PATENT SPECIFICATION (11) 1 461 238

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(21) Application No. 7576/75 (22) Filed 24 Feb. 1975
(31) Convention Application No. 22341/74 (32) Filed 27 Feb. 1974
(31) Convention Application No. 39499/74 (32) Filed 9 April 1974 in
(33) Japan (JA)
(44) Complete Specification published 13 Jan. 1977
(51) INT CL² C21C 7/02
(52) Index at acceptance
C7D 3G1E 3G3 3G7D 3G7J 3G7L 3G7M
C7M 202 215 218 21Y 22Y 232 235 238 23Y 275 278 27Y 285 288 28Y 30Y 38Y 40Y 42Y 462 483 486 503 513 553 556 586 663 683 703 760 773 783

(19)



(54) METHOD FOR DESULPHURIZING MOLTEN IRON

(71) We, AIKOH CO. LIMITED, a Japanese Company of No. 1—39, Ikenohata 2-Chome, Taito-Ku, Tokyo, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for desulphurizing molten iron.

Heretofore, alkali metal compounds, e.g. soda ash or sodium hydroxide, and alkaline earth metals, e.g. magnesium, or their compounds, such as calcium cyanamide or calcium carbide have been used as desulphurizing agents for molten iron. Methods for using these desulphurizing agents include, for example, a method in which the desulphurizing agent is placed first in a ladle, and then molten iron is poured into the ladle; a method in which a shaking ladle is used in order to promote mixing; a method in which an impeller is used for stirring, and an injection method in which the desulphurizing agent is blown into the molten iron together with an inert gas.

Because of its low cost and the simplicity of its use, soda ash has been regarded as the most practicable desulphurizing agent and has, in fact, been most commonly used. But the desulphurizing effect of soda ash varies and soda ash exhibits only a weak action in desulphurization when molten iron having a relatively low sulphur content is poured into a ladle. An object of the present invention is to provide an improved method for desulphurizing iron.

According to the present invention, there is provided a method of desulphurizing molten iron, which comprises adding, as a desulphurizing agent, to the molten iron, a dust collected from the smelting step of manganese and/or a dust collected from the smelting step of chromium.

Since such dust is normally discarded as a waste, the use of such a dust adds nothing to the cost of production of desulphurized iron.

The collected dust from smelting manganese or chromium may be used either alone or in admixture with commercially available soda ash containing sodium carbonate as a main component for supplementing the alkali content. Alternatively, collected dust having a relatively low alkali content may be blended as an auxiliary desulphurizing agent with soda ash so as to stabilize the desulphurizing activity of the soda ash, and to render the molten iron slag flowable. When it is necessary to prevent the scattering of the desulphurizing agent, for example, in the preplaced method, the dust may be used as a solid desulphurizing agent which further contains a cement containing CaO as the predominant component and water capable of hardening the cement.

The above cement can be, for example, Portland cement which contains CaO as the predominant component. Not only does the cement act as a binder, but also the action of CaO causes the Na_2S formed by desulphurization to be converted to CaS and thus results in a stabilization of the sulphur which helps to prevent re-sulphurization of the iron. The cement hardens under the action of water added at the same time. A suitable amount of the cement to be used as part of the desulphurizing agent is 2 to 25% by weight of the desulphurizing agent. If the amount of the cement is less than 2% by weight of the desulphurizing agent, the cement has a weak action as a binder, and is not effective. On the other hand, if the amount of the cement exceeds 25% by weight of the desulphurizing agent, the cement impedes the flowability of the slag and causes the contact between the desulphurizing agent and the molten iron to be poor, which in turn results in a reduction in the effect of desulphurization.

The water added simultaneously with the cement acts to harden the cement. Furthermore, steam is generated as a result of the heating of the water due to the heat of the molten iron at the time of desulphurization, and decomposes into hydrogen and oxygen upon contact with the molten iron. By an explosive reaction of these gases, the molten

iron is vigorously stirred, and consequently, the contact between the desulphurizing agent and the molten iron is promoted. Thus, the effect of the desulphurizing agent is increased. A suitable amount of water to be used in the desulphurizing agent is 3 to 30% by weight of the desulphurizing agent. If the amount of water is less than 3% by weight, the steam evaporates almost completely in the ladle before the pouring of molten iron, and no agitation results. On the other hand, if the amount of the water exceeds 30% by weight, water acts more vigorously than simply to agitate the molten iron, and the danger of an explosion and scattering can occur. Accordingly, amounts of water outside the above specified range are not desirable.

The collected dust described above is obtained by collecting the sublimed product and the scattered dust or smoke particles, generated by the furnace during the manufacture of, for example metallic manganese, ferromanganese, siliconmanganese, or ferrochromium, by the dry smelting of an ore or slag of manganese or chromium, using a dust collector which precipitates, absorbs and accumulates such a dust. The dust results from the freeing and subliming of a part of the alkalies (K_2O, Na_2O) in the crude ore due to a heating and a precipitation of these in the flue or dust collector in a condensed form. Therefore, the dust comprises the alkalies (K_2O, Na_2O) and CaO, SiO_2, Al_2O_3, C, FeO and MnO or a small amount of Cr_2O_3 as a result of the physical scattering of fine particles of the crude ore and/or any additives. Specifically, a manganese smelt dust for example, contains, by weight, 2 to 20% of Na_2O, 5 to 50% of K_2O, 20 to 40% of MnO, 5 to 30% of CaO, 3 to 20% of SiO_2, 3 to 10% of C, and not more than 5% of each of Al_2O_3, Fe_2O_3, and CaF_2. Chromium smelt dust contains by weight, 3 to 25% of Na_2O, 4 to 40% of K_2O, 4 to 15% of CaO, 5 to 30% of SiO_2, not more than 5% of Cr_2O_3, and not more than 5% of each of C, Al_2O_3, Fe_2O_3 and CaF_2. Since both of these dusts form low-melting slags having a melting point of less than 1000°C, and containing alkalies, they are effective for desulphurizing molten iron. When the alkali content is low, components such as CaO, MnO, SiO_2, FeO, Al_2O_3 and CaF_2 act as a flux to form a slag having good flowability and to assist the desulphurizing action of soda ash, and thus have an effect of promoting the contact between the desulphurized slag and the molten iron. If the components of the dust are basic, the dust can theoretically be used as the sole desulphurizing agent. Preferably, the dust has a:—

$$\frac{Na_2O\ (\%)+K_2O\ (\%)}{SiO_2\ (\%)+Al_2O_3\ (\%)}$$

value of at least 2.0. If this value is below 2.0, the dust is preferably used in admixture with soda ash.

A suitable mixing ratio of the collected dust with soda ash is 5 to 99% for the collected dust and 95% to 1% for the soda ash. If the amount of soda ash is less than 1% the soda ash does not effectively supplement the alkali content, and when less than 5% collected dust is added to soda ash, a poor effect of rendering the slag flowable results. The lower limits of the proportions of these are also the same when the desulphurizing agent is employed in a granulated form, i.e., with the cement hereinbefore described. In view of the fact that the proportions of cement and water for granulation are 2 to 25% and 3 to 30%, respectively, the proportion of the collected dust at the time of granulating the collected dust alone is 45 to 95%, and when the collected dust is mixed with soda ash, the amount of the collected dust is 5 to 94% and the amount of the soda ash is 90 to 1%.

The desulphurizing agent used in the desulphurizing method of this invention can be used in the preplaced method, the agitation method, or the blowing method. However, better results can be obtained by using a powdery dust with the blowing method or the agitation method, and a granulated dust with the preplaced method.

The desulphurizing agent used in the desulphurizing method of this invention may further contain a bulking agent such as scale, red iron oxide, iron ore powder or other iron oxides, or a flux as an auxiliary agent for desulphurization, such as calcium fluoride, magnesium fluoride, lithium fluoride or sodium fluoride.

The following examples are given to illustrate the present invention in greater detail. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

A powdery mixture of 50% by weight of a ferromanganese collected dust (comprising 15% Na_2O, 48% K_2O, 4% CaO, 10% SiO_2, 3% Al_2O_3, 15% MnO and the remainder being C and F) and 50% by weight of a collected ferrochromium dust (comprising 10% Na_2O, 40% K_2O, 8% CaO, 20% SiO_2, 4% Al_2O_3 8% C, 4% Cr_2O_3, and the remainder being Fe_2O_3 and F) was blown from lances into molten iron (with a sulphur content of 0.051%) placed in a ladle, using nitrogen gas. The amount of the powdery mixture was 4 kg per ton of the molten iron. The sulphur content of the molten iron after this desulphurization was 0.015%, and thus, the percentage desulphurization was 70.4.

EXAMPLE 2

A powdery mixture of 40% by weight of a collected ferromanganese dust (comprising

5% Na_2O, 23% K_2O, 15% SiO_2, 2% Al_2O_3, 3% Fe_2O_3, 18% MnO, 5% CaO, 6% C and the remainder being CO_2 and F) and 60% by weight of soda ash was blown into molten iron (with a sulphur content of 0.046%) in a ladle together with nitrogen gas using the same apparatus as used in Example 1. The amount of the powdery mixture was 4 kg per ton of the molten iron. The sulphur content of the molten iron after desulphurization was 0.013%, and thus, the percentage desulphurization was 71.7.

EXAMPLE 3

A mixture of 87% of the dust mixture used in Example 1, 6% by weight of Portland cement and 7% by weight of water was compressed with a granlator to form granules each with a size of 25 mm×25 mm×15 mm. This desulphurizing agent was placed in a ladle in an amount of 5 kg per ton of molten iron, and the molten iron was poured into the ladle. As a result, the sulphur content of the molten iron decreased from the original 0.055% to 0.028% after desulphurization, and thus, percentage desulphurization was 49.1.

EXAMPLE 4

A mixture of 25% by weight of the ferrochromium smelt dust used in Example 2, 55% by weight of soda ash, 10% by weight of Portland cement and 10% by weight of water was granulated to the same size as in Example 3 using the same procedure as in Example 3. The resulting desulphurizing agent was placed in a ladle in an amount of 5 kg per ton of molten iron, and the molten iron was poured into the ladle to desulphurize the iron. The sulphur content of the molten iron decreased from the original 0.051% to 0.025% after desulphurization. The percentage desulphurization was 51.8.

For comparison, soda ash was blown together with nitrogen gas into molten iron in an amount of 4 kg per ton of the molten iron. As a result, the sulphur content of the molten iron decreased from the original 0.049% to 0.023% after desulphurization, and thus, the percentage desulphurization was 52.2.

As a further comparison, 5 kg of molded soda ash was placed in a ladle per ton of molten iron, and then, the molten iron was poured into the ladle to desulphurize the iron. The sulphur content of the molten iron decreased from the original 0.048% to 0.029% after desulphurization, and thus, the percentage desulphurization was 38.5.

WHAT WE CLAIM IS:—

1. A method for desulphurizing molten iron, which comprises adding, as a desulphurizing agent, to the molten iron, a dust collected from the smelting step of manganese and/or a dust collected from the smelting step of chromium.

2. A method as claimed in Claim 1, wherein the desulphurizing agent is a mixture of 5 to 99% by weight of said dust and 1 to 95% by weight of soda ash.

3. A method as claimed in Claim 1, wherein the desulphurizing agent is a mixture of 45 to 95% by weight of said dust 2 to 25% by weight of a cement, and 3 to 30% by weight of water.

4. A method as claimed in Claim 1, wherein said desulphurizing agent is a mixture of 5 to 94% by weight of said dust, 1 to 40% by weight of soda ash, 2 to 25% by weight of a cement, and 3 to 30% by weight of water.

5. A method as claimed in any preceding Claim wherein said dust collected from the smelting step of manganese contains, by weight, 2 to 20% of Na_2O, 5 to 50% of K_2O, 20 to 40% of MnO, 5 to 30% of CaO, 3 to 20% of SiO_2, 3 to 10% of C, and not more than 5% of each of Al_2O_3, Fe_2O_3 and CaF_2.

6. A method as claimed in any preceding Claim, wherein said dust collected from the smelting step of chromium contains, by weight, 3 to 25% of Na_2O, 4 to 40% of K_2O, 4 to 15% of CaO, 5 to 30% of SiO_2, not more than 5% of Cr_2O_3 and not more than 5% of each of C, Al_2O_3, Fe_2O_3 and CaF_2.

7. A method as claimed in any preceding claim, wherein said dust has a

$$\frac{Na_2O\ (\%)+K_2O\ (\%)}{SiO_2\ (\%)+Al_2O_3\ (\%)}$$

value of at least 2.0.

8. A method as claimed in Claim 2, wherein said dust has a

$$\frac{Na_2O\ (\%)+K_2O\ (\%)}{SiO_2\ (\%)+Al_2O_3\ (\%)}$$

value of below 2.0.

9. A method of desulphurizing molten iron as claimed in Claim 1, substantially as hereinbefore described in Example 1; Example 2, Example 3 or Example 4.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

* C L M S *

5% Na_2O, 23% K_2O, 15% SiO_2, 2% Al_2O_3, 3% Fe_2O_3, 18% MnO, 5% CaO, 6% C and the remainder being CO_2 and F) and 60% by weight of soda ash was blown into molten iron (with a sulphur content of 0.046%) in a ladle together with nitrogen gas using the same apparatus as used in Example 1. The amount of the powdery mixture was 4 kg per ton of the molten iron. The sulphur content of the molten iron after desulphurization was 0.013%, and thus, the percentage desulphurization was 71.7.

EXAMPLE 3

A mixture of 87% of the dust mixture used in Example 1, 6% by weight of Portland cement and 7% by weight of water was compressed with a granlator to form granules each with a size of 25 mm×25 mm×15 mm. This desulphurizing agent was placed in a ladle in an amount of 5 kg per ton of molten iron, and the molten iron was poured into the ladle. As a result, the sulphur content of the molten iron decreased from the original 0.055% to 0.028% after desulphurization, and thus, percentage desulphurization was 49.1.

EXAMPLE 4

A mixture of 25% by weight of the ferrochromium smelt dust used in Example 2, 55% by weight of soda ash, 10% by weight of Portland cement and 10% by weight of water was granulated to the same size as in Example 3 using the same procedure as in Example 3. The resulting desulphurizing agent was placed in a ladle in an amount of 5 kg per ton of molten iron, and the molten iron was poured into the ladle to desulphurize the iron. The sulphur content of the molten iron decreased from the original 0.051% to 0.025% after desulphurization. The percentage desulphurization was 51.8.

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As a further comparison, 5 kg of molded soda ash was placed in a ladle per ton of molten iron, and then, the molten iron was poured into the ladle to desulphurize the iron. The sulphur content of the molten iron decreased from the original 0.048% to 0.029% after desulphurization, and thus, the percentage desulphurization was 38.5.

WHAT WE CLAIM IS:—

1. A method for desulphurizing molten iron, which comprises adding, as a desulphurizing agent, to the molten iron, a dust collected from the smelting step of manganese and/or a dust collected from the smelting step of chromium.

2. A method as claimed in Claim 1, wherein the desulphurizing agent is a mixture of 5 to 99% by weight of said dust and 1 to 95% by weight of soda ash.

3. A method as claimed in Claim 1, wherein the desulphurizing agent is a mixture of 45 to 95% by weight of said dust 2 to 25% by weight of a cement, and 3 to 30% by weight of water.

4. A method as claimed in Claim 1, wherein said desulphurizing agent is a mixture of 5 to 94% by weight of said dust, 1 to 40% by weight of soda ash, 2 to 25% by weight of a cement, and 3 to 30% by weight of water.

5. A method as claimed in any preceding Claim wherein said dust collected from the smelting step of manganese contains, by weight, 2 to 20% of Na_2O, 5 to 50% of K_2O, 20 to 40% of MnO, 5 to 30% of CaO, 3 to 20% of SiO_2, 3 to 10% of C, and not more than 5% of each of Al_2O_3, Fe_2O_3 and CaF_2.

6. A method as claimed in any preceding Claim, wherein said dust collected from the smelting step of chromium contains, by weight, 3 to 25% of Na_2O, 4 to 40% of K_2O, 4 to 15% of CaO, 5 to 30% of SiO_2, not more than 5% of Cr_2O_3 and not more than 5% of each of C, Al_2O_3, Fe_2O_3 and CaF_2.

7. A method as claimed in any preceding claim, wherein said dust has a

$$\frac{Na_2O\ (\%)+K_2O\ (\%)}{SiO_2\ (\%)+Al_2O_3\ (\%)}$$

value of at least 2.0.

8. A method as claimed in Claim 2, wherein said dust has a

$$\frac{Na_2O\ (\%)+K_2O\ (\%)}{SiO_2\ (\%)+Al_2O_3\ (\%)}$$

value of below 2.0.

9. A method of desulphurizing molten iron as claimed in Claim 1, substantially as hereinbefore described in Example 1; Example 2, Example 3 or Example 4.

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