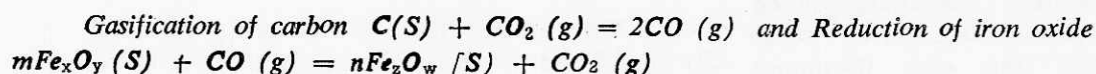


# KINETICS OF REDUCTION OF IRON OXIDES AND ORES BY CARBON

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## Abstract

**T**HEORETICAL considerations and experimental findings point out that reduction of iron oxides and ores by carbon proceed via the gas phase, whenever the latter is present. The overall reaction is a coupling of the following two component reactions, viz.,



Recent kinetic studies have established that the gasification reaction controls the rate of the overall process under the circumstances normally encountered.

A critical evaluation of these studies have been presented. The available information on the kinetics and mechanism of the two component reactions have also been critically reviewed.

On the basis of the above, first of all the scope of further work in this area have been assessed, and, finally the productivity of the rotary kiln process of sponge iron making has been examined.

Reduction of iron oxides and ores by carbon is a key metallurgical reaction. It was postulated in the nineteenth century that both "indirect" and 'direct' reduction were taking place inside an iron blast furnace. The former was meant to denote reduction by carbon monoxide, and the latter stood for reduction of iron oxides directly by carbon as follows.  $FeO + C = Fe + CO$  ...[1]

which takes place principally in the lower portion of the stack. The "direct" reduction as per equation (1) may be called carbothermic reduction too. For quite sometime the interest in it lay in connection with blast furnaces only. Of late however, a number of alternative iron making processes, such as rotary kiln processes, electric pig iron process etc. are employing carbon reduction of iron oxides and ores. The objective of this review is:

- (1) to present the salient features of the kinetic aspects of reduction of oxides of iron by carbon.
- (2) to critically assess the situation based on the above.

In doing so, the review as such shall be restricted to the fundamental investigations alone. The reduction is kinetically a complex process and there are many contradictions, controversies etc. An effort has been made to focus on these if they are important and to resolve them as much as possible.

## I. TRUE DIRECT REDUCTION VERSUS REDUCTION VIA GASEOUS MEDIUM:

Kinetically, a solid-solid reaction is expected to be much slower compared to a gas-solid one for two reasons. First of all, the solid-solid contact area is much smaller compared to gas-solid contact area. Secondly, solid-state diffusion is much slower compared to mass transfer in gases. Therefore, it was recognized even in early days that the overall reaction is perhaps

taking place in two stages, viz.

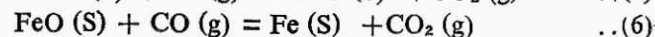
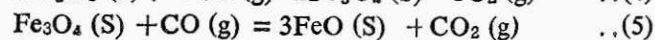
Reduction of iron oxides, which can be generalized as follows:



and, gasification of carbon:



Reaction (2) can be any one of the following:



It should be noted that wustite is non-stoichiometric. Hence equation (5) and (6) are simplifications.

Several investigators (1-4) attempted to measure the rates of true "direct" reduction, viz., the solid-solid reaction between iron oxide and carbon by continuous evacuation of the chamber in the overall temperature range of 700 to 1150°C and pressure range of  $5 \times 10^{-4}$ — $10^{-2}$  torr. They assumed that the gas phase were substantially eliminated by evacuation and hence the rates they obtained represented those of solid-solid reaction. Fig. 1 compares these experimental data with those obtained by Rao (5), who employed inert gas flushing.

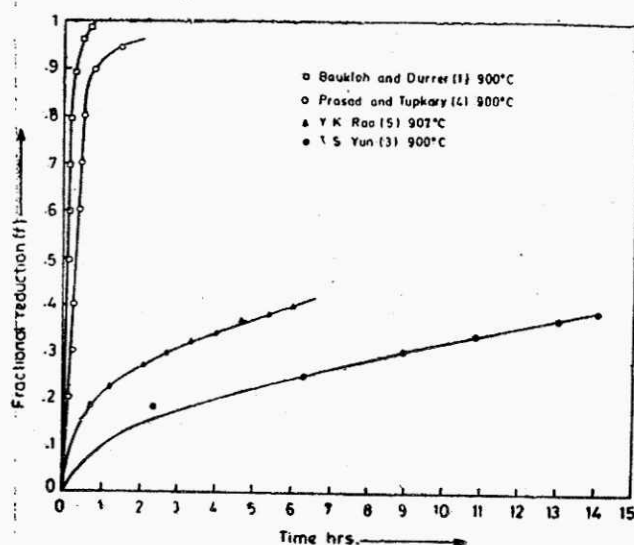


Fig. 1 Fractional reduction vs. time for carbon reduction.

It may be concluded from Figure 1 that the rates under inert gas flushing were even smaller compared to some of those obtained under evacuated conditions. Therefore as such there is no experimental proof to support the theoretical expectation that the rate of the solid-solid reaction should be much slower than that of the gas-solid reaction in this case. However, in these experiments fine iron oxide were mixed with powdered graphite and pressed into pellet. Although the chamber was evacuated the pressure

inside the fine pores of the pellets were likely to be appreciable because flow of CO and CO<sub>2</sub> from the interior of the pellet to the chamber would require a substantial pressure difference. The following sample calculation reveals it.

The flow of gas through a pore is 'molecular' or 'Knudsen' when the mean free path is larger than the pore diameter. This condition was very well met in the tiny pores of pellets under a reduced pressure. The through-put of gas per unit time (U) through such a cylindrical pore may be expressed by the following relationship (7):

$$pv = U = C (p_1 - p_2) \quad \dots (7)$$

where, v, is the volumetric flow rate in c.c./sec. at pressure p; (p<sub>1</sub>-p<sub>2</sub>) is the difference in pressure across the tube; C is known as the conductance and is given by:

$$C = 3,810 \sqrt{\frac{T}{M}} \frac{D^3}{l} \text{ c. c./sec.} \quad \dots (8)$$

where T is temperature in °K, M is molecular weight of the gas, D and l are diameter and length of the pore in cm. Noting that the pellet size is approximately 1 cm, the diameter of the pore to be of the order of 10μ, it can be shown with the help of equations (7) and (8) that the pressure inside the pellets should be at least 10 mm in order to allow flushing of CO and CO<sub>2</sub> out of the pellet into the evacuated chamber. If that is so, then the gas phase cannot be ignored in their experiments. Hence it is very doubtful whether the investigations (1-4) could at all measure the rate of the solid-solid reactions as such.

However, it may be stated here itself that there are a number of evidence in support of the contention that the overall reduction takes place via reactions (2) and (3), whenever a gaseous medium is present. These will be evident from the discussions in the following sections. Here a mention may be made of the experiments by Baldwin (7), who passed nitrogen over a heated bed of iron oxide and coke, and found that the rate of removal of oxygen decreased as the flow rate was increased. The possible explanation is that nitrogen was flushing out CO and CO<sub>2</sub> formed thus diluting their concentrations and decreasing the rates of gas-solid reactions. This could not have happened if the reaction was a solid-solid one.

Since it seems to be fairly well established as will be evident later that the carbon reduction takes place via reactions (2) and (3) in the presence of a gaseous environment, such as in industrial processes, the kinetic features of the

TABLE I

Experimental Conditions for investigation on kinetics of reduction by Carbon monoxide

Reference	Material	Practical size (dia)	Porosity	Gas Composition	Temp. range	Technique	Activation Energy
(1) Smith and Mckewan (12)	Hematite ore (pellets)	1.5-1.9 cm	Voids fraction-0.21	Pure CO	760°C-1120°C	Single pellet; Thermobalance	Porous pellet = 8.5 K Cal/mole Dense pellet = 8.0 K Cal/mole
(2) Khalafalla et. al. (13)	a) Magnetite pellets of ore	-6 + 8	—	70% CO 30% CO <sub>2</sub>	1000°C 1300°C	Packed bed; gas analysis	13 K Cal/mole
	b) Magnetite particles	"	—	"		"	45 K Cal/mole
(3) Bicknese and Clark (14)	FeO prepared from pure Fe <sub>2</sub> O <sub>3</sub> and Fe	-12 + 16	Surface area 0.0177 to 0.0213 Sqm per gram	1.88 mole N <sub>2</sub> for 1 mole of CO	1145°C	Packed bed; thermobalance	13.9 K Cal/mole
(4) Kawasaki et. al. (16)	Fe <sub>2</sub> O <sub>3</sub> prepared from pure Fe	1.5-4.4 cm sphere	Voids fraction-0.31	Pure CO	700-1200°C	Single layer of pellets; thermo balance	
(5) Khalafalla and Weston (17)	Wustite prepared from pure Fe <sub>2</sub> O <sub>3</sub>	-4 + 5 sphere	—	Pure CO	1000°C	Packed bed; gas analysis	

two component reactions [eqn. (2) and (3)] will be presented first and then the carbon reduction shall be taken up.

## II. KINETICS OF REDUCTION OF IRON OXIDES BY CARBON MONOXIDE:

Numerous fundamental investigations have been carried out in the past two decades on the kinetics of reduction of iron oxides by hydrogen (8-10). In comparison much less data are available on reduction by CO due to the problem associated with the deposition of carbon through the reaction:  $2\text{CO(g)} = \text{CO}_2\text{(g)} + \text{C(S)}$  during investigation.

Table 1 presents the important experimental conditions of some fundamental investigations of the kinetics of reduction of iron oxides by CO (11-17).

It should be noted that some of the investigators studied the reduction kinetics of FeO. Both single pellet-cum-thermobalance technique (12,15) as well as packed bed systems were employed (13, 14, 17). The particle size ranged anywhere from a fraction of a millimeter to 4 centimeters. The temperature ranged from 700°C to 1200°C and both CO as well as mixtures of CO and CO<sub>2</sub> were employed. However it must be emphasized here that all these are somewhat scattered studies. There is a definite need for comprehensive investigations in this area.

At low flow rates of CO or CO-CO<sub>2</sub> mixtures the rates of reduction were found to be dependent on the gas flow rate and increased with increasing flow rate (13, 14, 15), till there was no more influence. At this stage, reagent starvation as well as mass transfer in the gas phase has insignificant influence on the reduction rate.

For reduction of iron oxides and ores by hydrogen, the equation:

$$1 - (1 - f)^{1/3} = Kt \quad \dots (9)$$

has been found to be widely obeyed, especially in the middle ranges of the reduction curves (18). Here  $f$  denotes fractional reduction  $\left(\frac{\% \text{reduction}}{100}\right)$ .

$t$  is time from beginning of reduction and  $K$  is a constant. McKewan (19) interpreted it in terms of rate-control by slow chemical reaction at the Fe-Fe<sub>x</sub>O interface. However, it was shown later by Warner (20) as well as Olsson & McKewan (21) that mass transfer steps are also fairly slow and the reduction is a case of mixed control kinetics. Spitzer, Manning and Philbrook (22, 23) later analytically proved that equation (9) is

expected to be approximately obeyed in iron oxide reduction even if all transport steps as well as the chemical reaction step simultaneously control the rate. Also it appears to be immaterial whether the pellet is porous or dense as long as topochemical pattern of reduction is maintained. According to Ross (14), it has been found to be obeyed even when the reduction is completely internal.

Therefore, it is worthwhile to examine whether equation (9) is obeyed by CO reduction or not. Fig. 2 shows the data of some workers plotted this way.

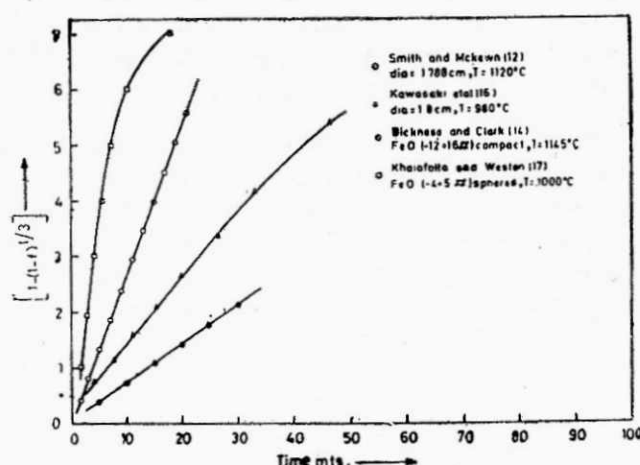


Fig. 2  $\left[1 - (1 - f)^{1/3}\right]$  vs. Time for Co-reduction.

From the straight line plot it can be said that equation (9) is generally valid even for CO reduction of iron oxides.

For chemical control,  $K$  of eqn. (9) should be inversely proportional to the diameter ( $d_p$ ) (in general, size) of the specimen. This was observed in some cases (11), but Bicknese and Clarke (14) found it to be independent of  $d_p$ . Microstructural observations revealed completely internal reduction due to porousness and smallness of the particles. In such a case individual grains of the particles have access to gas and themselves behave as tiny particles, thereby making the reduction rate independent of particle size.

For hydrogen reduction also experimental data (10) point out that time for certain fractional reduction is independent of  $d_p$  for completely internal reduction, proportion to  $d_p$  for limiting mixed control and proportion to  $d_p^2$  for diffusion in porous iron. To which case a situation shall belong to depends, amongst other things, the size of the pellet.



This conclusion can be strengthened by noting the finding of the following investigations. Kawasaki et al (16) employed large porous pellets of  $\text{Fe}_2\text{O}_3$  (dia. 1.8 cm—4.2cm), and found the rate to be controlled by diffusion through the porous product layer. They also observed stage-wise reduction, although it was not accompanied by the typical breaks in the rate curves as one would normally expect.

Khalafalla (17) found a marked promoter action of impurity oxides on the reduction of small  $\text{Fe}_2\text{O}_3$  particles (—4 mesh to +5 mesh) by CO. The extent of reaction rate enhancement was proportional to the ionic radius and electronic charge of the promoter additive. This points out to chemical control. Of course there are other factors which alter the control regime, but they are not that obvious in the above comparison.

Walker and Carpenter (15) found that addition of  $\text{CO}_2$  to CO decreased the rate of reduction of  $\text{Fe}_2\text{O}_3$  remarkably. Bicknese and Clark (14), in their experiments on reduction of synthetic and natural  $\text{FeO}$ , found this to contain an appreciable percentage of  $\text{CO}_2$  and, therefore, considered its likely influence. They could fit their rate data with the following equations:

$$\left[ \frac{1-(1-f)^{1/3}}{t} \right] = \left[ 4.3 \exp \left( -\frac{13,800}{RT} \right) \right] \times \left[ \frac{C_e - C}{C_e} \right] \quad (10)$$

where  $C$  is the concentration of  $\text{CO}_2$  at the metal-oxide interface and  $C_e$  is the concentration of  $\text{CO}_2$  at equilibrium with  $\text{Fe} + \text{O}$  and iron. Compliance with equation (10) implies that reaction (5) is a first order, reversible one. Churfarov et al (24) found  $\text{CO}_2$  to have quite a retarding effect on reduction of  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$  by CO expressed the influence of gas composition as:

$$v = K_{\text{pco}} \frac{n}{\text{pco}_2} \quad (11)$$

where  $v$  is the rate of reduction. This type of equation is to be found if  $\text{CO}_2$  is preferentially absorbed at the surface of the oxide thus blocking the number of bare surface sites. Further investigation is required in this area.

Activation energy of the reduction process has been obtained in two ways. In the first approach, a rate equation like equation (9) or (10) has been derived and then the constant  $K$  has been expressed as an Arrhenius-type equation as exemplified by equation (10). Alternatively, the rates have been determined from the slopes of the pct. reduction vs. time plots at constant  $f$  at various temperatures and the temperature dependence of the rate fitted with Arrhenius-type equation. The values of action energy were vari-

ously found as 8.5 K. cal/mole (12), 13.9 K cal/mole (14), 33-50 K cal/mole (13). Khalafalla (13) found an unusually large activation energy (33-50 K cal/mole) for reduction of coarse and crystalline  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ . He attributed it to a large negative heat of adsorption of CO on the oxide surface. However, the interpretation of the experimental data to substantiate this is not adequate.

It is recognized that the reduction process is complex. Such complexity arises from various sources. The product layer is porous and the diffusion process through the pores is influenced by the pore texture, which again depends on a number of factors. In addition considerable swelling of pellets, even to the extent of 10 times the original volume (25) has been observed. Cracking during reduction, especially in dense specimens, recrystallization of reduced iron layer and presence of unreduced oxide islands add to the complexity further. No wonder that the temperature dependence of reaction rate as well as occurrence of rate maxima and minima as found by various investigators are full of controversy (8). However, experiments on some recent analysis on the subject (26-28) that reduction by CO is 5 to 7 times slower as compared to that by  $\text{H}_2$ .

### III. Kinetic aspects of gasification of carbon by carbon dioxide

Because of the importance of this reaction, there have been numerous investigations over the past several decades, and investigators arrived at many divergent conclusions. Therefore, this brief review will be based on some recent analysis on the subject (26-28).

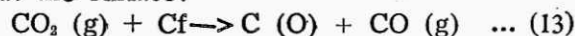
Cakes, carbon and synthetic graphites are highly porous with pores ranging from about  $10\text{\AA}$  to several microns in diameter. The kinetic steps involved are gas film diffusion, diffusion through pores and chemical reaction at gas-solid interface. It has been established that the chemical reaction is exclusively rate controlling below  $1100^\circ\text{C}$ , if the size of the graphite particle is not too large (diameter less than 1 cm.). Such a conclusion has been arrived at from evidences, such as high activation energy (80-90 K Cal/mole), and strong influence of solid and gaseous impurities even in trace quantities. For Chemical reaction control, the entire internal pore surface area should be active and the rate of loss of carbon should be proportional to the volume of the particle. Turkdogan et al (27) found it to be valid for particle diameter less than 1 cm.

By the very method of manufacture, carbon comes out with infinite spectrum of structural

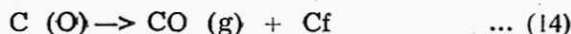
imperfections and surface defects. Again some solid inorganic materials, moisture,  $H_2$  etc. catalyze or inhibit the reaction strongly even if they are present in ppm. level. Regarding rate and mechanism of this reaction these were the sources of discrepancies in the past. Most authors (26) have found that the rate of the reaction can be represented by an equation of the form:

$$\text{rate} = \frac{K_1 pCO_2}{1 + K_2 pCO + K_3 pCO_2} \dots (12)$$

The first step in the reaction is the formation of a surface oxide,  $C(O)$ , on an active free (Cf) at the surface:



The second step is the breakdown of the surface oxide to form gaseous CO leaving a new active site behind:



Treatments of non-catalyzed reactions are modifications of Langmuir-Hinshelwood mechanism of surface reaction. Two mechanisms have been proposed to account for the inhibiting action of CO. In one mechanism, CO is assumed to adsorb reversibly on the active sites blocking them off. In the second mechanism, adsorption of CO has been assumed to be negligible and the retardation is stated to be caused by the reversible nature of reaction (13). The latter is more supported now-a-days because amongst other evidences the chemisorption of CO has been shown to be negligible (29). The mechanism, proposed by Turkdogan and co-workers (28) who explained the inhibiting action of CO in terms of chemisorption of CO, is at variance with the above.

A number of other rate equations have been proposed (26) giving different order of dependence on  $pCO_2$  and  $pCO$ . For example, Turkdogan and Co-workers (28) found the following:

(a)  $\text{rate} \propto pCO_2^{1/2}$  in absence of CO

(b)  $\text{rate} \propto (pCO_2 - pCO_2 \text{ equil})$  and smaller values of  $pCO_2$  in presence of CO.

and (c)  $\text{rate} \propto (pCO_2 - pCO_2 \text{ equil})^{1/2}$  at larger values of  $pCO_2$  in the presence of CO. It can be seen that these are not too different if the equation (12) is suitably simplified. It appears that all equations do not take care of all the factors influencing the rates and hence are not general. A general mathematical formulation is yet to appear, and it must be consistent with various physical measurements such as structural and adsorption studies. However, it may be pointed out here that the rate decreases enormously

with increase of percentage of CO in the gas. The rate of gasification with pure  $CO_2$  at 1 atm has been found to be  $10^2$  times larger compared to a gas of 90% CO—10%  $CO_2$  at  $900^\circ C$  (28).

For an equation, such as (12), there can be no simple activation energy. However such energy have been determined by investigators employing simple rate equations. The value is mostly between 80-90 Kcal/mole at  $850-1100^\circ C$  (26) for pure graphite. In the presence of catalyst it has been found to be as low as 15 Kcal/mole (30).

Specially relevant to sponge iron making in the marked catalytic effect of metallic Fe even at very low concentrations. This has been reported by a number of investigators. The rate has found to be enhanced even by a factor of 300 for graphite (26). The activation energy also goes down considerably. Walker and Co-workers (27) carried out magnetic susceptibility studies and found that iron is an effective catalyst only when it is present as metallic iron, mixed with a little  $FeO$ . Oxidation to  $Fe_3O_4$  and  $Fe_2O_3$  destroys the catalyst action. However, it can be again regenerated in a reducing atmosphere. The explanation put forward contends that oxygen transfer at the graphite surface is enhanced by alternate oxidation of Fe and reduction to  $FeO$ . The catalytic activity is helped by mobility of oxygen on the metal surface. Ni and Co also exhibit similar catalytic action.

The time-dependence of gasification rate is a complex phenomenon. The size of the particle shrinks. Pores get more and more enlarged. New pores open up as a result of which the pore surface area can increase even by a factor of 20(26). The impurities start concentrating on the surface as a result of "burn-off" of carbon. Therefore, the rate measurements ought to be done during the initial period only. Turkdogan and co-workers found that the rate of weight loss was constant during the first 20% of gasification and was proportional to the initial weight. Therefore, specific rate constant may be written as:

$$K = (dw/dt)/W_0 \quad (15)$$

where  $W_0$  is the initial weight.

Lastly, in many cases such as large particles and tiny forces, high temperature etc. pore diffusion may be partially controlling the reaction rate and cannot be ignored. This would be indicated if rate is proportional to square of diameter and would in effect lower the activation energy considerably.

#### IV. EXPERIMENTS ON REDUCTION ON IRON OXIDE BY CARBON IN GASEOUS ENVIRONMENT.

Several studies had been done in the past, but the ones of fundamental importance are mostly of recent origin and have been conducted by taking intimate mixtures of iron oxide and carbon particles (5, 14, 31, 32). Just from the weight loss of such a specimen it is not possible to find out the fractional reduction directly, since the weight loss is due to loss of oxygen and carbon both. Rao (5) has attempted to separate these two theoretically with the help of the rate equation for solution loss reaction proposed by Turkdogan et al (33). However, the approach suffers from some objectionable assumptions, notably constancy of gas composition with respect to time. On the other hand, Bicknese & Clarke (14) as well as Otsuka and Kunii (31) measured the quantities of gases evolved in conjunction with weight loss measurement. Ghosh and Tiwari (32) determined percentages of iron and carbon in the product. All investigators employed pure  $\text{Fe}_2\text{O}_3$  and C, except for Ghosh and Tiwari, who worked with Gua hematite iron and South Indian lignite coke.

Otsuka and Kunii (31) found a change in rate at approximately 33 per cent reduction, which

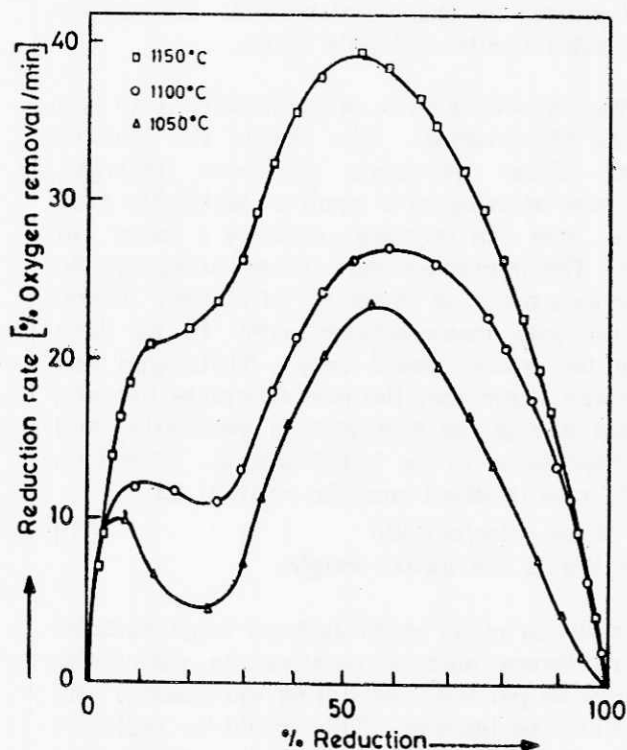


Fig. 3 Reduction Rate vs. Conversion according to Otsuka and Kunii (31)

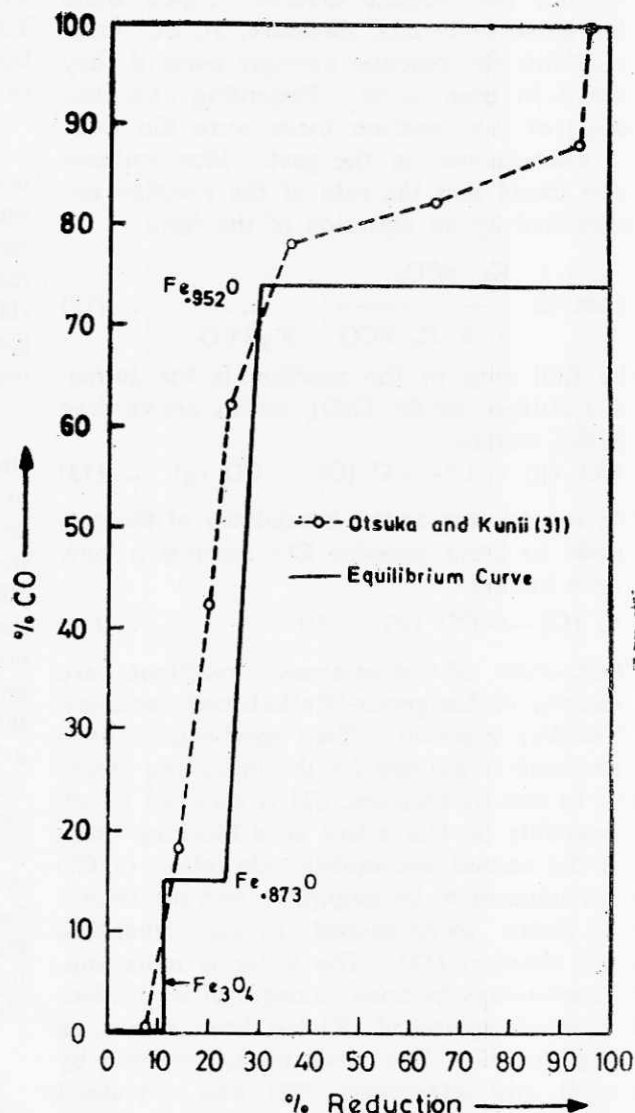


Fig. 4 % CO vs. % reduction at 1050°C.

corresponds to the  $\text{FeO}$  stage (Fig. 3). They also measured quantities of  $\text{CO}$  and  $\text{CO}_2$  evolved as a function of time by flushing with nitrogen and using gas chromatograph. The change in gas composition as reduction proceeds is shown against composition in equilibrium with various oxide mixtures (Fig. 4). It is evident that the gas is not reducing enough to allow formation of metallic  $\text{Fe}$  at the early stage.

The first stage was accompanied by a high activation energy (55-75 Kcal/mole). From this it was concluded that the rate-controlling step was the gasification reaction ( $\text{CO}_2 + \text{C} = 2\text{CO}$ ). As mentioned before activation energy values obtained by various investigations of the latter reaction (26-30) differed and ranged 80-90 Kcal/mole for uncatalyzed reaction and down to 15



Kcal/mole for strongly catalyzed reaction. Even then high activation energy definitely points out that the rate-controlling step is gasification, because the activation energy for CO reduction of oxides is much lower (13 Kcal/mole).

Further evidence were obtained by Otsuka and Kunii (31) in support of rate-control by gasification reaction for the 1st stage of reduction. The rate increased when the particle size of carbon was less. Similarly the rate was independent of the particle size of  $\text{Fe}_2\text{O}_3$ .

On the other hand, the second stage was characterized by a low activation energy (15-23.5 K cal/mole). The rate increased when the particle size of  $\text{Fe}_2\text{O}_3$  was decreased. From the above observations it would appear that in the second stage ( $\text{FeO} \rightarrow \text{Fe}$ ) the rate was controlled by the reduction step ( $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$ ). However there were evidence against this conclusion as noted below:

- (a) The actual gas composition (Fig. 4) was very close to that corresponding to  $\text{FeO}/\text{Fe}$  equilibrium.
- (b) Lower particle size of carbon also enhanced rates.

Therefore, Otsuka and Kunii proposed that the rate in the second stage was accelerated in the presence of metallic Fe which has been found to be a good catalyst for the gasification reaction (26-28). Their contention derives further support from the following observations:

(a) The rate at the second stage was accelerated if the rate of the gasification reaction was accelerated too, inspite of the fact that CO content of the gas was higher. This points out to catalysis.

(b) An increase in pelletizing pressure increased the rate in the second stage presumably due to better contact of metallic Fe with graphite and better catalytic action. This was held as the explanation for the enhancement of rate by lowering the particle size of  $\text{Fe}_2\text{O}_3$ , since that could lead to better contact.

(c) When the particle size of both  $\text{Fe}_2\text{O}_3$  and C were simultaneously altered there was no change in rate.

The lowering of activation energy is very large (approx. 20 K cal). However there are instances of such lowering due to impurity effects (30).

Rao (5) also found a high activation energy of the overall reaction. Lowering of particle size

of carbon enhanced the rate. In addition  $\text{Li}_2\text{O}$  enhanced the rate and  $\text{FeS}$  retarded it. It is known that these two compounds behave the same way for the gasification reaction. Hence it was concluded that the rate of overall reaction was controlled by that of the gasification reaction.

Ghosh and Tiwari (32) in their studies on Gua iron ore found all phases, viz.  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{Fe}$  to be present in the partially reduced pellets. Activation energy was determined as 18.7 K cal/mole between 56-91 per cent reduction. Although the authors inferred a slow reduction step from this, it has to be recognized that it has similarity with the second stage of Otsuka and Kunii (31) and may be a case of Fe-catalyzed gasification reaction.

From the above studies as well as the work of Baldwin (7) there seems to be no doubt that the rate of carbothermic reduction is controlled by the rate of the gasification reaction (eqn. 3). The catalytic effect of metallic Fe is also very likely. However the studies have been made only with powdered mixtures of oxide and carbon in intimate contacts and suffer from the following uncertainties:

- (i) Ill-defined size and geometry.
- (ii) Unknown factors such as catalytic effect of Fe on gasification reaction.

Moreover such studies cannot predict rates for situations where the ore size is much larger than the size of the reductant. Bicknese and Clark (14) did find some influence of the oxide on the rate. Mathematical description of such an assembly poses a problem too. Therefore, at best qualitative informations only can be obtained from such studies.

Bones, Reeves and Saunders (34) found that during CO reduction of iron oxides, carbon deposited within the pores and interstices of ore granules and it was confirmed by later workers (35). This can conceivably be imagined in the mixed pellets as well since metallic Fe is a good catalyst for it (36). This effect can substantially alter the detailed interpretations of experimental data. It is not out of place here that care is to be exercised to examine its influence on carbon monoxide reduction too.

## V. ASSESSMENT OF PRODUCTIVITY OF SPONGE-IRON MAKING IN ROTARY KILN.

The rotary kiln process of sponge iron making offers one important alternative method of iron production, especially for Indian conditions.



It has many merits, but one major disadvantage is that the productivity is very low (0.3 to 0.4 t Fe/m<sup>3</sup>/day compared to 2.5 to 3t Fe/m<sup>3</sup>/day for a modern blast furnace). Such low productivity originates basically from the slowness of reduction of oxides of iron by carbon. The salient features of the process, which are important from the kinetic point of view will be examined here very briefly.

Bogdandy and Engell(37) have presented some of the kinetic aspects, and analysis of the process in a very lucid manner. A reducing atmosphere prevails inside the charge, but an oxidizing one above it because of combustion air. The CO<sub>2</sub> arising from combustion also should react with carbon in addition to the CO<sub>2</sub> generated by reduction of the iron ore. Chemical reaction control was assumed for the gasification reaction and the following rate expression was employed on the basis of work Heddeu (38).

$$V_C = K_{\text{eff}} \left[ n_{\text{CO}_2}^{\circ} - \frac{n_{\text{CO}_2}^{\text{ed}}}{n_{\text{CO}_2}^{\text{eq}}} \right] \quad \dots(15)$$

$$\text{where } K_{\text{eff}} = McHc \exp \left[ \frac{-86,000}{RT} \right] \quad \dots(16)$$

Here V<sub>c</sub> is the rate of reaction in mole of C/cm<sup>3</sup>. Sec, Mc is the amount of C per c.c. of charge and Hc is reactivity. The range of McHc was taken as 0.4x10<sup>13</sup> to 10.4x10<sup>15</sup> per sec. n<sub>CO<sub>2</sub></sub><sup>°</sup> is the fraction CO<sub>2</sub> in the gas. n<sub>CO<sub>2</sub></sub><sup>eq</sup> is the CO<sub>2</sub> constant corresponding to the gasification equilibrium.

Equation (15) assumes the rate of reaction to be proportional to the volume of carbon. As already discussed this would be true only for short periods of time. With progress of gasification, porosity of carbon changes. There is going to be some impurity built up at the surface too as a result of burn-off. Therefore the value of K<sub>eff</sub> cannot be taken as a constant throughout the process even at a constant temperature. Moreover K<sub>eff</sub> also should exhibit an appreciable increase as soon as metallic Fe formation begins.

The reduction rate of the ore was expressed as follows on the basis of work by Krainer (39) on several ores:

$$V_o = K_{\text{Fe}} \left( n_{\text{CO}_2}^{\text{eq}} - n_{\text{CO}_2}^{\circ} \right) \quad \dots(17)$$

$$\text{where } K_{\text{Fe}} = H_{\text{Fe}} (1-R) (T/1173)^2 \frac{1}{n_{\text{CO}_2}^{\text{eq}}} \quad \dots(18)$$

Here V<sub>o</sub> is the rate of removal of oxygen in (mole per Cm<sup>3</sup>. Sec), H<sub>Fe</sub> is the reducibility of

ore, R, fractional reduction and n<sub>CO<sub>2</sub></sub><sup>°</sup> is the CO<sub>2</sub> content corresponding to Fe/Fe<sub>2</sub>O<sub>3</sub> equilibrium. The rate of reduction has been taken as proportional to the charge volume as well as fraction of unreduced ore. Diffusion control has been assumed. Since the reduction kinetics is complex in nature it cannot be off-hand generalized without proper studies of specific situations.

Assuming V<sub>o</sub> = V<sub>c</sub>, it has been shown by Bogdandy and Engells that the productivity kiln can be enhanced greatly by increasing Hc (reactivity of C) and temperature. H<sub>Fe</sub> has relatively small effect. Pilot plant trials have confirmed this temperature dependence. It has also been found that the C content of the gas is smaller than that required to reduce FeO to Fe at lower temperature. This would mean stagewise reduction in the kiln as well.

There of course would always be some engineering factors such as heat transfer or gas flow rate which may limit the rates of processes. However, the low productivity of the rotary kiln is originating basically from the slowness of the carbon reduction. It is worth examining how speeding up is possible. The following comments in this direction are based on the existing knowledge of the kinetics of the reaction.

(1) The temperature in the kiln should be as high as possible. This is being practised now.

(2) An ore-carbon pellet would lead to enhancement of reduction rate considerably due to intimate contact as well as catalyzing effect of metallic Fe.

(3) A porous pellet is to be very much preferred compared to a dense one because that would lead to faster rate of reduction as well as less cracking and distortion of the reduced pellet. Moreover it should prevent too much slowing down of reaction at high percentage of metallization.

(4) During the early stages of reduction, the reduction rate is fast. Hence it is necessary to speed up the gasification reaction. A low CO/CO<sub>2</sub> ratio is strongly advisable (28). This would offer other advantages. Stagewise reduction shall be induced and early formation of metallic Fe can be prevented. This on the one hand is expected to allow us to avoid the rate minima in iron oxide reduction (40), and on the other hand the tendency towards cracking should be less.

(5) Towards the end of the process the reduction is more of a problem, since it slows down. Therefore maintenance of a high CO/CO<sub>2</sub> ratio would be to our advantage. However the source of additional CO is a secondary problem because of the slow gasification reaction.

H<sub>2</sub> is a better reductant as compared to CO. Introduction of H<sub>2</sub> in the end of reduction zone is expected to speed up the last phase of metalization, which always poses a problem.

(6) As some additives have a strong influence on the gasification reaction, deliberate effort given to utilize this effect is going to be of considerable help. This of course would come under the general efforts to increase the reactivity of the solid reductant.

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