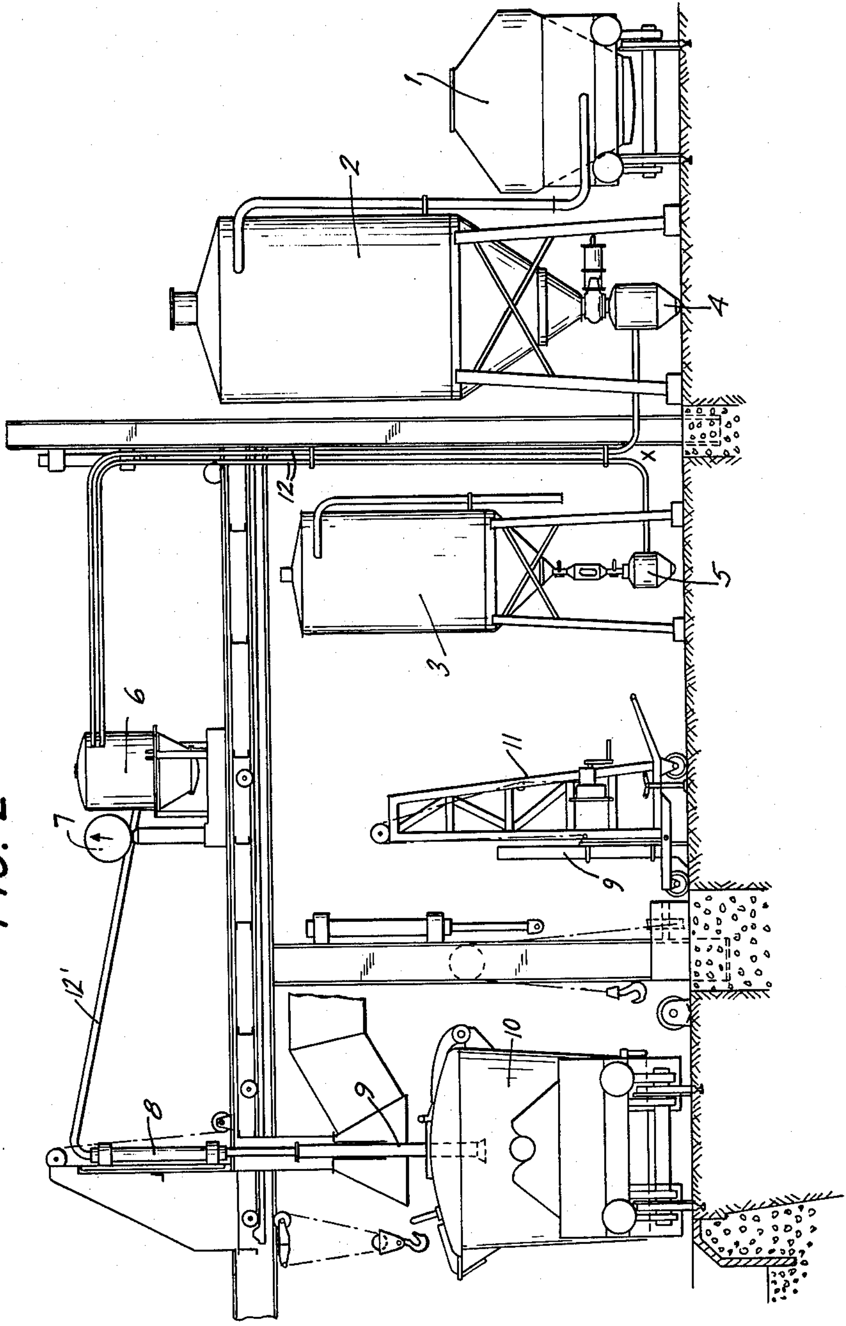
FIG. 2



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DESULFURIZATION METHOD

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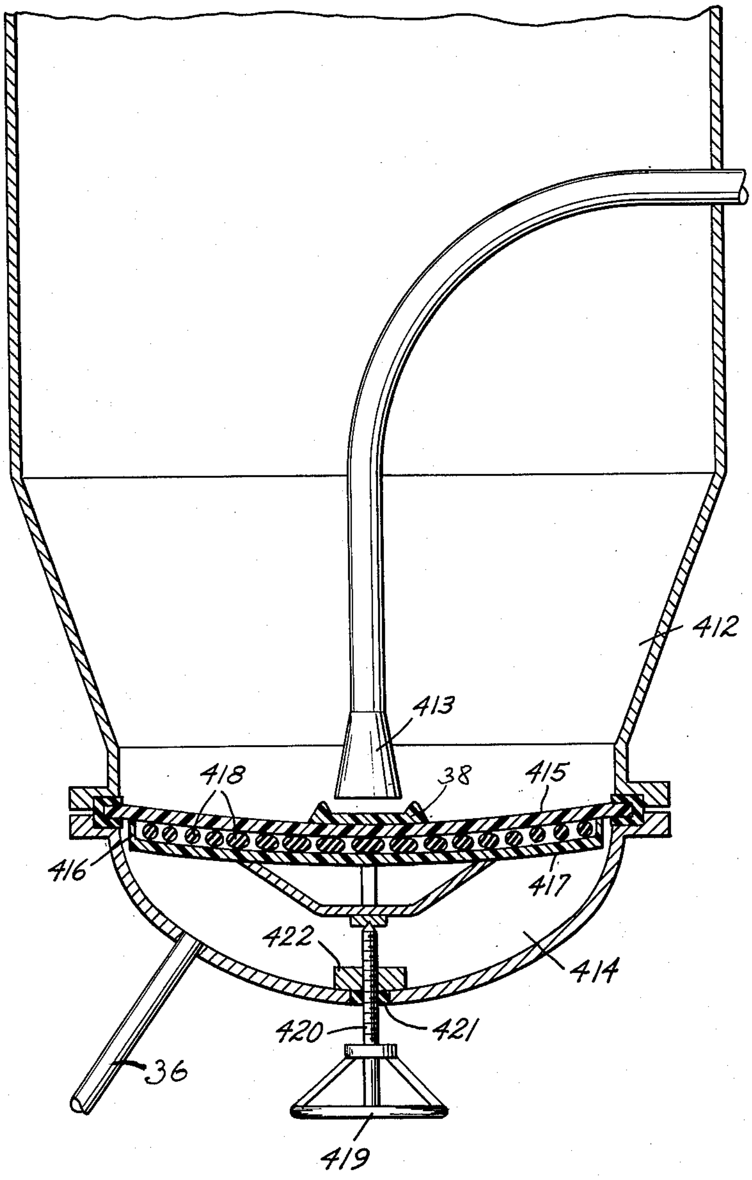
FIG. 4



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DESULFURIZATION METHOD

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14 Claims. (Cl. 75—55)

The present invention relates to the desulfurization of pig iron, and this application is a continuation-in-part of our copending application Serial Number 82,666, filed December 19, 1960, and entitled "Desulfurization Method," now abandoned.

Although several methods for the desulfurization of pig iron have been proposed and are in practical use, nevertheless, the search continues for a more effective and economical process for the desulfurization of pig iron and the like. Thus, it has been propesd to desulfurize molten pig iron with sodium carbonate or sodium carbonate-calcium oxide mixtures with or without the addition of fluorspar. It also has been proposed to blow a mixture of the above mentioned desulfurization agents into the molten bath, as well as to remove sulfur with finely subdivided lime. For the introduction of such pulverulent desulfurization agents either air or non-oxidizing gases were proposed.

However, certain disadvantages are connected with methods such as those broadly sketched out above. When air is used as a carrier gas, the oxygen content of the air and the oxidizing conditions caused by the same, will reduce the success of the desulfurization. Furthermore, particularly when pure calcium oxide is used as a desulfurizing agent, a dry but very firm slag cake is formed which firmly holds iron introduced into the slag during the blowing of pulverulent material into the molten pig iron. This causes difficulties with respect to the removal of the slag which first has to be brokin up and thereby is partially immersed in the bath of molten pig iron and thus absorbs additional iron. Apart from the manipulative difficulties involved, considerable iron losses are incurred in this manner.

It has also been suggested to use a shaking pan and to add to the molten pig iron therein pulverulent calcium oxide, whereby the addition of small quantities of sodium carbonate will to some extent prevent adherence of the slag to the walls of the pan. However, these experiments have shown that at least within the first five minutes of treatment no improved desulfurization can be achieved, although better results are obtained by continuing the treatment for 30 minutes or more. This relatively prolonged treatment causes undesirable cooling of the molten pig iron and furthermore, the installation and operation of shaking pans of the required size involves many difficulties and considerable expense so that the last mentioned method cannot be considered an adequate solution of the problems involved in effective desulfurization of pig iron.

It is therefore an object of the present invention to provide a method for the effective desulfurization of pig iron in a simple and economical manner.

It is further an object of the present invention to provide a method for desulfurization of pig iron which can be carried out in a relatively short period of time and which will result in a sufficiently large reduction of the sulfur content of the pig iron.

It is yet a further object of the present invention to provide a method for the desulfurization of pig iron with pulverulent desulfurization agents which method will be carried out under introduction of only very small quantities of gas into the molten metal bath, thus not subjecting the same to the undesirable effects of introduction of large quantities of gas irrespective of whether the gas is an inert gas or an oxidizing gas.

With the above and other objects in view, the present invention comprises in a method of desulfurizing pig iron, the step of introducing into a bath of molten sulfur-containing pig iron a suspension in a carrier gas of a pulverulent mixture of calcium oxide and sodium carbonate, the mixture comprising between 1% and 18% sodium carbonate and between 99% and 82% calcium oxide and the concentration of the suspension being such that one kilogram of the mixture is suspended in between about 3 and 7 liters of the carrier gas. Generally the percentage of sodium carbonate will be maintained between 5% and 15%, preferably between 8% and 12%, and frequently excellent results will be achieved with between 8% and 10% sodium carbonate, the respective balance being calcium oxide.

Particularly when the sodium carbonate content of the sodium-carbonate-calcium oxide mixture exceeds 7%, and up to a sodium carbonate content of 12%, a dry, loose slag is obtained which can be easily withdrawn and will hold relatively little iron. Increasing the sodium carbonate proportion to more than 12% will not have any marked effect on the consistency of the slag. Compared with conventional calcium oxide desulfurization, the sodium carbonate-calcium oxide desulfurization according to the present invention will achieve a higher degree of desulfurization with a lesser quantity of desulfurization agents. The loss of iron in the slag is reduced as well as the time required for withdrawal of slag.

Thus, according to the present invention, desulfurization of pig iron is carried out with a calcium oxide-sodium carbonate mixture, whereby reducing conditions are maintained in the reaction vessel and the mixture of reducing agents must contain certain proportions of the individual reactants dispersed in a small quantity of carrier gas.

Essentially, according to the present invention, desulfurization of the molten pig iron is carried out with between 1 and 18% by weight of sodium carbonate and between 99% and 82% by weight of calcium oxide, and a mixture of these two desulfurization agents in the indicated proportion is introduced into the molten pig iron suspended in a very small quantity of carrier gas so that for each kilogram of the pulverulent mixture between 3 and 7 liters of carrier gas are used, and, furthermore, it is essential that the suspension is introduced into the molten pig iron at relatively low overpressure, preferably through a lance at the orifice of which the suspension is under a pressure which is only between 0.1 and 0.5, preferably only between 0.1 and 0.2 atmospheres greater than the pressure in the area surrounding the lance orifice.

Calcium oxide is to be understood throughout the present specification to mean burnt lime which for the purpose of the present invention can be considered substantially pure calcium oxide and which generally does not contain more than 1.3% chemically bound water, corresponding to about 5⅓% calcium hydroxide. However, the degree of purity of the calcium oxide may of course vary within practical limits.

It has been found according to the present invention that the proportion of sodium carbonate in the calcium oxide-sodium carbonate mixture may be somewhat reduced with increasing temperatures of the molten bath. Thus, for instance at a temperature of the molten bath of pig iron of between 1200 and 1400° C. and at an initial sulfur content of between 0.10 and 0.25%, it will be desirable to introduce a mixture containing between 5 and 15% by weight of sodium carbonate and between 95% and 85% by weight of calcium oxide. However, if the bath temperature of a similar pig iron is below 1200° C., then the percentage of sodium carbonate is to be increased by between 3 and 5%, in extreme cases up to the maximum value of about 18%.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which:

FIG. 1 is a diagrammatic showing of preferred proportions of sodium carbonate and calcium oxide depending on the total amount of calcium oxide which is to be introduced per ton of pig iron;

FIG. 2 is a somewhat schematic elevational view of a desulfurization arrangement according to the present invention;

FIG. 3 is a schematic elevational veiw of a device for producing and conveying a suspension of pulverulent materials such as a suspension of desulfurization agents according to the present invention; and

FIG. 4 is another embodiment of a device for suspending and conveying pulverulent materials.

The total amount of calcium oxide which is to be introduced per ton of pig iron depends generally on the sulfur content of the pig iron, whereby it has been found that with increase in the addition of calcium oxide, the percentage of sodium carbonate in the desulfurization mixture should be somewhat increased, in order to obtain a slag of the desired consistency.

Thus, when the sulfur content of the pig iron is relactively very low, it may suffice to introduce per ton of pig iron 6 kilograms of calcium oxide in a mixture consisting of 99% per weight of calcium oxide and 1% per weight of sodium carbonate. However, with increasing sulfur content of the pig iron, the amount of calcium oxide which is to be introduced per ton of pig iron may rise to 40 kilograms or even more and in such case, the calcium oxide preferably will be introduced in the form of a pulverulent mixture which contains up to 18% sodium carbonate and, correspondingly, at least 82% by weight of calcium oxide.

Preferred proportions of sodium carbonate and calcium oxide depending on the total amount of calcium oxide which is to be introduced per ton of pig iron, are shown in FIG. 1.

Furthermore, according to the present invention, it is essential to use only such quantities of carrier gas which are actually required for conveying the pulverulent desulfurization agents, so that the carrier gas itself will be substantially without metallurgical effect with respect to the pig iron. In order to avoid even slight adverse side effects, it is preferred to use an inert gas such as nitrogen as the carrier gas, however, in view of the relatively very small quantities of gas involved, even other gases, for instance air, or other available industrial gases may be used. Nitrogen gas, of course, possesses the advantage of being a non-oxidizing gas. This may be important because an oxidizing atmosphere reduces the effect of the desulfurization. However, compressed air frequently is more easily available and more economical and in view of the small quantity of air which is required for conveying the pulverulent desulfurization agents into the molten pig iron, it is also possible to use compressed air for this purpose without experiencing any appreciable reduction in the effectiveness of the desulfurization. However, the use of air as carrier gas will have a slight desiliconizing effect.

Thus, in the process of the present invention, the exclusive purpose of the carrier gas is to convey the solid desulfurization agents and it is not intended that the carrier gas itself should have any metallurgical effect. Furthermore, the pressure at which the gaseous suspension of pulverulent desulfurization agents is introduced into the molten pig iron is to be only slightly greater than the counter pressure at the orifice of the lance through which the suspension is introduced. This slight pressure differential will achieve that the pulverulent desulfurization agents will leave the lance and will be introduced into the molten pig iron without appreciable pressure and thus that only very slight turbulence will be caused in the bath of pig iron. The pulverulent desulfurization agents have a lesser specific gravity than the molten metal and thus will slowly rise to the surface of the molten metal bath. During such rise, on the one hand, the calcium oxide will react with sulfur and there will also be a slight degree of reaction between calcium oxide and silicon, particularly if air has been used as the carrier gas. On the other hand, carbon dioxide will be freed and will slowly bubble upwardly through the molten metal bath, together with the carrier gas and will cause swelling or bloating of the slag surface. This process will be enhanced by incompletely decomposed sodium carbonate which reaches the slag and which forms carbon dioxide within the slag area.

A considerable portion of the thus introduced calcium oxide will also pass unaffected through the molten metal bath. At the surface of the bath, a portion of the silicon will be oxidized to silicon dioxide so that a slag is obtained which essentially will consist of about 30% calcium oxide, between 2 and 4% calcium sulfide, about 4% silicon dioxide and about 2% sodium oxide. The balance of the slag will be formed by granular iron or iron oxide.

This slag has a melting temperature which is about 300 to 400° C. higher than the temperature of the molten pig iron and thus can be considered a very dry slag. However, simultaneously, due to the addition of sodium carbonate to the desulfurization agent, not only localized swelling of the slag but also localized reduction of the melting point of the same will be achieved, so that the slag will not form a single firmly coherent cake or cover and due to this lack of adherence can be easily withdrawn and also will not attach itself to the walls of the treating vessel. The total iron content of the slag will thus be reduced from about 75% to about 50%. Thus, for instance upon desulfurization of a pig iron containing 0.15% sulfur, with the mixture of desulfurization agents according to the present invention, specifically with a mixture containing 8% sodium carbonate and 92% calcium oxide, the slag will contain about 30% less iron than upon desulfurization with pure calcium oxide. However, actually the reduction of iron loss is even more favorable, namely such that the loss of iron with the slag under the above described conditions including the addition of 8% sodium carbonate will only be about ⅓ of the loss of iron which is experienced by using calcium oxide alone. This greater reduction of loss of iron with the slag is due to the difference in the consistency of the slag and due to the ease with which the slag formed by introduction of the mixture of calcium oxide and sodium carbonate can be withdrawn. Thus, in the case of a charge weight of 40 tons, the iron recovery is improved by about 1 ton per charge and, furthermore, the desulfurization requires less time than heretofore.

A high silicon content of the pig iron does not interfere with the method of the present invention, but in fact, the degree of desulfurization is improved up to a silicon content of about 0.9%.

Preferably, the method of the present invention is carried out by starting to blow the suspension of desulfurization agents through a lance so that the orifice of the lance is upwardly spaced from the surface of the molten bath at the time the blowing of the suspension starts. The lance is then quickly immersed into the molten bath. By starting the blowing of the suspension while the lance is spaced from the molten bath, clogging up of the lance is prevented.

Preferably, the method of the present invention is carried out by introducing the pulverulent calcium oxide and the pulverulent sodium carbonate separately through pipe lines into a pneumatic mixing device, where the proportioned quantities of calcium oxide and sodium carbonate are mixed and suspended in a small quantity of carrier gas and the thus formed suspension is then blown through the lance into the pig iron bath.

The particle size of the pulverulent calcium oxide is preferably such that about 91.5% of the particles are smaller than 0.06 millimeter, about 6.5% of the particles have diameters of between 0.06 and 0.1 millimeter, about 1% between 0.1 and 0.15 millimeter, and about 1% between 0.15 and 0.20 millimeter, so that the pulverulent calcium oxide is substantially free of particles having diameters greater than 0.20 millimeter.

The diameter of the sodium carbonate particles should not exceed about 1 millimeter but may be considerably smaller, for instance similar to the particle size of the calcium oxide.

As described above, and by treating a pig iron containing about 0.15% sulfur, the use of a calcium oxide-sodium carbonate mixture containing 8% sodium carbonate, will increase the effectiveness of the desulfurization by about 20% above the effectiveness of blowing calcium oxide alone into the molten bath. This, of course, corresponds to a reduction in the consumption of calcium oxide of about 20% and, furtheremore, as compared with conventional desulfurization methods using sodium carbonate, a much better desulfurization is accomplished.

Due to the fact that the present method permits an accurate adjustment of the final sulfur content, it is not necessary, when operating as described herein to control and correct the sulfur content of the charge entering the Thomas converter.

It is also within the scope of the present invention to add to the desulfurizing mixture consisting of calcium oxide and sodium carbonate limited quantities of calcium carbonate, for instance between about 5 and 15 parts by weight, preferably about 10 parts by weight of calcium carbonate.

The addition of calcium carbonate will cause a loosening of the slag, particularly due to formation of carbon dioxide gas.

The following examples are given as illustrative only without however limiting the invention to the specific details of the examples.

EXAMPLE I

42.3 tons of pig iron containing 0.144% sulfur, 0.27% silicon and 0.53% manganese were treated in a ladle in accordance with the present invention. The temperature of the molten pig iron was 1,223° C. In the vicinity of the ladle, two containers were provided which were filled with calcium oxide and with sodium carbonate, respectively. The particle size of the calcium oxide was as described further above and the particle size of the sodium carbonate up to 0.6 millimeter. The two containers were connected by conduits to a pneumatic mixer in which mixing of calcium oxide and sodium carbonate was carried out in such a manner that a mixture of 100 parts by weight of calcium oxide and 8.7 parts by weight of sodium carbonate was formed.

A lance was arranged above the ladle containing the molten pig iron and a conduit led from the mixer to the lance. The lance could be lowered so that the lance orifice would then be a desired distance below the upper surface of the molten metal. After filling the ladle, blowing of the suspended mixture of calcium oxide and sodium carbonate was started with the lance orifice upwardly spaced from the surface of the molten metal and immediately thereafter, the lance was lowered into the ladle until the orifice of the lance was 1.20 meters below the surface of the molten metal. The depth of the molten metal bath was 2 meters so that the lance penetrated 60% of the height of the layer of molten metal. The mixture of calcium oxide and sodium carbonate was suspended in nitrogen gas so that 4 liters of nitrogen gas carried 1 kilogram of the mixture. In this maner, within three minutes, 528 kilograms of the calcium oxide-sodium carbonate mixture were introduced into the pig iron at an absolute pressure of 2.1 atmospheres.

After such treatment, the sulfur content of the pig iron was 0.06%, the silcon content 0.20% and the manganese content 0.49%. The same process was then repeated with the lance immersed to a greater depth into the molten pig iron, however, deeper immersion of the lance did not result in an improved desulfurization.

Thus, the process described in the present example resulted in the reduction of the sulfur content of 0.084%, of the silicon content of 0.07% and of the manganese content of 0.04%. This amounts to a degree of desulfurization equal to 57.7% and to an effective utilization of the calcium oxide of 11.6%.

The slag was loose and could be easily withdrawn, so that the total iron loss was only 0.61 ton, or 1.49%, as compared with 1.80 tons or 4.3% when blowing pure limestone in a pan similarly filled with 41 tons of pig iron.

It has been found desirable to introduce the lance orifice to a depth of about 120 centimeters into molten pig iron baths having a total depth of between about 150 and 200 centimeters. The purpose of starting blowing the desulfurizing suspension prior to immersion of the lance orifice is to assure maintenance of the open and unblocked condition of the lance orifice or orifices, whereby the slight loss of desulfurization agents can be disregarded for all practical purposes.

The present method is suitable for the desulfurization of all types of pig iron, including so-called steel-iron, i.e., the liquid charge for open hearth furnaces and the like, also cast iron and liquid steel. However, particularly with respect to liquid steel, the present method may be of somewhat reduced practical importance.

The pulverulent material which is thus blown into the molten bath will rise due to its lower specific weight and this will not require a deeper penetration of the bath by the lance, particularly since due to the blowing of the material into the bath, in combination with the degassing of the pulverulent desulfurization agents, an intensive mixing of the bath is effected and a high degree of desulfurization thus guaranteed.

Broadly, the optimum depth of immersion of the lance into the molten metal will be about two-thirds of the depth of the bath, the minimum about one-half of the depth of the bath and the maximum immersion would be such that the orifice of the lance would be located in the vicinity of the bottom of the bath. However, as stated above, there is no appreciable advantage in lowering the lance beyond about two-thirds of the depth of the bath.

By comparison of the conditions described in the example hereinabove with the conventional blowing of calcium oxide suspended in oxygen, it can be found that according to the present method no appreciable metallurgical effect of the gas is intended or takes place, since only 4 liters of gas were used per kilogram of suspended pulverulent material, while refining in accordance with the oxygen gas process requires between 0.4 and 8 kilograms of pulverulent material per Nm.^{3}, or at least 125 meters of gas per kilogram of pulverulent material.

There is a similarly marked difference between the pressures at which the suspension is introduced according to the present invention as compared with prior art methods, since, as stated above, in the example, a pressure of 2.1 atmospheres absolute, corresponding to an overpressure at the orifice of the lance which is less than 0.5 atmosphere, is employed as against pressures of between 5 and 20 absolute atmospheres according to the oxygen method. Other prior art desulfurization attempts by introducing calcium oxide suspended in nitrogen gas required at least 26 liters of carrier gas for each kilogram of desulfurization agent.

EXAMPLE II

Hereinbelow are given ranges and specific analyses of iron compositions which may be desulfurized in accordance with the present invention.

Thomas pig iron

C	3.20–3.80
Si	0.15–0.50
Mn	0.25–1.10
P	1.60–2.10
S	0.025–0.50

Typical individual analyses of pig iron

	Relatively Acidic Furnace Operation	Relatively Basic Furnace Operation
C	3.20	3.55
Si	0.17	0.69
Mn	0.56	0.70
P	1.82	2.19
S	0.185	0.071

Molten charge for open hearth furnace (steel-iron)

C	4.20
Si	0.50
Mn	1.80
P	1.80
S	0.20–0.80

The pig iron is drawn from the blast furnace into conveying ladles holding between about 40 to 50 tons. These conveying ladles are moved to the desulfurization installation where the blast furnace slag is removed and the residual pig iron is then desulfurized as described further above.

The time required for blowing the desulfurizing agent into the pig iron bath depends on the total amount of desulfurizing agent which is to be added and on the rate of introduction (kg./min.).

By introducing between 30 and 250 kg./min. and a total introduction per ladle or per about 40 tons of pig iron of between 200 and 1000 kg. of pulverulent desulfurizing agent, corresponding to between 5 and 25 kg./ton of pig iron, it normally takes between 4 and 5 minutes to blow the entire desulfurizing agent into the pig iron bars.

Starting temperature of the molten pig iron according to the present example is between 1080 and 1220° C. (in the case of Stahleisen up to above 1300° C.). The temperature loss while introducing the desulfurizing agent normally amounts to between 15 and 25° C.

The sulfur of the metal sulfides which are dissolved in the pig iron reacts with the calcium oxide under formation of calcium sulfide and oxygen. Sodium carbonate essentially reacts in the same manner, namely by binding sulfur as sodium sulfide.

A typical slag obtained in this manner may have the following composition:

Iron granules, 32.5%

the residual slag (free of iron granules) may contain:

	Percent
Total iron	4.55
Metallic iron	3.04
Mn	2.37
SiO_2	25.23
CaO	46.44
C	0.66
S	3.00
Na_2O	3.69
K_2O	0.44

The degree of desulfurization which is to be achieved according to the present invention depends on the subsequent metallurgical processes. Frequently, it is desirable to desulfurize so that the residual sulfur will amount to about 0.06%. However, when desired, for instance in the case of Stahleisen, it is also possible to desulfurize to a much greater extent for instance so as to obtain a residual sulfur content of less than 0.015%.

Sometimes, it is desirable to vary the rate of introduction of the desulfurization agent, for instance so that at the beginning of blowing desulfurizing agent into the molten pig iron, a quantity of 50 kilograms of desulfurizing mixture per minute is introduced and this rate of introduction is then continuously or intermittently increased for instance to a final rate of introduction of 150 kilograms per minute, or, however, it is also possible under certain conditions, to start with a higher rate of introduction of desulfurizing agents and to reduce the rate of introduction thereof during the desulfurizing process.

Sometimes it is desirable to start with the introduction of calcium oxide and to add sodium carbonate only after a certain minimum quantity of calcium oxide, for instance 6 kilos per ton of pig iron have been introduced. The purpose of proceeding in this manner is to provide as quickly as possible a sufficiently firm slag layer to prevent losses due to splattering of iron. For instance, it is possible to start desulfurization with calcium oxide alone until half of the desired amount of calcium oxide has been introduced and thereafter to add sodium carbonate so as to introduce a mixture of sodium carbonate and calcium with increasing sodium carbonate content, for instance, so that at the end of the introduction of the desulfurizing agents, the sodium carbonate content of the mixture amounts to 40%. However, the apportioning of the sodium carbonate will nevertheless be such that the total amount of sodium carbonate introduced will not exceed 18% by weight of the combined total of sodium carbonate and calcium oxide which is introduced into the molten pig iron.

Preferably, the calcium oxide and the sodium carbonate are stored separately and are then passed through suitable conduits into a pneumatic mixing device. Predetermined quantities of calcium oxide and sodium carbonate are introduced into the mixture in such a manner as to produce therein the desired percentage relationship between the two constituents of the desulfurizing mixture. The thus formed mixture is simultaneously suspended in a relatively small quantity of carrier gas and passes from the pneumatic mixer to the lance through which the suspension is introduced into the molten pig iron bars.

A desulfurizing arrangement according to the present invention is schematically illustrated in FIG. 2.

As shown in the drawing, calcium oxide or sodium carbonate reaches the desulfurization installation in hopper car **1** and is conveyed therefrom, in the case of calcium carbonate into storage vessel **2**, and in the case of sodium carbonate into storage vessel **3**. Storage vessel **2** has a capacity of 300 kilograms calcium oxide and storage vessel **3** has a capacity of about 70 kilograms sodium carbonate. Storage vessels **2** and **3** are connected with pressure feeding devices **4** and **5**, respectively, operation of which will cause the contents of the respective storage vessels to pass through conduit **12** into main mixing device **6**. Main mixing device **6**, for instance, may have a capacity of 1000 kilograms.

As illustrated, separate conduits **12** lead from storage vessel **2** and storage vessel **3** to main mixing device **6**. However, it is also possible to combine these two separate conduits into a single conduit for instance at the point indicated in FIG. 2 of the drawing with "X" so that in the single conduit then leading to main mixing device **6** already a premixing of sodium carbonate and calcium oxide will take place, due to the fact that pressure feed devices **4** and **5** are simultaneously operated. Furthermore, it is possible (however not illustrated in the drawing) to predetermine the rate of flow of pulverulent material from storage vessel **3** as well as from storage vessel **2** so as to obtain constant or changing desired proportions of the two constituents of the desulfurization mixture when the two constituents are intimately mixed in the main mixing device **6**. Conduit **12'** leads from mixing device **6** to lance **9** which is not cooled and which is movable in vertical direction. Reference numeral **11** indicates means for exchanging lances and reference numeral **8** indicates a hydraulic device for lowering lance **9** into ladle **10**.

Scale **7** serves to indicate the loss of weight of main mixing device **6** and thus the amount of pulverulent mixture which has been introduced into the molten metal through lance **9**. Thus, blowing will be discontinued when the weight reduction of main mixing device **6** has reached an amount equal to the amount of pulverulent mixture which is to be introduced into the ladle. Treating vessel **10** is mounted on wheels so that pig iron from the blast furnace can be introduced into the same and conveyed in treating vessel **10** to the desulfurization installation.

FIGS. 3 and 4 illustrate specific embodiments of mixing devices **6** which may be used according to the present invention and which have been found to be particularly advantageous.

According to the present invention as illustrated in FIGS. 3 and 4, the main mixing device **6** of FIG. 2 will be a pneumatic mixing and conveying vessel which includes an inner bottom dividing the interior of vessel **6** into an upper and a lower chamber, this inner bottom or wall being formed with portions of varying and controlled permeability, preferably so that the permeability of certain portions of the dividing wall can be adjusted as desired.

It is known to suspend finely granulated or pulverulent solid particles in a stream of gas and to convey the thus formed suspension through conduits such as pipe lines or hoses to their destination.

It is frequently desirable in such cases, particularly so in accordance with the present invention, to operate with the smallest possible consumption of energy and also with a relatively very small amount of carrying gas. The best prior art devices essentially are containers with an intermediate wall for loosening the pulverulent mass and with a withdrawal conduit located above such intermediate wall. Such devices have been found to have an effectiveness of up to 30% with respect to the utilization of energy in conveying the pulverulent material. Gas which passes upwardly through the intermediate permeable wall flows through the pulverulent mass located on top of the intermediate wall and loosens or fluidizes the same, provided that the gas passes through the permeable wall with a speed which is sufficiently great for the respective height of the layer of pulverulent mass, its specific gravity, particle size and particle configuration, which speed, however, will not reach or exceed the gravitational speed of the respective pulverulent material. The gas which thus passes through the pulverulent mass, loosening the same, will then form above such loosened pulverulent mass a pressure layer, so that upon opening of the valve controlling the withdrawal conduit, fluidized pulverulent material, i.e. pulverulent material suspended in the carrier gas will be pushed into the withdrawal conduit. The pressure required for this purpose may also be supplied in part by the addition of gas under pressure from above the loosened layer of pulverulent mass.

However, it has been found that devices such as the one broadly described above do not operate very effectively due to the fact that the gas will try to pass from the permeable wall into the withdrawal conduit along the shortest available path. Thus, while the direction of the flow of the gas which serves for loosening the layer of pulverulent material is upward prior to opening of the withdrawal conduit, this direction will be changed upon opening of the valve controlling the withdrawal conduit so that gas passing through the permeable wall after opening of the withdrawal conduit will generally flow along the shortest path from the permeable bottom to the opening of the withdrawal conduit. This will interfere with the fluidization of the pulverulent mass and reduce the concentration of suspended particles in the carrier gas. The relationship between the speed of the gas flowing towards the withdrawal conduit and the characteristics of the pulverulent mass is changed and distored when the direction of the gas now is no longer straight upwardly but angularly inclined toward the withdrawal conduit and, in fact, much higher speed of the gas flowing from the permeable wall towards the opening of the withdrawal conduit is required than would be required for fluidization of the material if the gas would flow straight upwardly through the pulverulent mass. It follows, that these conventional devices are rather inefficient, inasmuch as relatively large quantities of gas have to pass at a relatively high speed through the permeable wall and still will carry along only a relatively small quantity of particular material.

A further disadvantage of these devices is that the speed of the gas progressively increases due to the fact that channels are formed in the pulverulent mass and less and less resistance is offered for the gas passing from the permeable wall towards the withdrawal conduit. Eventually, these channels break down and the speed of gas is again reduced and consequently operation of these conventional devices will generally be carried out in a pulsating manner and from time to time they require shutting down of the device in order to again create conditions under which a relatively larger quantity of pulverulent material will be carried along.

The present invention eliminates the above described disadvantages and prevents channel formation within the pulverulent mass, by providing a permeable wall which possesses areas of varying permeability for instance in such a manner that in the case of a circular wall, several annular wall portions are provided wherein the gas permeability increases from the innermost annular portion towards the outermost annular portion, while the center portion which is surrounded by the innermost annular portion will be gas impermeable. Thereby, the outermost annular portion may be of relatively small width but of very great permeability so that nearly the entire quantity of gas which is required for loosening the pulverulent mass and for forming a suspension carrying the same along, will pass through this outermost annular zone. The intermediate annular zone between the outermost annular zone and the impermeable circular center zone, will then have a relatively small gas permeability so that the amount of gas flowing through this intermediate zone will thus suffice to overcome the frictional resistance of the pulverulent suspension which flows from the outermost zone past this intermediate zone towards the inlet opening of the withdrawal conduit, so that during passage of such suspension towards the withdrawal conduit precipitation of the pulverulent particles will be prevented. As stated above, the center portion of the intermediate wall which in this case preferably will be of circular shape is gas impermeable and has a diameter which is at least equal to the diameter of the opening of the withdrawal conduit. Furthermore, it is desirable to provide the horizontal gas impermeable center portion of the intermediate wall with a surrounding upwardly extending wall as will be described in more detail in the following description of FIGS. 3 and 4 of the drawing. Preferably, the impermeable portion of the intermediate wall is dish-shaped and is formed by a dish-shaped insert which is placed onto the center of the permeable wall. The outer diameter, or the diameter of the highest elevation of the dish-shaped impermeable structure is then preferably greater than the diameter of the inlet portion of the withdrawal conduit.

Permeability of the intermediate wall may either gradually increase from the impermeable center wall toward the most permeable outermost annular portion thereof, or there may be a stepwise increase of permeability in radial direction of the intermediate wall.

Thus, FIG. 3 illustrates an embodiment of the last-discussed device wherein the intermediate wall is formed of three zones of different gas permeability, whereby, of course, the outermost zone possesses the greatest gas permeability, while FIG. 4 shows an intermediate wall having an adjustable gas permeability, however, adjustable in such a manner that under all circumstances the greatest gas permeability will be found in the outermost annular portion of the intermediate wall.

Referring now specifically to FIG. 3, a container **31** is shown which is divided by intermediate wall **32** into an upper and a lower portion. Above intermediate wall **32** will be found withdrawal conduit **34** with inlet portion **33** and control valve **35**. Gas under pressure is introduced into the lower portion of container **31** via conduit **36**. The lower portion of the container which terminates upwardly in wall **32** is indicated by reference numeral **37**. Wall **32**, according to the embodiment illustrated in FIG. 3 consists of three areas, namely an impermeable center area **38** of dish-shaped configuration, an intermediate annular area **39** of limited gas permeability, and a highly gas permeable outer annular area **310**. The dish-shaped impermeable area **38** is formed with an upwardly extending annular wall **311**.

According to the embodiment of FIG. 4, reference numeral **412** indicates a frustoconical container into which extends a withdrawal conduit terminating in opening **413**. This frustoconical container or upper portion of the device terminates at its lower end in intermediate wall **415** which wall possesses even gas permeability throughout. Underneath gas permeable wall **415** and spaced therefrom is arranged a gas permeable wall **417** which is formed with an upwardly extending rim **416** contacting wall **415**. The interspace between walls **415** and **417** is partially filled with a single layer of resiliently deformable spheres **418**. Pressure may be exerted against wall **417** by actuating spindle **420**, for instance by operatitng hand wheel **419**. Spindle **20** is supported by bearings **422** and **421**. Thus, it is possible to reduce in the center portion of walls **415** and **417** the distance between the same and thereby, resilient spheres **418** will be deformed, more so in the center area of the space between walls **415** and **417** than in the peripheral area thereof. Consequently, gas permeability of the combined structure of walls **417** and **415** will be reduced by exerting pressure against the center portion of wall **417**, and this reduction will be most marked in the center portion and considerably less marked in the peripheral portion of the combined wall structure. In the illustrated embodiments, the outermost peripheral portion of gas permeable wall **415** is radially spaced from the entire gas permeable wall **417** and thus not effected by any reduction of gas permeability of the more centrally arranged wall portion. However, it is also possible to provide for instance an annular resilient tube located in the slot between the outer wall of permeable wal **417** and the container wall, and to control the gas permeability of the outermost annular portion by adjusting pressure in the resilient annular tube. The proportion of the various zones of different gas permeability relative to the total area of intermediate wall **415**, will be controlled depending on the desired effect of the entire device. For instance, for conveying pulverulent finely ground calcium oxide from a container having a total diameter of 400 millimeters, the gas impermeable circular center area may have a diameter of 130 millimeters, and the zone of main introduction of gas such as annular area **310** in FIG. 3 may have a width of 50 millimeters. The gas permeability of zone **310**, formed in a thickness of 5 millimeters has a gas permeability for dry air of 20° C. at a pressure differential of 100 millimeters which is equal to 1.24 liters per minute and square centimeter of zone **310**. The remaining gas permeable area, such as area **39** of FIG. 3 has a gas permeability of only 0.36 liter per minute and square centimeter under otherwise equal conditions. By introducing gas in the above described manner, it is accomplished that the gas has to flow along elongated paths from its main introduction area to inlet **33** of the withdrawal conduit. Thereby, channel formation in the pulverulent mass is safely prevented. In order to achieve this result, the distance which has to be travelled by the main portion of the gas after the same has passed through the gas permeable wall and until the gas reaches the inlet **33** of the withdrawal conduit should be at least twice as long as the diameter of the inlet portion of the withdrawal conduit.

What is claimed as new and desired to be secured by Letters Patent is:

1. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 5% and 15% sodium carbonate and between 95% and 85% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas.

2. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 8% and 12% sodium carbonate and between 92% and 88% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

3. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 5% and 15% sodium carbonate and between 95% and 85% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in about 5 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

4. In a method of desulfurizing pig iron, the steps of blowing at an overpressure of between about 0.1 and 0.5 atmosphere below the surface of a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 5% and 15% sodium carbonate and between 95% and 85% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blow into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

5. In a method of desulfurizing pig iron, the steps of blowing at an overpressure of between about 0.1 and 0.5 atmosphere below the surface of a bath of molten sul-

fur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 8 and 12% sodium carbonate and between 92% and 88% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in about 5 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

6. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein a pulverulent mixture consisting exclusively of between 5 and 15 parts by weight of sodium carbonate, between 95 and 85 parts by weight of calcium oxide and about 10 parts by weight of calcium carbonate, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blow into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

7. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein a pulverulent mixture consisting exclusively of between 8 and 12 parts by weight of sodium carbonate, between 92 and 88 parts by weight of calcium oxide and up to about 10 parts by weight of calcium carbonate, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

8 In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containnig pig iron nitrogen as a carrier gas being substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 5% and 15% sodium carbonate and between 95% and 85% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

9. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron nitrogen as a carrier gas being substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 8% and 12% sodium carbonate and between 92% and 88% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

10. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 5% and 15% sodium carbonate and between 95% and 85% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in between about 3 and 7 liters of said carrier gas and the total quantity of the thus introduced pulverulent mixture being equal to between about 6 and 40 kilograms of said mixture per metric ton of molten pig iron, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

11. A method according to claim **10**, wherein the sodium carbonate content of said mixture is gradually increased during introduction of the same.

12. In a method of desulfurizing pig iron, the steps of blowing into a bath of molten sulfur-containing pig iron a carrier gas of such type and in such amount as to be substantially without metallurgical effect with respect to said pig iron, said carrier gas having suspended therein as the only desulfurizing agent a pulverulent mixture of calcium oxide and sodium carbonate, said mixture consisting of between 8% and 12% sodium carbonate and between 92% and 88% calcium oxide, the concentration of said suspended mixture in said carrier gas being such that 1 kilogram of said mixture is suspended in about 5 liters of said carrier gas and the total quantity of the thus introduced pulverulent mixture being equal to between about 6 and 40 kilograms of said mixture per metric ton of molten pig iron, and the pressure at which said carrier gas with said desulfurizing agent suspended therein is blown into said molten bath being greater by up to 0.5 atmosphere than the bath pressure at the point of initial contact between said molten bath and said carrier gas having said desulfurizing agent suspended therein.

13. A method according to claim **10**, wherein initially pulverulent calcium oxide substantially free of sodium carbonate is introduced into said molten pig iron until up to 6 kilograms of calcium oxide per metric ton of pig iron have been introduced, and thereafter a mixture of calcium oxide and sodium carbonate with progressively increasing sodium carbonate content is introduced until per metric ton of molten pig iron up to about 40 kilograms of said pulverulent substances have been introduced.

14. A method according to claim **12**, wherein initially pulverulent calcium oxide substantially free of sodium carbonate is introduced into said molten pig iron until about 6 kilograms of calcium oxide per metric ton of pig iron have been introduced, and thereafter a mixture of calcium oxide and sodium carbonate with progressively increasing sodium carbonate content is introduced until per metric ton of molten pig iron about 40 kilograms of said pulverulent substances have been introduced, and wherein said pulverulent mixture is composed of between 8% and 10% sodium carbonate and between 92% and 90% calcium oxide.

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