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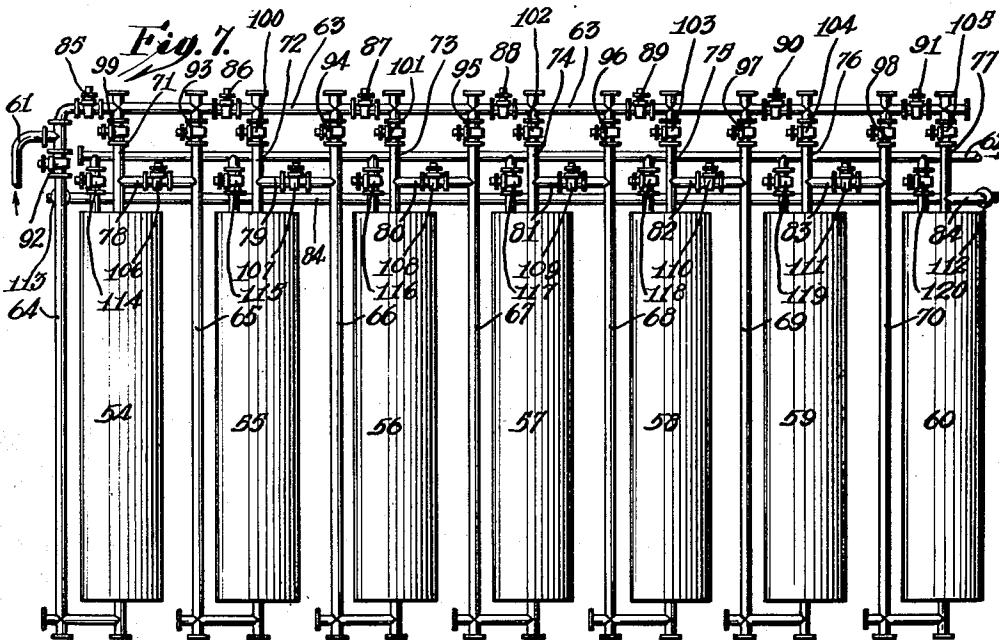
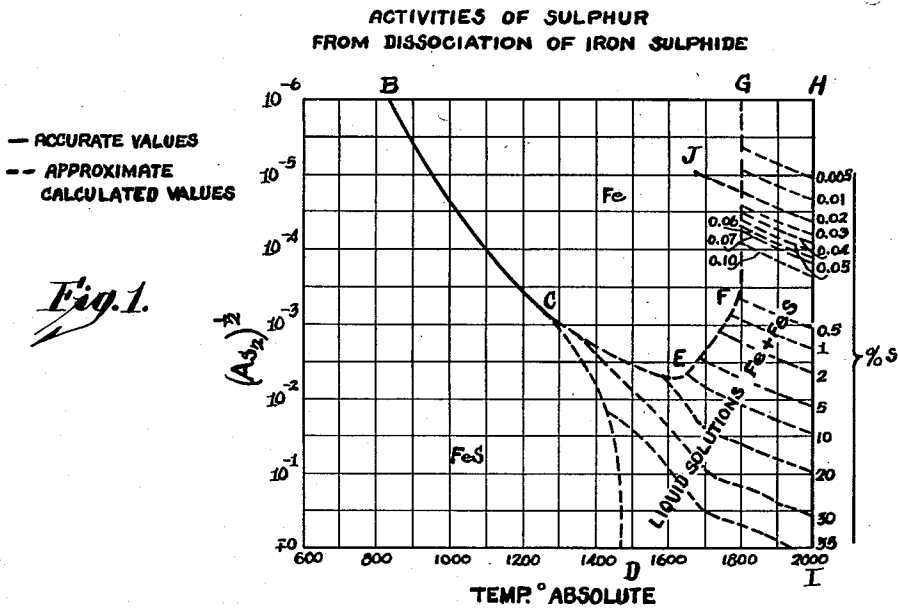
R. P. HEUER

2,110,066

IRON AND STEEL DESULPHURIZATION

Filed May 9, 1935

5 Sheets-Sheet 1



Witnesses:

Oliver W. Hacker
Walter Perry.

Inventor
Russell Pearce Heuer

by W. Steel Johnson and Son
Attorneys.

March 1, 1938.

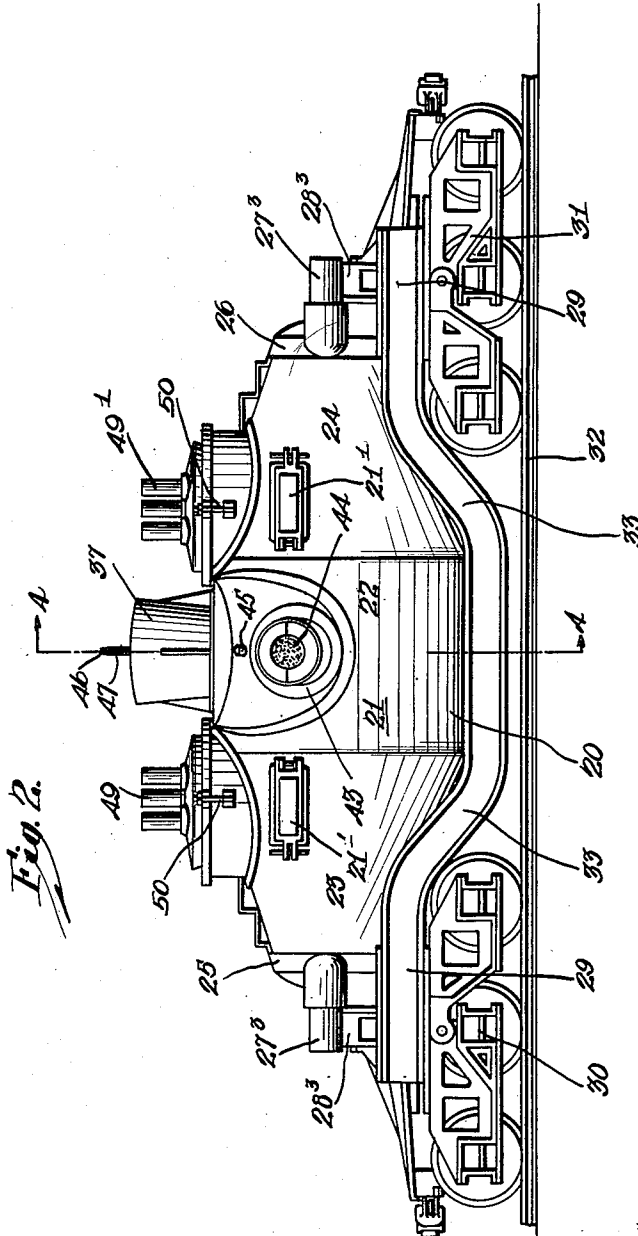
R. P. HEUER

2,110,066

IRON AND STEEL DESULPHURIZATION

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5 Sheets-Sheet 2



Witnesses:
Elmer W. Hicken
Walter C. Hicken

Inventor
Russell Pearce Heuer
by *W. Steel Johnson and Son*
Attorneys.

March 1, 1938.

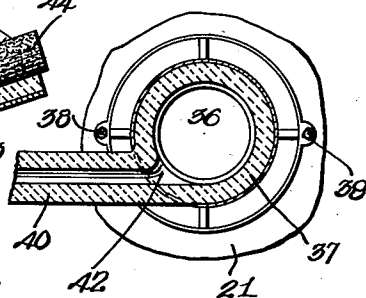
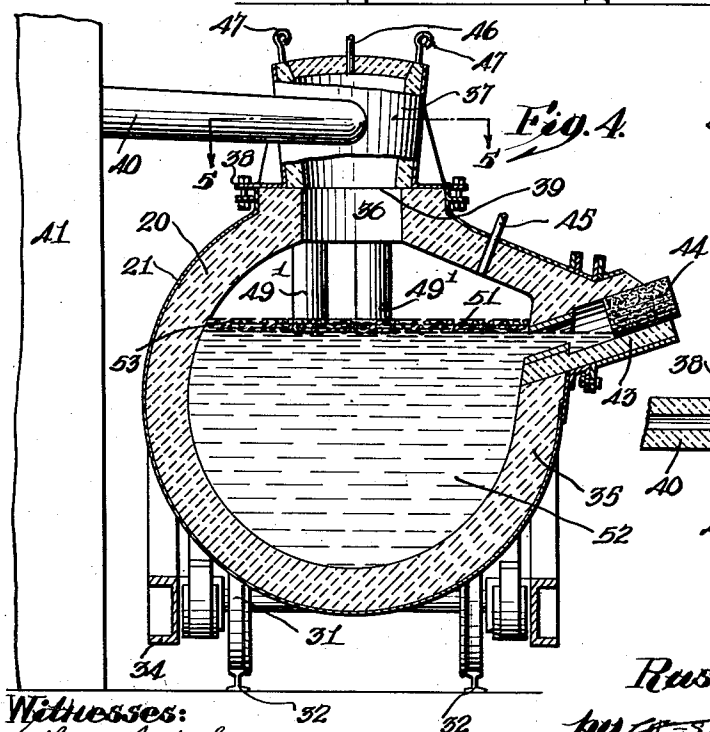
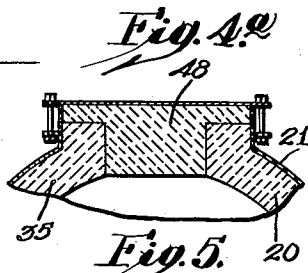
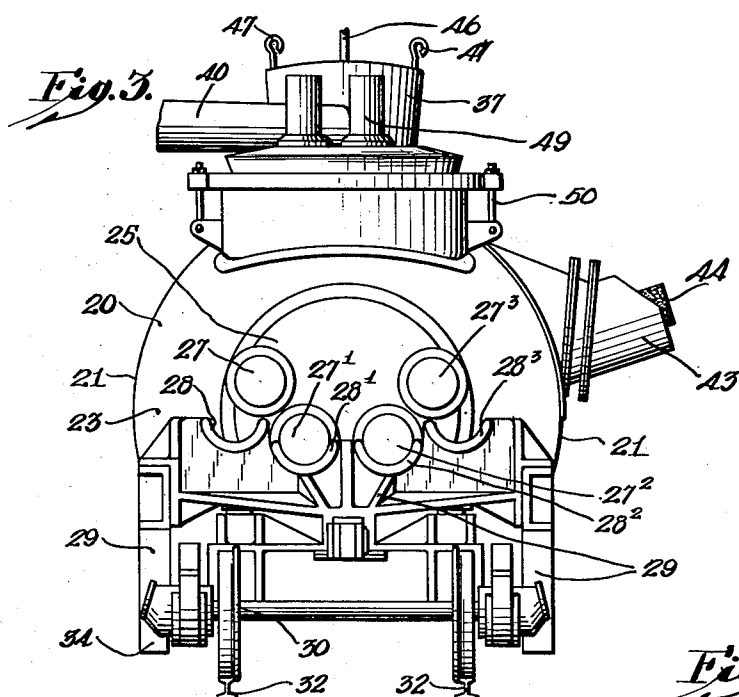
R. P. HEUER

2,110,066

IRON AND STEEL DESULPHURIZATION

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5 Sheets-Sheet 3



Inventor
Russell Pearce Hewer

by E. S. Hall Jackson and Son
Attorneys.

Witnesses:

Chas W. Hacker
Walter Cherry.

March 1, 1938.

R. P. HEUER

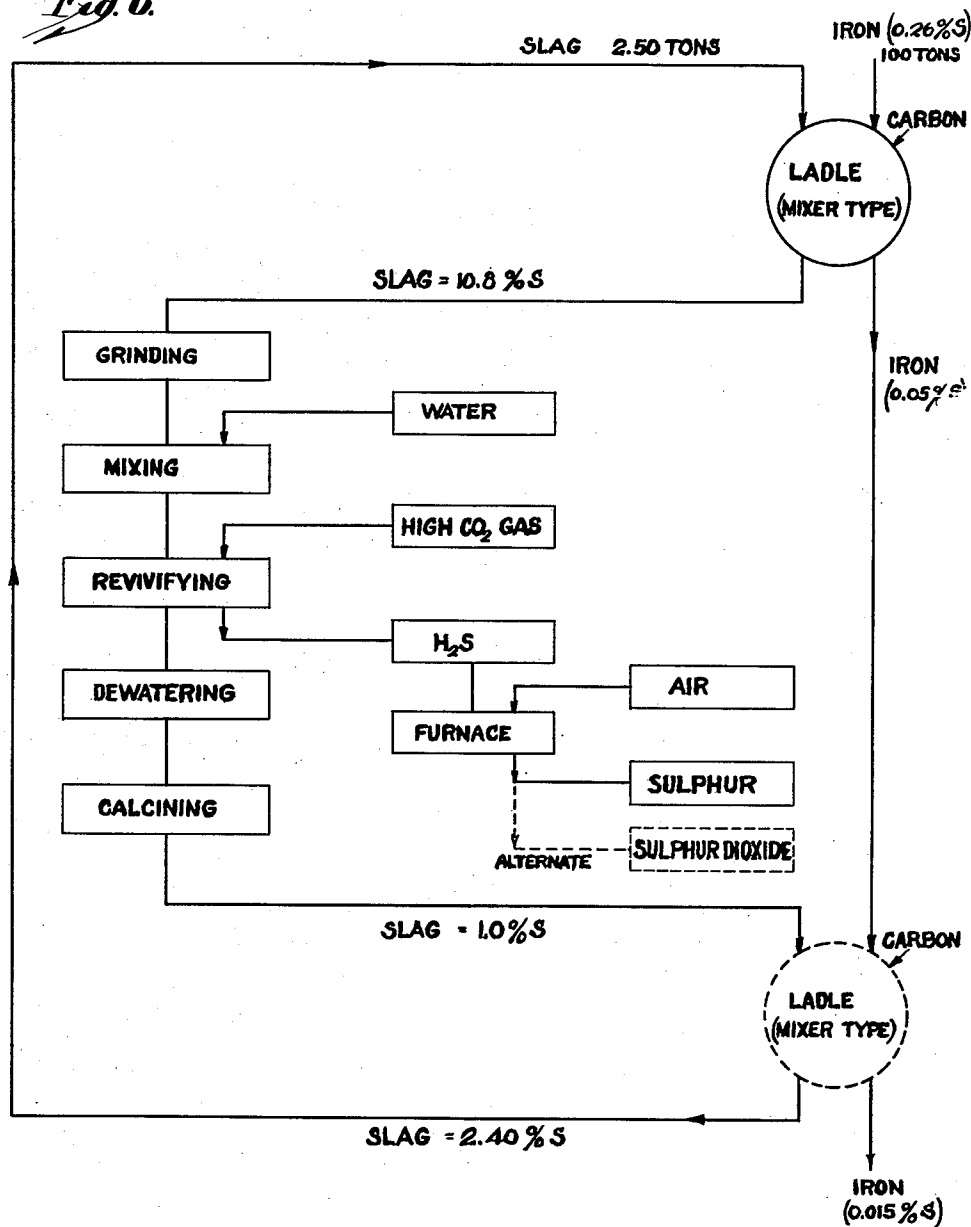
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IRON AND STEEL DESULPHURIZATION

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5 Sheets-Sheet 4

Fig. 6.



Witnesses:

Clara W. Hacker
Walter Chum

Inventor
Russell Pearce Heuer

by *W. Stull Johnson and Son*
Attorneys.

March 1, 1938.

R. P. HEUER

2,110,066

IRON AND STEEL DESULPHURIZATION

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Fig. 6a.

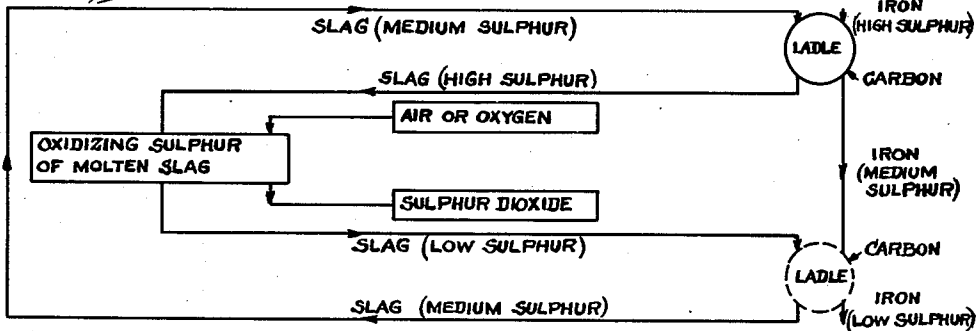


Fig. 6b.

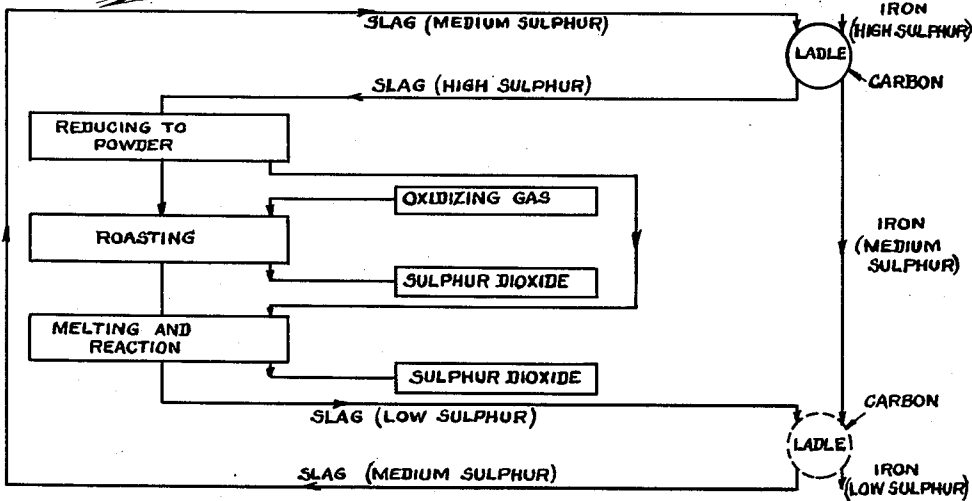
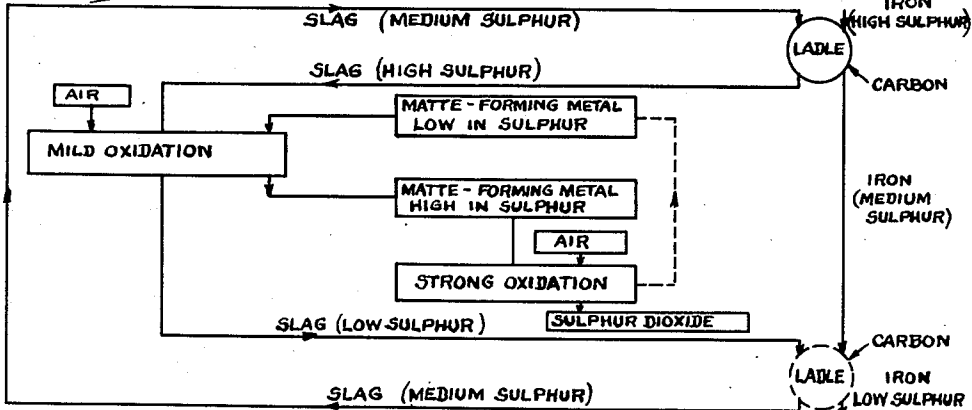


Fig. 6c.



Witnesses:
Emory W. Backer
Walter C. Hunt

Inventor
Russell Pearce Heuer
by *W. Steel Johnson and Son*
Attorneys

UNITED STATES PATENT OFFICE

2,110,066

IRON AND STEEL DESULPHURIZATION

Russell Pearce Heuer, Bryn Mawr, Pa.

Application May 9, 1935, Serial No. 20,555

36 Claims. (Cl. 75—55)

The invention relates to the manufacture of pig iron and the production of steel, and particularly to the desulphurization of pig iron.

A purpose of the invention is to lower the cost of pig iron production in the coke blast furnace by operating the blast furnace at lower temperature and/or with less basic slag, thus obtaining pig iron abnormally high in sulphur compared to present practice and substantially higher in sulphur than that ultimately desired, and to treat the molten pig iron external to the blast furnace hearth with a basic slag which is free-flowing below 1400° C. to remove sulphur while positively maintaining a strong reducing condition in the slag. The pig iron thus produced may be used in the form of cast iron, or used as a raw material, for example, for making steel.

A further purpose is to desulphurize molten pig iron in the presence of an excess of carbon, preferably as a carbon lining, by a reducing slag while excluding oxidizing gases.

A further purpose is to desulphurize pig iron objectionably high in sulphur, obtained by economical operation of the coke blast furnace, by treating the pig iron in molten condition with a basic desulphurizing slag freely flowing at 1200° C., and desirably containing more than 30% of oxides of the R_2O type, where R is a metal of the alkaline earth or alkali group, preferably calcium but permissibly strontium, barium, sodium, etc., and x is the numeral 2 or 1 depending upon the valence of the metal R.

A further purpose is to agitate pig iron during desulphurizing treatment with a basic slag under reducing conditions and with the exclusion of oxidizing substances.

A further purpose is to desulphurize molten pig iron excessively high in sulphur by treating it in a closed vessel with a basic desulphurizing slag in the presence of an excess of a noncontaminating reducing gas such as carbon monoxide, which serves to exclude oxidizing gases such as air and to maintain the reducing conditions requisite to desulphurization. The noncontaminating reducing gas such as carbon monoxide is desirably under sufficient pressure to prevent infiltration of air, and it may be mixed with nitrogen and/or nonoxidizing quantities of carbon dioxide.

A further purpose is to economize upon the use of desulphurizing slag in any of the processes disclosed herein by effecting the desulphurizing treatments in stepwise manner, preferably initially subjecting the pig iron to a first desulphurizing slag which is relatively high in sulphur

content and therefore limited in its ability to take up sulphur from the pig iron, and, after removal of the first slag, treating the pig iron with one or more further slags of lower sulphur content and correspondingly greater ability to remove sulphur. In this way, pig iron containing substantially more than 0.10% of sulphur, say 0.3% of sulphur or more, can have its sulphur content reduced to less than 0.05% sulphur (that is, to less than half) by treatment for an hour or more with slags which aggregate less than 8%, for example, only about 5%, of the weight of the pig iron.

A further purpose is to desulphurize molten pig iron with a slag capable of absorbing sulphur up to a percentage in the slag at least one hundred times the percentage present in the desulphurized pig iron, to separate the slag from the desulphurizing vessel and from the molten pig iron and to revivify the slag while it is out of contact with the molten pig iron to permit the reuse of the slag for desulphurizing more iron. The preferable slag for this purpose consists mainly of lime and fluorspar.

A further purpose is to desulphurize molten pig iron in a stepwise manner by initially treating it with a first slag relatively high in sulphur which has been used to desulphurize a previous charge of pig iron and not since revivified and by subsequently treating it with a second slag which is relatively low in sulphur, revivifying each slag when its sulphur content becomes high enough to prevent efficient desulphurization. In normal operation, the first slag after use is immediately revivified and the second slag after use is preserved for treatment of the next pig iron charge before revivification.

A further purpose is to revivify a pig iron desulphurizing slag by separating the slag from the desulphurizing vessel and from the molten pig iron and thereafter driving off sulphur from the slag as a volatile sulphur component.

A further purpose is to revivify pig iron desulphurizing slag and to recover elemental sulphur or a sulphur compound from the revivified slag, thus permitting reuse of the slag for further desulphurizing and crediting of the value of the recovered sulphur or sulphur compound against the cost of the process.

A further purpose is to desulphurize molten pig iron by a slag in such manner as to protect the slag from the influence of free oxygen, predominantly oxidizing oxides of carbon and water during the desulphurizing step, to subsequently treat the sulphur-bearing slag in the presence of

carbon dioxide and water to remove its sulphur content and to use the treated slag to desulphurize additional pig iron.

A further purpose is to reduce pig iron desulphurizing slag containing an alkaline earth sulphide such as calcium sulphide to a powder, to make it up into a slurry with water and to subject the mixture of water and powdered slag to the action of carbon dioxide gas to revivify the slag.

The carbon dioxide gas may preferably be obtained from the products of combustion of blast furnace gas.

A further purpose is to drive off sulphur from a pig iron desulphurizing slag containing an alkaline earth sulphide by treating the slag with carbon dioxide and water to generate hydrogen sulphide, and to burn the hydrogen sulphide either with sufficient oxygen to produce sulphur dioxide, or with the required amount of oxygen to obtain elemental sulphur.

A further purpose is to produce a pig iron desulphurizing slag which is fluid at 1200° C. and which has the property of self-disintegration when it solidifies and cools, to facilitate revivification of the slag and avoid the necessity of pulverizing the slag.

A further purpose is to desulphurize pig iron by a free-flowing basic slag, to separate the slag from the desulphurizing vessel and to revivify the slag by blowing a gas containing free oxygen through the slag in molten condition to oxidize the sulphur.

A further purpose is to revivify pig iron desulphurizing slag containing calcium sulphide or the like by reducing the slag to a powder, roasting the slag to produce calcium sulphate, mixing the roasted slag with the proper amount of slag containing calcium sulphide and calcining the mixture at a sufficiently high temperature to drive off sulphur dioxide.

A further purpose is to revivify pig iron desulphurizing slag by bringing the slag into contact with a molten matte-forming metal, such as copper, under mildly oxidizing conditions, and, after the matte-forming metal is separated from the slag, vigorously oxidizing the matte-forming metal to remove the sulphur.

A further purpose is to make up a pig iron desulphurizing slag containing from 30% to 55% of lime, from 20% to 50% of fluorspar and from 5% to 25% of silica, and preferably containing about 45% of lime, about 40% of fluorspar and about 15% of silica, the slag being freely flowing at 1200° C.

A further purpose is to pour pig iron into a desulphurizing vessel through a pouring head which excludes the air, and which preferably has an off-center inlet into a circular pouring opening.

A further purpose is to desulphurize pig iron in a ladle car having a carbon lining, and desirably provided with means for agitating the molten contents of the ladle car.

A further purpose is to use the pig iron desulphurized in the novel manner disclosed herein for the manufacture of steel, preferably as a continuous process in which the iron remains molten from the time it leaves the blast furnace until the time that it leaves the steel-making furnace.

Further purposes appear in the specification and in the claims.

The invention relates not only to the process involved, but also to the slag employed and to the apparatus used.

The apparatus is claimed in my application Ser. No. 171,800, filed Oct. 29, 1937.

The drawings are largely diagrammatic illustrations preliminarily intended to aid in understanding the invention, or to disclose apparatus which may be employed in performing the process. All apparatus shown is strictly schematic, and no effort has been made to complicate the disclosure by the illustration of detail within the routine skill of those in the art.

Figure 1 is a diagram whose ordinates are the square roots of activities of sulphur from dissociation of iron sulphide. The abscissae are absolute temperatures.

Figure 2 is a diagrammatic side elevation of a desulphurizing vessel which may be used in practicing the invention.

Figure 3 is a left end elevation of the structure of Figure 2.

Figure 4 is a transverse section of Figure 2 upon the line 4—4 thereof.

Figure 4a is a fragmentary view corresponding to a portion of Figure 4, with a door substituted for the pouring head.

Figure 5 is a horizontal section of Figure 4 on the line 5—5 thereof.

Figure 6 is a chart of a desirable process of desulphurizing pig iron and revivifying the slag in accordance with the invention.

Figures 6a, 6b, and 6c are charts of various processes of revivifying the slag in accordance with the invention.

Figure 7 is a diagrammatic view of apparatus which may be used for revivifying the slag.

In the drawings like numerals refer to like parts, and in the specification like symbols refer to like subject matter.

Throughout the specification, wherever reference is made to pig iron, it is intended to designate the product of the blast furnace which characteristically has a high carbon content, usually of 3% to 4%, or more, and always in excess of 2%, with varying contents of metalloids. The product of the blast furnace is referred to as pig iron whether it is intended to be used in the form of cast iron or whether it is to be used in making steel.

In the production of pig iron from low-sulphur burdens (such as wood charcoal and low sulphur ores) it is unnecessary to operate the blast furnace in such a manner as to obtain strong desulphurizing conditions in the hearth and bosh of the blast furnace. As a result the operation of the charcoal blast furnace is quite economical except for the excessive costs of charcoal and of low sulphur ores. In most instances, however, because of the high cost of wood charcoal, it is necessary to substitute coke for wood charcoal as a blast furnace fuel. When this is done, a strong desulphurizing action must be obtained in the hearth and bosh of the blast furnace in order to obtain a product having low enough sulphur to be commercially usable. For a strong desulphurizing action, it is necessary to have a higher temperature and a slag containing more lime. More fuel must be used in order to provide the higher temperature.

A typical slag from a charcoal blast furnace approximates

	Per cent	
SiO ₂	47.0	
Al ₂ O ₃	18.0	
CaO	27.0	
MgO	3.0	
S	0.10	

In the above slag the silica exceeds the lime plus magnesia. The sulphur in the pig iron approximates 0.02%.

A typical slag from a coke blast furnace has the following approximate composition

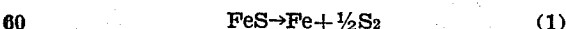
	Per cent
SiO ₂ -----	34.0
Al ₂ O ₃ -----	12.0
CaO -----	40.0
MgO -----	10.0
S -----	1.7

In the above slag the silica is less than the lime plus magnesia. The sulphur in the pig iron approximates 0.03%

The temperatures of the slag and pig iron tapped from a charcoal blast furnace are about 1450° C. and 1410° C. respectively. In the coke blast furnace, the respective temperatures of the slag and pig iron as tapped are approximately 1525° C. and 1475° C. Thus it is unnecessary for the charcoal blast furnace to expend as much heat to produce slag and pig iron as does the coke blast furnace.

From the above data it will be obvious that the cost of removing sulphur from the pig iron simultaneously with smelting of the ore in a blast furnace is considerable. It is one purpose of the present invention to cheapen the cost of manufacturing pig iron, whether for use as cast iron or for making steel, by omitting the strong desulphurizing action now considered necessary in the coke blast furnace because of the sulphur-bearing burdens. The iron is very desirably smelted in the coke blast furnace under conditions similar to those prevailing in charcoal blast furnaces, using a blast furnace slag in which the silica exceeds the lime plus magnesia. The smelting is conducted in the coke blast furnace under conditions of temperature and basicity of slag suitable to produce pig iron at lower cost but with a higher sulphur content in the iron than that ultimately desired. The sulphur content in the iron produced may be for example 0.25% sulphur. After production of this high sulphur pig iron, it is treated in novel manner as a wholly independent operation to remove the excess of sulphur. The cost of the desulphurization is small and it is possible to produce pig iron of desirable quality at a considerable saving.

The pig iron, containing a higher sulphur content than that ultimately desired, is transferred from the coke blast furnace to a suitable desulphurizing vessel as described later. The pig iron is there subjected to a strongly basic slag under reducing conditions. It is generally considered that the sulphur in pig iron is present as FeS. This iron sulphide will dissociate thus:



Due to this dissociation, there is a certain activity of sulphur in the molten pig iron which is measured at constant temperature by the equilibrium constant for equation (1), thus

$$\frac{(A_{\text{Fe}})(A_{\text{S}_2})^{1/2}}{(A_{\text{FeS}})} = K_1 \quad (2)$$

where

(A_{Fe}) = activity of iron

(A_{S₂}) = activity of sulphur

(A_{FeS}) = activity of iron sulphide

K₁ = equilibrium constant

The iron sulphide is considered to be present in solution in the molten pig iron and its activity

varies as the concentration. The relation of sulphur activity and sulphur concentration is expressed in Figure 1, taken from H. Schenck, *Physikalische Chemie der Eisenhüttenprozesse* (Verlag von Julius Springer, Berlin, 1932) volume 1, page 263. In this figure, the ordinates are square roots of the activities of sulphur from dissociation of iron sulphide and the abscissae are temperature in degrees absolute (K.). The curves are plotted for an iron-sulphur system free from carbon.

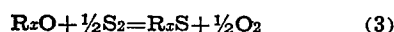
Within the area D C E F G H I, iron sulphide and iron occur as liquid solutions. In these solutions the sulphur activity is a function of the sulphur concentration. In Figure 1, diagonal dotted lines are shown corresponding to the sulphur percentages indicated by the numerals to the right of the dotted lines. The sulphur activity resulting from a given sulphur percentage in the melt and a given temperature is shown by these dotted lines. It would require a third dimension to show the relation of sulphur activity, sulphur concentration and temperature for liquids containing iron, iron sulphide and carbon. As an approximation for example to conditions prevailing in molten pig iron of 0.02% sulphur content at 1400° C. (1673° K.) we may extend the line for 0.02% sulphur outside the area D C E F G H I and into the area B C E F G until the temperature 1673° K. is reached and learn that at J the

$$(A_{\text{S}_2})^{1/2}$$

equals approximately 10^{-5.1} for 0.02% sulphur at 1400° C.

From Figure 1 it will be seen that, as the pig iron is subjected to conditions which lower the sulphur activity, the sulphur content will fall.

The desulphurizing slag contains basic oxides of the alkaline earth or alkali metals such as calcium oxide, barium oxide, strontium oxide, sodium oxide, etc. These are referred to generally as R_xO oxides, where R is an alkaline earth or alkali metal and x is the numeral 2 or 1, depending upon the valence of the metal. The oxides of the slag tend to react with sulphur of the pig iron thus:



For this reaction the equilibrium at constant temperature is expressed thus:

$$\frac{(A_{\text{R}_x\text{S}})(A_{\text{O}_2})^{1/2}}{(A_{\text{R}_x\text{O}})(A_{\text{S}_2})^{1/2}} = K_2 \quad (4)$$

where

(A_{R_xO}) = activity of R_xO

(A_{R_xS}) = activity of R_xS

(A_{O₂}) = activity of oxygen

K₂ = equilibrium constant

From reaction (3) it will be evident that there will be a low activity of sulphur and sulphur can be removed from the pig iron to enter the slag most efficiently if there is a low oxygen activity. In other words, the sulphur activity may be lowered directly by lowering the oxygen activity. The desulphurizing slag is therefore caused to act upon the pig iron in the presence of a reducing agent, preferably an excess of carbon. The carbon produces a low oxygen activity according to the reaction:



The equilibrium expression for this reaction is

$$\frac{(A_{CO})}{(A_C) \cdot (A_{O_2})^{1/2}} = K_3 \quad (6)$$

where

(A_{CO}) = activity of carbon
(A_{CO}) = activity of carbon monoxide
K₃ = equilibrium constant

The equilibrium constant K₃ may be calculated from the Gibbs free energy of reaction (5) by the equation:

$$-\Delta F_0 = RT \ln K_3 \quad (7)$$

where

−ΔF₀ = free energy change
R = gas constant
T = absolute temperature

The free energy change at a given temperature is expressed by the following equation, taken from International Critical Tables, volume VII, page 243:

$$\Delta F_0 = -26,600 - 2.15 T \ln T + 0.00215 T^2 - 0.0000002 T^3 - 8.20 T \quad (8)$$

At 1673° K. (1400° C.) the free energy change

$$\Delta F_0 = -61,938$$

Substituting this value in Equations (7) and (6), and assuming that the activities of carbon and carbon monoxide in Equation (6) are unity, since the carbon is present in excess and is available to supply an excess of carbon monoxide, it is evident that the oxygen activity of the slag in the presence of excess carbon can be reduced at equilibrium to

$$(A_{O_2})^{1/2} = 8.2 \times 10^{-9}$$

If, for the purpose of illustration, it be assumed that it is desired to desulphurize pig iron until the sulphur activity reaches a point at which

$$(A_{S_2})^{1/2} = 10^{-5}$$

Equation (4) may be solved using this value of

$$(A_{S_2})^{1/2}$$

and the previously determined value of

$$(A_{O_2})^{1/2}$$

thus:

$$\frac{(A_{R_2S}) \cdot (8.2 \times 10^{-9})}{(A_{R_2O}) \cdot (10^{-5})} = K_2 \quad (9)$$

$$\frac{(A_{R_2S})}{(A_{R_2O})} = (1.2 \times 10^3) K_2 \quad (10)$$

$$(A_{R_2S}) = (1.2 \times 10^3) (A_{R_2O}) K_2 \quad (11)$$

The value of (A_{R₂S}) is a measure of the concentration or percentage of R₂S in the desulphurizing slag. For most economical desulphurization it is desirable to have a high ratio of sulphur in the slag to sulphur in the pig iron, that is, a high percentage of R₂S in the slag when desulphurization is finished. This is accomplished by keeping the product (A_{R₂O}) K₂ high through choice of a slag of proper chemical composition.

Slags

A desulphurizing slag having the composition:

	Per cent
CaO	45
CaF ₂	40
SiO ₂	15

has been found to be very satisfactory. Such a slag can be readily synthesized by mixing lime and fluorspar of commercial grade, adjusting the silica to the desired percentage by the addition of silica sand, after allowing for the silica present as impurity in the lime and fluorspar. Magnesia present as a normal impurity in a good grade of lime is not objectionable. Alumina present as a small amount of impurity is also not objectionable. Indeed the addition of approximately 5% of alumina seems to be advantageous as it reduces somewhat the melting point of the desulphurizing slag. The above slag flows freely at 1200° C. and this property is very desirable for efficient desulphurization.

Molten pig iron high in sulphur (0.25% S) has been subjected to the action of the lime-fluorspar-silica slag above referred to at 1400° C. for one hour in a refractory container composed of carbon in the form of graphite. The slag and molten pig iron were under strong reducing conditions and the desulphurizing vessel was arranged so as to prevent direct contact with the atmosphere or with combustion gases high in oxygen, carbon dioxide or water. Under these conditions the slag picked up as much as 10.79% sulphur, and the pig iron had its sulphur content reduced to 0.03% sulphur, so that there was more than one hundred (in fact more than two hundred) times as high a sulphur percentage in the slag as in the pig iron after desulphurization. In other cases in which the pig iron initially contained only about 0.03% sulphur, the sulphur content of the pig iron was reduced to 0.002% sulphur and the slag picked up 0.11% sulphur. These results indicate that a very strong desulphurizing action is obtained in the above manner, and that the sulphur content of the iron may be reduced to less than one-half, or less than one-quarter, or even less than one-tenth of that in the iron before treatment by my invention.

Slags higher in lime than 45% may be used; for example, a slag containing

	Per cent
CaO	55
CaF ₂	33
SiO ₂	12

is a very efficient desulphurizer. It will be noted that this slag contains more than twice as much alkaline earth oxides as silica.

With rising lime content the viscosity of the slag increases and therefore excessive lime content is to be avoided. Where a lime fluorspar slag is to be employed, the lime content should be from 30% to 55%, the fluorspar content from 20% to 50% and the silica content from 5% to 25%. A desirable slag may contain lime in excess of 30%, fluorspar in excess of 20%, silica in excess of 5% and alumina from 1% to 5%, the composition being adjusted to make the slag freely flowing at 1200° C., or at least free-flowing at 1300° C. or 1400° C.

A study has been made of the use of soda slags as a substitute for lime slags. The desulphurizing action of soda, for example sodium carbonate, on pig iron is well known and this substitution can be made. It is found, however, that pure soda is readily attacked by carbon at temperatures of 1400° C. or even below, producing sodium vapor which is very effective in converting FeS into Na₂S and thus desulphurizing the pig iron. The sodium vapor causes difficulty in the handling of soda slags, and the reaction must be managed in such a way as to limit the forma-

tion of volatile soda derivatives in order to avoid excessive loss as fume. It is possible to use slags containing Na_2O , SiO_2 and Al_2O_3 with other oxides to overcome volatilization loss incident to sodium carbonate. Furthermore the revivification of soda slags to remove the sulphur and permit reuse presents special difficulties not present in the case of lime slags.

Detailed reference to the steps necessary when soda slags are used is therefore omitted, and the further discussion is generally confined to slags containing alkaline earth oxides as the preponderant active constituent. However, the use of slags containing soda or other alkali metal oxides as active desulphurizing ingredients, when used as substitutes for slags containing alkaline earth oxides such as lime as active ingredients, is claimed herein.

The quantity of oxides of the type R_2O in the slag should exceed 30% for best results.

Due to the cheapness and freedom from volatilization, it is preferable to use a lime slag, although such preference is subject to change under varying economic and metallurgical conditions.

In choosing the slag, it is desirable to have one which will be of low viscosity and workable at temperatures of 1400°C . and, for this purpose, the slag should preferably be freely fluid as low as 1200°C .

It is very advantageous to use a slag which shows a high ratio of sulphur concentration in the slag after use to sulphur concentration in the desulphurized or partially desulphurized pig iron. If, for example, 0.25% sulphur must be removed from the pig iron and if the slag will take up as much as 12.5% sulphur, then one ton of slag will desulphurize 50 tons of pig iron.

As noted in detail below, it is quite important to employ a slag which can be revived or treated to remove its sulphur so that it can be used over and over again. The lime slags referred to above fulfill this requirement.

The desulphurizing slag, after it has picked up, for example, 12% sulphur, is revived by removing the sulphur, until, for example, less than 1% sulphur remains. This revived slag is then used repeatedly to desulphurize further quantities of molten pig iron. The revivification of the slag may be accomplished in one of several ways discussed below.

Desulphurization

The pig iron used in the process will in most cases be pig iron produced in the coke blast furnace when operated under conditions of moderate temperature and moderate basicity of the slag suitable to produce pig iron at lower cost but with a higher sulphur content than that ultimately desired. The sulphur content of the pig iron produced in the coke blast furnace under such economical conditions may be 0.25%, 0.3% or even higher. Of course the invention may also be applied to pig iron of normal sulphur content, containing say 0.04% S. The pig iron is tapped from the coke blast furnace, and, of course, separated from the blast furnace slag at the time of tapping. The pig iron is then preferably brought at once into contact with the desulphurizing slag, while the pig iron is still molten from the blast furnace.

The actual desulphurization may, for example, be carried out in a vessel such as that shown in Figures 2 to 5, inclusive, which illustrate a ladle car of the general type disclosed in Pugh U. S.

Patent No. 1,534,187, granted April 21, 1925. The ladle car comprises a ladle body 20, covered with a metallic casing 21 having a cylindrical central portion 22 and conical end portions 23 and 24 which terminate in headers 25 and 26. The headers support trunnions 27, 27', 27², and 27³, which engage bearings 28, 28', 28², and 28³. The bearings 28, 28', 28², and 28³ are supported from a main frame 29, which in turn rests upon any suitable railway trucks 30 and 31, operating upon a track 32.

To permit tilting or rocking of the ladle car, the main frame 29 is bowed at 33. The hook of a crane may be engaged with the main frame, as at 34, to lift one side of the main frame, causing trunnions 27' to leave bearings 28' and eventually causing trunnions 27³ to engage bearings 28³. The lifting and lowering of one side of the main frame may be used to agitate the liquid contents of the ladle car, and may also be used in tapping the ladle car.

The means of rocking and tilting the ladle car need not be that shown, as any other suitable means may be employed. For example, the reaction vessel of the ladle car may be rotated by a conventional driving band and motor as shown, for example, in Hart U. S. Patent No. 1,916,170, granted June 27, 1933.

Inside the casing 21 is a lining 35 of suitable refractory material. It is contemplated that this will normally be a carbon refractory such as graphite, although any other suitable lining material, such as magnesite, for example, might be used. If carbon be used as a lining, it may be rammed in place with a tar binder or built into the desired form from blocks which have previously been fired.

Inlet to the ladle car is provided through a charging opening 36 which is engaged by a pouring head 37 detachably secured at 38 to the casing 21 and making a seal at 39 about the charging opening. The pouring head 37 desirably has a conical interior as shown in Figure 4. A runner or launder 40 suitably detachably connected to a coke blast furnace 41 enters the pouring head 37 at one side thereof as indicated at 42 so that pig iron flowing along the runner 40 enters the pouring head at 42 and receives a circular motion before entering the ladle car.

The discharge of slag from the ladle car is facilitated by a pouring spout 43 below the charging inlet. When the pouring spout is used, the ladle car will be tilted, and the pouring spout will normally be closed when not in use by a plug 44. The ladle car is provided with an inlet connection 45 for noncontaminating reducing gas as later described. A similar inlet opening 46 is desirably provided in the top of the pouring head so that a constant small escape of noncontaminating reducing gas takes place at the point 42 where the blast furnace runner enters the pouring head. The pouring head is equipped with lifting rings 47 to facilitate removal from the ladle car. When the pouring head is removed a door 48 is substituted to close the charging opening as shown in Figure 4a, and to prevent the introduction of air and gases of combustion high in oxygen, carbon dioxide or water vapor which would be oxidizing. Access to the interior of the ladle car for inspection purposes is provided through doors 21'.

Though not normally needed, the ladle car is equipped with suitable sets of electrodes 49 and 49' which may be connected to a suitable source of electrical energy to supply arc heating of the

ladle car. The electrodes are detachably connected to the ladle car, as at 50, and they may be removed and a door substituted to close the opening. In most cases no heating is necessary or desired, as the molten pig iron when charged into the ladle car has sufficient superheat to maintain itself freely molten during the desulphurization and to melt the slag where the slag is charged in solid form. Any other form of heating which is noncontaminating may be used instead of electric arc heating, if heating be desired.

It will of course be understood that, where an arc is not used, calcium carbide will not be formed in the slag.

An illustrative cycle of operations is indicated in Figure 6. The specific values given on this figure vary somewhat from those mentioned in other examples, and are given as a particular instance of the process, without intention to limit the disclosure.

The ladle car containing about 2.5 tons of molten slag, preferably slag which has previously been used to desulphurize a previous charge of molten pig iron, is filled with about 100 tons of molten pig iron from the coke blast furnace flowing through the blast furnace runner 40, and containing as much as 0.3% sulphur or more (say 0.26% sulphur). The molten slag is held in contact with the molten iron for as much as one hour or more until the sulphur content of the molten pig iron has fallen to about 0.03% sulphur to 0.10% sulphur (say 0.05% sulphur) and the sulphur in the slag has increased to perhaps 5% sulphur or a much higher figure (say 10.8% sulphur). With good operating conditions and efficient slags, as much as 12% sulphur can be built up in the slag with only 0.04% or 0.05% sulphur in the pig iron. It is desirable to have a high concentration of sulphur in the slag when the slag is to be revived since the amount of slag necessary is thereby reduced.

At this stage the slag is then removed from the ladle car by the pouring spout 43.

In the preferred process about 2.5 tons of a second slag similar in composition to the first slag are now added, and further desulphurization of the molten pig iron is accomplished. The pig iron and slag are maintained in contact with one another preferably for an additional hour or more, and the sulphur content of the metal may thereby be reduced to 0.015% sulphur, 0.01% sulphur or even less if desired. The sulphur content of the second slag may increase from a negligible quantity at the time it is charged to 1% sulphur or 2% sulphur or more. The molten iron is then separated from the second slag, as by tapping the second slag, then removing the molten iron, and then pouring back the second slag into the ladle car, or by retaining the molten slag in the ladle car during tapping of the iron, for example by submerging the pouring opening below the slag level before removing the plug from the pouring opening and then retaining the slag level above the pouring opening during pouring from the ladle car.

The ladle car is then returned to a source of high sulphur pig iron to receive a further charge of say 100 tons, and the further charge is desulphurized by a first treatment with the slag which was used as the second slag on the previous charge, removal of the high sulphur slag produced thereby, addition of fresh slag and so on.

It will of course be understood that a stationary

ladle, mixer or furnace can be employed, if it is suitably equipped to maintain sufficiently reducing conditions and, in the preferred process, exclude oxidizing gases such as free oxygen, predominantly oxidizing oxides of carbon and water vapor in high concentration.

The amount of slag required per ton of pig iron desulphurized will depend on the amount of sulphur to be removed from the pig iron and the amount of sulphur picked up by the slag. If, for example, a high sulphur pig iron containing 0.26% sulphur is desulphurized to 0.015% sulphur, then, for every 100 tons of pig iron, 0.245 ton of sulphur must be taken up by the slag. If the slag picks up 9.8% sulphur, 2.5 tons of slag will be necessary to treat 100 tons of pig iron.

In desulphurizing high sulphur pig iron, a stepwise process as described above is quite efficient since it removes the sulphur with a smaller amount of slag, and necessitates regeneration of a smaller amount of slag for further desulphurization. For efficient desulphurization the ratio of the percentage of sulphur in the slag to the percentage of sulphur in the pig iron after desulphurization may be as much as 250 to 1 or even a higher ratio. Thus a desulphurizing slag in contact with molten pig iron having 0.015% sulphur might have picked up 2.5% sulphur from the pig iron (corresponding to about 6% calcium sulphide). If 100 tons of iron were being treated to remove 0.25 ton of sulphur, 10 tons of slag might be needed if the desulphurization were done in a single step.

If the pig iron were desulphurized in a stepwise process as shown in Figure 6, reducing the sulphur first to about 0.05% sulphur and separating a sulphur-rich slag containing 10.8% sulphur, then adding a second and fresh slag to remove the balance of the sulphur in the iron down to 0.015% sulphur, then separating the iron from the second slag containing about 2.4% sulphur (corresponding to about 6% calcium sulphide) for use in the preliminary treatment of the next charge of sulphur-rich pig iron as above described, the removal of 0.245 ton of sulphur from 100 tons of iron can be accomplished with only 2.5 tons of slag, although 3.5 tons of slag, or more, may be used.

By stepwise treatment it is possible to reduce the sulphur content of molten pig iron from a value in excess of 0.10%, say 0.3%, to less than 0.01%, in one or two hours, by slags which aggregate less than 8% and generally not more than 5% of the weight of the pig iron.

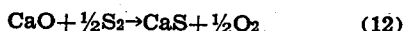
For best results the slag used should be very liquid at the temperature prevailing. It was found that 1400° C. was an economical and desirable temperature, although higher or lower temperatures may be used. If the slag flows freely at 1200° C., it will of course be very liquid at 1400° C. A very satisfactory slag may contain CaO 45%, CaF₂ 40% and SiO₂ 15%. In order to lower the slag fusion point, a little alumina may be added, for example using a composition of CaO 43%, CaF₂ 38%, SiO₂ 14% and Al₂O₃ 5%. With a slag of the character of one of those just noted, it is possible to absorb 10% or more of sulphur in the slag, and, under favorable conditions, to obtain a ratio of the percentage of sulphur in the slag to the percentage of sulphur in the iron at the end of desulphurization exceeding 250 to 1.

In the case of a lime slag, sulphur is retained

in the slag as calcium sulphide. Iron sulphide present in the iron phase dissociates:



5 The sulphur reacts with the lime or other R_2O oxide of the slag thus:



To drive the above reaction to the right and desulphurize the pig iron it is necessary to keep the oxygen activity low by reducing agents. The high carbon content of the pig iron itself has some reducing action, and it is decidedly preferable to desulphurize the iron while it still has its pig iron carbon content to aid in reduction than at a later stage when its carbon content has been lowered, for example to that of steel.

It is preferable to employ a carbon lining in the ladle car, and this serves to assist materially in maintaining reducing conditions. It is also very desirable where a carbon lining is used, and much more important where a carbon lining is not used, to introduce coke or charcoal into the slag, maintaining a substantial body of carbon floating on the molten pig iron. In the slag 51 floating on the molten pig iron 52 carbon is seen at 53.

The carbon lined ladle car is desirably so constructed as to positively exclude oxidizing gases, such as air, predominantly oxidizing mixtures of oxides of carbon, or water vapor, for example from products of fuel combustion. Exclusion is accomplished not only by the closed construction of the ladle car, but also by the pouring head 37, and the door 48 when the pouring head is not in place.

As a further assurance against introduction of air, oxidizing mixtures of oxides of carbon or water vapor into the interior of the ladle car, and as a protection against burning of the carbon lining, it is possible to introduce a noncontaminating reducing gas into the ladle car and also into the pouring head. The gas should suitably be maintained at superatmospheric pressure so that leakage through the inevitable cracks in the structure will be outward. The gas may suitably comprise carbon monoxide or a mixture of carbon monoxide, carbon dioxide and nitrogen which is preponderantly reducing due to the large proportion of carbon monoxide compared to carbon dioxide. Such a reducing gas consisting of a preponderantly reducing content of carbon monoxide, a small quantity of carbon dioxide whose oxidizing effect is more than overcome by the carbon monoxide and a large inert content of nitrogen may be obtained from the coke or charcoal gas producer. Where steel is to be made, hydrocarbon reducing gases may be used without harm.

If other reducing agents than carbon be desired to remove oxygen in Reaction (12), calcium carbide, ferro-silicon, or other reducing ferro-alloys may be added to the slag. The lower the oxygen activity, the higher the possible ratio of sulphur in the slag to sulphur in the pig iron at the end of desulphurization, the more complete the desulphurization and the more rapid the reaction.

To facilitate the desulphurization, agitation of the metal and slag may be used. Such agitation may be produced by rocking or rotating the ladle car, by raising and lowering one end of the ladle car as though running the car over an uneven track, introducing wood poles or rabbles into the ladle, blowing reducing gas such as carbon monoxide or hydrocarbons (where steel is to be made) through the molten mass, etc.

The presence of an excess of carbon monoxide at the point of desulphurization is of course assured by blowing a gas containing carbon monoxide upon or into the molten charge, although the same result is obtained by maintaining an excess of carbon in contact with the molten pig iron and/or slag, or by maintaining carbon monoxide gas on the surface of the molten charge.

The gas used either on the surface of the molten charge or to blow through it may be coke or charcoal producer gas which contains a predominantly reducing mixture of oxides of carbon plus nitrogen.

The desulphurized pig iron from the ladle car may be used in any form in which pig iron is suitably employed, as for example for gray iron or malleablized castings, etc. It is contemplated, however, that a large part of the desulphurized pig iron will be used in steel-making furnaces for the production of steel in much the same manner that the conventional low sulphur product of the coke blast furnace is now used.

Where steel is made, the economy in production of the raw material will effect an over-all economy in the steel process. A further important advantage in steel making is that it will in no case be necessary to take any precautions in steel making to eliminate sulphur, as is sometimes necessary when the blast furnace pig iron runs excessively high in sulphur. This is of especial importance in the manufacture of electric steel, in which case sulphur elimination takes a substantial part of the time and contributes to the cost. Nor will it be necessary to reject certain ores or coke on account of the sulphur content when smelting pig iron for steel-making purposes.

The detail of the refining of the pig iron to make steel is not part of this invention, and the desulphurized pig iron may be used in the acid or basic open hearth, the electric furnace, the Bessemer converter or in any other suitable manner to produce steel.

Revivification

There are several ways of revivifying the desulphurizing slag of the invention to lower its sulphur content so that the slag may be used again to desulphurize a further charge of pig iron, and so that the sulphur may be recovered. It is contemplated that the desulphurizing slag may be used repeatedly to treat further quantities of pig iron, with revivification when the sulphur content becomes so high that further desulphurization is impeded, and with addition of fresh slag when the losses of slag necessitate augmenting the quantity. It will be noted that, in accordance with the invention, the conditions are always reducing when the desulphurizing slag is in contact with the molten pig iron, thus minimizing the picking up of phosphorus, manganese, etc., by the slag. If the slag were in contact with the iron when oxidation was possible, pick-up of phosphorus, manganese, etc., by the slag would be excessive. Naturally, a substantial pick-up of phosphorus, for example, would render the slag unusable even though it were revived to lower its sulphur content, and therefore it is important to avoid having contact between the molten pig iron and the desulphurizing slag under unsuitable oxidizing conditions.

The slag is revived while it is out of contact with the molten pig iron, and preferably after separation from the desulphurizing vessel, as revivification involves oxidizing reactions which would be harmful to desulphurization.

It is preferred to effect the revivification by the principles underlying the process of Claus and Chance as used for removing the sulphur from calcium sulphide present in tank wastes produced in the Le Blanc soda process. See George Lunge, Sulphuric Acid and Alkali (D. Van Nostrand Co., N. Y., 1909) volume 2, part 2, page 943 et seq. This revivification process applies to slags containing any of the alkaline earth sulphides, but calcium sulphide, being the cheapest, is referred to below in the specific example. In accordance with this process the desulphurizing slag containing perhaps 35% of calcium sulphide is reduced to a fine powder, preferably to a state of subdivision such that it will pass through a 50 mesh per linear inch (387.5 mesh per square centimeter) screen. It is of course possible to reduce the slag to a powder by crushing and grinding and such a step is indicated on the process chart of Figure 6. It has been found, however, that it is a great convenience and economy to use a slag which is self-disintegrating, due to the volume changes which the alkaline earth silicates undergo when slowly cooled. The slag comprising

	Percent
CaO-----	45
CaF ₂ -----	40
SiO ₂ -----	15

is self-disintegrating, as it breaks up into a fine powder when cooled slowly to room temperature. The following slag is also self-disintegrating

	Percent
CaO-----	55
CaF ₂ -----	33
SiO ₂ -----	12

as are also the slags having compositions between those of the two examples just given. Self-disintegration of desulphurizing slags has been noticed in the case of the high lime-fluorspar slags used in the electric steel furnace.

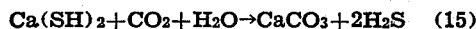
However the slag may be reduced to a powder, whether by crushing and grinding or by self-disintegration, it is next mixed with water to form a slurry. The slurry is then subjected to the action of carbon dioxide gas, and undergoes the following reactions



The hydrogen sulphide liberated may then react



Further treatment with carbon dioxide causes the reaction



Any suitable source of carbon dioxide may be employed. As a source of carbon dioxide which is very convenient and economical at an iron or steel plant, it is preferred to use the products of combustion issuing from furnaces employing blast furnace gas as fuel. For example, the products of combustion from the hot blast stoves used in preheating the air for blast furnaces may very conveniently and cheaply be employed. It is desirable that these gases contain as much carbon dioxide as is convenient. Any sulphur dioxide in these gases should be taken into account, but small quantities of sulphur dioxide are not seriously objectionable.

The products of combustion should be substantially cooled before being introduced into the slurry, to prevent difficulty through the production of steam in the revivification system.

The products of combustion are preferably blown or bubbled through the slurry in cast iron vessels such as are shown in Figure 7. Each of the vessels 54, 55, 56, 57, 58, 59, and 60 is a separate cylindrical tank about 3 feet (0.9 meter) in diameter and 15 feet (4.6 meters) tall. It is preferable to use about seven such tanks in conjunction, the exit gases from the tank receiving the gases rich in carbon dioxide passing through a series of other tanks to effect the desired reactions.

Each tank has a nitrogen cycle and a hydrogen sulphide cycle. During the operation of a given tank as the first tank in the train, the exit gases from this tank are initially nitrogen, which is inert, excess carbon dioxide and hydrogen sulphide produced by Reactions (13) and (15). These gases are passed into other tanks where both hydrogen sulphide and carbon dioxide are absorbed, until the final exit gas is substantially nothing but nitrogen, which can be exhausted. As the gas treatment continues, a stage is reached in one of the tanks in which the exit gases are rich in hydrogen sulphide and low in carbon dioxide. Such gases may be withdrawn and utilized for their sulphur content.

After sufficient carbon dioxide has been absorbed in a particular tank to complete Reactions (13), (14), and (15), the slurry may be withdrawn from this tank and the gas rich in carbon dioxide may be applied to another tank. The slurry withdrawn from the first tank will be found to contain less than 1% of sulphur.

At any time, gas rich in carbon dioxide enters the tanks of Figure 7 through the inlet pipe 61 and the exit gases leave through the outlet pipe 62. An inlet header 63 runs across all of the tanks and may be used to carry gas rich in carbon dioxide to any of them. Each tank is equipped with a down-flow pipe 64, 65, 66, 67, 68, 69, or 70, extending from the inlet header 63 to the bottom of the tank. Each tank also has at its top an up-flow pipe 71, 72, 73, 74, 75, 76, or 77, which joins the inlet header 63.

From the up-flow pipe of each tank to the down-flow pipe of the next tank is a cross-connection 78, 79, 80, 81, 82, 83, or 84 (the cross-connection 84 is a long pipe extending across the back of the tanks in Figure 7). The various elbows and T's are provided with suitable cap-flanges to permit ready access to the pipes.

Numerous valves are placed to permit change in the direction of gas flow. Between the junction with each downflow pipe and the junction with the next up-flow pipe, the inlet header 63 has a valve 85, 86, 87, 88, 89, 90, or 91. Between its junction with the inlet header 63 and its junction with its cross-connection, each down-flow pipe has a valve 92, 93, 94, 95, 96, 97, or 98. The inlet 61 lies between the valves 85 and 92. Between its junction with the inlet header 63 and its junction with its cross-connection, each up-flow pipe has a valve 99, 100, 101, 102, 103, 104, or 105. Each cross-connection 78, 79, 80, 81, 82, or 83 has a valve 106, 107, 108, 109, 110, or 111, while the cross-connection 84 has two valves 112 and 113. Each tank is connected with the outlet 62 through a valve 114, 115, 116, 117, 118, 119, or 120.

If it be assumed that the tank 60 is out of service, having its revivified slag removed, for example by taking off a cap-flange at the bottom, permitting air to enter at the top, and allowing the slurry to flow into any suitable drainage system, the tanks may operate as follows. Gas high

in carbon dioxide entering through the inlet 61 takes a route through valve 92 and down-flow pipe 64 into the bottom of tank 54 and bubbles up through tank 54.

5 A mixture of carbon dioxide, hydrogen sulphide and nitrogen may issue from tank 54. This gas is passed by up-flow pipe 71, cross-connection 78, including valve 106 in open position, and down-flow pipe 65 into the bottom of tank 55. Most of the carbon dioxide and hydrogen sulphide are absorbed in tank 55, but the gas is passed through up-flow pipe 72, cross-connection 79, including valve 107 in open position, and down-flow pipe 66 into the bottom of tank 56.

15 In tank 56 the remainder of the carbon dioxide and hydrogen sulphide are absorbed, and the effluent gas is substantially nitrogen, which passes through valve 116 into outlet 62. During the nitrogen cycle this effluent is allowed to escape.

20 As the blowing of tank 54 continues, more hydrogen sulphide passes over into tanks 55 and 56, and eventually the quantity of hydrogen sulphide in the effluent gas from tank 56 becomes appreciable. At this point, the effluent gas is led through tank 57 by closing valve 116 and directing the gas through up-flow pipe 73, cross-connection 80 (valve 108 in open position) and down-flow pipe 67 into the bottom of tank 57, and then by outlet valve 117 into outlet 62.

25 With increase in the hydrogen sulphide content of the effluent gas from tank 57, it may be desirable to add tank 58 to the train by closing outlet valve 117 and opening cross-connection valve 109 and outlet valve 118.

35 As the blowing of tank 54 proceeds further, the effluent gas from tank 56 (which is being carried to tanks 57 and 58) reaches such a high concentration of hydrogen sulphide that it can be utilized to recover the sulphur. This is the end of the nitrogen cycle and the beginning of the hydrogen sulphide cycle. Tanks 57 and 58 are cut out of the train by opening outlet valve 116 and closing cross-connection valves 108 and 109 and outlet valve 118. The outlet 62 is connected to suitable storage or recovery mechanism.

45 As the blowing of tank 54 continues still further, the hydrogen sulphide content of the effluent gas from tank 56 decreases and carbon dioxide begins to come over into the effluent gas from tank 56. This is the end of the hydrogen sulphide cycle and the beginning of another nitrogen cycle. Other tanks are then put back in train, for example by opening valves 108, 109, and 118, and closing valve 116.

55 Finally the contents of tank 54 are completely revived and gas rich in carbon dioxide is led to tank 55 by closing valves 92 and 106 and opening valves 85 and 93. Tank 54 can now be emptied and refilled with slurry to be revived. At the proper times in the cycle for tank 55, tank 59 is added to the train.

60 In general, other valves not mentioned during the above discussion are kept closed until it is necessary to open them when other tanks are in service.

65 The above discussion is merely illustrative of one manner of using the tanks, and is not intended to limit the disclosure, as other apparatus may be employed or this apparatus may be used in other ways.

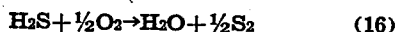
70 The revived slag can be removed from the tank in which the process is completed, filter pressed or run through a Dorr thickener or similar apparatus, dried and used for further desulphurization of additional charges of pig iron.

The drying may be done in a rotary drier if desired and the charge issuing from the drier may attain temperatures approximating 1000° C. At these temperatures, calcium carbonate is changed to calcium oxide. This hot discharge material can be placed in suitable containers to conserve its heat content and used as a desulphurizing slag for more pig iron.

10 It will be evident that the compounds used to revivify the slag in accordance with the above processes, namely water and carbon dioxide, are the very substances whose presence in substantial quantities is undesirable during desulphurization and which are preferably excluded from the desulphurizing vessel.

15 The point at which the slag is desulphurized will depend, of course, upon the exact process used. If the desulphurization is to be accomplished in stepwise manner, each desulphurizing slag is used twice, as a second slag on one charge and a first slag on the next charge, before it is revived. It would of course be possible to use the same slag three or a greater number of times before revivification, but this would complicate the process. In any case, when the sulphur content of the slag reaches a predetermined value, the slag is separated from the molten pig iron and revived.

20 The gas rich in hydrogen sulphide obtained from revivification may be used for its sulphur content. For example, it may be burned to sulphur dioxide by mixing it with sufficient air, and the sulphur dioxide may be made into sulphuric acid or other suitable compounds. Or, in the presence of a suitable catalyst, the hydrogen sulphide may be burned directly to sulphur trioxide. The hydrogen sulphide may also be converted into elemental sulphur by combustion with the required amount of air in accordance with the following reaction:



40 Whether the sulphur be changed to sulphuric acid, recovered as elemental sulphur or in some other form, the value of the resulting product may be credited against the cost of revivifying the slag, and may in some cases more than pay for the cost of revivification.

45 Figure 6 shows, by way of example, a series of steps which may be employed in the process. The ladle shown at the top of the chart may suitably contain 100 tons of molten pig iron of say 0.26% sulphur content. Into the ladle is charged about 2.5 tons of a first lime-fluorspar desulphurizing slag containing about 2.40% sulphur (corresponding to about 6% calcium sulphide). This high sulphur content is due to previous desulphurizing use of the slag subsequent to revivification. After suitable contact between the molten pig iron and the first desulphurizing slag in the ladle, the slag is separated from the pig iron. The first slag now contains, for example, 10.8% sulphur.

50 The slag is now ground to say 50 mesh per linear inch or allowed to self-disintegrate by slow cooling and pre-selection of the proper composition. The ground slag is then mixed with water to form a slurry and treated with a gas high in carbon dioxide, by which the slag is revived, and hydrogen sulphide gas driven off. The hydrogen sulphide gas may be burned in a suitable furnace to liberate sulphur, or, in the alternative, to form sulphur dioxide. The revived slurry is next dewatered and calcined to 55

produce a revived slag containing, say, 1% of sulphur.

The revived slag is then supplied to a subsequent charge in the ladle and there used as a second slag for treating pig iron which was initially desulphurized with a previous slag. The pig iron before treatment with the second slag may have a sulphur content of say 0.05% sulphur, but after treatment with the second slag its sulphur content will drop to perhaps 0.015% sulphur. The sulphur content of the slag, in the meantime, will increase from about 1% to about 2.40%. This second slag is then available for use as a first slag to treat a new charge of pig iron.

Through both of the desulphurizing treatments, the ladle is maintained under reducing conditions by the presence of carbon and desirably also by the positive exclusion of the atmosphere and combustion gases high in carbon dioxide and water vapor. The mixture of oxides of carbon present in the ladle is predominantly reducing due to the excess of carbon, and also desirably due to the introduction of harmless reducing gases at superatmospheric pressure.

It is contemplated that there will be certain losses of slag during the desulphurizing process, and that certain small amounts of impurities may be picked up, both of which features will necessitate additions of fresh slag-making materials from time to time. By the use of proper refractories in the ladle car, by the maintenance of reducing conditions when the slag is in contact with the molten pig iron, and by suitable treatment with carbon dioxide followed by proper processing of the slurry produced in that operation, the fresh slag-making materials required can be kept to a minimum in order to effect, to the fullest extent, the economies made possible by repeated use of the slag.

One process of revivifying the slag by driving off the sulphur as a volatile sulphur component in the form of hydrogen sulphide has just been discussed. This process may be varied by treating the powdered slag at higher temperature with steam and carbon dioxide gas, instead of carrying out the process by treating a slurry at moderate temperature.

There are a number of other processes by which revivification may be accomplished. For example, as indicated in Figure 6a, sulphur may be removed from the slag directly as sulphur dioxide gas, by maintaining the high-sulphur slag molten and at high temperature after it is removed from the ladle car and blowing air or oxygen through the slag. In this way sulphur dioxide will form readily and the sulphur content of the slag may be effectively reduced.

Another process of revivifying the slag, as shown in Figure 6b, is to allow it to cool, and reduce it to a fine powder, as by self-disintegration or by crushing and grinding. A portion of the slag is then roasted in a conventional furnace used for roasting sulphides, desirably to a temperature of about 1000° C. Calcium sulphide is thereby changed to calcium sulphate and some of the sulphur is driven off as sulphur dioxide.

The slag containing calcium sulphate is then mixed with a theoretical quantity of unroasted slag and melted to cause calcium sulphide and calcium sulphate to react:



This reaction is carried out with the slag in molten condition at about 1200° C. to 1400° C. In

this way the greater part of the sulphur from the sulphur-rich slag is driven off as sulphur dioxide, and may be used for manufacturing sulphuric acid or in other suitable manner.

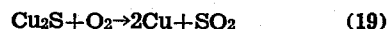
A serious difficulty with both of the last-mentioned processes for revivifying the desulphurizing slag is that they require that the slag be maintained molten under oxidizing conditions. Slags high in lime and calcium fluoride are rather corrosive to refractories other than carbon and; while carbon may be used in the ladle car under reducing conditions, it may not be used in operations involving the volatilization of sulphur dioxide where oxidizing conditions are necessary. It is therefore obligatory to have recourse to magnesite and similar refractories, and magnesite brick may be attacked by the slag.

Another process for revivifying the slag, as indicated in Figure 6c, involves the conversion of the sulphur in the slag to a metal sulphide capable of forming a molten phase immiscible with the molten slag, known as a matte. Copper is a suitable matte-forming metal; nickel might also be used. A sulphide of the type R_2S reacts with a matte-forming metal thus



Molten slag is brought into contact with molten copper, preferably at about 1200° C. and sufficient oxidation is brought about, as for example by blowing air mildly into the copper. Cuprous sulphide forms and enters the layer of copper below the slag. The revived slag may subsequently be separated from the matte and used for desulphurizing a further charge of pig iron.

The sulphur picked up by the copper may be eliminated by intensive oxidation of the matte through vigorous blowing with air, as for example in the conventional copper matte converter:



After removal of the sulphur from the copper, the copper bath may be used to desulphurize more slag.

The decision as to whether to revivify the slag by a wet process at low temperatures to eliminate hydrogen sulphide or by a dry process at high temperatures will depend upon the factors prevailing in individual cases. It is considered, however, that the wet process will be more economical in many instances.

Numerous examples have been given herein to aid in practicing the invention. It is not intended, however, to limit the disclosure by reason of the inclusion of these examples except where limitations are included in the claims or indicated by the specification to be essential.

In view of my invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of my invention without copying the structure shown, and I, therefore, claim all such in so far as they fall within the reasonable spirit and scope of my invention.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. The process of producing desulphurized pig iron, which comprises smelting the iron in a coke blast furnace under conditions of temperature and basicity of the slag suitable to produce pig iron at lower cost but with a higher sulphur

content in the iron than that ultimately desired, transferring the pig iron from the blast furnace to a vessel lined with carbon, maintaining the pig iron molten in the vessel free from the application of additional heat, and treating the molten pig iron in the vessel to reduce its sulphur content with a basic slag under reducing conditions while positively protecting the slag from oxidizing gases.

2. The process of desulphurizing pig iron, which comprises smelting it in a coke blast furnace under conditions which produce a substantially higher sulphur content than that ultimately desired, transferring the pig iron from the coke blast furnace and subsequently subjecting the molten pig iron without application of additional heat under reducing conditions to a basic slag containing fluorspar and lime totalling more than 50%, the lime alone being not more than 55%, silica and a substantial quantity of sodium oxide.

3. The process of producing pig iron of low sulphur content, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace, and treating the pig iron in a vessel in the presence of an excess of solid carbon free from substantial additions of oxidizing substances, with a desulphurizing agent containing calcium oxide, not more than 55%, fluorspar and silica, the fluorspar and silica totalling more than 25%, while maintaining the pig iron molten without the application of additional heat and without forming calcium carbide in the slag.

4. The process of producing pig iron of low sulphur content, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace, and desulphurizing the pig iron in a vessel in the presence of an excess of solid carbon, free from substantial additions of oxidizing substances, with a slag containing calcium oxide, calcium fluoride and silica and capable of removing the sulphur from the pig iron until not more than 0.015% of sulphur remains, while maintaining the pig iron molten at a temperature of 1400° C. or less, without the application of additional heat and without forming calcium carbide in the slag.

5. The process of producing pig iron of low sulphur content, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace, desulphurizing the pig iron in a vessel in the presence of an excess of solid carbon, free from substantial additions of oxidizing substances, with a slag containing calcium oxide, not more than 55%, calcium fluoride and silica, the calcium fluoride and silica totalling more than 25%, until the sulphur percentage in the slag is more than 250 times the sulphur percentage in the pig iron and maintaining the pig iron molten during the desulphurization at a temperature of 1400° C. or less without the application of additional heat and without forming calcium carbide in the slag.

6. The process of producing desulphurized pig iron, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace and desulphurizing the pig iron in

a vessel in the presence of an excess of solid carbon by a slag containing between 30% and 55% of calcium oxide, between 20% and 50% of fluorspar and between 5% and 25% of silica, while maintaining the pig iron molten without the application of additional heat and without forming calcium carbide in the slag.

7. The process of producing desulphurized pig iron, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace and treating the pig iron in a vessel with a desulphurizing agent containing fluorspar and silica, the fluorspar and silica totalling more than 25%, together with a substantial amount and not more than 55% of calcium oxide and another oxide of the type R_xO , where R is a metal of the group consisting of alkaline earth metals and alkali metals and x is a numeral determined by the valence of the metal, in the presence of an excess of solid carbon, until the sulphur content of the slag formed during the treatment exceeds 2.5% sulphur, while maintaining the pig iron molten during the treatment without the application of additional heat and without forming calcium carbide in the slag.

8. The process of producing desulphurized pig iron, which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace, maintaining the pig iron molten at a temperature below the blast furnace tapping temperature and in a vessel free from the application of additional heat, desulphurizing the pig iron in the vessel in the presence of solid carbon under strictly deoxidized conditions by a slag containing between 30% and 55% of calcium oxide, between 20% and 50% of fluorspar and between 5% and 25% of silica, and agitating the molten reactants during desulphurization.

9. The process of desulphurizing pig iron, which comprises treating a charge of pig iron in molten condition with a slag comprising between 30% and 55% of lime, between 20% and 50% of fluorspar and between 5% and 25% of silica which removes sulphur from the pig iron until the slag contains more than 5% sulphur, separating the slag from the molten pig iron, and treating the slag to lower its sulphur content while the slag is out of contact with molten pig iron.

10. The process of desulphurizing molten pig iron produced in a coke blast furnace, which comprises treating molten pig iron external to the coke blast furnace with a slag comprising between 30% and 55% of calcium oxide, between 20% and 50% of calcium fluoride and between 5% and 25% of silica, separating the sulphur-bearing slag from the desulphurized pig iron, treating the sulphur-bearing slag to lower its sulphur content and reusing the slag for desulphurizing a further charge of pig iron.

11. The process of desulphurizing pig iron, which comprises treating a charge of pig iron in molten condition in a carbon lining of a desulphurizing vessel with a slag which removes sulphur, concurrently excluding the atmosphere by a noncontaminating reducing gas, separating the slag from the molten pig iron, treating the slag to lower its sulphur content while the slag is out of contact with the molten pig iron and reusing the slag to desulphurize a further charge of pig iron.

12. The process of desulphurizing pig iron, which comprises treating a charge of pig iron in molten condition in a carbon lining of a desulphurizing vessel, with a slag which removes sulphur, concurrently excluding the atmosphere by carbon monoxide at superatmospheric pressure, separating the slag from the molten pig iron, treating the slag to lower its sulphur content while the slag is out of contact with the molten pig iron and reusing the slag to desulphurize a further charge of pig iron.

13. The process of desulphurizing pig iron, which comprises successively subjecting it in molten condition after it leaves the blast furnace to desulphurizing slags comprising between 30% and 55% of calcium oxide, between 20% and 50% of calcium fluoride and between 5% and 25% of silica and of progressively decreasing sulphur content and regenerating each of the slags when its sulphur content attains a percentage of sulphur in excess of 5%.

14. The process of desulphurizing pig iron, which comprises treating molten pig iron under reducing conditions with a basic slag capable of removing sulphur, separating the slag from the pig iron, revivifying the slag to permit its reuse for desulphurizing more pig iron and recovering the sulphur of the slag as elemental sulphur.

15. The process of desulphurizing pig iron, which comprises treating molten pig iron containing more sulphur than is desired under reducing conditions with a basic slag capable of removing sulphur while protecting the pig iron and slag from free oxygen, carbon dioxide and water vapor, separating the slag from the desulphurized pig iron, treating the sulphur-bearing slag in the presence of the carbon dioxide and water to remove its sulphur content and reusing the slag to desulphurize a further charge of pig iron.

16. The process of desulphurizing pig iron, which comprises treating the pig iron under reducing conditions with a lime slag which is fluid at 1200° C., the composition of the slag being adjusted so that the slag will self-disintegrate when it solidifies and cools, withdrawing the slag from the pig iron and allowing it to disintegrate and treating the slag with water and carbon dioxide to eliminate the sulphur and render the slag available for reuse.

17. In the manufacture of steel, the process which comprises smelting iron ore under conditions which produce pig iron having a substantially higher sulphur content than that ultimately desired, tapping the pig iron from the blast furnace, desulphurizing the pig iron in a vessel under strictly deoxidized conditions by a slag containing between 30% and 55% of calcium oxide, between 20% and 50% of fluorspar and between 5% and 25% of silica until the sulphur content of the pig iron is not more than 0.015%, while maintaining the pig iron molten at a temperature below the pig iron tapping temperature, without the application of additional heat and without forming calcium carbide in the slag, and then charging the pig iron into a steel making furnace for conversion into steel.

18. The process of producing desulphurized pig iron, which comprises smelting iron in a coke blast furnace under conditions which produce pig iron having a higher sulphur content than that ultimately desired, treating the molten pig iron under reducing conditions with a basic slag capable of taking up sulphur, separating the slag

from the iron, bringing the slag into contact with molten copper under mildly oxidizing conditions, separating the slag from the molten copper and vigorously oxidizing the copper to remove the sulphur.

19. The process of producing steel, which comprises smelting iron in a coke blast furnace under conditions which produce a substantially higher sulphur content than the sulphur content ultimately desired, transferring the pig iron excessively high in sulphur from the coke blast furnace, subsequently treating the molten pig iron direct from the coke blast furnace with a basic lime slag capable of removing sulphur from the pig iron in a carbon lining and in the absence of oxidizing gases, transferring the pig iron to a steel-making furnace and there changing it into steel, revivifying the slag to reduce its sulphur content and reusing the slag to desulphurize a further charge of pig iron.

20. The process of producing steel, which comprises smelting iron in a coke blast furnace under conditions which produce a substantially higher sulphur content than the sulphur content ultimately desired, transferring the pig iron excessively high in sulphur from the coke blast furnace, subsequently treating the molten pig iron under predominantly reducing conditions in the presence of an excess of carbon with a basic slag comprising between 30% and 55% of calcium oxide, between 20% and 50% of calcium fluoride and between 5% and 25% of silica, capable of absorbing sulphur until the sulphur content of the slag exceeds 5%, transferring the pig iron to a steel-making furnace and there changing it to steel, revivifying the slag to reduce its sulphur content and reusing the slag to desulphurize a further charge of pig iron.

21. The process of revivifying a pig iron desulphurizing slag containing a substantial amount of calcium sulphide or similar alkaline earth sulphide, which consists in treating the slag after separation from the molten pig iron with water and carbon dioxide, thereby eliminating the sulphur as hydrogen sulphide.

22. The process of revivifying a pig iron desulphurizing slag containing a substantial amount of calcium sulphide or similar alkaline earth sulphide, which comprises reducing the slag to a powder, mixing the slag with water and subjecting the mixture of water and powdered slag to the action of carbon dioxide gas.

23. The process of revivifying a pig iron desulphurizing slag containing a substantial amount of calcium sulphide or similar alkaline earth sulphide which comprises reducing the slag to a powder, mixing the slag with water and subjecting the mixture of water and powdered slag to the action of the products of combustion of blast furnace gas.

24. The process of revivifying a pig iron desulphurizing slag containing a substantial amount of calcium sulphide or similar alkaline earth sulphide, which consists in treating the slag with the products of combustion of blast furnace gas.

25. The process of revivifying a pig iron desulphurizing slag containing an alkaline earth sulphide which comprises reducing the slag to a powder by self-disintegration, making the slag into a slurry with water, bubbling gas containing carbon dioxide through the slurry, and de-watering and drying the slurry.

26. The process of revivifying a pig iron desulphurizing slag containing an alkaline earth

sulphide which comprises treating the slag with carbon dioxide and water to generate hydrogen sulphide, and burning the hydrogen sulphide with sufficient air to produce sulphur dioxide.

27. The process of revivifying a pig iron desulphurizing slag containing an alkaline earth sulphide, which comprises treating the slag with carbon dioxide and water to generate hydrogen sulphide, and burning the hydrogen sulphide with the required amount of oxygen to liberate elemental sulphur.

28. The process of revivifying pig iron desulphurizing slag containing alkaline earth or alkali sulphides, which comprises bringing the slag in molten condition into contact with a matte-forming metal under mildly oxidizing conditions, in separating the slag from the metal, removing the sulphur from the matte and reusing the metal for the desulphurization of further slag.

29. In the process of revivifying a sulphur-containing slag, the step which consists in removing sulphur from the slag by contact with a matte-forming metal.

30. In the process of revivifying a sulphur-containing slag, the step which consists in removing sulphur from the slag by bringing the slag into contact with molten copper.

31. A basic desulphurizing slag comprising lime, fluorspar and silica, which is free flowing above 1200° C. and which contains more than 5% of sulphur after use for desulphurizing pig iron.

32. A basic desulphurizing slag comprising principally lime, fluorspar and silica, which is free flowing above 1200° C. and which contains more than 2.5% of sulphur after having been used for desulphurizing pig iron, and is substantially free from calcium carbide.

33. A slag which has been used for desulphurizing pig iron comprising from 30% to 55% of lime, from 20% to 50% of fluorspar and from 5% to 25% of silica, and more than 2.5% sulphur, substantially free from calcium carbide.

34. A slag which has been used for desulphurizing pig iron comprising about 45% of lime, about 40% of fluorspar, about 15% of silica, and more than 2.5% sulphur.

35. A slag which has been used for desulphurizing pig iron comprising lime in excess of 30%, fluorspar in excess of 20%, silica in excess of 5%, alumina from 1% to 5%, and more than about 2.5% of sulphur, substantially free from calcium carbide.

36. The process of producing desulphurized pig iron which comprises smelting iron ore to produce pig iron containing more sulphur than the content ultimately desired, removing the pig iron from the blast furnace, subsequently maintaining the pig iron molten in a vessel lined with refractory containing magnesia as its principal ingredient free from the application of additional heat and treating the pig iron in the vessel as a wholly separate operation subsequent to the production of the pig iron under reducing conditions with a slag containing fluorspar not less than 20%, lime in an amount exceeding the fluorspar but not more than 55% together with silica and another oxide, in addition to the lime, of the type R_xO , where R is a metal of the group consisting of alkaline earth metals and alkali metals and x is a numeral determined by the valence of the metal, until the sulphur content of the slag formed during the treatment exceeds 2.5% sulphur.

RUSSELL PEARCE HEUER.