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[54] SINTERED DESULFURIZER FOR OFF-FURNACE USE

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[51] **Int. Cl.** **C21b 1/10,** C21b 3/02
[58] **Field of Search**....................75/58, 59, 76, 94, 55

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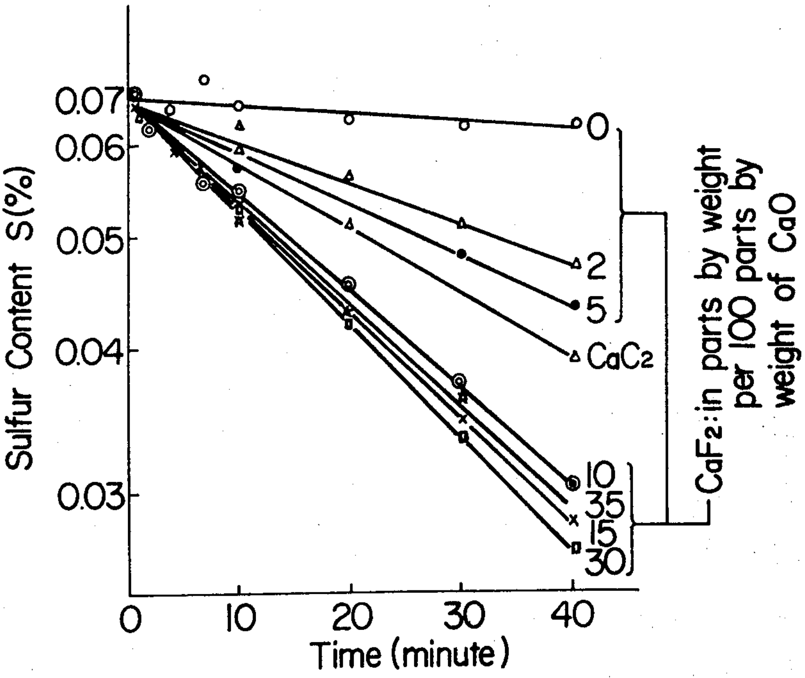
[57] **ABSTRACT**

A desulfurization composition for off-furnace use consisting of crushed particles of sintered material comprising 100 parts by weight of calcium oxide and 3 to 50 parts by weight, in total, of at least one compound selected from the group consisting of up to 30 parts by weight of calcium fluoride, sodium fluoride, magnesium fluoride, barium fluoride, and sodium silicofluoride, and up to 40 parts by weight, in terms of sodium carbonate, of sodium carbonate, sodium hydroxide, and sodium oxide.

6 Claims, 1 Drawing Figure


Sulfur Content S(%)
0.07
0.06
0.05
0.04
0.03
0
10
20
30
40
Time (minute)
0
2
5
CaC_2
10
35
15
30
CaF_2: in parts by weight per 100 parts by weight of CaO

SINTERED DESULFURIZER FOR OFF-FURNACE USE

This invention relates to a sintered desulfurizer for off-furnace use, and more particularly to a desulfurizer consisting of crushed particles of sintered material which is suitable for off-furnace use.

Recently, the use of converters has noticeably expanded in steel-making industries, and in order to ensure high efficiency of converters, increasingly high quality of molten pig iron is required as the input material thereto. Since it is particularly troublesome to remove sulfur from molten pig iron within the converter, the demand for low sulfur-content pig iron is pressing for the incoming molten iron to the converters.

Generally speaking, molten pig iron as delivered from a blast-furnace has a comparatively high sulfur-content. To obtain low sulfur-content pig iron from such iron from the blast-furnace for supplying it to the steel-making converter, a suitable desulfurizer agent is added in the pig iron in the course of transferring the molten pig iron from the blast-furnace to the converter, which molten pig iron is usually carried by a ladle. After adding the desulfurizer, the ladle is preferably vibrated, shaken, or stirred for thoroughly mixing the desulfurizer with the molten pig iron.

Conventional desulfurizers for such purposes consist of calcium carbide (CaC_2), because calcium carbide has a high desulfurizing ability. For instance, by using 4 to 6 Kg of calcium carbide per one ton of molten pig iron, 0.05 percent of sulfur-content can be reduced to 0.01 percent, or 80 percent of desulfurization can be achieved by such addition of calcium carbide.

Calcium carbide has another advantage in that it is available in solid phase and never melts by itself in the ladle while being stirred. Accordingly, such solid phase desulfurizer does not cause any chemical reaction either with the refractory bricks on the ladle wall, or with the blast-furnace slag. With the desulfurizer consisting of calcium carbide, sulfur once isolated from the molten pig iron seldom redissolves in the molten iron. Furthermore, the slag formed by the desulfurization by calcium carbide is easy to remove from the ladle.

On the other hand, calcium carbide has a serious drawback in that it is rather expensive, and that it quickly reacts with water and generates acetylene gas which is very easily inflammable. Accordingly, extra care is necessary in handling calcium carbide.

With the increase in the production of steel, the amount pig iron to be desulfurized by calcium carbide has greatly increased. Accordingly, the expenditure for the calcium carbide desulfurizer amounts to a considerable value. Accordingly, extra care is required to ensure the safety of personnel handling the desulfurizer.

In order to mitigate such shortcomings of calcium carbide, the applicants have carried out a series of studies and experiments, and has succeeded in finding out an improved desulfurizer for off-furnace use which is made by crushing sintered material of calcium oxide base composition.

Quick lime or calcium oxide itself has been known as a desulfurizer, which is mixed with a suitable flux material. When a known desulfurizer consisting of calcium oxide and a flux is added in a molten pig iron, the sulfur-capturing ability of the solid desulfurizer is extremely small, and reasonable sulfur-capturing ability can be obtained only after the calcium oxide is melted. In order to facilitate the melting of such desulfurizer including calcium oxide, a large amount solvent (e.g., silica SiO_2, alumina Al_2O_3, calcium fluoride CaF_2) has to be added. The use of large amount of such solvents tends to cool the molten pig iron.

In contrast to the aforesaid solid desulfurizer, the molten desulfurizer consisting of calcium oxide corrodes refractory bricks of the ladle. Accordingly, such combination of quick lime and flux material is not suitable for off-furnace use, because it causes temperature reduction of the molten pig iron.

It has been also known to add about 10 percent of soda ash (Na_2CO_3) and/or caustic soda (NaOH) in quick lime. The desulfurizing ability of such mixture, however, is inferior to that of calcium carbide. In fact, the desulfurizing ability of such mixture in the case of pig iron containing 0.05 percent of sulfur is 50 percent when the mixture is added at a rate of 10 Kg of the mixture per ton of the pig iron, 60 to 65 percent when 20 Kg/ton, and 70 to 75 percent when 30 Kg/ton. Thus, to achieve the same desulfurizing effects, about six times in weight of such mixture has to be added in comparison with calcium carbide. Although quick lime itself is fairly inexpensive, if a large amount of it is used, e.g., 20 Kg/ton, the total cost of desulfurizer consisting of such mixture becomes almost comparable with that of calcium carbide. Furthermore, the use of a large amount of desulfurizer results in an increase of slag, which means more man-hours for slag removal after the desulfurization. Thus, the overall efficiency of the desulfurizing process with such mixture is fairly poor.

Japanese Patent Publication No. 29,867/1968 discloses a desulfurizer consisting of a composite slag made by melting a mixture of quick lime, calcium fluoride (CaF_2), soda ash (Na_2CO_3), caustic soda (NaOH), and/or calcium carbide (CaC_2). The desulfurizer of this Japanese Patent is suitable for final desulfurization of molten steel, which is refined in a special furnace, but it is not suitable for off-furnace pretreatment of starting molten pig iron for steel-making, because it requires special equipment while using a considerably large amount of heat requiring a large expense.

Therefore, an object of the present invention is to obviate the aforesaid difficulties of conventional quick lime base desulfurizer, which consists of a mere mixture of quick lime and flux material or a molten slag of quick lime with suitable additives, by providing an improved quick lime base desulfurizer. The desulfurizer of the present invention retains all the advantages of solid desulfurizer, inclusive of a desulfurizing ability which is comparable with that of calcium carbide. The desulfurizer of the invention is featured in its low cost, so that it is particularly suitable for the production of a large quantity of low-sulfur steel.

The desulfurizer for off-furnace use, according to the present invention, consists of crushed particles of sintered material comprising 100 parts by weight of calcium oxide and 3 to 50 parts by weight, in total, of at least one compound selected from the group consisting of up to 30 parts by weight of calcium fluoride, sodium fluoride, magnesium fluoride, barium fluoride, and sodium silicofluoride, and up to 40 parts by weight, in terms of sodium carbonate, of sodium carbonate, sodium hydroxide, and sodium oxide.

What is meant by "in terms of sodium carbonate" refers to the number of sodium atoms in each of such compounds. For instance, 40 parts by weight of sodium carbonate is equivalent to 30 parts by weight of sodium hydroxide, as given by the following formula.

$$40 \times \frac{\text{1 molecular weight of NaOH}}{(\text{1 molecular weight of } Na_2CO_3)/2} \doteqdot 40 \times \frac{40}{106/2} \doteqdot 30$$

For a better understanding of the present invention, reference is made to the accompanying drawing, in which a single drawing is a graph illustrating the results of experiments on some sintered desulfurizers of the present invention.

The invention will now be described in detail by referring to examples.

Example 1:

Specimens of desulfurizer of the invention were prepared by adding 3 to 30 parts by weight of calcium fluoride having a particle size smaller than 0.3 mm, in 100 parts by weight of a main ingredient consisting of calcium oxide of a particle size smaller than 0.3 mm, sintering the mixture thus prepared at 1,200°C to 1,600°C, and crushing the sintered products to a particle size of 3 mm or less.

Tests were made on the desulfurizing speed by using the aforesaid specimens which consisted of different amounts of calcium fluoride added in calcium oxide and sintered at 1,300°C. Each of the specimens for the tests was in the form of a sintered cylinder of 25 mm diameter and 30 mm height. The specimen cylinders of the desulfurizer were immersed in a molten pig iron at 1,350°C, which contained about 0.07 percent of sulfur. Each specimen cylinder was rotated in the molten pig iron at 200 RPM. FIG. **1** shows the variation of sulfur content in the molten pig iron as time elapses.

For comparison's sake, test results with a known calcium carbide desulfurizer are also shown in FIG. **1**, which calcium carbide desurfurizer was also sintered and shaped in the same cylindrical form as that of the desulfurizer specimens of the present invention.

It is apparent from FIG. **1** that the addition of calcium oxide alone does not cause any material reduction in sulfur-content of the pig iron, while the desulfurizing effects increase with the addition of calcium fluoride in the calcium oxide and the desulfurizing ability of the specimens of the invention containing more than 10 parts by weight of calcium fluoride is superior to that of conventional calcium carbide. The desulfurizing speed of the desulfurizer of the invention increases with the content of calcium fluoride of up to about 15 parts by weight, but when the additional quantity of calcium fluoride further increases, e.g., to 35 parts by weight, the desulfurizing speed decreases, as shown in the figure. Thus, the desulfurizing speed of the desulfurizer of the invention saturates at a certain addition quantity of the aforesaid compound in calcium oxide, for instance at about 30 parts by weight of calcium fluoride per 100 parts of calcium oxide.

It was confirmed by tests that desulfurizers of the invention containing one or more of sodium flurode, magnesium fluoride, and barium fluoride also had a similar desulfurizing ability to that of FIG. **1**. The suitable addition quantity of such compounds to calcium oxide was found to be 3 to 30 parts per 100 parts by weight of calcium oxide.

It was also found that the calcium oxide to be used in actual desulfurization at plant can be replaced with calcium carbonate ($CaCO_3$) or calcium hydroxide ($Ca(OH)_2$), which are less expensive than calcium oxide. The sintering temperatures of 1,200°C to 1,600°C also apply to calcium carbonate and calcium hydroxide base desulfurizers, which are crushed into a particle size of 4 mm of less. According to the present invention, it is also possible to add a small amount, e.g., a few parts by weight per 100 parts of calcium oxide, of a suitable binder, such as sodium dihydrogen phosphate, calcium chloride, starch, and clay. With the addition of clay, the pellets of the desulfurizer is improved, so that during the sintering process, the shape of the desulfurizer pellets can be kept intact, and its workability is improved.

In preparing the desulfurizer of the invention, it is preferable to keep the particle size of the main ingredient calcium oxide and additive compound, e.g., calcium fluoride, to less than 0.3 mm, so as to shorten the sintering time and to achieve a higher desulfurizing ability.

As pointed out in the foregoing, calcium oxide alone is not effective in desulfurization, and what is effective in desulfurization seem to be dispersed mixture of calcium compound and the added compound, e.g., calcium fluoride, which mixture has a structure consisting of molecules of the ingredient compounds well dispersed therein by the sintering process. Such fact was confirmed by microscopic tests of the desulfurizer after the desulfurizing process.

If the particle size of the ingredients in the desulfurizer is too large, the sintering time increases. More particularly, if the particle size of the ingredients exceeds 0.3 mm, it is difficult to produce desulfurizer having a sufficient desulfurizing ability by sintering at 1,200°C, for several hours.

Table 1 shows the desulfurizing ability of simple mixtures of calcium oxide and calcium fluoride. Similarly, Table 2 shows the desulfurizing ability of the sintered desulfurizers of the invention. Table **2** also indicates the desulfurizers of non-sintered quick lime base desulfurizers containing calcium fluoride and sodium fluoride. The desulfurizing ability, or the rate of desulfurization, of Tables 1 and 2 were determined by adding the desulfurizers in about 60 tons of molten pig iron carried by a ladle, and stirring the contents of the ladle by a gate-type impeller. The desulfurizers of Table 2 were prepared by mixing calcium oxide having a particle size of about 0.2 mm with calcium fluoride having a similar particle size, sintering the mixture at 1,300°C for 30 minutes, and then crushing the sintered products into a particle size of about 2 mm.

Table 1

Simple mixtures consisting of 80 parts by weight of CaO and 20 parts by weight of CaF_2

Quantity of desulfurizer in pig iron (Kg/ton)	Temperature of molten pig iron (°C)	Treating time (minute)	Sulfur-content, before treating (%)	Sulfur-content, after treating (%)	Rate of desulfurization (%)
8.3	1350	10	0.043	0.023	46.5
8.4	1320	10	0.045	0.028	37.8

15.2	1300	10	0.049	0.026	46.9
16.4	1300	10	0.044	0.034	22.7
22.9	1370	10	0.051	0.009	82.4
24.3	1360	10	0.055	0.011	80.0

TABLE 2

[Sintered CaO-CaF$_2$ desulfurizers of the invention, as compared with known non-sintered desulfurizers]

CaF$_2$ (parts in 100 parts of CaO)	Quantity of desulfurizer in pig iron, kg./ton.	Temperature of molten pig iron (° C.)	Treating time, minute	Sulfur content before treating, percent	Sulfur content after treating, percent	Rate of desulfurization, percent
0	8.0	1,340	10	0.035	0.025	28.6
3	7.0	1,330	9	0.034	0.019	44.1
3	6.9	1,350	10	0.047	0.019	59.6
5	7.0	1,360	10	0.050	0.020	60.0
5	6.8	1,330	9	0.040	0.021	46.6
10	7.2	1,340	10	0.051	0.008	84.3
10	7.1	1,350	9	0.036	0.005	86.1
15	6.8	1,350	8	0.035	0.007	80.0
15	7.0	1,340	10	0.045	0.006	86.7
20	7.0	1,360	9	0.025	0.005	80.0
20	6.9	1,360	10	0.052	0.007	86.5
30	7.0	1,320	8	0.048	0.012	75.0
30	7.1	1,340	10	0.051	0.010	80.4
35	6.8	1,350	10	0.032	0.011	65.6
35	6.9	1,340	10	0.048	0.015	68.8
10*	15	1,340	10	0.051	0.032	37
15*	15	1,340	10	0.045	0.025	44.5
20*	15	1,340	10	0.052	0.07	48
NaF:						
5*	15	1,390	10	0.050	0.035	30
10*	15	1,340	8	0.051	0.030	41
30*	15	1,340	8	0.035	0.014	60

*Not sintered.

fluoride ingredient is contained in the form of solid desulfurizer and has a very limited contact area with such refractory bricks, so that there is no material corrosion.

It was confirmed that no substantial redissolution of sulfur was noticed by standing the molten pig iron for 1 hour after the desulfurization with the desulfurizers of the invention.

The slag removal after desulfurization by the desulfurizers of the present invention proved to be very easy, because the slag floats on the surface of the pig iron in solid state.

It is an important feature of the invention that the main ingredient is the inexpensive calcium oxide. Thus, the invention contributes greatly to the industry by providing a very inexpensive desulfurizer for off-furnace use.

Example 2:

Different specimens of the desulfurizer of the invention were prepared by thoroughly mixing ingredients as shown in Table 3, each having a particle size of smaller than 0.3 mm, shaping the mixture thus prepared into green pellets of 15 mm dia. by a pelletizer, drying the pellets at about 100°C, sintering the pellets at different temperatures, i.e., 900°C, 1,000°C, and 1,100°C, for 30 minutes, and crushing and sifting the pellets after cooling into particles of about 2 mm particle size.

TABLE 3.—UNIT: PARTS BY WEIGHT

Specimen number	CaCO$_3$	NaCO$_3$	NaOH	CaF$_2$	NaF	Na$_2$SiF$_6$	Remarks
2-1	98.9	1.1					
2-2	98.4	1.6					
2-3	94.2	5.8					
2-4	90.9	9.1					
2-5	83.3	16.7					
2-6	81.7	18.3					
2-7	80.0	20.0					
2-8	99.2		0.8				
2-9	97.3		2.7				
2-10	94.7		5.3				
2-11	90.0		10.0				
2-12	85.6		14.0				
2-13	81.7		18.3				
2-14	98.9	0.55		0.55			
2-15	98.3	0.6		1.1			
2-16	97.2	1.7		1.1			1.8% of NaH$_2$PO$_4$·2H$_2$O*.
2-17	92.2	1.8		6.0			1.3% of CaCl$_2$*.
2-18	85.6	1.9		12.5			
2-19	79.1	1.9		19.0			
2-20	94.2	2.9		2.9			
2-21	91.0	6.0		3.0			
2-22	87.8	6.1		6.1			
2-23	80.6	6.5		12.9			
2-24	79.9	6.7		13.4			
2-25	79.9	11.2		8.9			
2-26	86.4	12.4		1.2			
2-27	80.6	12.9		6.5			
2-28	96.2		1.1	2.7			
2-29	94.7		3.2	2.1			
2-30	90.9		4.0	5.1			
2-31	92.3		2.6		5.1		
2-32	92.3		5.1		2.6		
2-33	96.2	1.1			2.7		
2-34	93.7	5.2			1.1		
2-35	92.3		2.0			5.7	
2-36	95.7	1.6		1.6	1.1		
2-37	94.7	2.6	1.6	1.1			

*The addition quantity of the binder in each specimen is shown in percent by weight, based on the total weight of CaCO$_3$, Na$_2$CO$_3$, and CaF$_2$.

It is apparent from Tables 1 and 2 that the simple mixture of the ingredients do not have a high desulfurizing ability, but the sintered desulfurizer of the invention has a very desulfurizing ability.

It should be noted here that the desulfurizer of the invention retains the advantages of solid state desulfurizers. More particularly, flux which contains a fluoride usually tends to corrode the refractory brick of the ladle wall, but with the present invention, the

In those specimens which were sintered at 1,000°C or 1,100°C, calcium carbonate was almost completely decomposed into the form of calcium oxide, but in the specimens which were sintered at 900°C, most of the calcium carbonate was not decomposed. Tables 4-1 and 4-2 show the compositions of the specimens thus prepared, in which the content of calcium oxide is used as the base, regardless of whether it is in the form of calcium oxide or calcium carbonate. Tables 4-1 and 4-

2 also give the desulfurizing ability of the specimens, as determined by test operations. For comparison's sake, desulfurizers of known type were also tested, and the results are shown in the Tables.

The desulfurizing abilities, or the rates of desulfurization, in Tables 4-1 and 4-2 were determined by adding the desulfurizers into a ladle carrying 60 tons of molten pig iron, and stirring the contents of the ladle by a gate-type impeller with a rotary member having two vertical legs.

It is apparent from the Tables 4-1 and 4-2 that excellent desulfurizing effects can be achieved by the desulfurizers of the invention. If the sintering temperature is below 800°C, most of the calcium carbonate does not dissociate, and such residual calcium carbonate contains about 40 wt.% of carbon dioxide which does not participate in the desulfurization, so that it becomes necessary to increase the addition quantity of such desulfurizer in the molten pig iron. In Example 2, the desulfurizers which were sintered at 900°C provided similar high desulfurizing effects as those sintered at 1,100°C with an increased addition quantity.

If the sintering temperature is below 800°C, the desired desulfurizing effects cannot be achieved by using an economical amount of the desulfurizer.

It is an important feature of the present invention that the sintering temperature of the desulfurizer can be noticeably reduced by using calcium oxide material together with the aforesaid sodium compounds. In fact, the sintering temperature of the desulfurizer of Example 1 in the range of 1,200°C to 1,600°C can be reduced to the range of 900°C to 1,100°C of Example 2. As compared with the treating temperature of 2,000°C to 2,500°C necessary for the manufacture of conventional calcium carbide desulfurizers, the aforesaid sintering temperature range of 900°C to 1,100°C of this Example of the present invention is very low, so that the desulfurizers of the invention ensures considerable economy while retaining the high desulfurizing ability and other advantages of solid phase desulfurizers, as described hereinbefore referring to Example 1.

TABLE 4-1

Specimen number	Contents of ingredients, in parts by weight per 100 parts by weight of CaO			Sintering temperature (° C)	Amount of desulfurizer in molten pig iron (kg./ton)	Temperature of pig iron (° C.)	Treating time, minute	Sulfur content in pig iron (percent)		Rate of desulfurization (percent)	Remark
	Na_2CO_3	Na_2O	CaF_2					Before treating	After treating		
2-1	2			1,100	6.5	1,390	10.0	0.051	0.030	41	Reference.
2-2	2.9			1,100	6.5	1,430	10.0	0.038	0.015	61	
2-3	11.0			1,100	6.5	1,370	6.0	0.048	0.010	79	The invention.
				900	10.0	1,350	6.0	0.044	0.011	75	
2-4	18.0			1,100	6.5	1,410	10.0	0.033	0.007	75	
2-5	35.7			1,100	6.5	1,350	6.0	0.035	0.010	71	
				900	10.0	1,340	6.0	0.033	0.010	70	
2-6	40.0			1,100	6.5	1,420	10.0	0.032	0.008	75	
2-7	45.0			1,100	6.5	1,420	6.0	0.030	0.010	67	Reference.
2-8		1.2		1,000	6.5	1,350	6.0	0.054	0.031	42	
2-9		3.9		1,000	6.5	1,370	6.0	0.045	0.011	76	The invention.
2-10		7.8		1,000	6.5	1,350	6.0	0.050	0.010	80	
2-11		15.5		1,000	6.5	1,350	6.0	0.055	0.009	84	
2-12		23.2		1,000	6.5	1,369	6.0	0.043	0.014	68	
2-13		31.0		1,000	6.5	1,230	6.0	0.062	0.023	63	
2-14	1.0		1.0	1,100	6.5	1,260	6.0	0.045	0.030	33	Reference.
				900	10.0	1,350	6.0	0.047	0.033	20	
2-15	1.1		2.0	1,100	6.5	1,350	6.0	0.052	0.025	52	The invention.
				900	10.0	1,340	6.0	0.045	0.017	62	
2-16	3.2		2.1	1,100	6.5	1,250	6.0	0.038	0.010	74	
				900	10.5	1,260	6.0	0.040	0.012	70	
2-17	3.5		11.5	1,100	6.5	1,350	6.0	0.055	0.008	85	
				900	10.5	1,260	6.0	0.056	0.009	84	
2-18	3.9		26.0	1,100	6.5	1,360	6.0	0.052	0.006	89	
				900	10.5	1,250	6.0	0.046	0.006	89	
2-19	4.3		40.0	1,100	6.5	1,260	6.0	0.045	0.013	71	
				900	10.5	1,360	6.0	0.050	0.015	70	

TABLE 4-2

Specimen number	Contents of ingredients, in parts by weight per 100 parts by weight of CaO							Sintering temperature (°C.)	Amount of desulfurizer in molten pig iron (kg./ton)	Temperature of pig iron (° C.)	Treating time (minute)	Sulfur content in pig iron (percent)		Rate of desulfurization (percent)	Remark
	Na_2CO_3	Na_2O	NaOH	Na_2SiF_6	NaF	CaF	CaF_2					Before treating	After treating		
2-20	5.5						5.5	1,100	6.5	1,260	6.0	0.045	0.006	85	The invention.
								900	10.0	1,350	6.0	0.040	0.006	86	
2-21	11.8						5.9	1,100	6.5	1,250	6.0	0.050	0.007	86	
								900	10.0	1,370	6.0	0.044	0.008	82	
								------	6.5	1,350	6.0	0.053	0.026	51	
2-22	12.5						12.5	1,100	6.5	1,370	6.0	0.053	0.006	89	
								900	10.0	1,350	6.0	0.054	0.007	87	
2-23	14.3						28.6	1,100	6.5	1,260	6.0	0.050	0.012	76	
								900	10.0	1,260	6.0	0.055	0.012	78	
2-24	15.0						30.0	1,100	6.5	1,370	6.0	0.060	0.034	60	
								900	10.0	1,360	6.0	0.055	0.023	58	
2-25	25.0						20.0	1,100	6.5	1,230	6.0	0.065	0.029	55	
								900	10.0	1,260	6.0	0.045	0.021	53	
2-26	25.6						2.6	1,100	6.5	1,260	6.0	0.042	0.008	81	
								900	10.0	1,260	6.0	0.033	0.007	79	
								------	6.5	1,350	6.0	0.049	0.023	53	
2-27	28.6						14.3	1,100	6.5	1,260	6.0	0.050	0.011	78	
								900	10.0	1,370	6.0	0.045	0.009	80	
2-28		1.5					5.0	1,000	6.5	1,350	6.0	0.055	0.010	82	

TABLE 4-2 – Continued

Specimen number	Contents of ingredients, in parts by weight per 100 parts by weight of CaO: Na₂CO₃	Na₂O	NaOH	Na₂SiF₆	NaF	CaF	CaF₂	Sintering temperature (° C.)	Amount of desulfurizer in molten pig iron (kg./ton)	Temperature of pig iron (° C.)	Treating time (minute)	Sulfur content in pig iron (percent): Before treating	After treating	Rate of desulfurization (percent)	Remark
2-29		4.6					4.0	1,000	6.5	1,360	6.0	0.045	0.008	82	
2-30		6.2					10.0	1,000	6.5	1,360	6.0	0.040	0.005	88	
2-31		3.9			10.0			1,000	6.5	1,350	6.0	0.047	0.007	85	
2-32		7.7			5.0			1,000	6.5	1,340	6.0	0.055	0.009	83	
2-33	2.0				5.0			1,100	6.5	1,240	10.0	0.050	0.012	76	
2-34	10.0				2.0			1,100	6.5	1,330	10.0	0.060	0.012	80	
2-35		3.0		11.0				1,100	6.5	1,260	6.0	0.051	0.006	88	
2-36	3.0				2.0		3.0	1,100	6.5	1,240	10.0	0.045	0.007	84	
2-37	5.0	2.3				2.0		1,100	6.5	1,380	10.0	0.056	0.010	82	
	18								15	1,410	10.0	0.033	0.015	54.5	
	40								15	1,420	10.0	0.032	0.011	66	
			5.0						15	1,370	6.0	0.045	0.031	31	
			10.0						15	1,350	6.0	0.050	0.028	44	Reference.
			20.0					(1)	15	1,350	6.0	0.055	0.024	56	
	3				2		2		15	1,340	10.0	0.045	0.029	35.5	
	5		3			2			15	1,280	10.0	0.056	0.035	37.5	
			3.9	11.0					15	1,360	6.0	0.040	0.017	57.5	
	10				2				15	1,320	10.0	0.060	0.032	17.0	

[1] Not sintered.

Example 3:

Desulfurizers of the invention consisting of calcium carbonate and sodium silicofluoride were prepared by thoroughly mixing ingredients as shown in Table 5, each having a particle size of about 0.2 mm, sintering the mixture at 1,300°C for 30 minutes, and crushing the sintered product into particles of about 2 mm particle size.

Table 5

Unit: parts by weight

Specimen No.	$CaCO_3$	Na_2SiF_6
3–1	98.9	1.1
3–2	97.3	2.7
3–3	94.2	5.8
3–4	92.3	7.7
3–5	85.6	14.4
3–6	83.6	16.4

The desulfurizing ability of the desulfurizers of the invention thus prepared was tested by the same manner as Example 2, and the results are shown in Table 6. For comparison's sake, known desulfurizers of similar composition were prepared and tested. Table 6 also includes the properties of such known desulfurizers.

It is apparent from Table 6 that the sintered and crushed desulfurizer of the present invention has excellent desulfurizing ability.

TABLE 6

Specimen number	Contents of Ni₂SiF₆ in parts by weight per 100 parts by weight of CaO	Sintering temperature (° C.)	Amount of desulfurizer in molten pig iron (kg./ton)	Temperature of pig iron (° C.)	Treating time (minute)	Sulfur content in pig iron (percent): Before treating	After treating	Rate of desulfurization (percent)	Remark
3-1	2	1,300	6.5	1,330	10	0.053	0.026	51	Reference.
3-2	5	1,300	6.5	1,340	10	0.058	0.014	76	
3-3	11	1,300	6.5	1,350	6	0.040	0.006	85	The invention.
3-4	15	1,300	6.5	1,330	10	0.049	0.007	86	
3-5	30	1,300	6.5	1,370	10	0.036	0.008	78	
3-6	35	1,300	6.5	1,390	10	0.035	0.012	66	
	11	(1)	15	1,350	6	0.040	0.022	45	Reference.

[1] Not sintered.

The preferable temperature range for the sintering the material of the present invention is 800°C to 1,600°C. If the sintering temperature is below 800°C, the desired sintering effects cannot be obtained, and the desulfurizing ability of the products made by such a low sintering temperature is as low as that of simple mixture of the ingredients. On the other hand, for sintering at a temperature higher than 1,600°C, the desulfurizing ability of the products is not improved but the cost of the sintering furnace and the sintering operation increases in vain. The excessively high sintering temperature is, of course, undesirable from heat economy.

The particle size of the crushed particles of the sintered material is preferably smaller than 4 mm, in order to achieve the desirable quick desulfurizing speed for ensuring high efficiency in the desulfurizing process. More particularly, the desulfurizer of the present invention is a kind of solid desulfurizer, and from the macroscopic viewpoint, the particles of the desulfurizer are not melted in the molten pig iron but the particles act to capture sulfur at the surface thereof from the molten pig iron. As the sulfur is captured, the active surface area of the individual desulfurizer particles becomes smaller to reduce desulfurizing ability, and the desulfurizing time increases. Accordingly, the particle size of the desulfurizer should preferably be smaller than 4 mm.

What is claimed is:

1. A granular desulfurizer composition for quickly desulfurizing pig iron in off-furnace treatment consisting of crushed particles of material sintered at a temperature of 800°–1,600°C, whereby the sulfur content is substantially reduced, comprising 100 parts by weight of calcium oxide and 3 to 50 parts by weight, in total, of at least one compound selected from the group consisting of up to 30 parts by weight of calcium fluoride, sodium fluoride, magnesium fluoride, barium

fluoride, and sodium silicofluoride, and up to 40 parts by weight, in terms of sodium carbonate, of at least one compound selected from the group consisting of sodium carbonate, sodium hydroxide, and sodium oxide, the particle size of said desulfurizer composition being smaller than 4 mm and each granule of said desulfurizer composition includes calcium oxide particles of not greater than 0.3 mm diameter which are bonded by said compound, whereby the pig iron is substantially desulfurized in an off-furnace treatment.

2. The granular desulfurizer composition according to claim **1**, consisting of crushed particles of sintered material comprising 100 parts by weight of calcium oxide and 3 to 30 parts by weight of at least one compound selected from the group consisting of calcium fluoride, sodium fluoride, magnesium fluoride, barium fluoride and sodium silicofluoride.

3. The granular desulfurizer composition according to Claim **1**, consisting of crushed particles of sintered material comprising 100 parts by weight of calcium oxide and 3 to 40 parts by weight, in terms of sodium carbonate, of at least one compound selected from the group consisting of sodium carbonate, sodium hydroxide, and sodium oxide.

4. The granular desulfurizer composition according to Claim **1**, consisting of crushed particles of sintered material comprising 100 parts by weight of calcium oxide, and 3 to 50 parts by weight of at least two compounds, at least one of said two compounds being up to 40 parts by weight, in terms of sodium carbonate, of at least one compound selected from the group consisting of sodium carbonate, sodium hydroxide and sodium oxide, while the other one of said two compounds being selected from the group consisting of up to 30 parts by weight of calcium fluoride, sodium fluoride, magnesium fluoride, barium fluoride, and sodium silicofluoride.

5. A granular desulfurizer composition for quickly desulfurizing pig iron in off-furnace treatment according to claim **1**, characterized in that said sintered material comprises a binding amount of a binder selected from the group consisting of sodium dihydrogen phosphate, calcium chloride, starch, and clay.

6. A method of making granular desulfurizer composition for quickly desulfurizing pig iron in off-furnace treatment, comprising steps of thoroughly mixing 100 parts by weight of particles of calcium oxide, said calcium oxide particles being not greater than 0.3 mm in diameter, and 3 to 50 parts by weight, in total, of particles of at least one compound selected from the group consisting of up to 30 parts by weight of calcium fluoride, sodium fluoride, magnesium fluoride, barium fluoride and sodium silicofluoride, and up to 40 parts by weight, in terms of sodium carbonate, of at least one compound selected from the group consisting of sodium carbonate, sodium hydroxide and sodium oxide, said compound particles being not greater than 0.3 mm in diameter; sintering the mixture thus prepared at 800°C to 1,600°C, whereby the sulfur content is substantially reduced and so as to bind said calcium oxide particles with said compound; and crushing the material thus sintered into a particle size of 4 mm or smaller; whereby the pig iron is substantially desulfurized in an off-furnace treatment.

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