

US 20160168652A1

### (19) United States

## (12) Patent Application Publication MILLNER

# (10) **Pub. No.: US 2016/0168652 A1**(43) **Pub. Date: Jun. 16, 2016**

## (54) DESULFURIZATION OF GASES IN THE PRODUCTION OF PIG IRON

(71) Applicant: PRIMETALS TECHNOLOGIES AUSTRIA GMBH, Linz (AT)

(72) Inventor: Robert MILLNER, Loosdorf (AT)

(21) Appl. No.: 14/902,756

(22) PCT Filed: Feb. 6, 2014

(86) PCT No.: **PCT/EP2014/052280** 

§ 371 (c)(1),

(2) Date: **Jan. 4, 2016** 

#### (30) Foreign Application Priority Data

#### **Publication Classification**

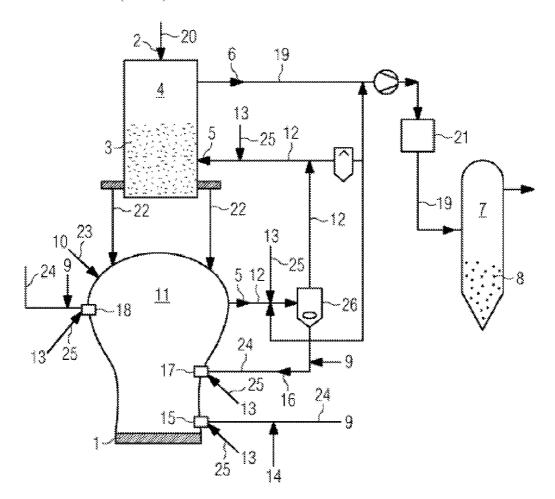
(51) Int. Cl. C21B 5/00 (2006.01) C21B 7/16 (2006.01) C21B 7/00 (2006.01)

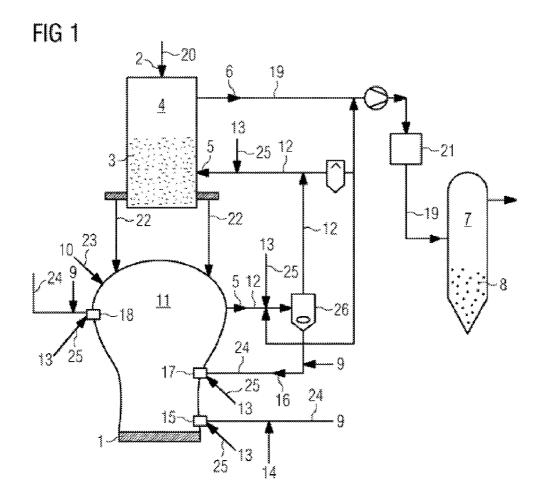
#### 

(2013.01); *C21B* 7/16 (2013.01); *C21B* 5/007 (2013.01)

#### (57) ABSTRACT

A process for producing liquid pig iron (1), in which charge materials (2) containing iron oxide are reduced by a reducing gas (5) in a first reduction plant (4) to form a partially reduced first iron product (3) and are melted in a fusion gasifier (11) to form the liquid pig iron (1). The spent reducing gas (5) is introduced as export gas (6) into a second reduction plant (7), wherein a sulfur-containing gas (13) is introduced together with an oxygen-containing gas (9) and/or together with dust (16) into the fusion gasifier (11) and/or into the reducing gas line (12). Also, a device for carrying out the process. It is therefore possible for sulfur-containing gas (13) to be used for production of liquid pig iron (1), or DRI, with a simultaneous increase in productivity, without damaging the environment or adversely affecting the quality of the liquid pig iron (1) or of the DRI.





## DESULFURIZATION OF GASES IN THE PRODUCTION OF PIG IRON

#### TECHNICAL FIELD

[0001] The invention relates to a process for producing liquid pig iron, said process comprising reducing iron oxide-containing charge materials to give a part-reduced first iron product in a first reduction unit by means of a reducing gas and drawing off the reducing gas used in the reduction as export gas, removing CO<sub>2</sub> from the export gas and introducing the export gas into at least one second reduction unit for producing a part-reduced second iron product, introducing the part-reduced first iron product, an oxygen-containing gas, and carbon carriers into a melter gasifier, gasifying the carbon carriers with the oxygen-containing gas and melting the part-reduced first iron product to give the liquid pig iron with formation of the reducing gas in the melter gasifier, and introducing at least a portion of the reducing gas into the first reduction unit by means of a reduction-gas line.

#### PRIOR ART

[0002] In the production of coke in a coking plant or the gasifying of coal with oxygen, gases are produced, an example being coker gas from a coking plant, that comprise not only a high fraction of hydrogen (H2) and carbon monoxide (CO) but also hydrogen sulfide (H2S) and methane (CH<sub>4</sub>). The coke-oven gas is often used to support the calorific value of blast-furnace top gas before it is utilized in blast heaters. Other known ways of utilizing the coke-oven gas are its deployment as fuel gas in slab reheater furnaces or roller hearth furnaces, its deployment in power stations for generating electricity, its blowing in via the air-blast tuyeres of blast furnaces for lowering the consumption of reducing agent. Moreover, the coke-oven gas is often used together with a further gas as the reducing gas in direct reduction units. In the direct reduction unit, iron oxide-containing charge materials are reduced to give directly reduced iron (DRI) irons, such as sponge iron, for example.

[0003] Where the coke-oven gas is utilized in direct reduction units, there are the following associated disadvantages:

[0004] coke-oven gas contains sulfur primarily in the form of hydrogen sulfide (H<sub>2</sub>S). H<sub>2</sub>S levels of between 300 mg per standard cubic meter of coke-oven gas and 500 mg per standard cubic meter of coke-oven gas are customary. If the coke-oven gas is introduced into the direct reduction unit, a large part of the hydrogen sulfide present in the coke-oven gas accumulates in the DRI or in the sponge iron, according to the reaction equation Fe (iron, DRI)+H<sub>2</sub>S (hydrogen sulfide)→FeS (iron(II) sulfide)+H<sub>2</sub>, and so increases the sulfur content of the DRI. The DRI is customarily processed further to liquid steel in an electric arc furnace (EAF) or in a basic oxygen furnace (BOF). The increased sulfur content of the DRI necessitates additional desulfurization of the DRI, either directly in the EAF or in the BOF, or of the liquid steel produced in the EAF or in the BOF.

[0005] Coke-oven gas contains methane as well as sulfur. Methane levels of between 20 and 25 volume percent in the coke-oven are customary. If the reducing gas comprising the coke-oven gas is introduced into the direct reduction assembly, the methane decomposes in an endothermic reaction with lowering of the reducinggas temperature. Especially in the case of a methane

content of more than 8 volume percent in the reducing gas, the reducing-gas temperature is lowered beneath a minimum temperature that is necessary for reduction of the iron ore-containing charge materials, and hence the productivity and unit performance of the direct reduction assembly are substantially reduced. Consequently, quantitative limitations are imposed on the deployment of coke-oven gas in direct reduction units.

[0006] In order to avoid these disadvantages, before being used for producing DRI, the coke-oven gas is subjected, by means of methods known from the prior art, for example, to desulfurization and/or to treatment in what is called a thermal reactor system to convert the methane contained in the coke-oven gas into carbon monoxide (CO) and hydrogen. Achieving this, however, necessitates inconvenient and costly techniques and units.

#### SUMMARY OF THE INVENTION

#### Technical Problem

[0007] The problem addressed by the present invention is that of providing a process and apparatus for desulfurizing gases in the production of liquid pig iron.

#### **Technical Solution**

[0008] This problem is solved by a process for producing liquid pig iron, said process comprising: reducing iron oxidecontaining charge materials to give a part-reduced first iron product in a first reduction unit by means of a reducing gas and drawing off the reducing gas spent in the reduction as export gas, removing CO2 from the export gas and introducing the export gas into at least one second reduction unit for producing a part-reduced second iron product, introducing the part-reduced first iron product, an oxygen-containing gas, and carbon carriers into a melter gasifier, gasifying the carbon carriers with the oxygen-containing gas and melting the partreduced first iron product to give the liquid pig iron with formation of the reducing gas in the melter gasifier, and introducing at least a portion of the reducing gas into the first reduction unit by means of a reducing-gas line, the process further comprising:

[0009] jetting or introducing a sulfur-containing cokeoven gas, a sulfur-containing natural gas, or a mixture of the sulfur-containing natural gas and the coke-oven gas [0010] together with the oxygen-containing gas and optionally together with fine coal into the melter gasifier by means of oxygen nozzles and/or

[0011] together with dust and the oxygen-containing gas into the melter gasifier by means of dust burners and/or

[0012] together with the oxygen-containing gas into the melter gasifier by means of oxygen burners and/or[0013] into the reducing-gas line.

[0014] The expression "sulfur-containing gas" refers in the context of this specification to

[0015] the sulfur-containing coke-oven gas,

[0016] the sulfur-containing natural gas, or the

[0017] mixture of the sulfur-containing natural gas and the coke-oven gas.

[0018] In the first reduction unit, by means of the reducing gas, the iron oxide-containing charge materials are reduced to give the first part-reduced iron product. The first reduction unit may be designed, for example, as a prior-art COREX

reduction shaft or as a fluidized bed reactor of a FINEX® reduction cascade. By iron oxide-containing charging materials are meant iron ore products. The reducing gas spent in the reduction is drawn off as export gas from the first reduction unit. This export gas is also customarily referred to by the expression "top gas". In the present specification, however, the export gas is introduced or exported into a second reduction unit, separate from the first reduction unit, optionally as a mixture of further gases. From the export gas, or from the mixture, the CO<sub>2</sub> is removed by means of facilities known from the prior art, examples being PSA units, and, after being heated, is introduced into the second reduction unit. The second reduction unit is designed preferably as a direct reduction shaft. Examples of known direct reduction shafts are MIDREX® high-pressure shafts or MIDREX® low-pressure shafts. Like the first reduction unit, the second reduction unit may be designed as a fluidized bed reactor of a reduction cascade. In the second reduction unit, further iron oxidecontaining charge materials are reduced to give the second part-reduced iron product, more particularly to give direct reduced iron (DRI) or sponge iron. The sponge iron is subsequently processed further to liquid steel in an electric arc furnace (EAF) or in a basic oxygen furnace (BOF). In the melter gasifier, with addition of the carbon carriers and the oxygen-containing gas, the part-reduced first iron product produced in the first reduction assembly is smelted to give liquid pig iron. The gasifying of the carbon carriers by the oxygen-containing gas produces the reducing gas, which is introduced by means of the reducing-gas line into the first reduction unit.

[0019] In accordance with the invention the sulfur-containing gas is jetted into the melter gasifier by means of the oxygen nozzles together with the oxygen-containing gas and optionally together with the fine coal. The sulfur-containing gas is produced, for example, during the production of coke in a coking plant or during the gasifying of coal with oxygen. More particularly, sulfur-containing gas refers to coke-oven gas from a coking plant. Such gases, in addition to a high fraction of hydrogen  $(H_2)$  and carbon monoxide (CO), also contain sulfur (S) and methane  $(CH_4)$ .

[0020] A typical composition of coke-oven gas is as follows:

[0021] between 60 and 65 volume percent hydrogen  $(H_2)$ ,

[0022] between 2 and 3 volume percent nitrogen  $(N_2)$ ,

[0023] between 6 and 6.5 volume percent carbon monoxide (CO),

[0024] between 20 and 25 volume percent methane  $(CH_4)$ ,

[0025] between 2.5 and 3.5 volume percent other hydrocarbons  $(C_nH_m)$ ,

[0026] between 1.5 and 1.5 volume percent carbon dioxide ( $CO_2$ ),

[0027] between 350 and 500 mg hydrogen sulfide  $({\rm H_2S})$  per standard cube meter coke-oven gas,

[0028] between 500 and 550 mg tar per standard cubic meter coke-oven gas, and

[0029] between 500 and 550 mg dust per standard cubic meter coke-oven gas

[0030] The jetted introduction of fine coal is known by the expression Pulverized Coal Injection (PCI). Serving on a standard basis as propellant gas in this case is nitrogen, as a result of which the reducing gas formed in the melter gasifier also includes a nitrogen fraction, which is of no effect in the

reduction of the iron oxide-containing charging materials. In accordance with the invention the nitrogen fraction is abated or substituted by the sulfur-containing gas, with the advantage of a more efficient reduction procedure both in the first and in the second reduction unit. Where the sulfur-containing gas is sulfur-containing natural gas, the  $\mathrm{CH_4}$  present in the sulfur-containing natural gas is reacted, together with the oxygen contained in the oxygen-containing gas, to form CO and  $\mathrm{H_2}$ , in addition to the substitution of the nitrogen fraction. Both CO and  $\mathrm{H_2}$  contribute to raising the efficiency of the reduction procedure.

[0031] In a further variant of the process of the invention, the sulfur-containing gas is jetted by means of dust burners into the melter gasifier together with the dust and the oxygen-containing gas, preferably with oxygen of technical purity. The dust originates, for example, from dry dedusting installations in the first reduction unit. As a result of the additional energy input of the oxygen in the oxygen-containing gas, it is possible to accumulate dust of low carbon content by means of dust burners, and so the dust is not carried out of the melter gasifier with the reducing gas.

[0032] The sulfur-containing gas may also be jetted together with the oxygen-containing gas by means of oxygen burners into the melter gasifier, or introduced directly into the reducing gas line. Located preferably in the reducing-gas line is a dedusting installation, more particularly a hot-gas cyclone, in which the reducing gas originating from the melter gasifier is dedusted before being introduced into the first reduction unit. Since the temperature of the sulfur-containing gas is below the temperature of the reducing gas drawn off from the melter gasifier, the introduction of the sulfur-containing gas into the reducing-gas line ahead of the dedusting installation—as viewed in the flow direction of the reducing gas—accomplishes cooling of the reducing gas. In this case, the sulfur-containing gas acts additionally as a cooling gas to set the optimum reduction temperature in the first reduction unit, and at the same time allows the amount of cooling gas needed to be reduced. Before being introduced into the reducing-gas line, the sulfur-containing gas is optionally preheated in a preheating installation, more particularly in a heat exchanger. In the preheating installation, for example, the sensible heat of a smelting-works gas is utilized. As a result, especially if the temperature of the sulfur-containing gas is very much lower than the temperature of the reducing gas, the amount of sulfur-containing gas that can be supplied is maximized.

[0033] If the sulfur-containing gas, comprising the sulfur primarily in the form of hydrogen sulfide (H<sub>2</sub>S), comes into contact with the iron (Fe) of the first part-reduced iron product, a reaction occurs in accordance with the reaction equation Fe+H<sub>2</sub>S→FeS (iron(II) sulfide)+H<sub>2</sub>. This reaction occurs either in the melter gasifier or in the first reduction unit. In the case of the production of liquid pig iron, not only the iron oxide-containing charge materials but also adjuvants such as CaO (calcium oxide) and/or MgO (magnesium oxide) are used. In that case, on contact of these adjuvants with the sulfur-containing gas, the following reactions occur: CaO (calcium oxide)+H<sub>2</sub>S→CaS (calcium sulfide)+H<sub>2</sub>O (water) or MgO (magnesium oxide)+H<sub>2</sub>S→MgS+H<sub>2</sub>O. The iron(II) sulfide, the magnesium sulfide, and the calcium sulfide are discharged by way of the slag, which floats on the liquid pig iron in the melter gasifier.

[0034] Hence there is a very eco-friendly desulfurization of the sulfur-containing gas, since the sulfur is bound predominantly in the slag and therefore does not enter the atmosphere. Moreover, by the jetting or introducing of the sulfur-containing gas into the process of the invention, the hydrogen content of the reducing gas is increased. Through an increase in the reaction kinetics, this results in an improvement in the reduction procedure in the first reduction unit. Through the direct utilization of the sulfur-containing gas in the process of the invention, there is no need for expensive and inconvenient installations for desulfurization, without any adverse effect on the quality of the liquid pig iron in terms of its sulfur content. The DRI in the second reduction unit as well is not adversely effected in terms of its sulfur content as a result of the sulfur-containing gas being introduced into the first reduction unit or into the melter gasifier, because the export gas which is introduced into the second reduction unit enters the unit in an already desulfurized form. Prior to or during the further processing of the DRI into liquid steel, therefore, there is no need for additional desulfurization procedures.

[0035] The coke-oven gas comprises not only sulfur but also  ${\rm CH_4}$  (methane),  ${\rm C_2H_4}$  (ethane),  ${\rm C_6H_6}$  (benzene),  ${\rm C_7H_8}$  (toluene), and  ${\rm C_{10}H_8}$  (naphthalene), which in some cases are toxic and are all unwanted in the process of the invention. In the melter gasifier or in the first reduction unit, these hydrocarbons present in the coke-oven gas are converted at least partly, as a result of the high temperatures prevailing therein and as a result of the oxygen present therein, into CO (carbon monoxide),  ${\rm CO_2}$  (carbon dioxide),  ${\rm H_2O}$  (water), and  ${\rm C}$  (carbon). By means of the process of the invention, the hydrocarbons present in the coke-oven gas are converted into elements and compounds that are comparatively undetrimental for the process of the invention, and compounds and elements that are comparatively unproblematic for the environment.

[0036] By means of the process of the invention, sulfurcontaining gas can be used in the production of liquid pig iron or DRI, with a simultaneous boost in productivity, without burdening the environment or adversely affecting the quality of the liquid pig iron or of the DRI.

[0037] One preferred embodiment of the process of the invention is characterized in that the first reduction unit comprises at least a first and a second fluidized bed reactor, in that the fluidized bed reactors are connected by means of connecting lines for introducing the reducing gas into the fluidized bed reactors and for drawing off the reducing gas after flowing through the two fluidized bed reactors is drawn off as export gas, and in the process further comprises: jetting or introducing the sulfur-containing coke-oven gas, the sulfur-containing natural gas and the coke-oven gas

[0038] together with the oxygen-containing gas into at least one of the connecting lines by means of oxygen burners and/or

[0040] directly into at least one of the connecting lines.
[0040] This embodiment typically involves fluidized bed reactors of a FINEX®—reduction cascade, which is well known from the prior art. The individual fluidized bed reactors are connected by means of the connecting lines, with the reducing gas being passed initially into the first fluidized bed reactor. Following reduction of the iron oxide-containing charge materials in the first fluidized bed reactor, the reducing gas is drawn off from this reactor by means of the connecting line and is passed into the other fluidized bed reactor for reduction of the iron oxide-containing charge materials located therein. Where more than two fluidized bed reactors

are present, this operation takes place, correspondingly, more often. Following passage of the flow through the last available fluidized bed reactor, the spent reducing gas is drawn off from this reactor as export gas. With this embodiment of the process of the invention, the jetting of the sulfur-containing gas together with the oxygen-containing gas takes place into at least one of the connecting lines by means of oxygen burners, and/or the introducing of the sulfur-containing gas takes place directly into at least one of the connecting lines. Direct in this context refers to the unmediated introduction of the sulfur-containing gas into the connecting lines. This means that the sulfur-containing gas is introduced into the connecting line without prior combustion in the oxygen burner.

[0041] In addition to the advantages already mentioned for the process of the invention, the reduction potential that is present in the sulfur-containing gas, and more particularly in the coke-oven gas, produces a further advantageous effect. Coke-oven gas typically contains between 60 and 65 volume percent hydrogen (H<sub>2</sub>) and between 6 and 6.5 volume percent carbon monoxide (CO). This means that there is reduction potential—meaning the capacity for reduction of iron-oxides to iron—in the coke-oven gas. In the case of the inventive introduction of sulfur-containing gas into the melter gasifier, into the reducing-gas line, and/or into the connecting lines, this reduction potential is utilized, thereby achieving a reduction in the consumption of reducing agent, in particular of the carbon carriers such as coal or coal briquettes in the melter gasifier.

[0042] A further subject of the present invention is apparatus for implementing the process of the invention, said apparatus comprising: a first reduction unit having an export-gas line and a supply line for supplying iron oxide-containing charge materials, a melter gasifier which is connected via a reducing-gas line to the first reduction unit, at least one second reduction unit which is connected by the export-gas line to the first reduction unit, a CO<sub>2</sub> removal unit disposed in the export-gas line and intended for removing CO<sub>2</sub>, at least one iron product supply line, which opens into the melter gasifier, and a carbon carrier supply line, one or more introduction elements which open into the melter gasifier and have an oxygen nozzle or a dust burner or an oxygen burner design, having in each case a media supply line for introducing a gas and/or a solid into the melter gasifier, wherein at least one process-gas line for supplying a sulfur-containing coke-oven gas, a sulfur-containing natural gas, or a mixture of the sulfurcontaining natural gas and the coke-oven gas, said line opens

[0043] into at least one of the media supply lines and/or [0044] into at least one of the introduction elements and/or

[0045] into the reducing-gas line.

[0046] A melter gasifier, in contrast to a blast furnace, is characterized in that it is operated predominantly with reducing agents in piece form, such as lump coal or coal briquettes, for example, with iron carriers that have undergone at least preliminary reduction, and with oxygen of technical purity: oxygen fraction greater than 90 volume percent. Moreover, in contrast to a blast furnace, a melter gasifier has a dome with a calming space.

[0047] The first reduction unit is connected via the reducing-gas line to the melter gasifier. The first reduction unit may be designed, for example, as a COREX® reduction shaft known from prior art or as a fluidized bed reactor of a FINEX® reduction cascade. By iron oxide-containing charge materials are meant iron ore products. The reducing gas spent

in the reduction of the iron oxide-containing charge materials in the first reduction unit is drawn off from the first reduction unit as export gas by means of the export-gas line. The exportgas line opens into the second reduction unit, which is different from the first reduction unit. The second reduction unit is designed preferably as a direct reduction shaft. Examples of known direct reduction shafts are MIDREX® high-pressure shafts or MIDREX® low-pressure shafts. Like the first reduction unit, the second reduction unit may also be designed as a fluidized bed reactor of a reduction cascade. In the second reduction unit, the DRI is produced. Disposed within the export-gas line is the CO<sub>2</sub> removal unit, preferably a pressure swing absorption unit (PSA unit) or a vacuum pressure swing adsorption unit (VPSA unit), for the removal of CO<sub>2</sub> from the export gas. Optionally there are additionally one or more compressor stages and/or heating installations and/or cooling installations disposed in the export-gas line. The melter gasifier has at least one iron product supply line, which opens into the melter gasifier, and a carbon carrier supply line. Via the iron product supply line, the first part-reduced iron product is introduced from the first reduction plant into the melter gasifier. Via the carbon carrier supply line, the carbon carriers, preferably lumps of coal or coal briquettes, are introduced into the melter gasifier. By means of the media supply lines, which open into the introduction elements of the melter gasifier, the gases or the solids are introduced into the melter gasifier. More particularly the oxygen-containing gas and the dust are introduced into the melter gasifier by means of the media supply lines.

[0048] The liquid pig iron is produced in the melter gasifier. The process-gas lines for supplying the sulfur-containing gas open, in accordance with the invention, in at least one of the media supply lines and/or in at least one of the introduction elements. The introduction elements are designed as oxygen nozzles or as dust burners or as oxygen burners. In accordance with the invention, one or more process-gas lines may also open into the reducing-gas line. Located optionally in the reducing-gas line are dedusting installations for dedusting the reducing gas. As viewed in the direction of flow of the reducing gas, the process-gas lines may open into the reducing-gas line ahead of and/or downstream of the dedusting installation. [0049] By means of the apparatus of the invention, sulfurcontaining gas can be used in the production of liquid pig iron or DRI, with a simultaneous boost in productivity, without burdening the environment or adversely affecting the quality of the liquid pig iron or of the DRI.

[0050] In one embodiment of the apparatus of the invention, the first reduction unit comprises at least a first and a second fluidized bed reactor, the fluidized bed reactors being connected by means of connecting lines for introducing the reducing gas into the fluidized bed reactors and drawing off the reducing gas from the fluidized bed reactors, one or more introduction elements which open into at least one of the connecting lines and are designed as oxygen nozzles, having in each case a media supply line for introducing a gas into the connecting line, are present, and there is at least one process gas line for supplying the sulfur-containing coke-oven gas, the sulfur-containing natural gas and the coke-oven gas, said line opening

[0051] into at least one of the media supply lines and/or[0052] into at least one of the introduction elements and/

[0053] into at least one of the connecting lines.

[0054] In one preferred embodiment of the apparatus of the invention, the process-gas line comes from a plant which produces the sulfur-containing coke-oven gas, the sulfur-containing natural gas, or the mixture of the sulfur-containing natural gas and the coke-oven gas, more particularly from a plant for producing coke and/or a coal gasification plant and/or from another source of the sulfur-containing natural gas.

[0055] Accordingly, sulfur-containing natural gas, or a mixture of the sulfur-containing natural gas and the coke-oven gas, can also be utilized and simultaneously desulfur-

#### BRIEF DESCRIPTION OF THE DRAWING

[0056] Shown exemplary and schematically by

ized during the production of liquid pig iron.

[0057] FIG. 1 are a process of the invention and apparatus of the invention for producing liquid pig iron 1, with utilization and desulfurization of coke-oven gas.

#### DESCRIPTION OF THE EMBODIMENT

[0058] FIG. 1 shows a process of the invention and apparatus of the invention for producing liquid pig iron 1, with utilization and desulfurization of coke-oven gas, in the version of a COREX® integrated direct reduction plant.

[0059] A first reduction plant 4, a COREX® reduction shaft with fixed bed, is supplied with the iron oxide-containing charge materials 2 via a supply line 20 for the supply of iron oxide-containing charge materials 2. These materials are reduced by means of a reducing gas 5 to give a part-reduced iron product 3, which is subsequently introduced into a melter gasifier 11 via a plurality of iron product supply lines 22 which open into the melter gasifier 11. Introduced additionally into the melter gasifier 11 are carbon carriers 10 in the form of lumps of coal, via a carbon carrier supply line 23, and oxygen-containing gas 9 via media supply lines 24. The carbon carriers 10 introduced into the melter gasifier 11 are gasified by means of the oxygen-containing gas 9 with formation of the reducing gas 5. The reducing gas 5 is introduced via the reducing-gas line 12 into the first reduction unit 4. The first iron product 3, introduced into the melter gasifier 11, is melted by the heat produced in the gasification of the carbon carriers 10, to form the liquid pig iron 1. The reducing gas 5 spent in the reduction of the iron oxide-containing charge materials 2 is drawn off from the first reduction unit 4 as export gas 6 via an export-gas line 19 and compressed, after which CO<sub>2</sub> removal takes place in a CO<sub>2</sub> removal installation 21 disposed in the export-gas line 19. The export gas 6 is subsequently introduced into a second reduction unit 7 for production of a part-reduced second iron product 8, more particularly direct reduced iron (DRI). The melter gasifier 11 possesses three introduction elements, which open into the melter gasifier 11 and which have an oxygen nozzle 15, a dust burner 17, and an oxygen burner 18 design. On the outside, relative to the melter gasifier 11, the introduction elements are connected to the media supply lines 24. There are five process-gas lines 25, with two of the process-gas lines 25 opening into the reducing-gas line 12, and one in each case opening into the oxygen nozzle 15, into the dust burner 17, and into the oxygen burner 18. Via the process-gas lines 25, the melter gasifier 11 is supplied with sulfur-containing gas 13, in this specific case with coke-oven gas having a typical composition of

[0060] 65 volume percent hydrogen  $(H_2)$ ,

[0061] 2.5 volume percent nitrogen (N<sub>2</sub>),

[0062] 6 volume percent carbon monoxide (CO),

[0063] 22 volume percent methane  $(CH_4)$ ,

[0064] 3 volume percent other hydrocarbons ( $C_nH_m$ ),

[0065] 1.5 volume percent carbon dioxide  $(CO_2)$ ,

[0066] 350 mg hydrogen sulfide (H<sub>2</sub>S) per standard cubic meter coke-oven gas,

[0067] 500 mg tar per standard cubic meter coke-oven gas, and

[0068] 500 mg dust per standard cubic meter coke-oven

[0069] The coke-oven gas is supplied by jetting of the cokeoven gas into the melter gasifier 11; in the first case, the coke-oven gas is jetted into the melter gasifier together with the oxygen-containing gas 9 and fine coal 14 by means of the oxygen nozzle 15, in the second case together with dust 16 and the oxygen-containing gas 9 by means of the dust burner 17, and in the third case together with the oxygen-containing gas 9 by means of the oxygen burner 18. In the fourth case the sulfur-containing gas 13, or the coke-oven gas, is introduced directly into the reducing-gas line 12 by means of the processgas lines 25. As viewed in the direction of the flow of the reducing gas 5, this takes place in one instance ahead of a dedusting installation 26 disposed in the reducing-gas line 12, and in another instance downstream of that installation. The process-gas lines 25 come from a plant—more particularly a coking plant—that produces the sulfur-containing gas 13.

[0070] In summary the invention relates to a process for producing liquid pig iron 1, wherein iron oxide-containing charge materials 2 are reduced in a first reduction unit 4 by means of a reducing gas 5 to give a part-reduced first iron product 3 which is melted in a melter gasifier 11 to give the liquid pig iron 1, the spent reducing gas 5 being introduced as export gas 6 into a second reduction unit 7, and a sulfur-containing gas 13 being introduced into the melter gasifier 11 and/or into the reducing-gas line 12 together with an oxygen-containing gas 9 and/or together with dust 16.

[0071] The invention further relates to apparatus for implementing the process.

[0072] Accordingly, sulfur-containing gas 13, more particularly coke-oven gas, can be used in the production of liquid pig iron 1, or DRI, with an accompanying boost in productivity, without burdening the environment or adversely affecting the quality of the liquid pig iron 1 or of the DRI.

[0073] Despite the invention being described in detail and illustrated more closely by the preferred working example, the invention is not confined by the example disclosed, and other variations can be derived from it by the skilled person without departing the scope of protection of the invention.

#### LIST OF REFERENCE NUMERALS

[0074] 1 liquid pig iron

[0075] 2 iron oxide-containing charge materials

[0076] 3 part-reduced first iron product

[0077] 4 first reduction unit

[0078] 5 reducing gas

[0079] 6 export gas

[0080] 7 second reduction unit

[0081] 8 part-reduced second iron product

[0082] 9 oxygen-containing gas

[0083] 10 carbon carrier

[0084] 11 melter gasifier

[0085] 12 reducing-gas line

[0086] 13 sulfur-containing gas

[0087] 14 fine coal

[0088] 15 oxygen nozzle

[0089] 16 dust

[0090] 17 dust burner

[0091] 18 oxygen burner

[0092] 19 export-gas line

[0093] 20 supply line for supplying iron oxide-containing charge materials

[0094] 21 CO<sub>2</sub> removal unit

[0095] 22 iron product supply line

[0096] 23 carbon carrier supply line

[0097] 24 media supply line

[0098] 25 process-gas line

[0099] 26 dedusting installation

1. A process for producing liquid pig iron, the process comprising:

reducing iron-oxide containing charge materials to produce a part-reduced first iron product in a first reduction unit, the reducing being by means of a reducing gas and then drawing off the reducing gas spent in the reduction as export gas;

removing CO<sub>2</sub> from the export gas and then introducing the export gas into at least one second reduction unit for producing a part-reduced second iron product;

introducing the part-reduced first iron product, an oxygencontaining gas, and carbon carriers into a melter gasifier;

in the melter gasifier, gasifying the carbon carriers with the oxygen-containing gas and melting the part-reduced first iron product to produce the liquid pig iron with formation of the reducing gas;

introducing at least a portion of the reducing gas into the first reduction unit by a reducing-gas line;

jetting or introducing a sulfur-containing coke-oven gas, a sulfur-containing natural gas, or a mixture of the sulfurcontaining natural gas and the coke-oven gas

together with the oxygen-containing gas and optionally together with fine coal into the melter gasifier by oxygen nozzles; and/or

together with dust and the oxygen-containing gas into the melter gasifier by dust burners (17) and/or

together with the oxygen-containing gas into the melter gasifier by oxygen burners; and/or

into the reducing-gas line.

2. The process as claimed in claim 1, wherein

the first reduction unit comprises at least a first and a second fluidized bed reactor, the fluidized bed reactors are connected by connecting lines for introducing the reducing gas into the fluidized bed reactors and for drawing off the reducing gas from the fluidized bed reactors, and the process further comprising:

after flowing the reducing gas through the two fluidized bed reactors, drawing off the reducing gas as export gas; and

the jetting or introducing the sulfur-containing coke-oven gas, the sulfur-containing natural gas, or the mixture of the sulfur-containing natural gas and the coke-oven gas

together with the oxygen-containing gas is into at least one of the connecting lines by means of oxygen burners; and/or

directly into at least one of the connecting lines.

3. An apparatus configured for implementing a process as claimed in claim 1, the apparatus comprising:

a first reduction unit having an export-gas line for outlet of export gas and a supply line for supplying iron oxidecontaining charge materials to the first reduction unit;

- a melter gasifier connected via a reducing-gas line to the first reduction unit;
- at least one second reduction unit connected by the exportgas line to the first reduction unit;
- a  $\tilde{CO}_2$  removal unit disposed in the export-gas line and configured for removing  $CO_2$ ,
- at least one iron product supply line, which opens into the melter gasifier, and a carbon carrier supply line into the melter gasifier;
- one or more introduction elements which open into the melter gasifier and the one or more introduction elements include an oxygen nozzle or a dust burner or an oxygen burner each having a media supply line for introducing a gas and/or a solid into the melter gasifier;
- at least one process-gas line for supplying a sulfur-containing coke-oven gas, a sulfur-containing natural gas, or a mixture of the sulfur-containing natural gas and the coke-oven gas, the process gas line opening

into at least one of the media supply lines; and/or into at least one of the introduction elements; and/or into the reducing-gas line.

4. The apparatus as claimed in claim 3, further comprising: the first reduction unit comprises at least a first and a second fluidized bed reactor, the fluidized bed reactors being connected by connecting lines for introducing the

reducing gas into the fluidized bed reactors and for drawing off the reducing gas from the fluidized bed reactors;

one or more introduction elements which open into at least one of the connecting lines and comprise oxygen nozzles, each introduction element having a media supply line for introducing a gas into the respective connecting line, and at least one process gas line for supplying the sulfur-containing coke-oven gas, the sulfur-containing natural gas, or the mixture of the sulfur-containing natural gas and the coke-oven gas;

the at least one process gas line opening into at least one of the media supply lines; and/or into at least one of the introduction elements; and/or into at least one of the connecting lines.

- 5. The apparatus as claimed in claim 3, wherein the process-gas line comes from a plant which produces the sulfurcontaining coke-oven gas, the sulfur-containing natural gas, or the mixture of the sulfur-containing natural gas and the coke-oven gas.
- **6**. The apparatus as claimed in claim **3**, wherein the process gas line comes from a plant for producing coke and/or a coal gasification plant and/or a source of the sulfur-containing natural gas.

\* \* \* \* \*