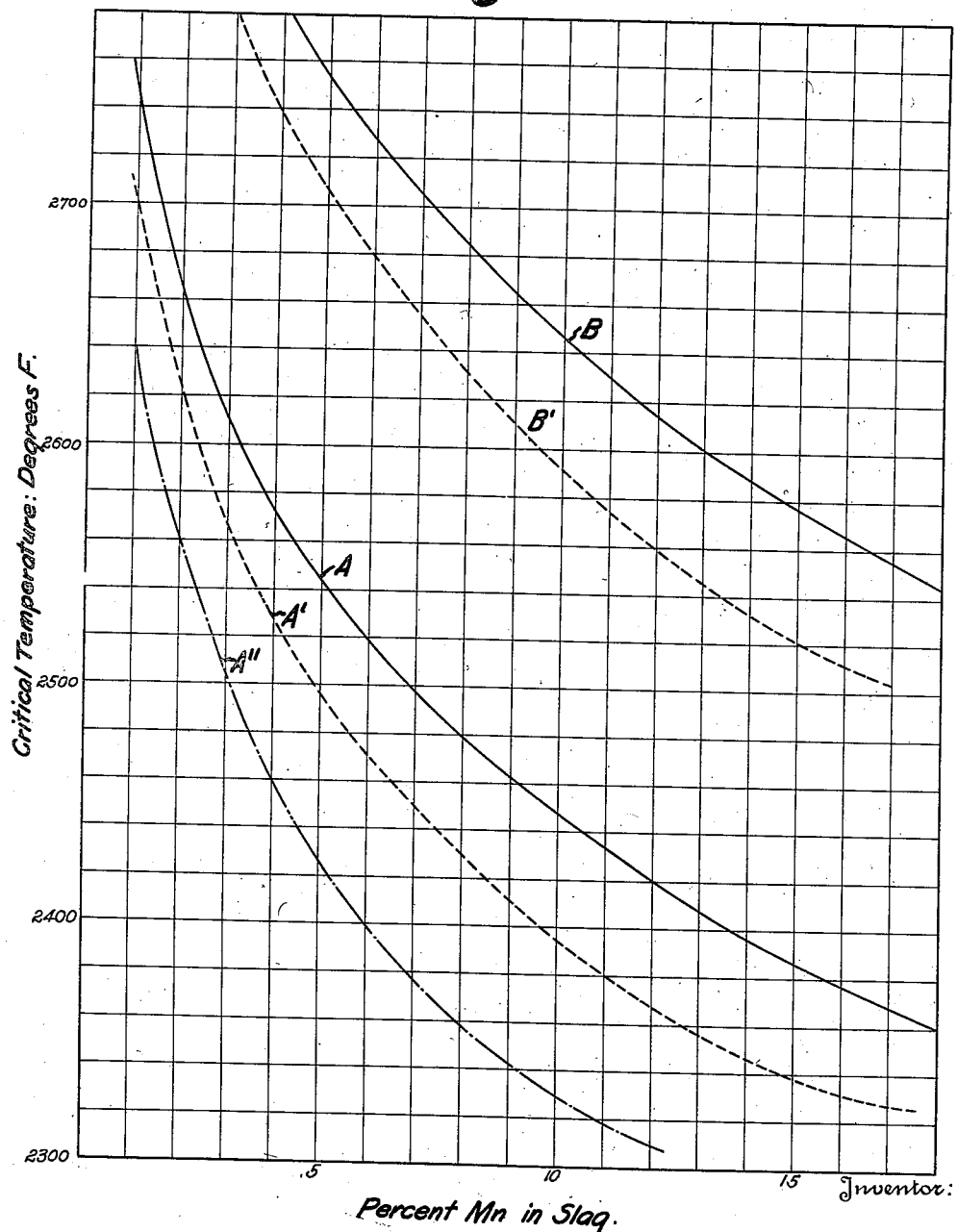
Dec. 9, 1941. P. H. ROYSTER 2,265,866

SMELTING MANGANESE ORE

Filed March 9, 1939 2 Sheets-Sheet 1

Fig. 1.



Inventor:

Percy H. Royster

By Potter, Pierce & Scheffler

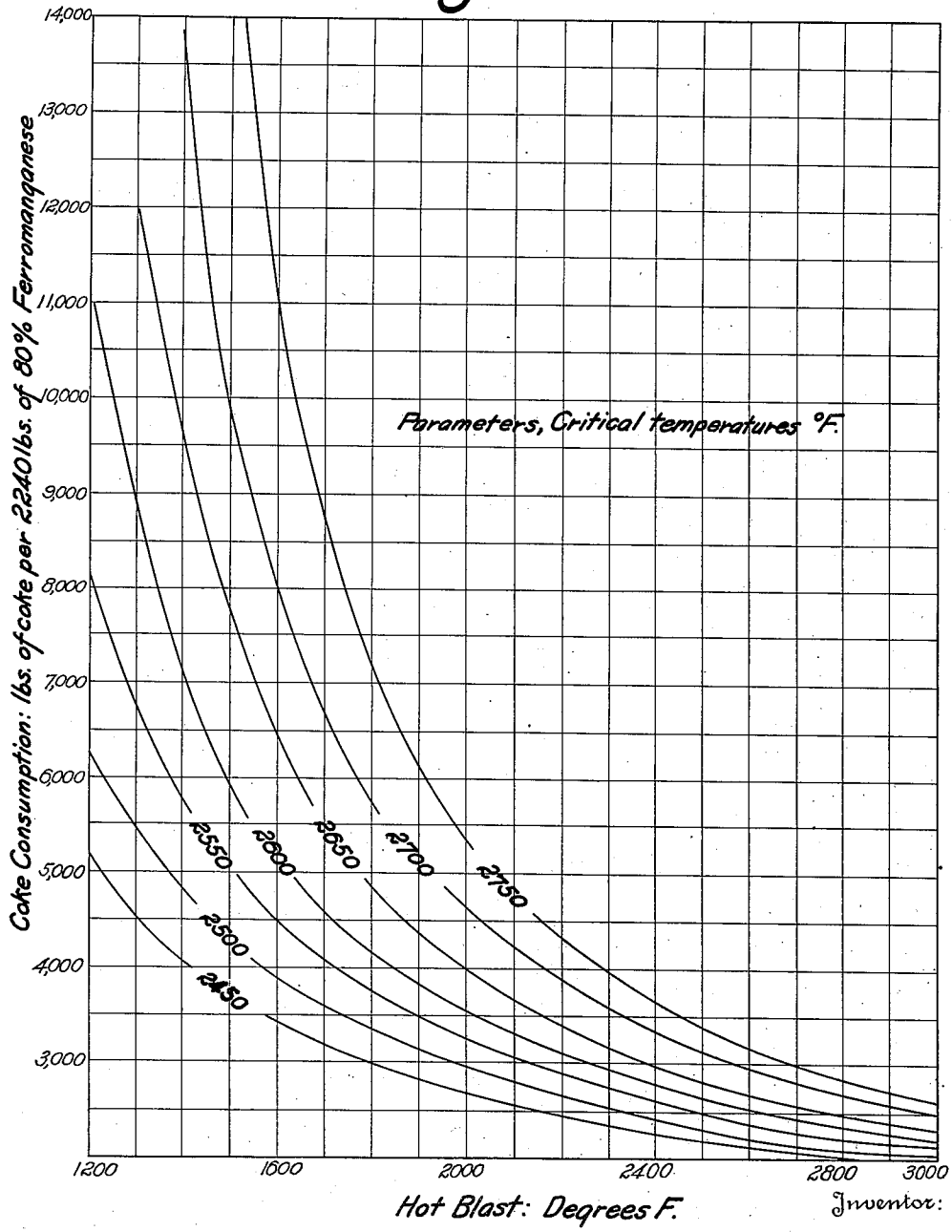
Attorneys.

Dec. 9, 1941. P. H. ROYSTER 2,265,866

SMELTING MANGANESE ORE

Filed March 9, 1939 2 Sheets-Sheet 2

Fig. 2.



Inventor:

Percy H. Royster

By Potter, Pierce & Scheffler

Attorneys.

Patented Dec. 9, 1941

2,265,866

UNITED STATES PATENT OFFICE

2,265,866

SMELTING MANGANESE ORE

Percy H. Royster, Bethesda, Md.

Application March 9, 1939, Serial No. 260,867

4 Claims. (Cl. 75—131)

This invention relates to the smelting, in the blast furnace, of natural ores, beneficiated ores, and the like, containing reducible manganese compounds, whereby to metallize their manganese contents. The invention is concerned more particularly with an improved smelting process for the production, in the blast furnace, of alloys of manganese and iron.

The improved smelting process of the invention is applicable to the metallization of manganese occuring in ores (or in metallurgical equivalents thereof) containing reducible manganese compounds, with or without reducible compounds of other metals, commingled with much silica. Production, in the blast furnace, of ferro-manganese of "80%" grade from ores (or metallurgical equivalents thereof) containing much silica and/or other acidic refractory oxides is a particular object of this process, although production of alloys containing from 50% to 90% of manganese is within the purview of the invention.

By the expression "manganese ore or metallurgical equivalent thereof" I mean to include both naturally occurring and synthetically produced mineral compositions containing oxides of manganese and iron, silica and alumina, in which compositions the manganese and iron are present in ratios adapted to yield ferromanganese of at least 50% grade. In the appended claims the expression "ore" includes metallurgical equivalents of a naturally occurring ore.

In the smelting of an ore in which the silica is low with respect to manganese content, the ore does not melt to a fluid fusion product until relatively high temperatures are reached. For example, a manganese ore containing 48% to 52% Mn and 6% to 12% SiO_2, when melted, forms a fusion product in the binary system MnO-SiO_2 containing from 89.4 to 81.4 molar per cent of MnO and 10.6 to 18.6 molar per cent of $MnSiO_3$. While the eutectic in the binary system MnO-$MnSiO_3$ is low-melting and fluid, the great preponderance of MnO in this low silica ore in excess of said eutectic composition renders said ore high-melting and viscous. In the blast furnace smelting of such an ore, a liberal supply of limestone or dolomite would be added to the furnace burden where, as the ore and stone descended through the shaft, incipient fusion initially would take place between the CaO and MgO (resulting from calcination of the stone, at about 1,650° F.), and progressive fusion of the ore and bases would form reaction products in the ternary system MnO-CaO—SiO_2. Some of the silica would be combined with CaO and MgO to form the metasilicates $CaSiO_3$ and $MgSiO_3$, thereby reducing the relative amount of the low-melting and fluid $MnSiO_3$ formed. The success heretofore attained in the blast furnace production of ferro-manganese has depended in large measure upon the retention of the manganese oxide of the ore in a non-fluid state in the furnace shaft above the tuyères and in the path of the ascending heated gases, so that a large part of the heat necessary for effecting the reduction of the MnO to metal by solid carbon could be brought into a satisfactory approach to equilibrium. The reduction of MnO by solid carbon according to the equation

$$MnO+C \rightleftarrows Mn+CO \qquad (1)$$

is strongly endothermic, absorbing about 2,300 B. t. u. per pound of manganese.

The above outline of the conduct of a metallurgical grade of manganese ore, i. e., a manganese ore having a relatively low SiO_2 content, in its descent to the blast furnace hearth is given in order to explain the differences between its pyrometallurgy and the pyrometallurgy of an ore (or metallurgical equivalent, containing much contaminating silica. I have found experimentally that such an ore-melt, when maintained at 2,100° F., could quite readily be stirred with a carbon rod, and that the temperature of the melt had to be reduced to below 2,050° F. before the same could be called "sluggish" or "slow flowing."

When such a mineral composition as that just described is subjected to treatment according to conventional ferro-manganese blast furnace practice, the results are metallurgically unsatisfactory and economically unacceptable.

The charge material liquefies too early in its downward course through the furnace shaft, promptly flows into the hearth where it ceases to be in contact with hot reducing gases, and resists reduction.

This latter course of events probably explains the prior art conception that it was impossible to reduce to metal the manganese content of such an ore (or metallurgical equivalent) typified by manganese-bearing material containing 18% or more of SiO_2 or containing 25% or more of gangue material, without at the same time reducing considerable (e. g., 10% to 25%) of the SiO_2 content thereof.

As a result of conventional practice applied to such ores, the manganese content of the resulting slag is high, a great increase in coke

consumption over conventional practice is necessary (in order to maintain even unsatisfactory operation of the furnace), large additions of flux are required, daily tonnage of metal is low, and excessive losses of manganese and of heat result from the large volume of gases produced in the furnace, which gases leave the latter at an excessively high temperature, thereby adversely influencing vaporization of manganese. The fraction of total manganese charged which is lost in the final slag is great, due to two causes: first, the actual manganese content of the final slag is high, and second, the "slag volume" (i. e., pounds of slag per long ton of metal produced) is very much greater than are the slag volumes met with in smelting standard manganese ores.

From the foregoing discussion is will be appreciated that economical metallization, in the blast furnace, of manganese from such high-silica ores (or metallurgical equivalents) cannot be effected by carrying out the ferro-manganese blast furnace procedure which is conventionally considered "good practice."

It is an object of the present invention to provide an improved process for the economical metallization, in a blast furnace operation, of manganese from a "high silica" manganese ore (or metallurgical equivalent thereof) containing manganese and common acidic refractory oxides (e. g., SiO_2, Al_2O_3, etc.) in a ratio less than 4 to 1. The invention also has as its object the provision of a blast furnace smelting process which minimizes losses of manganese into the slag and out the stack. Another object of invention is the provision of an improved blast furnace process of smelting low manganese-high silica ores (or metallurgical equivalents), which improved process involves the consumption of relatively small amounts of solid fuel (e. g., materially less fuel than ore, by weight).

These, and other, inventive objects are realized by the process of the present invention, according to which at least the major part of the manganese contained in a siliceous manganese ore of relatively low Mn-to-SiO_2 ratio of the types just described, is metallized in a blast furnace operation conducted under chemical and thermal conditions adapted to increase the quantity of available heat supplied to the furnace hearth and to promote the reaction of reduction of MnO in solution in the slag by contact of the latter with solid carbon.

In smelting a manganese-SiO_2 mixture (e. g., an ore of the sort above described), I charge the blast furnace with appropriate amounts of the mixture, solid fuel (e. g., coke), and a suitable basic fluxing agent (e. g., a limestone and/or dolomite, natural or calcined), and blow the charge with a preheated blast. For increasing the quantity of available heat supplied to the furnace hearth I may:

I. Increase the blast temperature, and/or
II. Decrease the critical temperature of reduction of the manganese, and/or
III. Decrease the partial pressure of the gaseous product of the reduction of MnO by solid carbon, and/or
IV. Increase the activity of the manganese compound existent in solution in the slag, and/or
V. Increase the time of contact of slag, metal and carbon, and/or
VI. Decrease the dimensions of the oxidizing zone adjacent the blast entrance.

A fuller explanation of these six measures follows:

I. By increasing the blast temperature beyond that which has heretofore been employed in the blast furnace production of ferro-manganese I desirably increase the total sensible heat of the blast gases (oxygen and nitrogen) entering the furnace, and increase the amount of available heat per unit of fuel consumed without changing the amount of unavailable heat. In general it is a feature of the process of the present invention to preheat the blast to a temperature of at least 1600° or 1650° F. Increasing the blast temperature tends to increase the temperature of the gases produced in the combustion zone without concurrently increasing the "critical temperature" (J. E. Johnson, Jr., "Principles, Operation and Products of the Blast Furnace") of reduction of MnO.

II. The critical temperature of the reduction of manganese may, when the blast temperature is maintained at a sufficiently elevated value, be decreased by increasing the non-oxidizing constituents of the blast (i. e., operate with a blast containing a lesser proportion of oxygen than has ordinary atmospheric air). This expedient is effective for reducing "Tc", since dilution of the blast with nitrogen decreases the partial pressure of the carbon monoxide in the hearth: As the partial pressure of the carbon monoxide is decreased the content of MnO in the slag decreases in direct linear proportion.

III. I may decrease the partial pressure of the gaseous product of reduction of NnO by solid carbon,—and hence decrease the critical temperature of the reduction,—either by

(*a*) Lowering the hydrostatic pressure inside the furnace hearth, or by
(*b*) Decreasing the percentage of CO present in the furnace hearth gases.

Measure (*a*) may be effected by operating the furnace under "slow blowing" conditions, permitting time for the CO (produced from the MnO reduction) to diffuse from the carbon-manganese oxide interface and for dilution of the gases at the interface with non-reactive nitrogen to take place; or, by shortening the charge column of the furnace to a height materially less than conventional for said furnace (whereby hearth pressure is reduced); or, by decreasing the vertical height of the slag bath (whereby the hydrostatic pressure of the slag, and its MnO content, is reduced); or, by mechanically removing furance gases by means of an "induced draft" or "vacuum" applied to the exhaust conduit system of the furnace. Maintaining the hydrostatic pressure in the slag at a low level (as by keeping the slag bath shallow by frequent flushes between consecutive casts) accelerates the rate of movement of CO from the slag. Rapid removal of CO from the slag displaces to the right the equilibrium in the reaction expressed by Equation 1 and hastens the conversion of the MnO of the slag to metallic manganese and decreases the content of MnO remaining in the slag.

Measure (*b*) above may be effected by suitably diluting the air, employed in the blast of the furnace, with nitrogen or equivalent non-oxidizing gas. In this connection it is noted that CO is not the equivalent of nitrogen since the former, under the conditions obtaining in the furnace hearth, exerts oxidizing properties with respect to metallic manganese. It is to be noted, also, that measure (*b*) above becomes available

only as the blast temperature is so greatly elevated as to approach the critical temperature of reduction of MnO.

IV. The activity of the manganese compound existing in the slag may be increased by increasing the basic oxide content of said slag, whereby the chemical combination between CaO and/or MgO and the Al_2O_3, Cr_2O_3, SiO_2, TiO_2 and other acidic oxides of the slag (forming silicates, aluminates, alumino-silicates, etc., of the bases) is increased, and chemical "fixation" of the manganese as silicates, aluminates, or alumino-silicates of manganese is decreased.

As appears from the foregoing, the smelting of high-silica manganese ores in which the ratio of manganese to silica is 3-to-1 or less, e. g., a manganese-iron ore (or equivalent) in which the ratio of manganese to silica is less than 3-to-1 and in which the ratio of iron to manganese is less than 1-to-8, by conventional blast furnace practice is uneconomical for the following reasons:

(*a*) Increased "fuel consumption" (i. e., pounds of fuel per long ton of metal) is necessary, due to the increased weight of material to be smelted per unit of metallized product;

(*b*) Increased addition of basic fluxing agent is required because of the greater weight of acid gangue oxides in the lower grade ore and because of the increase in fuel ash by reason of (*a*) above;

(*c*) Greater "slag loss" of manganese is encountered because of the increased "slag volume" (i. e., pounds of slag per long ton of metal), since the measure of the "slag loss" of manganese is the product of the "slag volume" multiplied by the weight per cent of manganese retained in the slag;

(*d*) The "reducibility" of the MnO in the charge is low because of dilution of the MnO with a large volume of the gangue oxides contained in such ore; and

(*e*) The "reducibility" of the MnO in the charge is further decreased by chemical combination of MnO with acidic gangue oxides to form silicates, aluminates, and aluminosilicates of manganese.

The increase in amount of fluxing agent employed is a necessary result of the composition of the siliceous ore and cannot be obviated. In fact, in the process of the present invention the increase in amount of fluxing agent is greater than the proportional increase in acidic gangue oxides, since it is desirable to increase the "basicity of the slag"—i. e., ratio of (CaO plus MgO) to (Al_2O_3 plus SiO_2) by weight.

The principles of the process of the present invention will be described with greater particularity in the following paragraphs, with reference to the accompanying drawings, in which

Fig. 1 is a chart comprising graphs showing relationships between critical temperature "Tc" and content of manganese (in percent by weight) in the resulting slag, and

Fig. 2 is a chart composed of a family of curves showing relationships between blast temperature, coke consumption and critical temperature.

In carrying out the process of the present invention I employ an extremely basic slag whenever the same is economically feasible. Thus, when limestone is relatively cheap (e. g., less than $1.00 per ton) and when coke is relatively expensive (e. g., more than $5.00 per ton), I employ a basicity ratio higher than hitherto has been employed either in pig iron practice or in ferro-manganese practice, e. g., a basicity ratio as high as 1.5.

For a blast furnace with a hearth pressure of 7 lbs./sq. in. (gauge) producing 80% ferro-manganese, in a case where the slag basicity is sufficiently high, e. g., 1.5, the critical temperature "Tc," in degrees F., may be plotted against the weight per cent of metallic manganese in the slag as shown in curve A of the graph designated Fig. 1 of the accompanying drawings.

On the contrary, when coke is relatively cheap and limestone is relatively expensive the basicity of the slag must, for economical reasons, be decreased, and can be made less than unity with resulting economy. With decrease in the basicity of the slag, the critical temperature of reduction of manganese is shifted upwardly. Thus, in the case of an extremely acid slag (e. g.,

$$(CaO+MgO)/(Al_2O_3+SiO_2)=0.85$$

or less).

Tc may be plotted as curve B in Fig. 1.

For slag basicities intermediate 0.85 and 1.5 there exist a family of curves lying between curve A and curve B. This family of curves is represented by the following equation:

$$\log_{10}\frac{21.7m}{PM}=V-\frac{W}{Tc+460}$$

wherein

m=Mn in slag, in weight per cent,
M=Mn in metal, in weight per cent,
P=hearth pressure, in lbs./sq. in., absolute,
Tc=critical temperature, in °F.
Tc+460=critical temperature, absolute, and V and W are parameters whose values are given by the equations,
$V=7.23+0.6G$, and
$W=28{,}240-200G$,
where

$$G=\frac{CaO+MgO}{Al_2O_3+SiO_2}$$

A considerable decrease in critical temperature of reduction of manganese can be effected by lowering the hearth pressure. Hearth pressure may be reduced as low as, say, 1 lb./sq. in. by one or another, or by a combination of two or more, of the following measures:

1. Employing a larger diametered furnace of standard height;
2. Employing a shorter furnace shaft, with "standard" diameter;
3. In a "standard" furnace, carrying the stock line lower than customary;
4. Blowing the furnace at a lower rate than customary.

The effect of such a drop in hearth pressure is to shift curve A (Fig. 1) downwardly into the position shown as curve A^1. Similarly, critical temperatures, for 1 lb./sg./in. hearth pressure, is shown in curve B^1.

I may, with very desirable results, reduce the hearth pressure,—e. g., to a value below atmospheric pressure,—by the use of an exhauster, or induced draft blower, operating upon the outlet gases. Illustrative of the effect of this measure is the following: For the case of a hearth pressure of 5 lbs./sq. in. below atmospheric, the critical temperatures illustrated in curve A, Fig. 1, are shifted downwardly to those in curve A^{11}, and in curve B to curve B^{11}.

The effect of lowering the critical temperature Tc is to effect a remarkable decrease in coke con-

sumption, in producing ferro-manganese, by increasing the fraction of the heat, supplied to the combustion zone, which is available for manganese reduction. For example, when one pound of coke-carbon is burned at the blast entrance by air (60% humidity, 60° F.) to form CO and N_2 (plus 1.2% H_2), there are generated 3,990 B. t. u. If the blast be preheated to 2,000° F., its sensible heat is 2,940 B. t. u., making a total (gross) value of 6,930 B. t. u., from which latter must be subtracted 117 B. t. u. for the endothermic reaction of blast moisture with carbon and 630 B. t. u. lost to the tuyère and bosh water-cooled devices and for conduction through the brick work, leaving a net combustion zone heat of 6,183 B. t. u. per pound of carbon burned by the O_2 of the blast. If the reaction of Equation 1 is carried out at a reduction temperature of, say, 2,500° F. (6.9% Mn in the slag,—curve A of Fig. 1), the combustion zone gases cannot be cooled below 2,500° F. by absorption of heat in carrying on the endothermic reduction reaction (Equation 1); therefore, these gases carry away from the reduction zone the sensible heat which was required to heat them up to 2,500°, i. e., 4,525 B. t. u. per pound of carbon burned to CO. In other words, 73% (4.525/6,183) of the net combustion zone heat is "unavailable" for manganese reduction. This situation is made even worse when Tc is raised to 2,700° F., in which latter event the "unavailable" heat is 4,925 B. t. u./lb. of carbon, or 79.7% of the net heat.

In order to make completely clear the relationship between the critical temperature Tc, the blast temperature and the coke consumption, I have computed the thermal requirements for producing one long ton of 80% ferro-manganese, in a typical blast furnace; these results are given in Fig. 2 as a family of curves with blast temperatures as abscissa and coke consumption as ordinates, and with the critical temperature as a parameter for each curve as marked by 50 degree (F.) steps from 2,450° to 2,750° F.

In the following I shall describe my process as applied to the production of ferro-manganese of "80%" grade from an ore of the following analysis:

	Per cent
Mn (as metal)	35.5
Fe (as metal)	3.2
SiO_2	21.5
Al_2O_3	5.3
MgO	2.5
CaO	0.8
BaO	0.7

This ore would, under conventional practice, be considered "non-merchantable" because of its high concentration of the acidic gangue oxides SiO_2 and Al_2O_3.

A "standard" grade of ore operable under current practice for production of ferro-manganese has an analysis, for example, of: Mn—49.25%, Fe_2O_3—4.5%, SiO_2—8.0%, Al_2O_3—3.0%, CaO—1.5%, MgO—1.25%, and BaO—0.85%. In smelting this latter ore in accordance with conventional "best practice," one would charge into a blast furnace 4,375 lbs. of the ore, 950 lbs. of limestone and 4,100 lbs. of coke, blow the furnace charge with air at 1,550° F., and produce 1 long ton (2,240 lbs.) of 80% ferro-manganese and 1,300 lbs. of a slag analyzing 8.0% manganese. With manganese at 33¢ per unit, coke at $3.50 per ton, and limestone at $1.75 per ton, the "smelting cost" would be $9.45, including $7.18 for coke, $0.74 for flux and $1.53 for manganese "lost" in the slag.

With the siliceous ore given hereinbefore, the slag volume (in the immediately preceding example) is increased to about 4,500 lbs. In order to hold the manganese slag loss to the 104 pounds of the above example, or to a lesser figure, when employing the above siliceous ore, it is necessary so to operate the blast furnace that the slag contains not more than 2.3% Mn. Reference to Fig. 1, however, shows that the critical temperature of manganese reduction for a 2.3% manganese slag is 2,650 F. Reference to Fig. 2 shows that with 1,550° F. hot blast the coke consumption at Tc=2,650 F. is 7,000 pounds per ton of metal, which figure represents an increase in fuel cost of $5.25 per ton of metal. For a "neutral" slag, the siliceous ore requires 3,300 pounds of limestone per ton of metal, which figure represents an increase in flux cost of $1.86. The total increased materials cost called for by use of the siliceous ore under the furnace conditions just mentioned is $7.11.

But when the furnace is blown with air preheated to 1,870° F. the coke consumption is reduced to 4,100 pounds,—a figure equal to the "standard" ore's competition in this respect,—and when the furnace is blown with air preheated to 2,300° F. the coke consumption (corresponding to Tc=2,640° F.) is reduced to 3,050 pounds. This latter reduction in coke consumption "cancels" the added expense of the flux, thereby showing that the metallurgical penalty on the siliceous ore can be obviated by raising the blast temperature from the conventional figure of 1,550° F. to 2,300° F.

It is to be noted that if, in the above example, the loss of manganese into the slag is maintained at, say, 4.3%, instead of at 2.3%, the temperature of the hot blast must be elevated to about 2,600° F. in order to make the smelting of this ore competitive with smelting a "standard" ore.

Another example of application of the concepts of the present invention to smelting of an ore containing 21% SiO_2 in competition with an ore containing only 8% SiO_2 is as follows, in which example coke is valued at $5.00 per ton, limestone at 85¢, and ore at 26¢ per unit: When smelting an ore containing 8% SiO_2, using a blast temperature of 1,550° F., 4,100 lbs. of coke and 950 lbs. of limestone are employed. The slag volume is 1,300, and the slag contains 8% Mn. When employing the siliceous ore (21% SiO_2), I use a blast temperature of 2,000° F., a coke consumption of 3,600 pounds (corresponding to Tc=2,610° F.,—Fig. 2), and a flux consumption of 3,300 pounds. Under these conditions the slag volume is 4,500, and the content of manganese in the slag is 2.95%. The materials cost is substantially identical with that of the just mentioned "standard" practice applied to ore of 8% SiO_2.

Substantially the same end can be attained by reducing fuel consumption to 3,400 pounds and holding the blast temperature at 2,000° F. (thereby raising the content of manganese in the slag to 4% and lowering Tc to 2,572° F.)

Reference to Figs. 1 and 2, and knowledge of prevailing unit costs of ore, coke and flux, will enable the operator to adjust the operation of the blast furnace for smelting a given siliceous ore under the economically most favorable conditions.

I claim:

1. Process of producing ferro-manganese con-

taining at least 50% of manganese, in the blast furnace, from a manganese-bearing ore containing more than 18% silica, which comprises feeding the furnace with a charge consisting essentially of the ore, a basic fluxing agent and a solid carbonaceous fuel; and blowing the charge with a gas, containing oxygen and nitrogen, preheated to a temperature equal to the critical temperature of reduction of manganese, the blown gas containing a lesser proportion of oxygen than does atmospheric air.

2. In the process of producing, in the blast furnace, ferro-manganese of at least 50% grade from a manganese-bearing ore, the improvement which consists in blasting a furnace charge, consisting essentially of the ore, a basic fluxing agent and a solid carbonaceous fuel, with a blast preheated to a temperature in excess of 1,600° F., and simultaneously sufficiently decreasing the hydrostatic pressure of the CO within the resulting slag bath, by reducing the hearth pressure to a value of the order of 1 lb./sq. in. gauge, as materially to lower the critical temperature of reduction of manganese.

3. Process of producing ferro-manganese containing at least 50% of manganese, in the blast furnace, from a manganese-bearing ore containing more than 18% silica, which comprises feeding the furnace with a charge consisting essentially of the ore, a basic fluxing agent and a solid carbonaceous fuel; blowing the charge with a gas, containing oxygen and nitrogen, preheated to a temperature in excess of 1,600° F.; and so adjusting the rate of introduction of the preheated blast, with respect to the dimensions of the furnace, and the particle size and proportions of the charge ingredients, as to maintain the static pressure of gases within the furnace hearth at not to exceed 5 lbs./sq. in. above atmospheric pressure.

4. In the process of producing manganese alloys in the blast furnace, the improvement which consists in maintaining the furnace hearth at a static pressure less than atmospheric pressure by accelerating the exhaust of furnace gases by means of an induced draft.

PERCY H. ROYSTER.