

Feb. 26, 1952

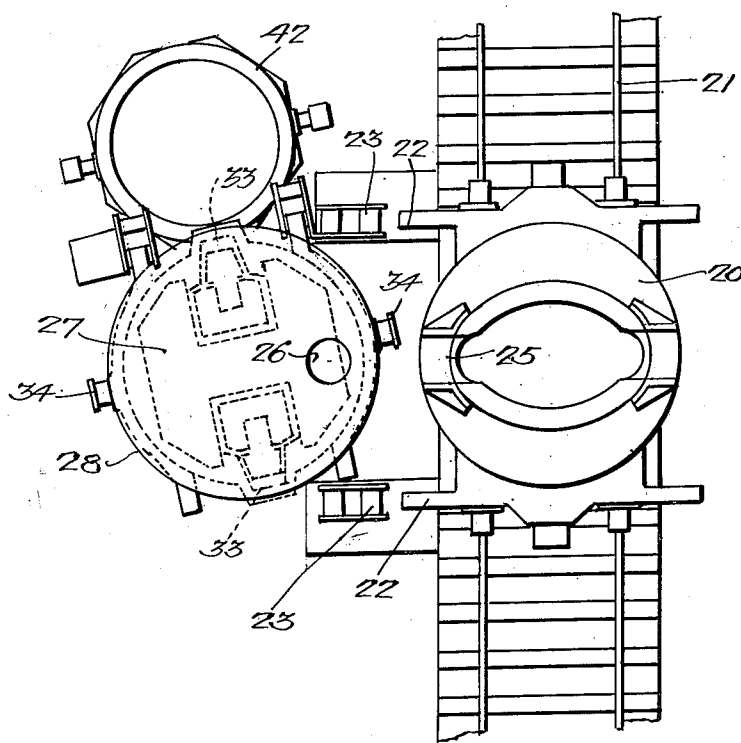
D. J. WYNNE
DESULFURIZING PROCESS

2,587,573

Filed June 9, 1949

4 Sheets-Sheet 1

Fig. 1.



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2,587,573

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Fig. 2.

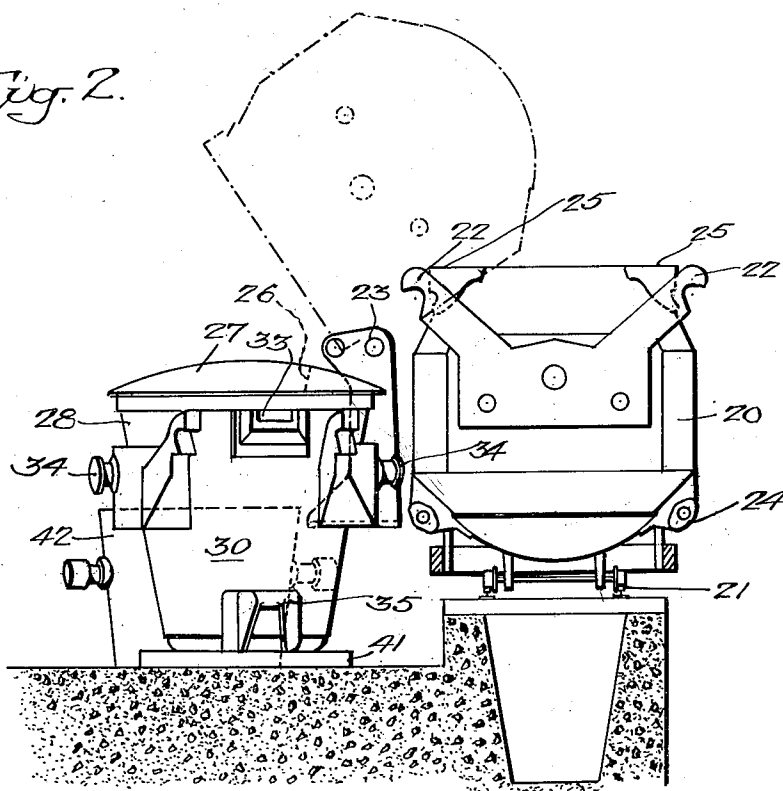
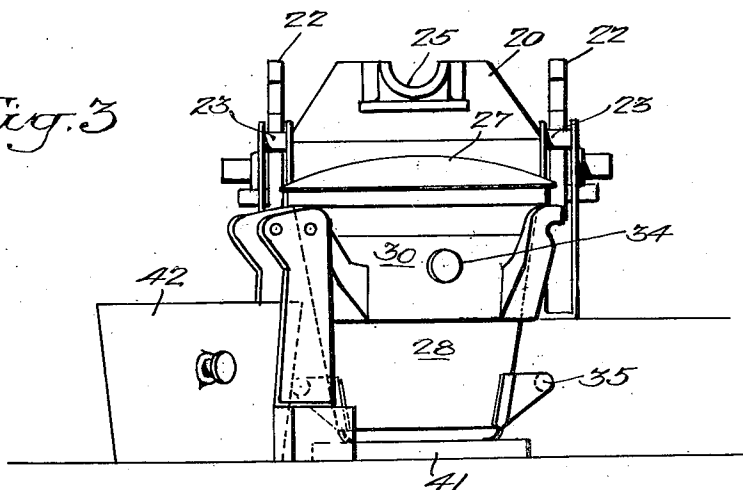


Fig. 3



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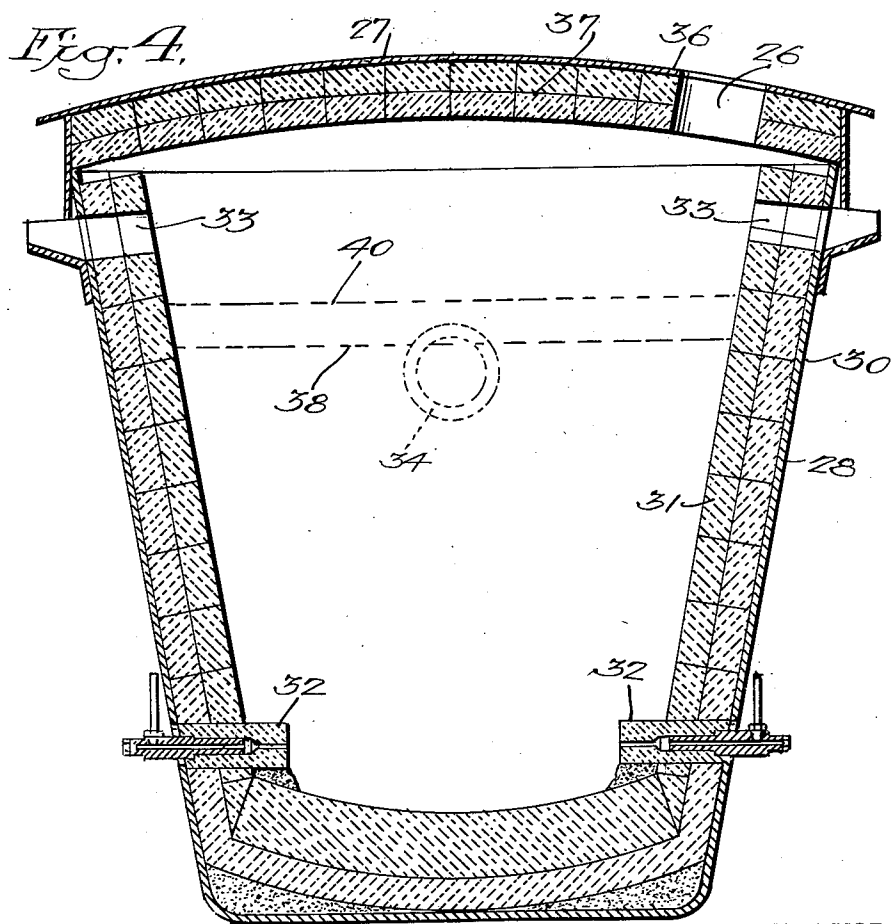
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DESULFURIZING PROCESS

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4 Sheets-Sheet 3



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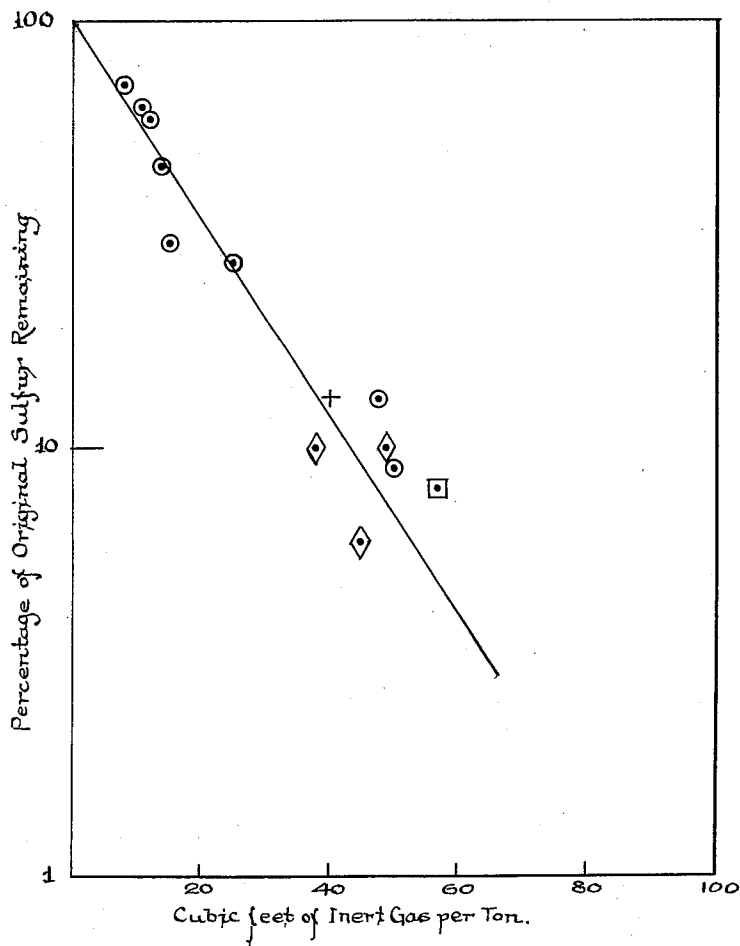
DESULFURIZING PROCESS

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○ 70000 Lbs.
◇ 30000 Lbs.
□ 140 Lbs.
+ 20 Lbs.

Fig. 5.



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UNITED STATES PATENT OFFICE

2,587,573

DESULFURIZING PROCESS

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Application June 9, 1949, Serial No. 97,959

3 Claims. (Cl. 75-51)

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The present invention relates to the process of desulphurizing pig iron.

A purpose of the invention is to chemically intensify the desulphurization and physically accelerate the agitation while desulphurizing molten pig iron at pressures not less than atmospheric pressure.

A further purpose is to maintain a bath of molten pig iron in a desulphurizing vessel in contact with a desulphurizing slag, to enclose the molten pig iron and slag to exclude oxidizing gases including the atmosphere and maintain strong reducing conditions around the molten pig iron and slag and to blow through the molten pig iron an inert gas free from substantial quantities of compounds which, under the conditions, are more oxidizing than carbon monoxide and free from carbon monoxide in excess of 33 percent to chemically intensify the desulphurization and physically accelerate the agitation, while maintaining a pressure of at least atmospheric pressure above the molten pig iron and slag.

A further purpose is to accomplish the objectives of the preceding paragraph and obtain desulphurization at an acceptable commercial rate relatively independent of the depth of the iron bath and therefore at an increased rate in a deep bath by passing the inert gas through at least half the depth of the molten iron at a rate in excess of one-third cubic foot of gas per minute per ton of iron measured at atmospheric temperature and pressure.

A further purpose is to accomplish the objective of the next preceding paragraph by passing through a depth of at least two feet of pig iron an inert gas which is not combustible in the air and is free from substantial quantities of compounds more oxidizing than carbon monoxide, leading the gas from the vessel out into the atmosphere and there initially burning the gas and continuing the passage of the inert gas through the iron beyond the point at which the gas coming out into the atmosphere from the vessel is combustible.

A further purpose is to employ a calcium desulphurizing agent capable of reacting with sulphur in the molten iron to form calcium sulphide, which may or may not be molten at the temperature of the reaction.

A further purpose is to employ lime as a de-

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sulphurizing agent, preferably along with fluor-spar and waste blast furnace slag.

A further purpose is to utilize an inert gas predominantly by volume consisting of nitrogen and permissibly having carbon monoxide as its chief minor constituent, limited, however, to not over 33 percent carbon monoxide by volume.

A further purpose is to employ an inert gas predominantly by volume consisting of hydrogen and permissibly having carbon monoxide as the chief minor constituent, the carbon monoxide content, however, being not over 33 percent.

A further purpose is to employ as an inert gas, a gas predominantly by volume consisting of blast furnace gas, in which the content of carbon dioxide has been reduced to not more than 3 percent and the content of carbon monoxide has been reduced to not more than 33 percent by volume.

As well known, it is customary to operate many furnaces under slightly diminished pressure because of the suction of a stack, etc. An operation employing slightly less than atmospheric pressure in order to facilitate movement of gases would, therefore, be considered an operation at normal pressure as compared with the high vacua set forth in Heuer U. S. Patent 2,110,067.

Further purposes appear in the specification and in the claims.

The present application is a continuation in part of my application Serial No. 601,654, filed June 26, 1945 for Desulphurization of Pig Iron and my application Serial No. 757,756, filed June 28, 1947 for Desulphurization of Pig Iron, both now abandoned.

The drawings illustrate one type of apparatus applicable to the invention.

Figure 1 is a diagrammatic top plan view of apparatus by which the invention may be applied.

Figure 2 is an end elevation of the structure of Figure 1, the base being shown in section.

Figure 3 is a left end elevation of Figure 2.

Figure 4 is a diagrammatic central vertical section of the desulphurizing vessel.

Figure 5 is a graph relating the percentage of original sulphur remaining in the pig iron to logarithmic coordinates as ordinates and the number of cubic feet of inert gas per ton at atmospheric temperature and pressure which has been

passed through the iron to linear coordinates as abscissae.

Where reference is made herein to pig iron it is intended to designate the alloy of iron with a high content of carbon—3 to 4 percent or more—with varying contents of silicon, manganese, phosphorus and sulphur as conventionally obtained from the iron blast furnace, the cupola, the air furnace, or from any other source.

The treatment of molten pig iron with lime bearing desulphurizing slags was taught by Heuer in U. S. Patent 2,110,066. Heuer taught that carbon monoxide is a non-contaminating gas which can be blown through the molten mass to provide agitation. He stated that it was possible to absorb 10 percent of sulphur in the slag "under favorable conditions" and obtain a ratio of the percentage of sulphur in the slag to the percentage of sulphur in the iron of 250:1.

In U. S. Patent 2,110,067 Heuer taught that the desulphurizing reaction should take place below the normal atmospheric pressure, as for example, at a pressure of 76 millimeters of mercury. Mechanical agitation was suggested.

In U. S. Patent 2,193,593 Heuer taught the use of reducing agents other than carbon to reduce the oxygen activity in the desulphurizing process and thereby improve the desulphurizing action of the lime slags. As reducing agents Heuer disclosed metallic aluminum, magnesium or calcium. Mechanical agitation was suggested.

In U. S. Patent 2,290,961 Heuer taught that the rate of sulphur removal using his previously described slags was too slow since it required approximately 12 minutes for each one inch of depth of metal bath in order to reduce sulphur from 0.07 percent to 0.005 per cent, a reduction to less than 10 percent of the original sulphur content. Thus for a depth of 60 inches of metal the time required would have been 720 minutes. Heuer sought to secure thorough and rapid desulphurization by means of violent agitation.

"A further purpose is to expedite the desulphurizing reaction between a basic desulphurizing slag and molten pig iron by producing local agitation adjacent the slag-pig iron interface, and preferably by projecting streams of molten pig iron into the slag." Page 1, column 1, lines 22 to 27.

"A further purpose is to agitate molten pig iron during desulphurization under the action of a basic slag, by introducing beneath the surface of the slag and pig iron, a stream of noncontaminating gas, suitably nitrogen, carbon monoxide, producer gas, or coke oven gas, at a pressure substantially above that at the surface of the pig iron and at a temperature substantially below that of the molten pig iron, and desirably also to maintain subatmospheric pressure above the surface of the molten pig iron so as to cause the gas to do a maximum of work upon the pig iron." Page 1, column 1, lines 28 to 40.

"A further purpose is to introduce a stream of agitating gas beneath the surface of molten pig iron being desulphurized by a basic slag, the gas being at a high enough pressure or low enough temperature, either or both, to undergo rapid expansion while flowing through the metal and to concurrently evacuate the vessel, removing gas at a rate at least as great as that at which gas is supplied so as to maintain subatmospheric pressure in the vessel. The reduced pressure then performs a dual function; it chemically intensifies the desulfurization and it physically

accelerates the agitation." Page 1, column 2, lines 5 to 17.

Heuer intended to utilize the subatmospheric pressure to perform a dual function of chemically intensifying the desulphurization and physically accelerating the agitation. Heuer had previously taught that by reducing the pressure he could chemically intensify the desulphurization. He had also taught in U. S. Patent 2,110,066 that agitation could be accelerated by blowing carbon monoxide through the molten bath without the use of subatmospheric pressure. By blowing carbon monoxide through the molten pig iron to physically accelerate the agitation it is not, however, possible to perform the other one of the dual functions of chemically intensifying the desulphurization without evacuating the vessel.

I have discovered that by substituting for the carbon monoxide gas an inert gas such as nitrogen or hydrogen, the passage of the inert gas through the molten pig iron will remove carbon monoxide from the molten pig iron in addition to accelerating agitation, favoring the liberation of calcium to react with the sulphur according to the following reactions:



It will be evident on principles of mass action that removal of carbon monoxide in reaction (2) favors the liberation of metallic calcium, favors the combination of the metallic calcium with the sulphur and so favors desulphurization. Thus blowing an inert gas such as nitrogen or hydrogen through the molten bath in accordance with the present invention chemically intensifies the desulphurization and promotes the agitation without evacuating the vessel.

Heuer in U. S. Patent 2,290,961 inextricably confuses good and bad in that he does not teach the proper method of choosing the chemical composition of the gas and the proper method of application of the gas in order to chemically intensify the desulphurization if the desulphurizing vessel is maintained at atmospheric pressure, although Heuer's teaching of the selection of gas composition and method of application of the gas is correct when applied to subatmospheric pressure.

Heuer taught in U. S. Patent 2,290,961 that the removal of sulphur from the molten pig iron proceeds at a rate which is dependent upon the depth of the bath. In contrast to the disclosure of Heuer U. S. Patent 2,290,961, however, I have discovered that if gas is blown through a sufficient depth of molten pig iron at a rate beyond one-third cubic foot of gas per minute per ton of pig iron measured at atmospheric temperature and pressure the sulphur is removed from the molten pig iron at a rate which is independent of the depth of the pig iron bath and is much greater than that obtained by following the teaching of this Heuer patent.

Thus, unlike the experience reported in Heuer U. S. Patent 2,290,961, under my conditions of inert gas flow large commercial pig iron baths can be desulphurized at the same low elapsed time intervals which are obtained in the case of small laboratory melts.

Thus proceeding according to the invention, using 140 pounds of pig iron having an initial sulphur content of 0.041 percent I have reduced the

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sulphur to less than 10 percent of its original content in less than 90 minutes, employing a lime desulphurizing slag by blowing commercially pure nitrogen through the metal-slag system in amounts of about 60 cubic feet per ton, measured at normal atmospheric temperature and pressure.

Using the same procedure, I have applied the same principle to the desulphurization of 30,000 pounds of molten pig iron and have also reduced the sulphur content to less than 10 percent of its original value in less than 90 minutes using 40 cubic feet per ton. Still further and using the same process I have treated 70,000 pounds of molten pig iron and have reduced the sulphur content to less than 10 percent of its original in value in less than 90 minutes for about 45 cubic feet gas flow per ton.

The chart in Figure 5 shows a curve relating the percentage of original sulphur remaining in the various melts described above and the cubic feet of nitrogen per ton passed through the metal. If I desire to remove 90 percent of the original sulphur from the metal I find that a satisfactory rate is obtained if about 40 cubic feet per ton is passed through the metal in 90 minutes or even if this time is extended to 120 minutes, measured at atmospheric temperature and pressure. I therefore recommend a gas flow exceeding about one-third cubic foot of gas per minute per ton of iron measured at the atmospheric temperature and pressure, irrespective of the depth of metal or area of the metal surface.

Under the aforesaid conditions it is possible to increase the size from a laboratory sample of 140 pounds to 70,000 pounds with relatively no increase in the time required for the desulphurization. This feature was not obtained in the Heuer patents.

Heuer in U. S. Patent 2,290,961 claimed invention in reducing the time of desulphurization from 12 hours to 4 hours, a decrease of 66⅔ percent. By the present invention I can still further decrease the time required to desulphurize a 60 inch depth of molten pig iron from four hours to one and one-half hours, a reduction of 62½ percent. This same reduction can be obtained in depths of molten pig iron exceeding the 60 inch depths to which Heuer refers, up to depths of the order of 15 feet, and down to depths of the order of three feet or over one foot.

By the present invention all the difficulties inherent in metallurgical apparatus operating under vacuum are avoided.

In carrying out the invention I bring the molten pig iron and suitable desulphurizing slag or other agent into contact in a substantially closed vessel which protects the contents from the oxidizing action of the atmosphere.

A suitable inert gas is then blown into the molten pig iron by means of a tuyère or tuyères. The gas rises through the molten pig iron and escapes through a vent in the upper part of the desulphurizing vessel. When an incombustible inert gas is used, and when the gas is made to rise through a substantial depth of metal exceeding two feet, the gas escaping through the vent in the desulphurizing vessel at the beginning of the cycle contains carbon monoxide picked up from the molten pig iron system and it ignites spontaneously in the atmosphere. As the blowing continues and carbon monoxide is gradually removed from the system, the amount of carbon monoxide in the exit gas decreases until the exit gas contains too little carbon monoxide to burn,

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and the flame will go out. I continue to blow beyond the point at which the flame goes out.

This removal of carbon monoxide which is effected at atmospheric pressure by the proper passage of the inert gas, reduces the partial pressure of carbon monoxide within the desulphurizing vessel and reduces the partial pressure of oxygen in the desulphurizing vessel, so that the desulphurizing action of the slag is chemically intensified.

The flow of a suitable gas as described above through the molten pig iron then performs a dual function, it chemically intensifies the desulphurization and it physically accelerates the agitation.

The gas used should, of course, not contaminate the pig iron and therefore a gas carrying a substantial sulphur content such as hydrogen sulphide or sulphur dioxide should be avoided.

As inert or non-reactive gases nitrogen, helium, hydrogen, ammonia, and the other rare inert gases such as argon are desirable, either alone or in mixtures with one another in any proportions, the balance impurities. Gases of this type are either chemical elements or chemical compounds which, upon contact with molten iron, are decomposed into their elements, and thus, for the purposes described herein, may be considered as chemical elements.

I have treated molten pig iron containing 0.035 percent sulphur with a lime bearing desulphurizing slag and chemically pure nitrogen in accordance with the present invention and obtained in 70 minutes a desulphurized iron containing 0.001 percent sulphur. The final desulphurizing slag contained more than 10 percent of sulphur, and the ratio of the percent of sulphur in the slag to the percent of sulphur in the iron exceeded 10,000:1.

I am familiar with the fact that the passing of the gas into molten iron in the presence of slag has been used to speed up the rate of desulphurization. The desirable desulphurizing result above reported was not merely the result of rapid desulphurization which would be caused by any kind of gas.

For example, a similar trial was made with the same analysis of molten pig iron and slag, under otherwise identical conditions, but carbon monoxide was substituted for nitrogen in similar amount. The desulphurized iron after 70 minutes still contained 0.015 percent of sulphur, and the ratio of sulphur in the slag to sulphur in the molten pig iron was only approximately 600:1. Thus the use of nitrogen gas accomplishes a desulphurizing effect which is unusual because it performs a dual function of chemically intensifying the desulphurization and physically accelerating the agitation.

Carbon monoxide, on the other hand, merely performs the single function of accelerating the agitation without intensifying the desulphurization reaction.

Mixtures of nitrogen gas with carbon monoxide may be used satisfactorily if the carbon monoxide does not exceed 33 percent by volume. The carbon dioxide should not exceed 3 percent by volume. A suitable gas containing a mixture of inert gas and a small amount of carbon monoxide can be prepared if natural gas, methane or similar hydrocarbon is mixed with air and reacted as follows:



The resulting gas will comprise about 20 per-

cent carbon monoxide and the remainder will consist of hydrogen and nitrogen. Such a gas mixture is suitable for use in place of hydrogen or nitrogen gas as described above.

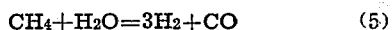
Mixtures of nitrogen gas and other gaseous compounds containing oxygen may be used without the presence of large amounts of hydrogen. Blast furnace gas itself may be used as a source of such a gas mixture. A typical blast furnace gas contains the following constituents by volume:

N ₂ -----	59.4
CH ₄ -----	1.8
H ₂ -----	1.2
CO-----	23.8
CO ₂ -----	13.8
	<hr/>
	100.0

This gas should be treated to remove carbon dioxide, in any suitable manner as by compressing to about 250 pounds per square inch and washing it with water in a packed tower. A product containing less than 1 percent CO₂ and a ratio of nitrogen to carbon monoxide in excess of 2 to 1 by volume is obtained. The ratio of nitrogen to carbon monoxide can be further increased, for example, to 5 or more to 1 by volume if the blast furnace gas is burned preferably with a deficiency of air to convert some of the carbon monoxide to carbon dioxide and is then compressed and washed to remove carbon dioxide.

I have used hydrogen gas instead of nitrogen gas and have obtained satisfactory results. As a source of hydrogen gas I may use hydrogen gas prepared by electrolysis. I may also use hydrogen gas prepared from steam in the conventional manner by reacting with a reducing agent such as carbon, followed by suitable treatment to remove the oxides of carbon which are formed.

It is not necessary to use pure hydrogen gas. For example, a mixture of about three parts of hydrogen gas by volume to one part of carbon monoxide is suitable. Such a gas may be made by mixing natural gas comprising principally methane with about an equal volume of steam. The mixture is heated to about 900° C. in contact with a suitable catalyst. The following reaction occurs:



The gaseous product may be used directly for the treatment of iron in the desulphurization vessel. In using a mixture of hydrogen gas and carbon monoxide it is important that the carbon monoxide should not exceed 33 percent by volume.

Hydrocarbon gases such as coke oven gas, methane or propane deposit carbon in the tuyères and are likely to stop the flow of gas. While these gases are otherwise suitable, they are not to be recommended because of this deposition of carbon.

From the foregoing it is evident that many different gases or combinations may be used, depending upon their availability and the results desired. In general the cheapest and best gas for use in many cases will be comprised principally of hydrogen and/or nitrogen with the amount of any accompanying gases containing oxygen reduced to a practical minimum, and, in the case of carbon monoxide not exceeding 33 percent by volume and in the case of carbon dioxide not exceeding 3 percent by volume.

In order to desulphurize large masses of iron at a rate which is the same for different depths and which, therefore, is unusually rapid for large

commercial quantities of molten pig iron, it is necessary not only that highly active agitating conditions exist, but also that very dynamic desulphurizing reaction conditions occur due to the chemical intensification of the desulphurization.

Unless these two effects are simultaneously achieved the results will be unsatisfactory. For example, W. C. Newell, A. J. Langner and J. W. Parsons experimented with ideas communicated to them by Heuer and reported the desulphurizing results obtained in Foundry Trade Journal, vol. 85, (1948) No. 1668, pages 165-172. These experimenters used desulphurizing slags containing fluorspar and tricalcium silicate. They brought the slag into contact with molten iron and passed nitrogen through the iron-slag system. They concluded that "the role of nitrogen when bubbled into the slag seemed to be solely that of a mixer of slag and metal, and no desulphurizing action proportional to the volume bubbled was observed." The highest ratio of sulphur in the slag to sulphur in the iron which these workers were able to obtain with such slags was 56:1. Thus, the results were unsatisfactory and not the desirable results which I have obtained as shown in Figure 5. It is possible that their failure was due to the fact that they passed the nitrogen into the slag-metal system at a point only slightly below the slag-metal interface and thus obtained mixing action solely without chemical intensification. I have found that it is necessary to have the nitrogen gas pass through a substantial depth of metal before coming to the slag-metal interface. It is for this reason I recommend that tuyères be located at a depth of approximately one-half the metal depth or preferably even lower than that. In any event the record indicates that the mere passing of nitrogen gas through a pig iron-slag system does not necessarily achieve the fine results which I have accomplished, and indicates that these prior workers, following the teachings of Heuer, were unable to get results in any respect approaching those which I have obtained.

Thus it will be evident that in desulphurizing pig iron at a rate relatively independent of depth of bath, a molten pig iron bath should be maintained having a depth of from one to fifteen feet, a desulphurizing slag or other agent should be brought into contact with the molten pig iron, the molten pig iron and slag or other agent should be enclosed to exclude oxidizing gases including the atmosphere and to maintain strong reducing conditions around the molten pig iron and slag, an inert gas free from substantial quantities of compounds which under the conditions are more oxidizing than carbon monoxide and free from carbon monoxide in excess of 33 percent by volume should be blown through a sufficient depth of the molten pig iron at a rate in excess of one-third cubic foot of gas per minute per ton of iron measured at room temperature and atmospheric pressure, and a pressure not less than atmospheric pressure should be maintained in the vessel. If these conditions are followed the partial pressure of carbon monoxide in the iron is reduced and at least 90 percent of the original sulphur content of the iron is removed to the slag in 90 to 120 minutes irrespective of the depth of the molten pig iron bath.

Under the desulphurizing conditions above described, it is possible to obtain practically complete removal of sulphur from pig iron using

simple and inexpensive slags, such as for example, a slag containing 45 percent burned lime, 40 percent fluorspar and 15 percent silica. This slag when added to molten pig iron and treated with an inert gas such as nitrogen produces a desulphurized iron containing as low as 0.001 percent sulphur or lower.

Other slags containing, for example, 30 percent of conventional waste iron blast furnace slag, 40 percent burned lime and 30 percent fluorspar when used in cooperation with treatment with an inert gas such as nitrogen will produce desirable results. The latter slag will pick up from the iron 10 percent or more of its weight in sulphur. An equivalent weight of lime originally present in the slag will be converted into calcium sulphide which remains in the slag. For each 32 parts by weight of sulphur entering the slag as calcium sulphide, 56 parts of lime are used up, and 72 parts of calcium sulphide are formed in the slag. Thus the initial slag containing 30 parts blast furnace slag, 40 parts burned lime and 30 parts fluorspar, after picking up 10 parts of sulphur, then contains the original 30 parts of blast furnace slag and 30 parts of fluorspar, but only 22.5 parts of burned lime and 22.5 parts of newly formed calcium sulphide. This slag still has a good desulphurizing power and is capable of producing iron containing 0.001 percent sulphur or less.

Another suitable slag contains 70 percent conventional waste iron blast furnace slag, 20 percent burned lime and 10 percent fluorspar. Intermediate ranges of lime, silica, fluorspar and the like may be used. A typical analysis for iron blast furnace slag (before use) is:

	Percent
CaO	44
MgO	4
Al ₂ O ₃	15
SiO ₂	37
	100

The desulphurizing power of lime slags is generally better with higher ratios of lime to silica and with higher percentages of fluorspar. Lower ratios of lime to silica and lower percentages of fluorspar than illustrated above may still be utilized. Ordinary waste blast furnace slag alone may be used with considerable effect. In addition to lime in the slag, other oxides of the type R₂O, where α is either integer one or two, as for example Na₂O, and R is a metal of the alkali or alkaline earth group, may be advantageously used as desulphurizing agents. The desulphurizing agent need not be a fluid, but may be a plastic mass or a solid. For example, powdered burned lime may be used, or powdered burned lime along with too little silica or fluorspar to make the mass molten may be employed.

As explained above, the reaction is attributable to the calcium, or similar metal, and calcium may be contributed by other materials instead of or along with calcium oxide, such as calcium carbide or calcium silicate or any compound capable of forming calcium sulphide.

Molten pig iron having sufficient superheat to go through the desulphurizing treatment without application of external heat is conveniently brought from the blast furnace or other source of molten pig iron in a ladle car 20 operating on rails 21 and carrying tilting supports 22 which in the desired position of tilting engage fixed trunnions 23 positioned in spaced relation beside

the track. The ladle car is desirably tilted by the lifting of a crane which engages the ladle at 24. Figure 2 shows in dot-and-dash view the tilting position.

The ladle car pours through one of its spouts 25 into a small charging opening 26 in the removable cover 27 of a desulphurizing vessel 28 supported in suitable position beside the track. The desulphurizing vessel generally will not be provided with heating means.

The desulphurizing vessel comprises a metallic casing 30, a refractory lining 31 and tuyères 32, located adjacent the bottom, and in any case far enough down so that the gas will pass through more than half the height of the molten pig iron. The ladle can pour from either pouring opening 33. For pouring purposes the ladle has trunnions 34 and tilting supports 35 which are engaged by a crane for tilting the ladle.

The cover has a metallic casing 36 and refractory lining 37.

The refractory for lining the desulphurizing vessel and the cover will preferably be carbon refractory bricks or carbon refractory rammed lining. However, the desulphurizing agent need not be a slag but may be a solid or plastic mass, such as powdered lime or burned lime or powdered burned lime mixed with too little silica or fluorspar or both to make the mass a fluid at the temperature of the molten iron and the refractory lining may desirably be of some other character, such as burned magnesite, or other basic material.

The desulphurizing vessel when operating contains a charge of molten pig iron 38 and a slag or other desulphurizing agent 40 floating thereon. During desulphurization, the desulphurizing vessel conveniently rests on a base 41.

From the desulphurizing vessel, the desulphurized pig iron is removed by a transfer ladle 42 of conventional character, which receives the pig iron poured from one of the spouts 33.

The desulphurizing slag is removed by a similar transfer ladle, not shown.

In operation, assuming all of the vessels are initially empty, a desulphurizing slag or desulphurizing agent, sufficient in quantity to form from 1 to 30 percent of the weight of the pig iron to be treated, preferably one percent, is charged into the covered desulphurizing vessel. A charge of molten pig iron in the ladle car is then brought from the blast furnace or other suitable source. A flow of inert gas such as nitrogen as before explained is then started through the tuyères and iron is poured into the vessel through the charging opening 26. Gas is emitted through the charging opening 26 or through the pouring spouts, but during the operation of blowing these openings should be partially closed as by luting to keep out air infiltration. Even though the gas employed may be substantially pure nitrogen, the pig iron, initially having a normal sulphur content in excess of 0.02 percent and commonly of the order of 0.034 percent, will introduce so much carbon monoxide in the gas due to the desulphurizing reaction that the gas emitted at the beginning of the desulphurization will contain sufficient carbon monoxide to burn with a characteristic flame when it comes in contact with the atmosphere.

In order to take advantage of both the agitation and the accentuation of the desulphurizing reaction, the gas flow is continued using gas from any suitable source supplied at super-atmospheric pressure and room temperature, at a

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rate in excess of one-third cubic foot of gas per minute per ton of molten pig iron measured at room temperature and atmospheric pressure' The charge of molten pig iron will preferably be about 150 tons, and the depth of molten pig iron will be desirably about seven to ten feet. The maximum diameter of the molten pig iron under treatment will preferably be not over twice the depth.

The flow of gas will be continued for a suitable time until the desired percentage of original sulphur is removed. Usually about 90 to 120 minutes will remove 90 percent of the original sulphur content of the pig iron. The metal can then be removed from the vessel. The slag can be removed before the metal is removed or may be retained in the vessel and removed after the metal, for example using one of the pouring spouts for the slag and another for the metal. It is desirable to obtain a sharp separation between the slag and the molten pig iron while the molten pig iron remains under strong reducing conditions, as otherwise resulphurization may occur. If necessary, a second slag can be introduced for wash purposes after the first slag has been removed, to assure more complete separation, the second slag being if desired, used as the desulphurizing slag for the next cycle.

When reference is made herein to percentages or proportions in gases they are by volume, whereas in solids or liquids they are by weight. Tons are tons of 2,000 pounds.

When reference is made to impurities in the gaseous content, it will be understood that carbon dioxide is included as such an impurity.

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 process shown, and I, therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

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

1. The process of desulphurizing pig iron, which comprises maintaining a bath of molten pig iron in a desulphurizing vessel in contact with a calcium desulphurizing agent capable of reacting with sulphur in the molten pig to form calcium sulphide, enclosing the molten pig iron and desulphurizing agent to exclude oxidizing gases including the atmosphere and maintain strong reducing conditions around the molten pig iron and the desulphurizing agent, blowing through at least a two foot depth of molten pig iron an inert gas which is free from carbon monoxide in excess of 33 percent by volume, not combustible in the air and is free from substantial quantities of compounds which, under the conditions, are more oxidizing than carbon monoxide while maintaining a pressure of at least atmospheric in the vessel, leading the inert gas after it has passed through the vessel out of the enclosed space and continuing the blowing with the inert gas beyond the point at which the effluent gas is combustible in the atmosphere.

2. The process of desulphurizing pig iron,

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which comprises maintaining a bath of molten pig iron having a depth of between 1 and 15 feet in contact with a lime desulphurizing agent in a desulphurizing vessel, enclosing the molten pig iron and agent to exclude oxidizing gases, including the atmosphere, and maintaining strong reducing conditions around the molten pig iron and agent, blowing through at least one-half of the depth of the molten pig iron an inert gas which is free from carbon monoxide in excess of 33 percent by volume, noncombustible in the air, free from substantial quantities of compounds which, under the conditions, are more oxidizing than carbon monoxide at a rate in excess of one-third cubic foot of gas per minute per ton of iron measured at atmospheric temperature and pressure to chemically intensify the desulphurization and physically accelerate the agitation while maintaining a pressure in the vessel at least as great as atmospheric pressure, leading the inert gas after it has passed through the vessel out into the atmosphere and there initially burning the same and continuing the blowing with the inert gas beyond the point at which the gas is combustible when it comes out into the atmosphere.

3. The process of desulphurizing pig iron, which comprises maintaining a bath of molten pig iron having a depth of at least two feet in contact with a calcium desulphurizing agent in a desulphurizing vessel, enclosing the molten pig iron and agent to exclude oxidizing gases, including the atmosphere, and maintaining strong reducing conditions around the molten pig iron and agent, blowing through at least a two foot depth of molten pig iron an inert gas which is free from carbon monoxide in excess of 33 percent by volume, noncombustible in the air and free from substantial quantities of compounds which under the conditions are more oxidizing than carbon monoxide, at a rate in excess of one-third cubic foot of gas per minute per ton of iron measured at atmospheric temperature and pressure to chemically intensify the desulphurization and physically accelerate the agitation while maintaining a pressure in the vessel at least as great as atmospheric pressure, leading the gas after it has passed through the vessel out of the enclosing space and continuing the blowing with the inert gas beyond the point at which effluent gas is combustible in the atmosphere.

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