

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

by W Bleloch

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Errata

- (a) The final sentence in the penultimate paragraph, left hand column p. 34 of the text should read: 'In the hot regions of the bosh and stack the $C + CO_2 = 2CO$ reaction proceeds to CO from coke carbon *and carbon* dioxide generated by reduction of iron oxides by CO (the so-called solution loss of carbon)'. The italicised words have been omitted in the text.
- (b) Temperature in Fig. 3 is K not C.
- (c) In Fig. 9, connection from top plate of column 10 to heat exchanger 9 has been omitted.

DISCUSSION

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Dr Bleloch's paper has outlined the advantages of recycling stack-gas of low nitrogen content in the blast furnace. In the first instance it would appear to be extremely beneficial in controlling the hearth temperature and allowing a 100 per cent oxygen-blast to be used.

On a second point however we have to disagree. It is claimed that heat is liberated in the combustion zones by the oxidation of CO to CO_2 near the tuyeres and in the subsequent reduction of the CO_2 by CO. The author has hypothesized as follows, and we quote:

'The $C + CO_2 = 2CO$ reaction in the outer combustion zone at about $1700^\circ C$ is no longer endothermic due to loss of stability of CO_2 and its consequent dissociation into CO and free oxygen.'

This statement requires closer examination. If we consider the individual events occurring with the CO in the recycled topgas, with the oxygen in the blast and

with the coke in the burden, as done by Dr Bleloch, the following heat considerations emerge. All heats of reaction are calculated from the enthalpy values of each reactant and product, as well as the temperature dependence of their molar heat capacities.

- (a) At the tuyeres: $CO + \frac{1}{2} O_2 \rightarrow CO_2$ (1)
CO, CO_2 at $500^\circ C$; O_2 at $25^\circ C$.

$$\Delta H_{\text{reaction}} = -65\,000 \text{ cal/mole CO}$$

The reaction (1) is exothermic.

- (b) In the outer combustion zone: $CO_2 + C \rightarrow 2CO$ (2)
C, CO at $1700^\circ C$; CO_2 at $500^\circ C$.

$$\Delta H_{\text{reaction}} = +56\,000 \text{ cal/mole CO}$$

Reaction (2) is endothermic.

The overall heat gain of reactions (1) and (2) is

$$\Delta H = +56\,000 - 65\,000 = -9\,000 \text{ cal/mole CO}$$

i.e. the overall reaction is slightly exothermic, the amount of heat liberated is however smaller than suggested by Dr Bleloch.

- (c) The dissociation $CO_2 \rightarrow CO + \frac{1}{2} O_2$ (3)
is a highly endothermic reaction at $1700^\circ C$, requiring $82\,000 \text{ cal/mole } CO_2$ to proceed to completion.

Furthermore, this reaction (3) is energetically not favoured from proceed, as can be observed from the free energy-temperature relationship of figure (3), which favours the formation of CO_2 at $1700^\circ C$. Hence direct dissociation of CO_2 at $1700^\circ C$ appears to be unlikely.*

The concept of recycling topgas is however still intriguing from many other points of view. Apart from providing a very efficient method of hearth temperature control, it will create a much higher CO partial pressure in the stack.

Whether the rate of indirect reduction in the stack will be proportional to this partial pressure or not is un-

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certain and will depend on whether the rate controlling step is a surface reaction, gaseous diffusion or another mechanism.

	$\frac{P^2_{CO} \cdot P_{O_2}}{P^2_{CO_2}}$	T °K	log Kp
*For $2 CO_2 \rightleftharpoons 2 CO + O_2$ Kp =		1 000	-20.13
		1 500	-10.25
		2 000	- 5.37

Our own experience and that of many other co-workers appears to indicate that this depends on many factors — not the least of which is the nature of the iron containing burden and the size of the material in the furnace shaft. For this reason it is felt that the effectiveness of the increased partial pressure of the CO would have to be proved in practice.

It is certainly true, as Dr Bleloch has pointed out, that another effect of the increased CO partial pressure would be to increase the rate of carbon deposition. Here our experience would indicate that this could have serious consequences if allowed to proceed unchecked. Experiments done at Iscor have indicated that under certain conditions, when reducing with 100 per cent CO, the rate of carbon deposition can outstrip by far the rate of indirect reduction and can in fact block the indirect reduction mechanism almost completely. This then leaves the greater part of the reduction to be done directly in the hearth and this, as is well known, can be expensive from the point of view of coke requirements.

Once again it is felt that this would have to be proved in practice and could certainly be of little consequence in a system such as envisaged by Dr Bleloch due to the steep thermal gradient which should exist with this type of furnace arrangement.

The principles involved in the cold blast oxygen iron production however remain sound and it would be interesting to see a practical trial carried out. The economics of the principle appear very attractive, but are, of course, based on a number of theoretical assumptions. To add to this, it is by now well known that the construction of theoretical models of blast furnaces are always fraught with difficulties and the capital outlay needed to erect a plant of a size suitable for obtaining the required information for the construction of a production plant could be more than considerable. It is this kind of consideration that makes the practical testing of a project such as this one so very difficult.

It is to be sincerely hoped that Dr Bleloch will find some way of doing this in the not too distant future.

AUTHOR'S REPLY

Oxygen enters the furnace in the blast and in the oxides of the metals being reduced; and almost all of it leaves the furnace as oxides of the carbon fed into the furnace. It follows that the greater the CO₂ content of the top gas the greater is the overall efficiency of the use of carbon in the coke and injected fuel for reduction of iron oxides and other reducible oxides. It is well known that increase in partial pressure of carbon monoxide increases the rate of carbon deposition in the stack. By increasing the carbon deposition in the upper stack, and so increasing the CO₂ content of the top gas, the top gas recycle proposal of the text has as its main objectives:

- (i) the attainment of significant carbon economy

- (ii) a high and controllable hearth temperature for reduction of metals other than iron concurrently with iron itself (e.g. vanadium, chromium, manganese)

- (iii) an adequate rate of combustion of formed coke and other grades of coke of low reactivity in the hearth.

Hearth heat demand for the cold oxygen and recycled top gas proposal is taken as 1.2×10^6 Kilo-calories per t pig iron made, *including* the enthalpy of the blast at 1 200 °C. As nitrogen is purged from the system to low levels under steady-state conditions in the recycle proposal, this total heat demand is diminished by the enthalpy of nitrogen in the hot blast, between the blast temperature of 1 200 °C and the hearth temperature of about 1 700 °C, amounting, as calculated in the text, to approximately 0.2×10^6 kilo-calories, leaving as stated a total hearth heat demand of about 1.0×10^6 kilo-calories/t of iron.

In conventional hot blast operation the enthalpy of nitrogen between 1 200 °C blast temperature and 1 700 °C hearth temperature is used in part to heat burden in the stack. This source of stack heat is absent in the cold oxygen/recycled top gas proposal but is compensated to an extent which is at present indeterminate by the exothermic carbon deposition reaction, and possibly by the greater heat transfer from the low-nitrogen stack gas due to its longer residence time in the stack. It would, in the practical operation of the top gas recycle proposal, be finally compensated by variation of the top-gas/oxygen ratio during running.

In the text the demand of 1.0×10^6 kilo-calories is met by reaction in the hearth of 410 kg of carbon with 615 kg of oxygen taking the heat of reaction of $2C + O_2 = 2CO$ to be 5.88×10^4 kilo-calories for 24 kg of carbon. Whether the CO₂-carbon reaction is endothermic or exothermic in any given region at any given temperature is entirely irrelevant to this calculation of hearth-heat generation.

In the text the quantity of 410 kg carbon/t iron consumed in the hearth is reduced, as a purely arbitrary estimate, to 280 kg of carbon, because of the re-cycling of carbon in the stack by the carbon deposition reaction; and likewise the oxygen is reduced to 400 kg of injected oxygen as 95-98 per cent gas because of the reaction of carbon deposited on the iron oxides by disproportionation of its monoxide under the high partial pressure in the stack, with those oxides (especially Fe₂O₃ in the sinter) on their journey down the stack into regions of temperature above about 750 °C.

It is agreed that dissociation of CO₂ to CO and oxygen is highly endothermic at 1 700 °C. That this is so is clearly stated in the text by curve 3 of Fig. 3; but CO₂ is reduced to CO by carbon above about 1 000 K.

That disproportion of CO₂ to CO and carbon is exothermic below about 1 000 K, as shown in curve 4 of Fig. 3 of the text, is known from the established thermodynamic data of reaction of carbon with oxygen.

In the low temperature range of curve 4 Fig. 3 the carbon deposition reaction can proceed only if adequately catalysed. It is considered that any hindrance of stack reduction by deposited carbon is more than compensated by the re-cycling of carbon back to the bosh and hearth for direct reduction in that region.