

Theory of cold-blast iron production with stack-gas of low nitrogen content

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SYNOPSIS

The feasibility of rejection of nitrogen from stack gas by recycling of top-gas with cold-blast 95 to 98 per cent oxygen is assessed. It is concluded that nitrogen could be removed to a level below 3 per cent of the stack-gas using recycled cleaned cold top-gas and 95 to 98 per cent oxygen produced by a single-column air separation plant with liquid-air reflux instead of liquid nitrogen reflux. The partial pressure of carbon monoxide in the stack-gas could be doubled without top pressure and the deposition of carbon and reduction of iron oxides by the stack gas could be markedly increased. It is concluded that rate of stock descent could be doubled compared with present-day practice and an iron make of 4 400 kg/m² of hearth area/hour may be attainable with a working volume of 129 m³/m hearth diameter by this method. Oxygen consumption is estimated at possibly 280 m³ (0.4 t)/t iron† made and carbon consumption at possibly 280 kg/t iron. Power consumption for oxygen including auxiliaries is estimated at 304 kWh/t 100 per cent oxygen as 95 to 98 per cent gas. The air separation cycle due to Schufltan is discussed in some detail, and the components of a 1 600 metric ton/day separation plant are briefly discussed. The paper is a theoretical essay.

INTRODUCTION

Thirty-five years ago the average unit size of blast furnace in Britain could make about 600 metric tons of iron a day. In the United States the 1 000 t/day furnace had been built and was then regarded as approaching the ultimate in unit size; but in the 1950's single furnaces of 2 000 t/day became standard practice and in the early 1960's unit size had increased to 3 000 to 4 000 t/day. Present day top-rate practice is 6 000 t/day and design of furnaces to make 10 000 t/day is proceeding. Some idea of the size of these large furnaces may be gained from the blast volume of 5 000 m³ (175 000 ft³) per minute at 240-340 kN m⁻² (35-50 lb/in²) requiring 28 000 kW for compression for a 6 000 t/day furnace.

This ever-increasing unit size has been caused primarily by the increase in world demand for pig-iron which has had to be met despite the ever-increasing cost of raw materials and wages. The graph of Fig 1 shows the trend¹ in pig-iron output from the level of about 22 million tons in 1900 to the present output which, having topped 380 million tons in 1967, is likely to be about 430 million tons in 1970. This trend has followed the equation (curve of Fig 1).

$$\log_e \frac{p}{y} = \frac{rt}{100} \text{ where } r \text{ is } 4.25 \text{ per cent p.a.}$$

t is number of years from 1900, y is the 1900 A.D. production and p is the yearly total output. The steel-plant wage rate in the U.S.A. increased approximately by 5.2 per cent p.a. compounded between 1954 and 1964² and therefore has more than doubled in the past 16 years. These trends have been off-set as far as possible by increase in unit size and productivity, automation, improved burden by sintering and pelletizing, fuel injection, high top pressure, (proposed by Avery in 1938³), and increase in blast temperature from an average of about 500°C to 700°C 35 years ago to 1 200°C to 1 400°C at the present time. Metallurgical coke of high shatter index has trebled in cost over the past three decades, but the many improvements in blast furnace practice have reduced consumption of coke from about 800-1 000 kg/t pig-iron 35 years ago to the present good practice level of about 475 kg/t.

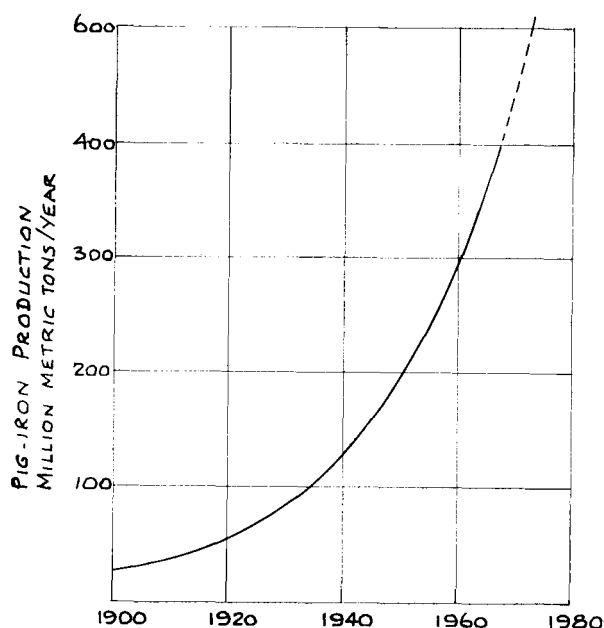


Fig. 1

The nitrogen content in the stack-gas of the modern 6 000 t/day furnace is about 55 per cent by volume. This means that in the course of one day over 7 000 metric tons (5.8×10^6 m³) of nitrogen are compressed, heated to about 1 200°C, and passed through the hearth, bosh and stack. The compression and transfer of this weight of nitrogen, which reacts only to an infinitesimal extent in the chemistry of the process, is the direct consequence of using air as the source of oxygen for the process. Many attempts have been made in the past to lower the nitrogen burden by addition of oxygen to the air, and by steam injection; but for the reasons set out by Colclough⁴ the extent to which oxygen enrichment can be successfully carried out with hot-blast is strictly limited.

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†Note that throughout this paper, gas volumes are expressed in cubic metres at N.T.P.

The object of this paper is to assess the engineering feasibility and the consequences of cold-blast iron production with 98 per cent oxygen and a stack-gas low in nitrogen (less than 3 per cent by volume). Among the consequences of operation of a blast furnace with low-nitrogen stack gas are a smaller stack volume for a given output of iron, increased partial pressure of carbon monoxide in the stack, elimination of Cowper stoves; and finally the consequences of the thermo-physics of the carbon deposition reaction and the effect of low-nitrogen stack-gas on the thermal balance of the furnace.

The decomposition of carbon monoxide to carbon and carbon dioxide takes place under sufficient partial pressure and residence time of carbon monoxide in the cooler regions of the stack in contact with iron and its oxides, which act as catalysts and cause deposition of finely divided carbon in the iron ore of the burden. This reaction is of importance in the iron blast furnace in that the carbon so deposited is an efficient reducing agent in the bosh and hearth of the furnace, and the deposition reaction is exothermic.

The carbon deposition reaction was discussed at some length in a paper by the author in 1950⁵ in which cold-blast operation without nitrogen was analysed. At that time fuel injection at the tuyeres was virtually unknown and the proposal then envisaged entailed the separation of CO₂ from the top gas by chemical extraction or high pressure water extraction. The present paper is to an extent complementary to the earlier paper but a different means of ensuring low-nitrogen stack gas is proposed.

REMOVAL OF NITROGEN FROM STACK-GAS

The modern high capacity blast furnace has been developed entirely on air blast. Massive fuel injection and oxygen enrichment of the air blast have both so far proved impracticable⁶. The highest recorded level of fuel injection and simultaneous oxygen enrichment is that of the Osaka furnace⁶ in which coke consumption was reduced to as low as 370 kg/t of pig-iron produced, by injection of 157 kg/t of oil and enriching the air blast to 27 per cent by volume. The ever-increasing blast rate, at present over 5 000 m³/min at 1 200°C coupled with the design problems created by hearth diameters of over 11 metres, is on the point of causing levitation or fluidization of the shaft contents. The attainment of a blast rate of 5 000 m³/min on an 11.2 m hearth at No. 2 furnace at Fukuyama was apparently assisted by the fact that the great increase in furnace volume to 2 626 m³ in order to attain 6 000 t/day output, was attained by its designers by increasing the hearth diameter rather than the stack height, which is only 20.775 m including the height of the bosh. The furnace has relatively squat lines reminiscent of the original low shaft oxygen furnaces built in Germany in the 1940's using > 95 per cent oxygen blast, with low nitrogen content.

There are many difficulties in reducing the nitrogen content of the stack gas by oxygen enrichment either with or without simultaneous fuel injection. In the first place it is necessary to have a minimum coke rate in order to maintain an effectual permeability of the stack contents to permit passage of the blast. The attainment of 370 kg of coke per metric ton of iron made at Osaka is apparently a near approach to this minimum, which is nevertheless still unknown, but must ultimately set a maximum to fuel injection. Oxygen enrichment of air blast, even to the Osaka level of 27 per cent, which is probably the highest yet attained in continuous operation, requires large quantities of oxygen, and there is an upper ill-defined

limit to this enrichment set by the increasing temperatures in the combustion zone with increasing oxygen content of the hot blast.

On the other hand, if the process of nitrogen removal described in this paper can be successfully carried out in practice, and there seems to be no valid reason why this cannot be done, then at low nitrogen levels, for example less than three per cent, the very reverse could be expected. The hearth combustion temperatures could be controlled even at 98 per cent oxygen content in the blast; both the partial pressure and the residence time of carbon monoxide in the stack would be approximately doubled and the total liberation of heat in the hearth would be unaffected, so that the same heat transfer to the stack solids from the stack-gas would be attained; and finally the efficiency of ore reduction would be increased because of the higher partial pressure of carbon monoxide. A further advantage of importance would be gained by low nitrogen content and increased partial pressure of carbon monoxide in that the disproportionation of carbon monoxide to carbon and carbon dioxide catalysed by ferric oxide and hydrogen in the upper regions of the stack would be increased by the longer residence time of the monoxide in contact with iron oxides. The carbon so deposited is finely disseminated in the iron oxide and acts as an efficient reducing agent in the lower hot regions of the bosh and hearth, thereby further reducing the coke consumption.

Apart from these considerations the stack volume for a given rate of iron production would be greatly reduced and of so low a height that a coal char made from non-coking or partially coking coal and having a low micum value or shatter index could be effectively used.

RECYCLING OF TOP GAS

The proposal for separation of nitrogen from stack gas described in this paper is based essentially on re-circulation of top gas. Probably the earliest known extensive recirculation of the top-gas of a working furnace is that of the electric shaft furnace built at Aosta in the 1920's by Electro-metals Limited⁸. Here roughly two thirds of the top gas was separated, freed of tar by water scrubbing and blown by fans into the hearth of the electric shaft furnace, which generally resembled a small blast furnace in which the tuyere combustion zone was replaced by electric arcs between carbon or graphite electrodes in a relatively wide hearth. As this furnace had no air blast, nitrogen was in any case virtually absent and the sole objective in re-cycling the top gas was to transfer heat from the hearth to the solids up the stack and to generate some monoxide from the carbon dioxide of the top gas by reaction with carbon present in the hearth.

In 1926 the Electro-metals idea at Aosta was developed further by Bradley⁹ who proposed the use of a mixture of CO₂ and O₂, in the proportions that would give the right hearth temperatures and hearth heat evolution when used as a cold blast. The CO₂ in Bradley's proposal was to be obtained as stated in his patent by "any suitable method" but possibly by burning some of the stack gas in an external combustion chamber with oxygen to yield "a gas high in CO₂ and low in nitrogen". Bradley's proposals were evidently never put into operation probably for the reason that they offered little if any advantage over conventional hot-blast operation with oxygen enriched blast. In 1950 the author⁵ investigated the feasibility of achieving what Bradley set out to do, by separating CO₂ from top gas by high pressure scrubbing with water, or by ethanolamine extraction, and then using the CO₂ with

oxygen as a cold blast. This proposal could not bear the cost of CO_2 separation; but when fuel injection had proved to be feasible, it was later concluded that if part of the top gas was re-cycled after cleaning and cooling and injected at the tuyeres as an auxiliary fuel, then massive fuel injection in the shape of top gas together with > 95 per cent oxygen as cold blast would be possible and nitrogen could be purged from the system to low levels in the stack gas¹⁰.

Briefly the system would be to draw off a stream of cleaned water-saturated top gas and compress this for injection at the tuyeres in a water cooled blow-pipe concentric (inner or outer) with the water cooled oxygen blow-pipe so that the two gas streams mix and react only in the combustion zones at the delivery end of the tuyeres. This system would be initiated with a light burden with air blast or oxygen-enriched air blast via the oxygen blow-pipe, venting the top gas to atmosphere via a candle. When sufficient hearth-heat has developed, top gas would be diverted to its concentric blow-pipe at each tuyere via a conventional bustle pipe system and the oxygen content of the cold blast gradually increased to > 95 per cent, while adjusting the volume of injected top gas to maintain the required hearth temperature and rate of burning of carbon in the combustion zone. The burden would then be increased to the target level of output while adjusting oxygen and top-gas injection until target rate of make is attained. In this way the content of nitrogen in the stack gas would follow the course indicated by Fig 2. The curve has been estimated by taking the decrement in nitrogen of the top gas in successive theoretical cycles and smoothing out the curve to simulate a continuous rejection of nitrogen-bearing top gas either to atmosphere after burning or for other fuel purposes. It is apparent that this system will be self-maintaining only if the weight rate of oxygen used to burn carbon and carbon monoxide in the tuyere combustion zone is sufficient to provide the equivalent of heat generation of hot-blast operation, including the enthalpy of the hot blast itself. The CO of top gas acts as an injected fuel in the tuyere combustion zone and also, after reacting with hearth carbon, as a reductant in the upper hearth, bosh and stack, especially at the increased partial pressure due to removal of diluent nitrogen.

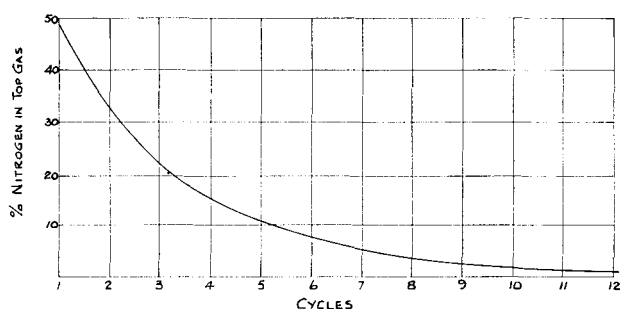


Fig. 2

The enthalpy of conventional air hot-blast is, in point of fact, supplied by the CO of the top gas. In the present proposal this CO is injected into, and burned directly in the hearth instead of in the Cowper stoves. The balancing of these sources and sinks of heat in the hearth is attainable by adjusting the flow rate of cold oxygen and of cold cleaned top gas to give the heat required:

(a) to melt and superheat the iron and slag produced,

- (b) to pre-heat adequately the stack gas (now predominantly CO in the bosh and $\text{CO} + \text{CO}_2$ in the upper stack) in order to heat the coke and burden to about 700-1 000°C in the bosh and lower stack, wherein it will be assisted by the exothermic reduction of iron-oxide by CO.
- (c) to maintain a temperature of about 450 to 600°C in the upper stack decreasing to about 200 to 250°C at the stock-line in order to provide heat to initiate the exothermic disproportionation of CO to CO_2 and carbon, known as "carbon deposition", in this region of the stack.
- (d) to provide for a number of minor heat consumptions such as radiation and cooling water losses, decomposition of water-vapour in the blast, reduction of oxides other than iron oxides, enthalpy of top gas leaving the furnace, and others in the thermal balance.

The carbon deposition reaction of (c) above is of importance in the proposed re-cycle of top gas with low nitrogen content, in that it re-deposits in the stack with evolution of heat, much of the carbon lost lower in the stack with heat absorption by the carbon reduction reaction. In the earlier small furnaces using conventional hot blast at low rates of make, for example 500 to 700 metric tons/day of iron, the carbon deposition in the upper cooler regions of the stack was of considerable importance. It took place in the main because of the low blast rate of these small furnaces and the resulting longer residence time of the stack gas even though the partial pressure of carbon monoxide was low. In the modern large furnace working on conventional hot-blast at high rates of stack gas flow this reaction is to some extent suppressed; and even in the older small furnaces its objective was usually defeated by bad burden preparation and sizing, resulting in poor catalysis of the reaction, and marked channelling of the gas streams which greatly suppressed the reaction. In the present proposed operation with low nitrogen stack gas with a modern highly permeable uniform self-fluxing sinter burden, the carbon deposition reaction would take place to a greater extent than that previously attained because of good contact, good catalysis by iron oxide and hydrogen, high partial pressure of carbon monoxide, and virtual absence of channelling of stack gas. For this reason the thermodynamics of the carbon deposition reaction and its catalysis by hydrogen and iron oxide are examined in some detail in this paper.

HEAT DEMAND

The thermal balance of the iron blast-furnace process is extremely complicated and there is a voluminous literature on the subject. The main items of heat input and consumption for a modern 6 000 t/day furnace, are given in Table I which represents present advanced hot blast (1 200°C) practice with crushed sized ore and sinter, without pellets, based on operating results recorded by Suzuki⁷.

It is estimated that in the proposed cold-blast oxygen operation with recycled cold cleaned top gas, the reaction of oxygen with carbon and carbon monoxide in the tuyere combustion zone must satisfy the heat demand:

- (a) of 630 000 kilocalories by the reaction $2\text{C} + \text{O}_2 = 2\text{CO}$ and
- (b) the enthalpy of the hot blast between day temperature and about 1 200°C amounting to 470 000 kilocalories.

TABLE 1.

HEAT INPUT	kilogram calories* per metric ton of pig iron
Combustion of C to CO (coke & injected fuel)	630 000
Exothermic CO reduction of iron	45 000
Enthalpy of hot blast (1 200°C)	470 000
Enthalpy of moisture in blast	20 000
Heat generated in slag formation	35 000
	1 200 000
HEAT CONSUMPTION	
Enthalpy top gas	90 000
Enthalpy hot metal	300 000
Enthalpy slag	130 000
Reduction of oxides excepting iron	50 000
Decomposition of water in blast	50 000
Endothermal hydrogen reduction	15 000
Carbon solution loss	300 000
Radiation and cooling & unaccounted	265 000
	1 220 000

*1 kilogram calorie (kilocalorie) = 4 186.8J (The kilocalorie has been used in preference to Joules, as all the data was published in kilocalories).

It is difficult to reconcile the figures quoted by Suzuki⁷ of about 630 000 kilo cal for carbon burned at the tuyeres per t/pig iron, and the enthalpy of the 1 200°C hot blast at 5 100 m³/min as about 470 000 kilo cal per t/pig iron with the Cowper stove gas volume of 67 000 m³/hr, when allowance is made for the CO₂ content of the top gas. It is considered that these figures should be 870 000 kilocalories/t iron and 230 000 kilocalories/t iron respectively. This does not alter the total heat consumption of 1.1×10^6 kilo cal/t pig iron for these items which is considered to be reasonably correct. This total of 1.1×10^6 kilocalories per metric ton, is about 92 per cent of the total heat demand, the balance of about 8 per cent being common to both cold-blast oxygen/top gas and conventional hot-blast working. An assessment of the way in which cold-blast oxygen operation with recycled cold clean top gas meets the total heat demand of 1.2×10^6 kilo cal/t of iron is based on the following considerations:

The combustion zone at the front of the tuyeres, in which the reaction $C + O_2 = CO_2$ predominates, is roughly spheroidal and of about 0.75 m, as determined from measurements by the U.S. Bureau of Mines Experimental Station, Pittsburgh¹¹. These authors found that in a zone surrounding this inner sphere and of about 0.3 m thickness the reaction $C + CO_2 = 2CO$ predominates. External to these spherical zones the carbon of the coke heated to about 1 500-1 700°C in the hearth and bosh reduces iron oxides (here predominantly FeO) to metallic iron and the slag is melted, while the carbon monoxide, in rising through the stack, reduces the higher oxides of iron to FeO and partly to sponge iron in the stack regions above 600-700°C, and at lower temperatures disproportionates to C and CO₂ (carbon deposition). In the hot regions of the bosh and stack the $C + CO_2 = 2CO$ reaction proceeds to CO from coke carbon generated by reduction of iron oxides by CO. (the so-called "solution" loss of carbon).

The essential points here are:

- the $C + O_2 = CO_2$ reaction in the inner sphere of the tuyere combustion zone has a free energy in the temperature range 298 k-2 200 k which is determined by a small entropy term, and therefore

remains nearly constant over this whole temperature range. Whether the oxygen blast is pre-heated, or is cold, therefore does not affect the heat evolution in this zone, excluding the enthalpy of the reactants.

- in the reaction of CO₂ with C to form CO in the outer combustion zone of the tuyeres, hot CO₂ from the inner zone (1 700°C) reacts with hot (1 500-1 700°C) carbon. The free energy equation of this reaction has a negative entropy term, so that at the prevailing temperature the CO₂ dissociates to CO and oxygen which combines with the hot carbon present to form CO. In this zone the CO₂-C reaction is no longer endothermic.

The result is that the CO₂ of the recycle gas does not react in the inner combustion zone but becomes heated to the reaction zone temperature (1 700°C) and then passes into the outer combustion zone where it reacts exothermally with carbon to form CO. The CO of the recycle gas is oxidized exothermally to CO₂ in the inner zone and the resulting CO₂ reacts as the rest of the CO₂ does, in the outer combustion zone. As only part of the top gas is recycled the nitrogen is bled off from the system to low levels, e.g. < 3 per cent depending on the N₂ content of the oxygen blast.

The heat demand, including the enthalpy of the oxygen and the recycled top gas, must therefore be met by combustion of C to CO₂ and CO to CO₂ in the inner combustion zone at the tuyeres. The relative amounts of C and CO burned to CO₂ in the inner zone cannot at present be estimated on any sound basis, because the concept of the top recycle process with cold oxygen blast as described in this paper¹² is apparently novel and there is no data available, as far as the author is aware, on pilot or large-scale operation of the process. The actual result in practice would depend among other factors on the quantity of top gas recycled and its carbon monoxide and dioxide content.

Whatever is the actual proportion of oxygen and recycle top gas used for any particular burden and rate of iron make, the absence of nitrogen reduces the total heat demand below that of conventional air hot blast by the enthalpy of the nitrogen of the air hot blast in being heated from blast temperature (1 200°C) to hearth temperature (1 700°C). Based on the high temperature specific heat of nitrogen averaged to 8.6 calories per gram mole (0.306) this heat quantity in terms of the operating results quoted by Suzuki⁷ (1.25 t nitrogen/t pig iron) is approximately 200 000 kilocalories/t pig iron.

Since the carbon solution reaction may be regarded as no longer endothermic at the temperature of the hearth, the heat demand for the recycle process is estimated to be of the order of 10^6 kilocalories per t pig iron. This would be met in the limiting case neglecting the heat from oxidation of CO to CO₂ by combustion of C to CO in the hearth zone of 410 kg of carbon (about 465 kg coke) per ton pig iron with 615 kg of 100 per cent oxygen as 95-98 per cent gas. These amounts of carbon and oxygen are to be regarded as an upper limit and are likely to be significantly lower in practice (possibly 280 kg carbon and 400 kg of oxygen) because of the enhanced reduction and carbon deposition in the upper stack due to increased partial pressure of CO and longer residence time (decreased stack gas velocity) in a sized self-fluxing sinter burden, and because of the presently incalculable quantity of heat from oxidation of CO in the inner tuyere combustion zone. This last quantity is considered likely to be about equal to the heat from combustion of 270 m³/t

of pig iron (67 000 m³/hr) of top gas of 1.1/1 CO/CO₂ ratio in the hot blast stoves as quoted by Suzuki⁷ in hot blast operations at Fukuyama. The thermodynamics and equilibrium conditions on which these conclusions are based, are discussed in the next section.

THERMODYNAMICS AND EQUILIBRIUM CONDITIONS OF CARBON-DIOXIDE REACTIONS

(a) Combustion of C to CO with cold oxygen blast.

From the available data on heat demand it is evident that success of the top gas recycle with oxygen cold-blast is dependent on the near-invariance of the free energy of the C + O₂ = CO₂ reaction in the temperature range 298 K-2 500 K. The equation for the free energy of this reaction from 298 K to 2 500 K has been averaged from the data of Thomson¹³ by Richardson¹⁴ to the straight line relationship.

$$\Delta G^{\circ}_{T_1 \rightarrow T_2} = -94\,200 - 0.20T \dots\dots\dots 1$$

On the same basis the reaction 2C + O₂ = 2CO has been averaged to

$$\Delta G^{\circ}_{T_1 \rightarrow T_2} = -53\,400 - 41.90T \dots\dots\dots 2$$

and the reaction 2CO + O₂ = 2CO₂ to

$$\Delta G^{\circ}_{T_1 \rightarrow T_2} = -135\,100 + 41.5T \dots\dots\dots 3$$

The free energy curve for the reaction C + CO₂ = 2CO has been derived from Boudouard's paper of 1901¹⁵.

$$\Delta G^{\circ}_{T_1 \rightarrow T_2} = +40\,900 - 42.0T \dots\dots\dots 4$$

These straight lines are plotted in Fig 3 and it is evident from them that at the operating hearth temperature of about 1 700°C, the heat evolution in the inner combustion zone of CO₂ formation is virtually independent of temperature; that the C + CO₂ = 2CO reaction in the outer combustion zone also at about 1 700°C is no longer endothermic due to loss of stability of CO₂ and its consequent dissociation into CO and free oxygen; and finally that the curve of equation 3 at the average hearth temperature of about 1 600°C to 1 700°C shows that the heat of combustion of CO to CO₂ in the tuyere zone can without significant error be estimated to be 30 000 kilocalories/kg mole of carbon or 2 500 kilocalories/kg of carbon as its monoxide.

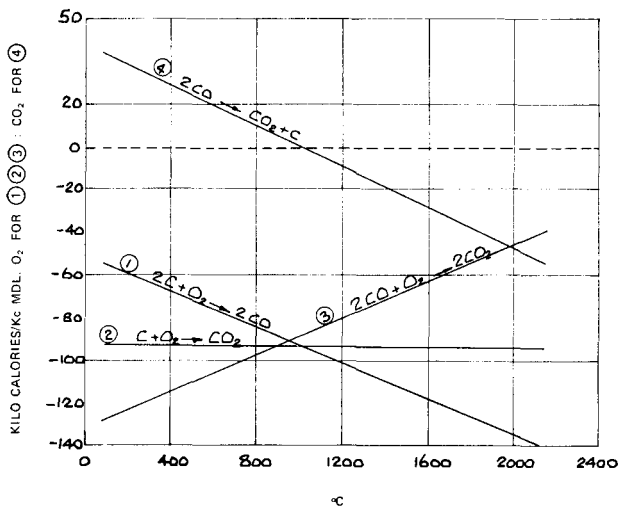


Fig. 3

(b) The Carbon Deposition Reaction.

Because of the decrease in volume on carbon deposition from its monoxide, the main effect of stack gas of low nitrogen content on this reaction is to assist carbon deposition; but this effect is complicated and is effective only over a critical temperature range lying approximately between 800 K and 1 200 K. The reason for this lies in the thermo-physics and catalysis of the reactions involved.

The variation of free energy with temperature in this reaction may be calculated from the equation

$$\Delta G^{\circ}_T = 41.533 - 4.97 \times 10^{-3} T \log_e T + 4.95 \times 10^{-6} T^2 + 5.1 \times 10^{-10} T^3 - 12.66T \dots\dots\dots 5$$

wherein the value of 41.533 in kilocalories per kilogram-molecule of CO₂ is a little higher than (40.91) given in the International Critical Tables over the temperature range 1 123 K to 1 473 K. The entropy term of (5) may be averaged for the relevant range of temperatures to 42.04 kilocalories/K to give the straight line (averaged) relationship.

$$\Delta G^{\circ}_T = 41.500 - 42.04T \dots\dots\dots 6$$

which falls nearly along the plot of (4) and (5) and is shown together with a plot of equation (4) and of k for this reaction in Fig. 4.

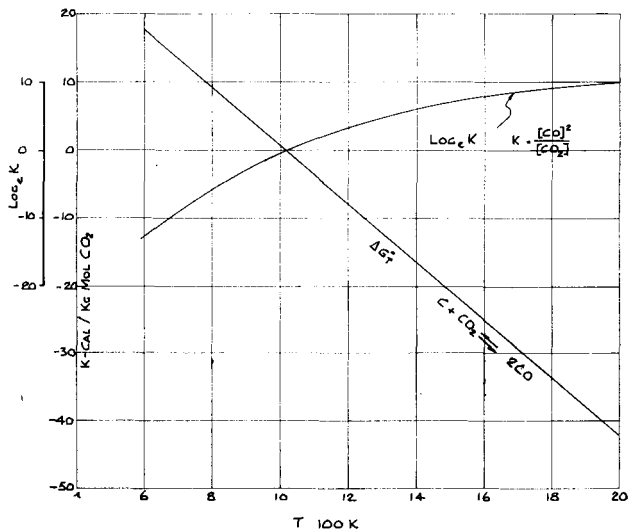


Fig. 4

Based on equation (6) and $\Delta G^{\circ}_T = -RT \log_e k$ the values of $\log_e k$ and $k = (\text{CO})^2/(\text{CO}_2)$ have been calculated as in Table II.

TABLE 11.

K	$\log_e k$	k
600	-13.7	1.14×10^{-8}
800	-4.97	6.93×10^{-3}
1 000	0.225	1.3
1 200	3.755	43
1 400	6.198	490
1 600	8.105	3 250
1 800	9.550	14 000
2 000	10.800	43 800

Fig. 5 shows the plot of weight per cent of CO_2 in $\text{CO}_2 + \text{CO}$ at equilibrium as calculated from the values of k in Table II (solid line) as compared with Boudouard's measurements¹⁵ and it can be seen that there is a close agreement. It can be seen from the plot of Fig. 4 that ΔG°_T passes through zero at about 1 000K and here the value of $\log_e k$ becomes zero and k passes through unity. At higher temperatures than 995K the reaction is exothermic due to decreased stability of CO_2 but at lower temperatures it is endothermic. Above 1 400 K the reaction goes nearly to completion in the formation of CO , whereas at about 350K to 400K the reaction for carbon deposition tends to go to completion in the reverse direction but can do so only in the presence of catalysts, of which iron oxides and water vapour promote the deposition of carbon at these lower levels of temperature.

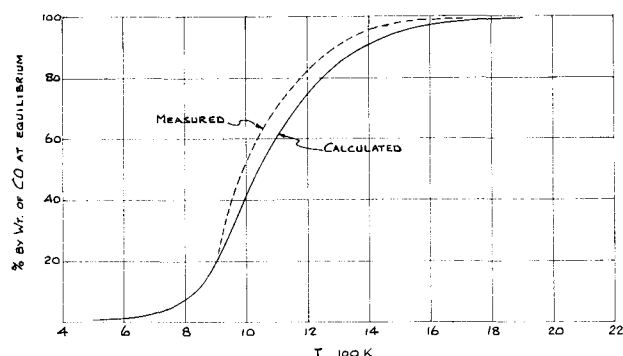


Fig. 5

The significance of these factors in the operation of a blast furnace with low nitrogen stack gas is that both in the low temperature regions where the reaction goes nearly to completion to carbon deposition and in the high temperature range where it goes nearly to completion in the reverse direction, the effect of the partial pressure of carbon monoxide is insignificant; but in the intermediate ranges of temperature of about 900K to 1 100 K, wherein the value of k lies between about unity and 3, increased partial pressure of carbon monoxide attainable by low nitrogen content of stack gas, and if desired in addition high top pressure operation, has a significant effect on carbon deposition. Rhead and Wheeler measured this equilibrium of CO in presence of carbon at 800°C to 900°C with the results shown in Fig. 6 from which it can be seen that the equilibrium partial pressure of CO_2 (and therefore carbon deposition) is increased about three-fold on increasing the pressure of $\text{CO} + \text{CO}_2$ from 30 Nm^{-2} to 100 Nm^{-2} . It is therefore to be expected that with stack gas of low nitrogen content carbon deposition in the region of the stack where the burden and stack gas temperatures are between about 500 K to 1 200 K carbon deposition will be greater than that encountered with the 50 per cent nitrogen stack gas of conventional operation and will be stepped up by high top pressure operation.

Catalysts of the carbon deposition reaction could be expected to be best attained by the iron oxides of well oxidised basic sinter rather than by self fluxing basic pellets. This is borne out by the performance of the Fukuyama furnace⁷ which first achieved 6 000 metric tons per day using a burden with no pellets but only crushed ore and sinter in the proportions of 30 and 70 parts by weight respectively. Catalysts of the carbon reaction by hydrogen and/or water vapour was measured

by Bone¹⁷ using a carbon monoxide-nitrogen mixture simulating ordinary stack gas. The ore used in these measurements was a Barrow haematite of high ferric oxide content of the following analysis.

	%
Fe_2O_3	82.36
FeO	Nil
CaO	0.9
SiO_2	14.53
Al_2O_3	0.23
MgO	Nil
MnO	trace
$\text{H}_2\text{O}(150^\circ\text{C})$	0.6

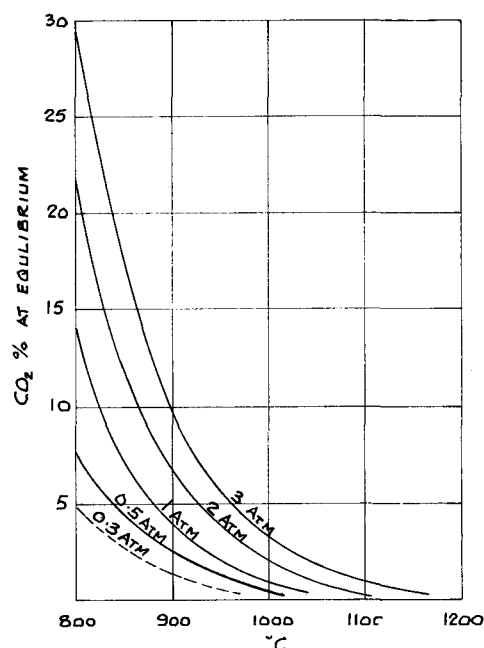


Fig. 6

The high ferric oxide content of this ore would closely simulate a well oxidised good quality basic down-draught sinter.

Fig. 7, based upon the Bone's data shows the catalytic effect of the ferric oxide (i) with dry hydrogen-free carbon monoxide, and (ii) with 1 per cent of hydrogen present. To the effect of the hydrogen catalysis of this reaction is due at least some if not all of the benefit of adding relatively small amounts of water vapour to the conventional hot blast system. Any blast furnace operated with low-nitrogen stack gas by re-cycle of top gas as described in this paper would normally have the required optimum concentration of water vapour in the blast, the actual rate of injection of water being varied to suit operating conditions as it is in normal hot-blast operation; but under the conditions of high partial pressure of CO and CO_2 in low-nitrogen stack gas the rate of carbon deposition is likely to be increased in the region of the stack with temperatures lying between about 900 K and 1 200 K.

COLD-BLAST LOW NITROGEN FURNACE LINES

There is so marked a general similarity in conventional hot-blast furnace lines used for reducing ores of widely differing physical and chemical properties that it is at

times assumed that the lines of a furnace, comprising the stack and bosh heights, and the in-wall and out-wall batter of the stack and bosh, are more or less fortuitous. In modern designs of high productivity with carefully prepared self-fluxing sintered burdens this is far from the truth. The bosh height and angle, and to a less degree the stack height and angle, are of importance in obtaining high productivity from any given ore, flux and coke. For any given burden and coke the height and angle of the stack must be determined to ensure the required rate of stock descent so that despite swelling and generation of fines from the burden particles, the designed stack-gas flow can be maintained at the expected pressure drop across the stack height, and so that stock arrives at the top of the bosh in the pasty condition.

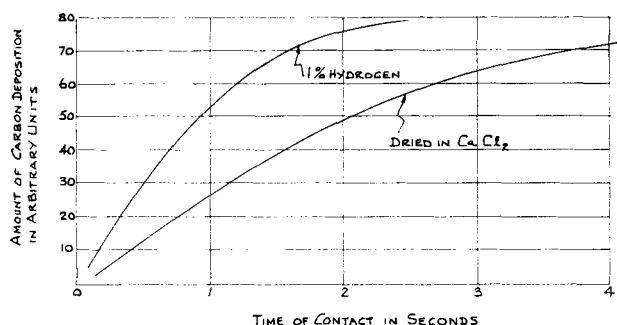


Fig. 7

During descent in the stack pre-reduction of iron to lower oxides and metal takes place to some extent, the burden becomes heated to incipient melting or pastiness at the base of the stack, carbon deposition takes place, but there is little or no shrinkage. In the bosh the reverse is true. Marked shrinkage takes place due to coke consumption, slag formation, and completion of reduction of oxides of iron and the oxides of such constituents as phosphorus, vanadium, silicon and manganese; and at the base of the bosh on delivery to the tuyere zone little remains to be done but the combustion of carbon and the superheating of slag and iron, in the hearth. For these reasons the bosh can and must have an outwall batter.

When using modern blast temperatures of 1 200°C to 1 400°C in high productivity furnaces with sized sintered burden and sized coke the stack and bosh heights and their angles differ surprisingly little from those of smaller hot-blast furnaces of 35 years ago. The chief difference in lines has been the increase in diameters of hearth, bosh, and stack, presumably in order to take advantage of the fact that with carefully sized burden and coke, resistance to stack-gas flow, which as a limiting factor transcends all others (even that of rate of stock descent) decreases closely with the square of these diameters. While the limit of rate of stock descent is still far off, modern blast rates have already reached in hot-blast practice over 5 000 m³/min and are being talked up to 8 000 m³/min at power input for blast alone of 45 000 kW. It is evident that these blast rates must be approaching levitation or fluidization of the burden in the stack even at the presently planned hearth diameters of about 17 m.

Table III compares a hot-blast furnace at South Works, Illinois Steel Company making 700 t/day in the late 1920's on a 6.5 m hearth (then one of the largest in the world) with the Fukuyama furnace making 6 000 t/day on a 11.2 m hearth in 1969.

TABLE III.

	South Works 700 t/day	Fukuyama 6 000 t/day
Stack height	17m	19.8 m
Stack angle	85°	83° 57'
Bosh height	4.5 m	3.8 m
Bosh angle	80° 32'	82° 27'
Hearth diameter	6.5 m	11.2 m
Hearth area	33.2 m ²	98 m ²
Bosh diameter	7.5 m	12.2 m
Bosh area	43.9 m ²	109 m ²
Stack diameter (top)	5.2 m	10.0 m
Working volume	460 m ³	2 255 m ³
Blast temp.	600°C	1 200°C
Blast rate	1 300 m ³ /min	5 100 m ³ /min
Blast pressure (max)	1.2 kg/cm ²	3.7 kg/cm ²
Iron make/m ² hearth area/hr	860 kg	2 560 kg

It can be seen that in this advance in productivity the heights and angles of stack and bosh are about the same, but the hearth bosh and stack diameters have about doubled giving roughly a four-fold increase in area traversed by stack-gas. Even so, blast pressure has been increased three-fold. It is therefore to be concluded that in conventional hot-blast operation stock descent rate is not the limiting factor but that the blast rate is the limiting factor and has required a three-fold increase in pressure despite the much greater permeability of burden attained by careful sizing. In S.I. units the Blast Furnace Output Index¹⁸ of the South Works furnace is 42 and that of the Fukuyama furnace is 137.

Elimination of nitrogen from the stack gas virtually halves the blast rate for a given rate of burning of C to CO at the tuyeres, and at the same time about doubles the CO concentration in the bosh and lower stack. Although in the opinion of the author the B.O.I. estimate fails at so great a rate of production as that of the Fukuyama furnace, it does show that there is no apparent valid reason why the rate of stock descent corresponding to a make of 2 500 kg/m²/hr, which is, for a burden yield of 59 per cent iron, equivalent to approximately 4 200 kg/m²/hr of stock should not be increased by 50 per cent to 6 300 kg/m²/hr. or even doubled. The increased rate of stock descent is mainly a matter of increasing the stack angle to accommodate the descent of stock before a significant decrease in volume takes place and to reduce the bosh angle to accommodate the increased rate of descent during the reduction and melting stage. Bosh height and stack height would follow normal design lines depending on ore, flux, and coke properties as stated by Sarek¹⁹.

Modern high capacity furnaces have a working volume of approximately 200 m³/m of hearth diameter. Based partly on Sarek's data and on the modern high capacity lines for hot blast at 1 200°C to 1 400°C, the lines and performance of a furnace of rated output of 4 000 t/day from a sized sinter burden of 59 per cent iron content and coke of 14 per cent ash content are estimated in terms of the foregoing analysis of the low nitrogen stack gas proposal, to be as follows:

Stack height	17 m
Stack angle	86° 42'
Bosh height	3.5 m
Bosh angle	78° 42'
Bosh diameter	8.5 m
Bosh area	57 m ²
Hearth diameter	7 m
Hearth area	38 m ²
Working volume	900 m ³

Working volume/m hearth diam.	129 m ³
Iron make kg/m ² hearth area/hr.	4 400
95—98 % oxygen m ³ /t iron	270—290
Carbon burned at tuyeres kg/t iron made	280
Top pressure	$2 \times 10^4 \text{ Nm}^{-2}$
Blast pressure	$15 \times 10^4 \text{ Nm}^{-2}$
Slag volume kg/t iron	350
t iron/hr	170
t iron/day	4 000
Oxygen 95—98 % t/day	ca 1 500—1 800

The performance of the Fukuyama furnace at 6 000 t/day when reduced to its iron make per m² of hearth area per hour (which is 2 560 kg), does not appear to be such a cataclysmic advance when it is remembered that over 50 years ago a furnace of Bochum Verein in Germany averaged no less than 2 300 kg of iron/m²/hr on a 3.9 diameter hearth with only a 460 m³ working volume or 118 m³/m of hearth diameter. The Bochum furnace moreover operated with a blast temperature of 560°C. The Bochum output was achieved with a burden yielding 49 per cent of iron but unprepared in any other way, as compared to the 59 per cent yield at Fukuyama with a carefully prepared and sized sinter and crushed ore burden. The coke rate at Bochum in the 1920's was as low as 790 kg/t.

PROVISION OF OXYGEN

Any significant degree of oxygen enrichment of the blast to over 25 per cent in normal sized and larger furnaces requires large daily tonnages of oxygen. The

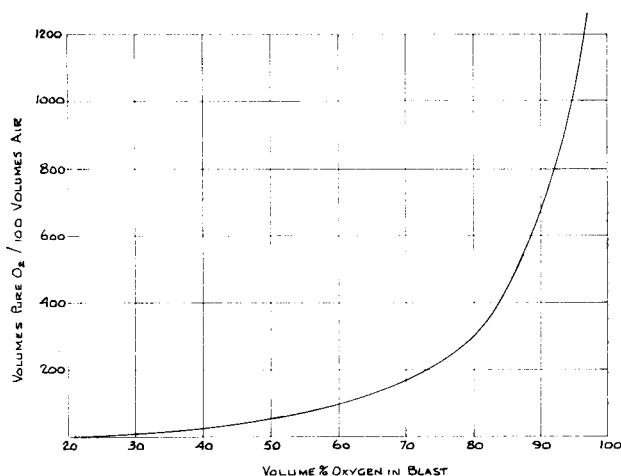


Fig. 8

graph of Fig. 8 shows the rate of increase of volume of oxygen that must be added to attain a given oxygen enrichment of the blast. Colclough⁴ claimed that in normal hot blast working with oxygen enrichment, the increased heat absorption in the bosh zone, coupled with decreased volume of stack gas due to increasing oxygen enrichment, leads to a decreasing quantity of heat passing up the stack, until, at about 25 per cent oxygen content of the blast, the stack heat available is insufficient, and descending stock reaches the bosh unheated and un-reduced with the result that direct reduction in the hearth increases. These authors stated that the stage at which this imbalance is reached is ill-defined, but that the permissible limit of oxygen enrichment is about 25 per cent of oxygen in the blast. That Colclough's deductions regarding lack of stack-heat and greater direct

reduction in the hearth are erroneous was later established by the results of the Osaka furnace⁶ which attained the record low of 370 kg of coke per metric ton of iron with as much as 27 per cent oxygen in the hot blast.

In the present proposal for limiting the nitrogen of stack gas to small percentages, stack-gas for heat transfer is provided by carbon monoxide which acts purely as an inert heat transfer gas in the hearth and lower bosh, but in the upper bosh and stack acts both as a heat transfer gas and as a reductant and in addition liberates heat in the upper stack by the exothermic carbon deposition reaction.

The oxygen added to the re-cycled cold low-nitrogen stack gas must be approximately the equivalent of that taken into any given furnace working on normal hot blast. The graph of Fig. 8 shows that low nitrogen is unattainable by straight enrichment of blast with oxygen, because the temperature of the tuyere combustion zones would be too high, and could not be diminished and controlled; but with re-cycled cold top gas the combustion temperature at the tuyeres is controllable by the rate of admission of cold top gas which will carry as much heat up into the stack as is necessary, but unlike inert nitrogen will strongly reduce the ore burden in the stack and cause useful carbon deposition at the same time.

On the basis of the estimates presented in this paper it can be expected that in normal haematite practice with properly prepared self-fluxing burden an average of 0.42 tons (290 m³) of 97 per cent oxygen per ton of pig iron produced will be required to maintain the action of the furnace. If nitrogen is rejected from the process by injection at the tuyeres of cold clean recycled top gas, all of this oxygen must come from air-separation plant, but its purity can be between 95—98 per cent by volume. The separation plant for blast furnaces of capacity of 4 000 to 6 000 tons of iron per day must therefore be of large capacity, of the order of 1 500 to 2 500 t/day of this medium purity oxygen.

Air separation plants of this size are generally designed on the basis of low-pressure cycles. Two fundamental inventions have made these plants possible:

- the use of the regenerator heat exchange principle for low temperature heat exchangers proposed by Mathias Frankl in 1925, and
- the use of liquid air as reflux in a single column distillation unit in place of liquid nitrogen as reflux in a double column distillation unit.

Low pressure high tonnage air separation cycles could not be worked with conventional tubular heat exchangers, but proved to be readily workable on the regenerative principle. When Frankl's regenerators were used it was unexpectedly discovered that air could be compressed into the cycle without previous removal of water vapour and carbon dioxide as these impurities could be frozen out in the regenerators in the cooling cycle and re-evaporated under clearly defined conditions by waste nitrogen in the heating cycle. The use of Frankl's regenerators was also dependent on the development of efficient low pressure expansion engines. These regenerators came into large-scale use with the development of both radial and axial flow turbines in Europe and North America.

The use of liquid air reflux in a single distillation column for large tonnage oxygen 95—98 per cent purity was proposed by Schuftan²⁰ in 1955. The flow-sheet is shown in Fig. 9²¹ in which Schuftan's numbering of some plant items has been retained for comparison with his description.

dioxide, but also to provide an efficient and flexible source of cold for production of the desired amount of liquid oxygen and a means of pre-heating the L.P. air stream in exchanger 5 immediately before the expansion turbine passing this stream into the distillation column. The high pressure air system is shown in figure 9 and is conventional in that a small part of the wet cooled I.P. air stream is freed of CO₂ by caustic soda in a contact tower, compressed and finally dried by alumina in a pair of contact towers and expanded in a conventional reciprocating expander generating a small amount of power.

The waste nitrogen path is shown in Fig. 9 from the top of the column 10 via heat exchanger 9 through to group 1 and 2 of the regenerators. Provision is made, at reduced demand, for part of the I.P. stream to be diverted at the exit of equaliser 7 to expansion turbines 15 via heat exchanger 14 and is expanded directly into the waste nitrogen line so as to provide, if desired, an additional liquid oxygen supply at the expense of total oxygen yield.

It is of interest to note that in the large-scale operation of Schuftan's process aluminium alloy heat exchangers are used, but the original coiled corrugated aluminium foil trays of Frankl's regenerators have been replaced by stone on the grounds that stone has a higher heat capacity which permits a longer cycle time of about 8 minutes and smaller change-over losses with less disturbance in the operation of the plant.

Schuftan's plant is simple and robust and is capable of supplying, at remarkably low power consumption, large tonnages of 95–98 per cent oxygen for the relatively steady demand of the blast furnace. When producing 97 per cent oxygen with minimal output of liquid oxygen a power consumption including all auxiliaries of 0.434 kWh per m³ of 100 per cent oxygen can be attained²². This power input is 304 kWh/t 100 per cent oxygen.

At a power cost of 0.4 cents/kWh (South African currency), power per metric ton of 100 per cent oxygen is R1.22. Allowing that total power costs are 40 per cent of total costs of oxygen including amortization of plant, the cost of a ton of 100 per cent oxygen is R3.05. A cost recently quoted⁶ for tonnage oxygen in the U.K. is 1s. 9d. (pre-devaluation) per 1 000 standard cubic feet or R4.35 per metric ton which is in fair agreement, allowing power costs in U.K. at 0.6 cents/kWh.

GENERAL CONDITIONS

(i) Time of Stock Descent.

The Fukuyama No. 2 furnace produces 6 000 t/day from a 59 per cent burden yield. This is estimated to require 2.2 tons of burden and coke occupying 1.85 m³/t of iron. With a working volume of 2 255 m³ time of stock descent is therefore about 5.8 hours.

In the theoretical 4 000 t/day furnace operating the top-gas recycle process as quoted in this paper, time of stock descent with an equivalent burden, and at the coke rate estimated, would be 2.9 hours or approximately twice the rate of the Fukuyama furnace, to produce 4 400 kg iron/m² hearth area/hr as against the Fukuyama No. 2 make of 2 560 kg/m² hearth area/hour.

(ii) Oxygen Plant.

For the theoretical 900 m³ cold oxygen blast furnace quoted in this paper an oxygen capacity of 1 600 t/day of 100 per cent oxygen would be required. This would be

constructed on the Schuftan cycle with one main compressor of 23 000 kW power input for the L.P. and I.P. streams, and one H.P. compressor of 2 000 kW input, and an expansion engine for "balancing" air. These compressors would be arranged to operate two 800 t/day or four 400 t/day distillation columns in conjunction with a battery of six groups of two regenerators each. This arrangement could supply some air blast direct to the furnace to allow for short-term outage of the distillation units. The H.P. system can have short-term outage without undue interference with the main distillation plant.

(iii) Water Vapour.

For the same reasons that hot-blast furnaces are operated with a water vapour content in the blast, the cold oxygen blast would also have an adjustable water vapour content by addition of steam at the tuyeres. The beneficial action of small amounts of water vapour in blast furnace air is appreciated by most hot-blast operators but is not yet fully explained. The primary objective is to catalyse carbon deposition in the upper regions of the stack.

CONCLUSION

Over and above production of ordinary grades of iron and ferro-manganese, a potential use for the low nitrogen stack gas proposal is to reduce sinters of vanadium-bearing titaniferous iron ores and sinters of iron ores containing other alloying elements for direct conversion to alloy steels in the oxygen converter.

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