United States Patent [19]

Takemura

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[54] **PROCESS FOR DESULFURIZATION OF MOLTEN PIG IRON**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **75/58;** 75/51; 75/53

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

[58] **Field of Search** 75/53–60, 51, 75/52

[56] **References Cited**

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Attorney, Agent, or Firm—Toren, McGeady and Stanger

[57] **ABSTRACT**

A process for desulfurization of molten pig iron, which comprises mixing calcium carbide with a gas generating substance and adding the mixture into the molten pig iron with a carrier gas.

5 Claims, 3 Drawing Figures

FIG. 1

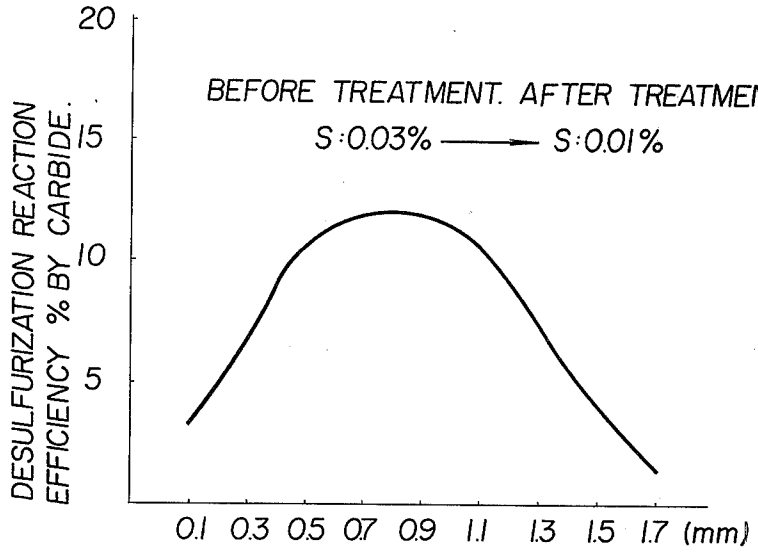

20
15
10
5
DESULFURIZATION REACTION EFFICIENCY % BY CARBIDE.
BEFORE TREATMENT. AFTER TREATMENT.
S:0.03% ——→ S:0.01%
0.1 0.3 0.5 0.7 0.9 1.1 1.3 1.5 1.7 (mm)
SIZE OF DESULFURIZING AGENT (mm)

FIG. 2

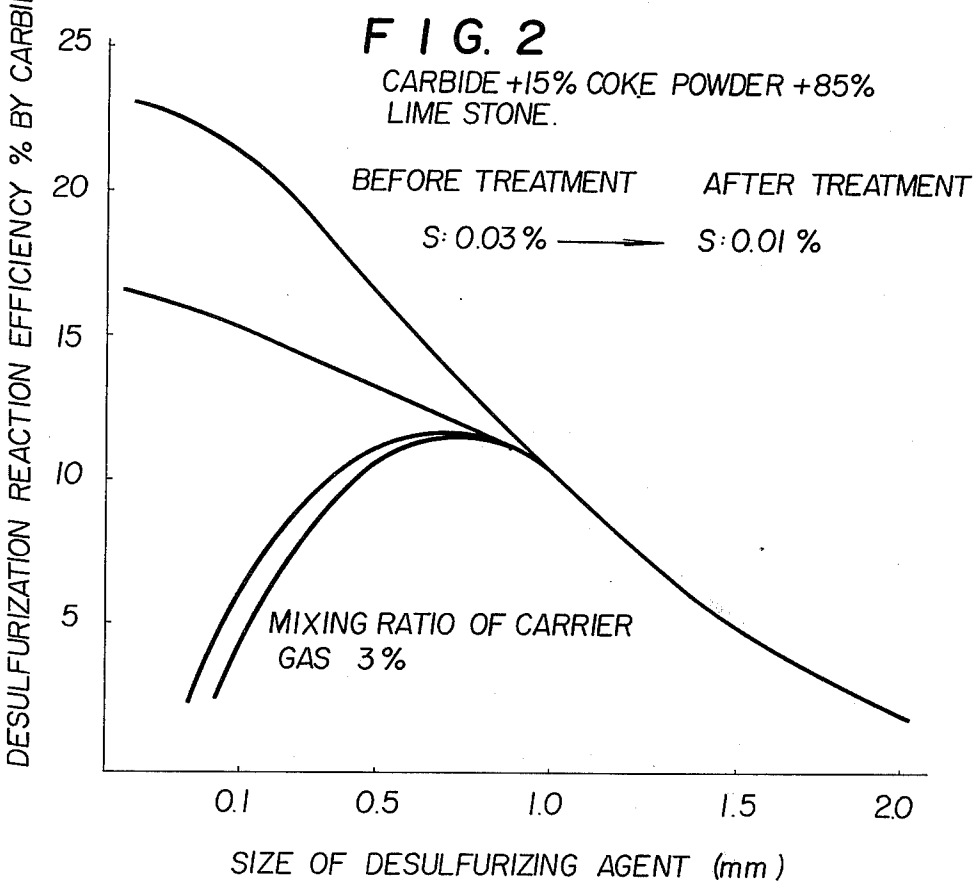
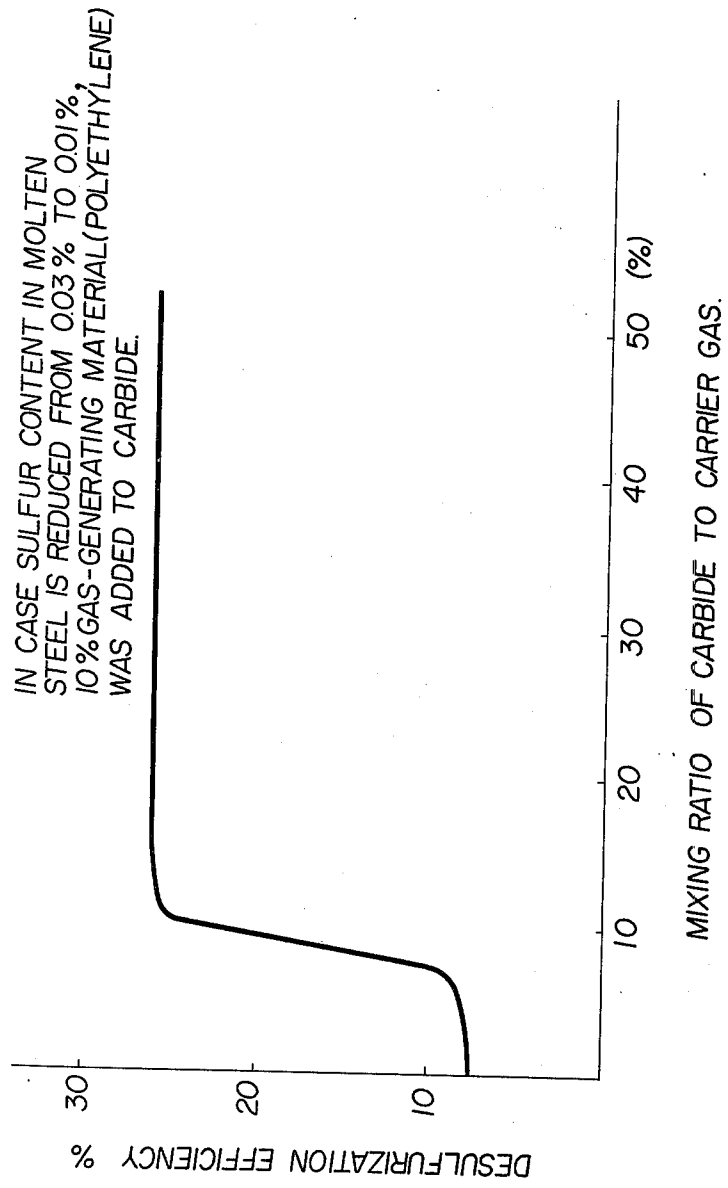

25
20
15
10
5
DESULFURIZATION REACTION EFFICIENCY % BY CARBIDE.
CARBIDE +15% COKE POWDER +85% LIME STONE.
BEFORE TREATMENT
AFTER TREATMENT
S: 0.03% ——→ S: 0.01 %
MIXING RATIO OF CARRIER GAS 3%
0.1 0.5 1.0 1.5 2.0
SIZE OF DESULFURIZING AGENT (mm)

FIG. 3


IN CASE SULFUR CONTENT IN MOLTEN STEEL IS REDUCED FROM 0.03% TO 0.01%, 10% GAS-GENERATING MATERIAL (POLYETHYLENE) WAS ADDED TO CARBIDE.
DESULFURIZATION EFFICIENCY %
30
20
10
10
20
30
40
50 (%)
MIXING RATIO OF CARBIDE TO CARRIER GAS.

PROCESS FOR DESULFURIZATION OF MOLTEN PIG IRON

The present invention relates to a process for desulfurization of molten pig iron.

In the conventional process for desulfurization of molten pig iron, calcium carbide has been hitherto added. The desulfurization shows a reaction efficiency of 5 to 15 percent when it is added through a carrier gas and of 20 to 25 percent when it is mechanically agitated for desulfurization, for example, by an impeller. Thus, the reaction efficiency is particularly low with carrier gas.

The present invention provides an excellent method to improve the efficiency when a carrier gas is used and is characterized by (1) a process for desulfurization of molten pig iron in which calcium carbide having a particle size of of about 10 mm or less is mixed with a gas generating substance and added to the molten pig iron through a carrier gas; (2) a process for desulfurization of molten pig iron, in which carbide is mixed with a gas generating substance and added to the molten pig iron through a carrier gas, having a reducing gas therein; (3) a process for desulfurization of molten pig iron, in which a granulated desulfurizing agent, made of carbide mixed with a gas generating substance is added to the molten pig iron; (4) a process for desulfurization of molten pig iron, in which petroleum substances are added to the molten pig iron to promote the desulfurization; and (5) a desulfurizing agent for molten pig iron composed of calcium carbide mixed with a gas generating substance, in which 10 to 50 percent of said carbide is admixed with a foaming gas.

The present invention shall be explained in detail, referring to the drawings, in which

FIG. 1 is a diagram, showing the relation of the size of the desulfurizing agent (carbide) to the desulfurization effect;

FIG. 2 is a diagram, showing the relation of the size of the sulfurizing agent and the ratio of mixing in the carrier gas (including the gas generating substance) to the desulfurization efficiency; and

FIG. 3 is a diagram showing the relation between the ratio of the desulfurizing agent, mixed with the carrier gas (foaming gas) and the desulfurization efficiency.

According to the result of various investigations made by the present inventors on the relation between the desulfurization reaction and the desulfurizing agent (carbide), as shown in FIG. 1, carbide having a particle size of 0.5 to 1.1 mm shows the increase of the desulfurization efficiency, but it is not possible to improve the desulfurization efficiency when sizes different from those shown in the drawing are used. For particle sizes of about 1.1 mm or above, the surface of the desulfurizing agent becomes small and the area to be contacted with molten pig iron becomes small, so that it is natural that the desulfurization efficiency is decreased. Though it is a common-sense view that if the size becomes about 0.5 mm or below, the desulfurization effect is improved by the large area per unit weight of contact with the molten pig iron, the efficiency is decreased as shown in the drawing when the size of the desulfurizing agent becomes about 0.5 mm or below. We have found that it is due to the following reason:

When the desulfurizing agent is blown (added) into the molten pig iron through a carrier gas, it is desirable to introduce the agent in the bottom part of the vessel

in order to increase the efficiency by elongation of the contact time with the molten pig iron. The time depends upon the capacity of the vessel, but it generally takes about 1.0 sec. for the foam of carrier gas to be floated from the point at which it is blown in to the surface of the molten pig iron. It is necessary that the desulfurizing agent, blown in through the carrier gas, is sufficiently contacted with the molten pig iron during this time. However, a large amount of the desulfurizing agent, blown in through the carrier gas enters, enter into the foam of the carrier gas and some of the desulfurizing agents in the foam reach the peripheral part of the foam under their own weight in the process of floating toward the surface of the molten pig iron, while the others remain in the foam and continue to be floated up. Therefore, the desulfurizing agent for contact with the molten pig iron diminishes, so that the desulfurization efficiency is decreased.

That is to say, particle size range which enables the the movement of the agent toward the periphery of the foam by its own weight, is 0.5 to 1.1 mm. If the size is about 0.5 mm or below, the agent floats in the foam and comes to the surface of the molten pig iron without contacting the molten pig iron. Consequently, the desulfurization efficiency can be significantly increased if the floating foam is broken and the desulfurizing agent in the foam is fully contacted with the molten pig iron.

Therefore, the desulfurizing agent is mixed with a foam breaking substance. For example, a substance which generates gas when treated and is added i.e., blown into in the molten pig iron through a carrier gas, whereby gas can be generated in the molten pig iron from the gas generating substance contained in the foam, and the foam may be expanded and thus broken (exploded), so that the desulfurizing agent, contained in the foam is fully contacted with the molten pig iron to increase the desulfurization efficiency. For the gas generating substance, a reducing agent, for example, petroleum substances, such as heavy oil, tar or the like, cokes, Al powders or polyester, are mixed in a CO_2 gas generating substance, such as, limestone or $MgCO_3$ to convert CO_2 to CO (a reducing gas). Thus, oxidation of the surface of the desulfurizing agent can be prevented by CO_2 so that the desulfurization efficiency can be increased. The quantity to be added in the desulfurizing agent is 7 to 20 percent. To break the foam, a mixing ratio with the carrier gas as explained below is used. The mixture of the desulfurizing agent and the gas generating substance can sufficiently break the foam in the molten pig iron when the mixing ratio with the carrier gas, i.e.:

$$\frac{\text{Quantity of CO, generated from the desulfurizing agent/min.}}{\text{Quantity of carrier gas/min.}} \times 100$$

is from 10 to 50 percent. If the quantity (ratio) of the gas generating substance to be added in the desulfurizing agent is about 7 percent or below, the quantity of gas generated is not enough. It can scarcely expand the foam and sometimes it becomes impossible to break the foam. If the ratio is about 20 percent or above, the flame or boiling becomes vehement and the operation become dangerous. Accordingly, when the amount of gas generating substance is 20 percent, the ratio of the carrier gas mixed with the gas generating substance, including the desulfurizing agent, is about 50 percent or

below in order to break the foam fully. The desulfurization efficiency can be increased as shown in FIG. 2, when the mixing ratio with the carrier gas is about 10 percent or above. Moreover, according to the present invention, the desulfurization can be efficiently performed by adding the desulfurizing agent through the carrier gas. Such excellent desulfurization effects can be brought about easily and simply.

The relation of the mixing ratio of the desulfurizing agent and the carrier gas (foaming gas) to the desulfurization efficiency is shown in FIG. 3.

If such a gas generating substance is mixed to generate gas in the molten pig iron, carbide is oxidized by CO_2 gas in the reaction: $CaC_2 + CO_2 \rightarrow CaO + CO$ and becomes less active for the desulfurization reaction. The desulfurization efficiency thus is sometimes decreased.

In this case, if a reducing gas, such as, H_2, CH_4, C_2H_4 or C_3H_8 is contained in the carrier gas and the carbide, mixed with the beforementioned gas generating substance is carried in the molten pig iron, CO_2 generated in the molten pig iron is reduced in the reaction of CO_2 + reducing gas $\rightarrow$ CO. The carbide can be prevented from the surface oxidization of CO_2 gas. The surface of carbide, dispersed in the molten pig iron by the breaking of the foam, can be contacted with the molten pig iron in the active condition, so that the desulfurization reaction may be significantly improved. If the reducing gas is used in this manner according to the present invention, the reaction of CO_2 + reduction $\rightarrow$ CO is instantaneously carried out as compared with the case of a solid substance, such as C, used as the reducing agent. Therefore, carbide is almost not oxidized and the desulfurization effect can be largely improved.

Further, the present inventors have found that when calcium carbide, a desulfurizing agent, is granulated after mixing with a gas generating substance and added to the molten pig iron, gas is generated by the heat of the molten pig iron to pulverize or explode the desulfurizing agent in the molten pig iron, whereby the area of the desulfurizing agent, contacted with the molten pig iron is increased, so that the desulfurization efficiency can be improved.

Further, the present inventors have learned that when carbide is added through the carrier gas, the carbide, blown in the molten pig iron, is confined in the bubble of the carrier gas and often comes to the surface of the molten pig iron without taking part in the desulfurization reaction, so that the yield of the desulfurizing agent is sometimes decreased.

The present inventors have found that in order to eliminate such a difficulty advantageously, a process, in which petroleum substances are added with carbide into the molten pig iron, is favourable in the case of carbide being added to the molten pig iron for desulfurization.

For the petroleum substance to be used according to the present invention, any such substance in the form of a gas, liquid and solids will do. Gases, such as, propane, butane liquids, such as, heavy oil, tar, kerosene, naphtha, solids, and such as, polyethylene, and vinyl chloride may be used.

When a solid is used, it is divided into fine particles of about 0.1 mm or below and mixed with carbide so that the desulfurization effect can be improved.

It seems that the petroleum substance has C and H as the main ingredient and when it is added in molten pig iron, a cracked gas (H_2) is first generated at the temperature, whereby the oxide film is peeled from the carbide to expose the surface, which possesses a high activity and this surface is contacted with the molten pig iron to improve the desulfurization effect.

The carbide is covered with the cracked gas (H_2) to interrupt the reaction of N_2, O_2 and carbide, so that the change of $CaC_2 \rightarrow CaO$ and $CaCN_2$ does not occur. Further, when it is added in the molten pig iron through the carrier gas, the foam is broken by the cracked gas (H_2) of the petroleum substance and the carbide, contained in the foam, is contacted with the molten pig iron to react, whereby the desulfurization effect can be improved.

Accordingly, the quantity of petroleum substance to be added may be so determined as to be 0.04 to 1.0 percent, computed on the basis of the quantity of H_2 gas to be generated

$$\frac{\text{Quantity of } H_2 \text{ generated from the petroleum substance Kg}}{\text{Quantity of carbide Kg}}$$

whereby the desulfurization efficiency can be advantageously increased.

If it is less than about 0.04 percent, the quantity of H_2 gas (cracked gas) generated is very small and the improved effect will not be obtained. If it is about 1.0 percent or above, the cracked gas (H_2) is increased, and flaming and boiling becomes vehement, and is dangerous.

Examples of the inventive process are as follows:

Inventive examples	Desulfurizing agent	Size of desulfurizing agent	Ratio of gas generating substance to reducing agent			Ratio to carrier gas (mixing ratio)
1	calcium carbide	0.5 mm	coke 7%		$CaCO_3$ 93%	10%
2	"	1.0	10		90	20
3	"	0.3	15	Al 5	80	40
4	"	0.1	20	10	70	30
5	"	0.1	polyester 10		lime stone 90	25
6	"	0.05	heavy oil 10		raw dolomite 90	45
Comparative examples						
1	"	0.5				
2	"	1.0				
3	"	0.3				
4	"	0.1				

Quantity of desulfurizing agent to be added in molten pig iron a6	Rate of desulfurizing agent to be added in molten pig iron	Sulphur in molten pig iron before desulfurization	Sulfur in molten pig iron after desulfurization	Reaction efficiency
kg/t-pig	kg/t-min.	%	%	%
2.5	0.1	0.03	0.01	19
2.6	0.2	0.04	0.015	23
4.1	0.3	"	0.005	20
1.5	0.06	"	0.02	30
1.0	0.5	0.03	0.01	40
1.2	0.2	0.04	0.015	32
4.7	0.15	0.03	0.01	10
4.7	0.3	0.04	0.015	12
11.8	0.3	"	0.005	7
9.5	0.33	"	0.02	5

Note 1:
The molten pig iron of 1200°C was filled in a ladle and blown in under the surface of molten pig iron.
Note 2:
The ratio to carrier gas is the volumetric ratio of the mixture of a desulfurizing agent and a gas generating substance, thrown in the carrier gas:

$$\frac{\text{Quantity of CO gas, generated from the gas generating substance/min.}}{\text{Quantity of carrier gas/min.}} \times 100$$

Note 3:
The reaction efficiency is:

$$\frac{\text{Quantity of } CaC_2\text{, taking part in the desulfurization reaction}}{\text{Quantity of } CaC_2 \text{ to be added}} \times 100$$

Inventive examples	Desulfurizing agent	Size of desulfurizing agent	Ratio of mixing in gas generating substance and carbide	Carrier gas
7	calcium carbide	0.5 mm	$CaCO_3$: 15 %	N_2
8	"	1.0	$MgCO_3$: 10	"
9	"	0.3	$CaCO_3$: 10 $MgCO_3$: 10	Ar
10	"	0.1	$CaCO_3$: 10	N_2
Comparative examples				
5	"	0.5	carbide singly	N_2
6	"	1.0	"	Ar
7	"	0.3	$CaCO_3$: 15	N_2
8	"	0.1	$MgCO_3$: 10	"

Ratio of addition in reducing gas and carrier gas	Desulfurization reaction		Unit of desulfurizing agent	Reaction efficiency
	S before desulfurization	S after desulfurization		
CH_4 : 10 %	0.03	0.01	2.0 kg/t-pig	26.5 %
C_2H_6 : 5	0.05	0.015	3.0	31.5
C_3H_8 : 3	0.03	0.01	1.5	35.5
" : 3	0.05	0.015	2.7	34.5
	0.03	0.01	4.5	11.8
	0.05	0.015	6.0	15.5
	0.03	0.01	5.5	9.7
	0.05	0.015	8.0	11.6

Note :
The molten pig iron of 1200°C was filled in a ladle and blown in under the surface of molten pig iron.

Inventive examples	Size of calcium carbide	Gas generating substance	Ratio of gas generating substance, added to carbide	Size of gas generating substance after addition
11	below 0.2 mm	lime stone + C 85% + 15%	10%	1 ~ 2 mm
12	"	tar + C 80 + 20	5	2 ~ 3
13	below 0.05 mm	lime stone 100	30	1 ~ 2
14	below 0.2 mm	polyester 100	5	1 ~ 3
Comparative examples				
9	0.2 to 1.0 mm			
10	below 0.2 mm			
11	"			
12	0.2 to 1.0 mm			

Quantity of desulfurizing agent	Sulphur in molten pig iron before desulfurization	Sulphur in molten pig iron after desulfurization	Reaction efficiency
1.5 kg/t-pig	0.03 %	0.016	25 %
2.0	0.04	0.017	30
2.5	"	0.008	35
"	"	0.008	"
2.7	0.03	0.015	15
2.5	0.04	0.033	7
"	"	0.023	6
3.0	"	0.015	13

Note 1:
The molten pig iron of 1250°C was filled in a ladle (250 t) and added with the above mentioned desulfurizing agent as the molten pig iron being agitated by an impeller at 80 r.p.m.
Note 2:
The desulfurizing agent was added at the almost uniform rate of addition for 10 minutes. In all cases, the molten pig iron was agitated by an impeller for 16 minutes after the beginning of the addition.

Inventive examples	Desulfurizing agent	Size of desulfurizing agent	Mixing ratio of a gas generating substance and a reducing gas generating substance		Quantity of gas generating substance, added to carbide
15	calcium carbide	0.05 mm	lime stone	: 90 %	6 %
			polyester	: 10	
16	"	0.10	$MgCO_3$	: 80	15
			plastic	: 20	
17	"	0.30	dolomite	: 85	11
			coke particle:	15	
18	"	0.01	polyester	: 100	18
19	"	0.5	soda ash	: 93	
			oil	: 7	
Comparative example					
13	"	0.01			

Ratio of mixing in carrier gas (foaming gas)		Quantity of desulfurizing agent, added to molten pig iron	Rate of desulfurizing agent to be added	S in molten pig iron before desulfurization	S in molten pig iron after desulfurization	Reaction efficiency
gas generating substance	rest: carrier gas	kg/t-pig	kg/t-min.			
10		2.5	0.1	0.03 %	0.01 %	19 %
30	"	2.7	0.2	0.04	0.015	23
50	"	4.1	0.3	"	0.005	20
40	"	1.5	0.06	"	0.02	30
25	"	1.0	0.5	0.03	0.01	40
		4.7	0.15	0.03	0.01	10

Note 1:
The molten pig iron of 1200°C was filled in a ladle (250 t) and the desulfurizing agent was blown in under the surface of the molten pig iron.
Note 2:
N_2 was used for the carrier gas (foaming gas).

Inventive examples	Quantity of carbide to be added	Petreluem substance	Computed in terms of quantity of H_2 gas to be generated
20	2.0 kg/t-pig	heavy oil	0.25 %
		20 kg/t-carbide	
21	2.0	"	1.00
		100	
22	2.2	tar	0.3
		40	
23	1.5	polyethylene	0.1
		50	
24	1.3	propane(liquid)	0.5
		80	
Comparative examples			
14	4.0		
15	4.0		
16	3.0		

Dusulfurization method	S in molten pig iron before desulfurization	S in molten pig iron after desulfurization	Desulfurization efficiency CaC_2, taking part in desulfurization reaction / added CaC_2 × 100
addition with carrier gas	0.028%	0.012	21.3%
"	0.033	0.006	50.0
"	0.040	0.010	40.0
agitation	0.035	0.005	36.2
"	0.030	0.005	44.0
addition with carrier gas	0.028	0.011	10.8
"	0.040	0.020	13.3
agitation	0.030	0.011	17.0

Note 1:
The addition with carrier gas, shown in the column "desulfurization method", means that a desulfurizing agent (calcium carbide) was carried with N_2 gas, the carrier gas, to be added into the molten pig iron. The agitation shows that the molten pig iron is mechanically agitated by an impeller and added with a desulfurizing agent to further the contact with the molten pig iron.
Note 2:
In the examples 20, 21 and 22, the petroleum substances and the desulfurizing agent (carbide) were added. The petroleum substance in the example 23 was pulverized an average of 0.1 mm and mixed with carbide to be added.
Note 3:
The molten pig iron was desulfurized at 1320°C.

What is claimed is:

1. A process for desulfurizing molten pig iron comprising introducing a mixture of calcium carbide and a solid material selected from the group consisting of polyethylene, vinyl chloride, and polyester, in a carrier gas, to the molten pig iron.

2. The process of claim 1 wherein a substance which generates carbon dioxide selected from the group consisting of limestone and magnesium carbonate is added to the mixture.

3. The process of claim 2 wherein the ratio of amount of carbon dioxide generated to carrier gas is from 10 to 50 percent.

4. A process according to claim 1, in which the particle size of the calcium carbide is from 0.5 to 1.1 mm.

5. A process according to claim 1, in which H_2, CH_4, C_2H_2, or C_3H_8 is contained in the carrier gas.

* * * * *

Notice of Adverse Decision in Interference

In Interference No. 99,220, involving Patent No. 3,876,421, Y. Takemura, PROCESS FOR DESULFURIZATION OF MOLTEN PIG IRON, final judgment adverse to the patentee was rendered Oct. 12, 1976, as to claims 1 and 2.

[*Official Gazette February 1, 1977.*]