# United States Patent

[11] 3,619,171



[72] Inventors **Hermanus Bakkerus Voorburg; Bernardus J. J. van der Holst, Delft, both of Netherlands**



[21] Appl. No. **780,555**

[22] Filed **Dec. 2, 1968**

[45] Patented **Nov. 9, 1971**



[73] Assignee **Nederlandse Organistie Voor Toegepast-Natuurweten-Schappelijk Onderzoek Ten Behoeve Van Nijverheid, Handel En Verkeer The Hague, Netherlands**



[32] Priorities **Dec. 5, 1967**

[33] **Netherlands**

[31] **6716522;**

**Nov. 6, 1968, Germany, No. P 18 07 322.0**


---

[54] **METHOD AND A MIXTURE FOR THE PREPARATION OF AN IRON MELT WITH A LOW SULPHUR CONTENT**

**18 Claims, No Drawings**


[52] **U.S. Cl.** ..... **75/55,** 75/58, 75/130

[51] **Int. Cl.** ..... **C21c 7/02**

[50] **Field of Search** ..... 75/53, 58, 130, 55



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,755,180 | 7/1956 | DeLaval | 75/58 X |
| 2,834,668 | 5/1958 | Barnes | 75/58 |
| 3,051,564 | 8/1962 | Drenning | 75/58 X |
| 3,158,465 | 11/1964 | Brown | 75/58 X |
| 3,258,328 | 6/1966 | Goss | 75/53 X |

FOREIGN PATENTS

| | | | |
|---|---|---|---|
| 812,410 | 4/1959 | Great Britain | 75/53 |



*Primary Examiner*—L. Dewayne Rutledge
*Assistant Examiner*—Joseph E. Legru
*Attorney*—Spencer & Kaye


---


**ABSTRACT:** (1) A method for the preparation of an iron melt with a low sulfur content wherein a mixture is added to the melt, the mixture comprising $Na_2CO_3$, calcium compounds and a quantity by weight of NaCl which is at least one-third and at most three times the quantity (by weight) of $Na_2CO_3$ while, of the total mixture, at least one-third consists of calcium compounds and (2) said mixture for adding to an iron melt.

# METHOD AND A MIXTURE FOR THE PREPARATION OF AN IRON MELT WITH A LOW SULPHUR CONTENT

The invention relates to a method and a mixture for the preparation of an iron melt with a low sulfur content. Many iron ores, and fuels used for smelting these in a furnace, have a high sulfur content, and attempts have been made to reduce the sulfur content by adding substances while charging the furnace. Some of such added substances produce side effects on other constituents of the melt, however, and many difficulties may also arise with the furnace lining and the slag.

Preference is therefore given to desulfurizing outside the furnace, either by adding special agents to the stream of melt, or by collecting the melt in special devices and desulfurizing it in these, such as vibrating ladles or ladles with injection lances, stirring devices or dippers. These special devices are expensive and unsuitable for continuous operation, and the treatment must be continued for a fairly long time to obtain the desired desulfurization.

Examples of desulfurizing agents for pig iron are CaO and $CaC_2$. This desulfurization is not very effective or takes a very long time because the melt temperature is fairly low.

$Na_2CO_3$ is also used as a desulfurizing agent, but it is very aggressive and attacks all linings.

It is known to use a mixture of CaO and $Na_2CO_3$ which is blown with a lance into a ladle, in the form of fine granules suspended in nitrogen or air, in amounts of from 10 to 25 kg. per ton of melt. In larger amounts, it makes the slag unworkable, and a large percentage of $Na_2CO_3$ in the mixture results in a very severe attack on the lining.

According to another method, in addition to about 17 kg. of calcium compounds, such as CaO and $CaF_2$, 2 to 7 kg. of $Na_2CO_3$ per ton of melt is added to a bath. This bath is then agitated for a number of minutes with the aid of a low-frequency electric current.



For this purpose a mixture is introduced into the melt, the mixture consisting of $Na_2CO_3$, and at least one calcium compound, such as $CaC_2$ and possibly CaO, to which, according to the invention, a quantity (by weight) of NaCl (at least one-third and at most three times the quantity of $Na_2CO_3$) is added. Preferably equal amounts of NaCl and $Na_2CO_3$ are added, but the amount of neither substance is more than that of the calcium compound(s).

In order to minimize the generation of gas, less than one fourth NaCl and less than one fourth $Na_2CO_3$ should be employed in the mixture; the resulting slag can then be properly removed and aggressiveness obviated.

Excellent results are obtained if the sum of the amounts of NaCl and $Na_2CO_3$ does not exceed one third of the quantity of the calcium compound(s). Unlike $CaC_2$, such a mixture provides better desulfurization at a lower melt temperature than at a higher temperature; it can therefore also be used in desulfurizing pig iron.

These mixtures enable continuous addition without expensive extra devices, the quantity of the mixture being relatively small and not giving rise to attack or dangerous gas generation, while the slag moreover, is easy to remove.

Preferably, not more than 20 kg. mixture is added per ton of melt because this amount can already lead to desulfurization of over 40 percent, with both an initial sulfur content of 0.2 and of 0.04 percent.

The fast-acting mixture can also be added to the melt with the aid of conventional devices, such as in a ladle with a lance, an agitator, or a dipper or in a vibrating ladle. Desulfurization takes place more quickly than usual, and higher desulfurization percentages are possible.

Some examples of mixtures added to a stream of melt, and the results obtained with them are mentioned in the following tables.

TABLE A

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization, percent | Notes |
|---|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | | |
| 20 | 20 | | | 0.094 | 0.079 | 16 | 1a |
| 20 | 15 | 5 | | 0.096 | 0.057 | 40.7 | 2a |
| 20 | 10 | 7.5 | 2.5 | 0.084 | 0.045 | 42 | 2c |
| 20 | 10 | 5 | 5 | 0.100 | 0.045 | 55 | 3c |
| 20 | 15 | 3.5 | 1.5 | 0.107 | 0.051 | 52.3 | 2b |
| 20 | 15 | 2.5 | 2.5 | 0.100 | 0.042 | 58 | 2b |
| 20 | 10 | 2.5 | 7.5 | 0.104 | 0.043 | 58.6 | 3d |
| 20 | 15 | 1.5 | 3.5 | 0.100 | 0.046 | 54 | 3b |
| 20 | 10 | | 10 | 0.096 | 0.056 | 42 | 4d |

NOTE.—1=Very little gas generation; 2=Very little gas; 3=Much gas; 4=Very much gas; a=Very easy slag removal; b=Easy slag removal; c=Difficult slag removal; d=Very difficult slag removal.

For Thomas steel a desulfurizing method is known according to which per ton of melt about 5 kg. $Na_2CO_3$ and 2 kg. $Na_2CO_3 \cdot H_2O$ are added in addition to $CaC_2$. This reaction produces very large amounts of gas and is dangerous.

The desulfurizing agent used for cast iron, which has a higher temperature than pig iron, is mainly $CaC_2$. It is expensive and does not work quickly. Its use, moreover, may adversely increase the carbon content of the melt. According to one method blocks of $CaC_2$ are melted on the melt bath in a ladle by means of an electric arc, and NaCl is used as a flux in the slag. Finally, a mixture of $CaC_2$ and NaCl may be introduced in the form of a briquette into the ladle by means of a dipper. The quantities used generally do not exceed 25 kg. per ton of melt, whereas the reaction time is fairly long.

The object of the present invention is a method whereby an inexpensive desulfurizing mixture with a very short reaction time so that it can be introduced into the melt without any adverse effects, for instance by adding it on or in the stream of melt.

In these cases the mixture was added to the stream of melt, and the final sulfur percentage was determined immediately after deslagging.

Table A shows that $CaC_2$ alone has hardly any effect in this short time. Addition of $Na_2CO_3$ considerably increases the desulfurization percentage but the slag becomes more difficult to work, while the aggressiveness of the $Na_2CO_3$ continues to exist and the lining is attached.

Addition of NaCl to the mixture according to the invention results in an improvement of desulfurization while the slag can be worked better and gas generation remains within reasonable limits. Replacement of all the $Na_2CO_3$ by NaCl makes the slag unworkable, and also entails considerable gas generation, while the desulfurization percentage is considerably reduced.

On the whole, the best result is obtained with approximately equal amounts of $Na_2CO_3$ and NaCl.

Tests were next made to ascertain how effective a mixture in accordance with the invention is with low sulfur contents, and what quantity is advisable.

TABLE B

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization, percent | Notes |
|---|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | | |
| 17 | 15 | 1 | 1 | 0.047 | 0.025 | 47 | 1a |
| 20 | 15 | 2.5 | 2.5 | 10.4 | 0.022 | 45 | 2b |
| 30 | 22.5 | 3.75 | 3.75 | 0.04 | 0.022 | 45 | 3b |
| 40 | 30 | 5 | 5 | 0.04 | 0.021 | 47 | 3c |

TABLE C

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization, percent | Notes |
|---|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | | |
| 20 | 15 | 2.5 | 2.5 | 0.2 | 0.085 | 57.5 | 2b |
| 30 | 22.5 | 3.75 | 3.75 | 0.2 | 0.07 | 65 | 3b |
| 40 | 30 | 5 | 5 | 0.2 | 0.065 | 67.5 | 3c |

TABLE D

| Total kg./ton melt | Kg./ton melt | | | Initial S, percent | S after— | | | Desulphurization percentage after— | |
|---|---|---|---|---|---|---|---|---|---|
| | $CaC^2$ | $Na^2CO^3$ | NaCl | | 1 min. | 3 min. | 8 min. | 1 min. | 8 min. |
| 20 | 20 | | | 0.036 | 0.031 | 0.027 | 0.022 | 14 | 39 |
| 20 | 15 | 2.5 | 2.5 | 0.04 | 0.024 | 0.019 | 0.016 | 40 | 60 |
| 20 | 10 | 5 | 5 | 0.04 | 0.023 | 0.020 | 0.017 | 42.2 | 57.4 |
| 20 | 6.7 | 6.7 | 6.7 | 0.044 | 0.024 | 0.023 | 0.02 | 45.4 | 52.3 |

TABLE E

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization, percent | Notes |
|---|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | | |
| 20 | 20 | | | 0.094 | 0.079 | 16 | 1a |
| 16.5 | 15 | 0.75 | 0.75 | 0.012 | 0.059 | 42 | 1a |
| | | | | 0.111 | 0.05 | 55 | 1a |
| 17 | 15 | 1 | 1 | 0.099 | 0.043 | 56.5 | 1a |
| 18 | 15 | 1.5 | 1.5 | 0.107 | 0.045 | 58 | 2b |
| 20 | 15 | 2.5 | 2.5 | 0.1 | 0.042 | 58 | 2b |
| 25 | 15 | 5 | 5 | 0.1 | 0.04 | 60 | 3c |
| 30 | 22.5 | 3.75 | 3.75 | 0.1 | 0.042 | 58 | 3b |
| 40 | 30 | 5 | 5 | 0.1 | 0.04 | 60 | 3c |

TABLE F

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization, percent | Notes |
|---|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | | |
| 18 | 18 | | | 0.082 | 0.059 | 28 | 1,570° C. |
| 18 | 18 | | | 0.091 | 0.078 | 14 | 1,450° C. |
| 20 | 15 | 2.5 | 2.5 | 0.116 | 0.061 | 48 | 1,600° C. |
| 20 | 15 | 2.5 | 2.5 | 0.104 | 0.052 | 50 | 1,540° C. |
| 20 | 15 | 2.5 | 2.5 | 0.097 | 0.041 | 56 | 1,450° C. |

TABLE G

| Total kg./ton melt | Kg./ton melt | | | S, percent | | Desulphurization,[1] percent |
|---|---|---|---|---|---|---|
| | $CaC_2$ | $Na_2CO_3$ | NaCl | Initial | Final | |
| 3.6 | 2.7 | 0.45 | 0.45 | 0.066 | 0.04 | 40 |
| 3.8 | 2.8 | 0.5 | 0.5 | 0.069 | 0.043 | 38 |
| 5.7 | 4.2 | 0.7 | 0.7 | 0.046 | 0.025 | 46 |
| 7.8 | 5.8 | 1 | 1 | 0.041 | 0.023 | 44 |

[1] Determined after approximately 25 minutes.

TABLE H

| Total kg./ton melt | Kg./ton melt | | | | Initial S, percent | S, percent | | Desulphurization percentage | |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | $CaC_2$ | $Na_2CO_3$ | NaCl | | Immediately | After 1 min. agitation | Immediately | After 1 min. |
| 15 | 15 | | | | 0.094 | | 0.085 | | 10 |
| 20 | 10 | | | 10 | 0.094 | | 0.072 | | 23 |
| 20 | 15 | | 2.5 | 2.5 | 0.102 | 0.072 | 0.050 | 30 | 51 |
| 20 | 10 | 5 | 2.5 | 2.5 | 0.110 | 0.061 | 0.037 | 45 | 66 |
| 20 | 5 | 10 | 2.5 | 2.5 | 0.086 | 0.042 | 0.023 | 51 | 73 |
| 17 | 5 | 10 | 1 | 1 | 0.107 | 0.059 | 0.038 | 45 | 65 |
| 20 | | 15 | 2.5 | 2.5 | 0.102 | 0.058 | 0.045 | 43 | 56 |

Table B shows that a quantity of more than 30 kg. per ton of melt, containing one-eighth $Na_2CO_3$ and one-eighth NaCl, provides little improvement in desulfurization, but gives rise to increasing drawbacks as regards the generation of gas and with regard to the slag.

In order to ascertain whether the mixture is also effective for high sulfur contents, and what quantity is then advisable, the following tests were carried out.

Again, a quantity of more than 30 kg. per ton of melt proves to offer no advantage.

Desulfurization with the mixtures is effected in a short time Tests were carried out in which the sulfur content was determined after 1 minute, after 3 minutes and after 8 minutes. The mixture was not introduced in the stream of melt but was added to a small amount of melton the bottom of the ladle, after which the ladle was immediately filled with melt. No agitation in the ladle was applied.

The quantities of mixture in fact caused no serious drawbacks as regards gas and slag.

Equal amounts of the three substances do give a saving in $CaC_2$, but desulfurization declines compared with a mixture containing less $Na_2CO_3$ and NaCl The main desulfurization effect is already reached after 1 minute however, and is equal to or higher than desulfurization with $CaC_2$ after 8 minutes

For cast iron melts containing about 0.1 percent sulfur, the minimum amounts of NaCl and $Na_2CO_3$ and the maximum quantity of mixture of the best composition compared with $CaC_2$ only were also determined

Preferably, not more than 10 kg. $Na_2CO_3$+NaCl should be added. More than 25 kg. mixture per ton of melt does not im-

prove the result. Less than 1.5 kg. $Na_2CO_3$+NaCl seems to have little result as regards cast iron, the more so as the saving in $CaC_2$ is then unimportant.

The above-mentioned tests were all conducted at a melt temperature of about 1450° C. It is known that when $CaC_2$ is used at a higher melt temperature, the desulfurization percentage increases. With a mixture of three-fourth $CaC_2$, one-eighth $Na_2CO_3$ and one-eighth NaCl the desulfurization percentage surprisingly rises as the temperature is reduced.

As with a cast iron melt, the preferred mixture results in greater desulfurization at a lower temperature than at a higher temperature, a number of tests were carried out with pig iron, which has a much lower temperature. The mixture was introduced into a ladle holding 25 tons, the bottom of which was covered with pig iron, and the ladle was filled with pig iron in two to three minutes. The quantity of the mixture was very small but gas generation was great. The slag was crumbly to firm, but easy to remove. With continuous addition to the stream gas generation is much slighter.

As $CaC_2$ may give rise to the increase of the carbon content in the melt under certain conditions, it was ascertained whether there would also be any advantage in using a mixture according to the invention also with CaO or mixtures of $CaC_2$ and CaO.

As CaO acts more slowly than $CaC_2$, the mixture was introduced in subsequent tests along with the stream of cast iron into the ladle and the sulfur content was determined once immediately and once more after the contents of the ladle had been agitated for 1 minute.

Addition of equal amounts of $Na_2CO_3$ and NaCl thus gives an immediate and very great improvement in all cases, while a further improvement is effected later because the CaO continues to work for some time.

In this case, of course, agitation is an additional complication.

We claim:

1. A mixture for desulfurizing a sulfur-containing iron melt outside a furnace, consisting essentially of (a) $Na_2CO_3$, (b) NaCl and (c) a material, each component of which is a desulfurizing calcium compound; the weight of NaCl being at least one-third and at most three times the weight of $Na_2CO_3$, and the material comprising at least one-third of the mixture.

2. A mixture according to claim 1 wherein the material consists essentially of calcium carbide.

3. A mixture according to claim 1 wherein the material comprises a calcium compound selected from the group consisting of $CaC_2$ and CaO.



4. A mixture according to claim 3 containing equal amounts of NaCl and $Na_2CO_3$.

5. A mixture according to claim 3, less than one-fourth of which consists of NaCl.

6. A mixture according to claim 3, less than one-fourth of which consists of $Na_2CO_3$.

7. A mixture according to claim 3 wherein the sum of the weights of NaCl and $Na_2CO_3$ is at most one-third the weight of the material.

8. In a method for reducing the sulfur content of a sulfur-containing iron melt by adding a composition to the melt, the improvement wherein the composition is the mixture according to claim 1.

9. In a method for reducing the sulfur content of a sulfur-containing iron melt by adding a composition to the melt, the improvement wherein the composition is the mixture according to claim 2.

10. In a method for reducing the sulfur content of a sulfur-containing iron melt by adding a composition to the melt, the improvement wherein the composition is the mixture according to claim 3.

11. A method according to claim 10 wherein the mixture contains equal amounts of NaCl and $Na_2CO_3$.

12. A method according to claim 22 wherein at least one of NaCl and $Na_2CO_3$ comprises less than one-fourth of the mixture.

13. A method according to claim 10 wherein the sum of the amounts of NaCl and $Na_2CO_3$ in the mixture is not more than one-third of the quantity of the calcium compound content thereof.

14. A method according to claim 10 wherein the mixture is continuously added along with the stream of melt.

15. A mixture according to claim 1 wherein the material consists essentially of at least one member selected from the group consisting of $CaC_2$ and CaO.

16. In a method for reducing the sulfur content of a sulfur-containing iron melt by adding a composition to the melt, the improvement wherein the composition is the mixture according to claim 15.

17. A method according to claim 16 wherein the mixture contains equal weights of the sodium chloride and of the sodium carbonate.

18. A method according to claim 16 which comprises introducing the mixture into a stream of said melt before the melt enters a ladle.

* * * * *

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,619,171 Dated November 9th, 1971

Inventor(s) Hermanus Bakkerus and Bernardus J.J. van der Holst

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading of the patent, line 8, change "Organistie" to --Organisatie--; line 16, change "P 18 07 322.0" to --P 18 07 332.0--. Column 1, line 52, change "$Na_2CO_3 \cdot H_2O$" to --$Na_2CO_3 \cdot 10H_2O$--. Column 2, line 57, change "attached" to --attacked--; in Table B, the second amount in the column under "Initial" should be changed from "10.4" to --0.04--. Table D, at the top of the second column, change "$CaC_2$" to --$CaC_2$--; at the top of the third column, change "$Na_2CO_3$" to --$Na_2CO_3$--. Column 3, line 71, after "time" insert a period --.--. Column 4, line 67, after "NaCl" insert a period --.--; line 69, after "minutes" insert a period --.--; line 70, change "0 1" to --0.1--; line 73, after "determined" insert a period --.-- . Column 6, line 24, change "22" to --10--; line 32, change "10" to --8--.

Signed and sealed this 2nd day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334