

REDUCIBILITY OF ASWAN ORE AND SINTERS WITH VARYING BASICITY RATIOS

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Abstract

THE RESULTS of the study of the reduction kinetics of sinters of different basicity ratios (0.2—2.0) as well as of Aswan ore of definite grain size (6—10) mm. by H_2 gas at a definite "Redox" potential (100 l./g. O_2 /hr.) at $950^\circ C$ have shown that the general shape of the reduction functions of time are unique—partly parabolic and partly topochemical in nature—and that they obey the general Jeschar equation for the overall reduction process.

A specific case of the general equation has been checked among other 6 formulas by modern computing techniques using an IBM electronic computer type 1620 and found to be in good agreement with the experimental results.

The equation could be derived on a theoretical basis and considers a reduction mechanism that is controlled mainly by both diffusion and chemical reaction processes as being the slowest pertaining and hence the rate determining factors in the complex reduction mechanism.

Aswan ore is far more reducible than any of the other different kinds of studied fluxed or non-fluxed sinters. Also fluxed sinters made from Aswan ore by adding increasing amounts of lime are far more reducible by gases at a temperature level of $950^\circ C$ —normally prevailing in the shaft of a blast furnace than nonfluxed sinters. The reasons underlying this are the following:

I) The gradual formation of highly reducible ironbearing minerals replacing the very weakly reducible fayalite ($2 FeO \cdot SiO_2$)

II) The gradual decrease of the amount of glassy silicates beyond basicity 1.0 accompanied with gradual increase of crystalline silicate minerals replacing the glassy form. A completely micro-crystalline texture is reached beyond 1.6 basicity accompanied with the formation of a net-work of inter-connected micropores distributed all over the sinter. Micropores proved to have a pronounced effect contributing to the reduction kinetics of fluxed sinters as the basicity increases above 1.6. Beyond this range, both the reaction velocity constant (K) and the diffusion coefficient (D) are markedly increasing but the latter increases with a faster rate leading to a more reaction controlled reduction mechanism in highly basic sinters $Da = K/D = 0.21$ compared to less basic ones $Da = 0.31$).

The best range of reducibility of Aswan ore sinters lies therefore above 1.6 basicity. However reducibility is markedly improved beyond 1.0 up to 1.6 by the combined effect of the gradually increasing chemical reaction and diffusion rates.

Introduction

Perhaps one of the biggest changes likely to occur in the next twenty or thirty years will be brought about by the increased challenge to the supremacy of the blast furnace as the principal method for iron production. Over the last forty years a remarkable rise in standards has taken place in blast furnace technology. Daily output of 100 t/day were considered remarkably good in 1930's 7000 t/day are now being achieved and 10,000 t/day are being forecast. These advances in blast furnace technology have enabled the blast furnace to ward off competition from alternative ways of ironmaking over the last twenty years or so. However this supremacy is now seriously threatened by the growing shortage of metallurgical coking coal. Even allowing for a coke consumption rate of 300 kg/t., world requirements for coking coal would rise by the year 2000 to more than double the present requirement of the blast furnace. (1)

This situation has led to the urgent search for the question of the "Reducibility" of iron ores or of sinters and pellets made of reducibility therefore gained its importance both to the blast furnace in a trial to bring its coke consumption to minimum and to the gas reduction processes as well. These latter processes include all direct reduction processes producing Sponge Iron and in which the required reductant is fed into the reactor as gas right from the start. The success of any of these processes is governed by its economic viability; this depends primarily on the chemical utilization of the gases during reduction. Gas utilization efficiency is determined by its rates of reaction with the ore (reduction kinetics), equilibria in the iron oxide-gas systems (thermodynamics) and the heat requirements and heat losses of the individual reactions.

None of the naturally occurring or industrially used gases—however—are suitable for direct use in the reduction of iron ores for the simple reason that all of them have fairly high hydrocarbon contents. Therefore the production of reducing gases is a separate technology apart from the technology of the reduction itself occurring inside the sponge iron reactor. The reducing gas production technology can be based equally important either on solid, liquid or gaseous fuel basis.

Although "Reducibility" in its industrial sense as a (2 & 3) measure has enabled the classification of either blast furnace or sponge iron

reactor materials in order to choose its best feed; it has initiated however a tremendous curiosity for the thorough comprehension of the kinetics of the reduction processes that take place either in porous or in dense particles.

It is the aim of the present article to take the kinetics of reduction of Aswan iron ore in comparison to different sinters made of it with different basicities from 0.5—2.0 as denoted by CaO/SiO_2 . It embraces also a trial to formulate a theory to explain the physico-chemical change as it proceeds from its initial to its final state of reduction and passing through different intermediate stages.

EXPERIMENTAL

A—Preparation of Sinter from Aswan Ore and Suitable Fluxes with Different Basicities

The change of basicity index was achieved by changing the amount of lime used in the sinter mix prior to sintering. The main iron bearing material used was a mixture of Aswan Ore fines and pyrite cinders with a ratio of 3:1 in order to simulate the normal production plant conditions.

The different kinds of sinter for the purpose of this investigation were prepared in a "Loesche" type pilot sinter plant of 20 cm pan diameter, provided with a suction fan capable of attaining a vacuum of 500 mms W. G. (Fig. 1).

It may be observed, however, that some of the internal factors affecting the reducibility could not be kept strictly constant, while changing the basicity index, namely the degree of oxidation of iron oxides (D_{ox}) and the microporosity or texture. This must be expected to affect the reductions kinetics under study and have to be taken, therefore, into consideration in the discussion of the all over effect of the basicity variation.

The external factors, on the other hand could be kept reasonably constant while changing the basicity index.

Chemical analyses of all charge ingredients are done before the sintering process (Table I) and this enabled the careful calculation of the necessary limestone added as a flux to attain different basicities required. The sinters after preparation were also analysed to determine their actual basicities (Table II).

Table I
Chemical analyses of the raw materials

| Raw material | Fe | FeO | Fe ₂ O ₃ | SiO ₂ | Al ₂ O ₃ | CaO | MgO | P ₂ O ₅ | Mn |
|---------------|------|-------|--------------------------------|------------------|--------------------------------|-------|------|-------------------------------|------|
| Ore fines | — | — | 50.47 | 26.16 | 6.67 | 4.68 | 1.75 | 1.35 | 0.85 |
| Flue dust | — | 10.39 | 25.81 | 16.60 | 5.94 | 18.77 | 1.92 | 1.01 | 0.67 |
| Pyrite cinder | — | 2.09 | 79.22 | 8.62 | 1.64 | 1.50 | 0.72 | 0.10 | 0.08 |
| Limestone | — | — | 0.76 | 2.06 | 0.30 | 53.60 | 1.56 | 0.06 | 0.04 |
| Scale | 20.1 | 45.12 | 30.24 | 1.42 | 1.23 | 0.80 | 0.52 | 0.10 | 0.37 |
| Coke ash | — | — | 35.90 | 45.06 | 12.12 | 4.55 | 2.37 | — | — |
| Calcined lime | — | — | — | 3.28 | 0.84 | 79.91 | 0.60 | — | — |

Table II
Chemical analyses of the sintered samples

| $\frac{\text{CaO}}{\text{SiO}_2}$ | SiO_2 | CaO | MgO | Fe (Total) | Fe (met.) | FeO | Fe_2O_3 | Al_2O_3 |
|-----------------------------------|----------------|-------|------|---------------|--------------|-------|-------------------------|-------------------------|
| 0.44 | 22.70 | 9.90 | 0.72 | 43.30 | — | 19.90 | 39.70 | 6.66 |
| 0.56 | 22.06 | 12.40 | 0.64 | 42.40 | — | 17.00 | 41.40 | 6.34 |
| 0.69 | 21.61 | 14.80 | 1.30 | 39.40 | — | 18.50 | 35.70 | 6.45 |
| 0.77 | 20.22 | 15.40 | 0.75 | 39.20 | — | 18.50 | 35.40 | 6.42 |
| 0.83 | 21.20 | 17.60 | 0.94 | 38.60 | — | 15.42 | 38.30 | 6.27 |
| 0.95 | 20.29 | 18.92 | 0.82 | 38.40 | — | 23.40 | 28.40 | 6.10 |
| 1.00 | 20.64 | 19.93 | 0.91 | 38.20 | — | 28.60 | 21.70 | 5.77 |
| 1.13 | 20.43 | 22.64 | 0.72 | 38.80 | — | 27.30 | 28.10 | 5.97 |
| 1.23 | 20.16 | 24.72 | 0.57 | 36.20 | — | 24.80 | 24.10 | 6.00 |
| 1.31 | 19.85 | 25.97 | 0.63 | 37.20 | — | 22.00 | 28.50 | 6.04 |
| 1.34 | 18.55 | 25.00 | 2.01 | 34.65 | 3.08 | 9.22 | 34.89 | — |
| 1.60 | 17.32 | 27.78 | 1.85 | 34.65 | 3.08 | 11.33 | 32.54 | — |
| 1.85 | 18.45 | 34.47 | 1.40 | 27.16 | 1.55 | 14.41 | 20.60 | — |
| 2.00 | 17.48 | 34.91 | 1.30 | 28.62 | 1.55 | 10.16 | 27.41 | — |
| 2.68 | 15.00 | 40.23 | 1.28 | 27.16 | 3.10 | 10.03 | 23.25 | — |

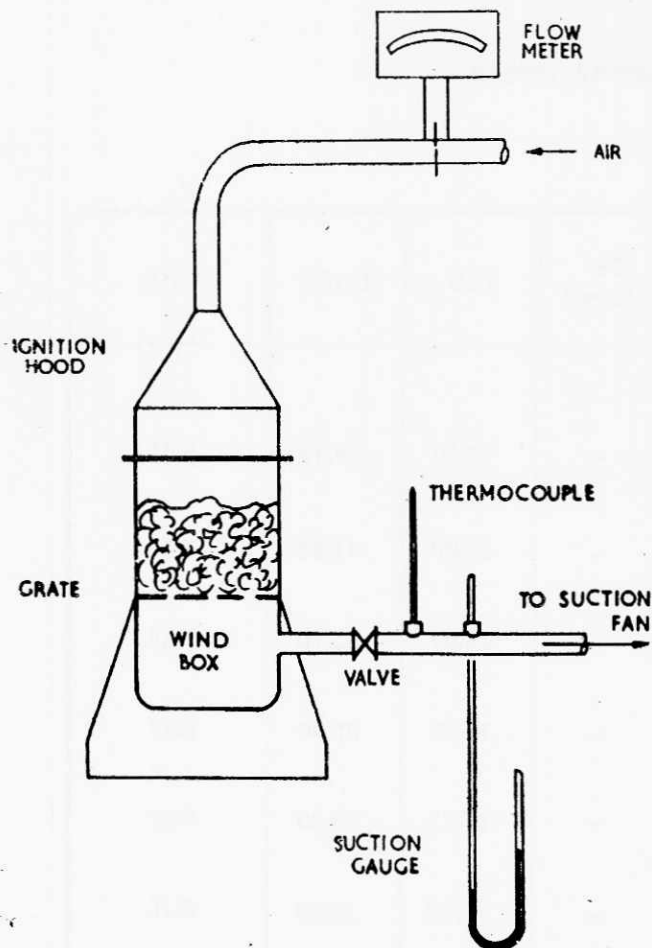


Fig. 1. Pilot Sintering Pan

B—Apparatus used in the study of the kinetics of Sinter reduction

The method of the determination of the loss in weight undergone by a reduced sample against time has been followed during this work. This procedure has been found more adequate than other methods known for the study of reduction kinetics due to its simplicity in outfit especially if it is proved to be of the same standard of accuracy. This is due to the fact that the sinter agglomerate as well as the ore have been freed totally from all its volatile contents before the loss in weight due to reduction has been recorded by means of a single pan "sartorius" balance. This was achieved by heating the sample placed inside the reduction crucible (Fig. 2) at a temperature of 950°C in an inert atmosphere using pure dry N₂ gas provided by a suitable gas column, until a reasonably constant weight is attained. An electrical tubular furnace capable to attain 1200°C in its central Zone where the sample is hanged within the reduction vessel

was used. Temperature regulation as well as accurate temperature measurement equipments were attached to the furnace in order to ensure that the reduction process is carried throughout the test under the constant temperature of 950°C plus or minus 5°C inside the reduced sample.

The details and the assembly of the apparatus consisting of the reduction crucible (Fig. 2), the balance, the furnace with temperature regulation and the reducing gas line are represented in Fig. (3).

C—Standardization of the Experimental Conditions and their Significance

i) Weight of the sample

It varied from 60-80 grms. according to the oxygen concentration in the sample containing different ways of Iron-Oxygen combinations. It is therefore the weight of the oxygen contained in the sample that was kept constant to maintain

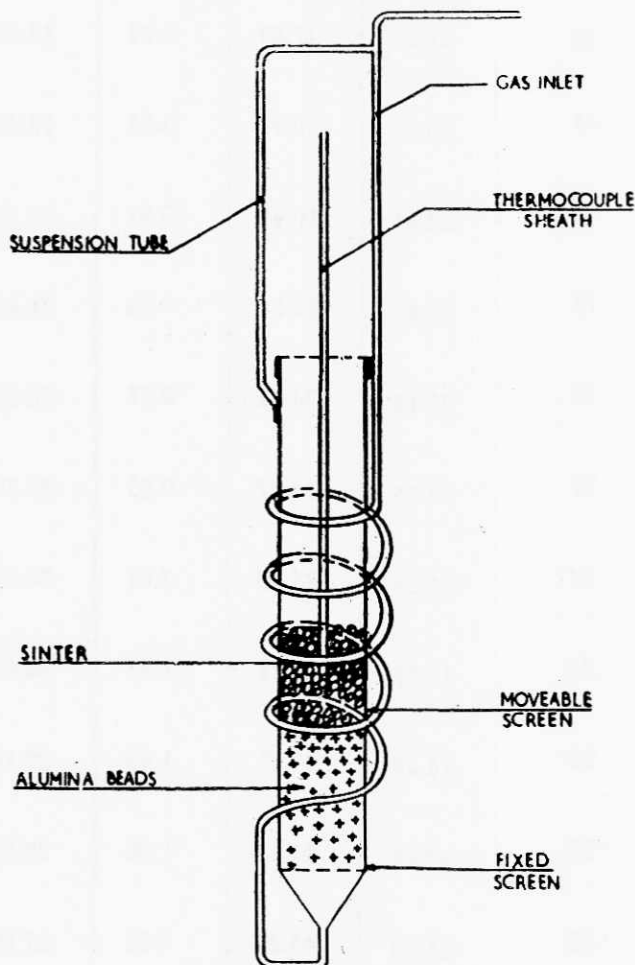


Fig. 2. Reduction Crucible

a constant oxidation—reduction potential. This weight is considered to be well representative for a prepared amount of sinter of 2.5 kilograms using an experimental pilot sintering pan of 20 cms. diameter. Naturally a bigger sample would have been more desirable to assimilate the industrial conditions, but the capacity of the balance of 1 Kg. was the main restricting factor in this respect. However this small size of the reduced sample was helpful in excluding the so-called "bed-effect" i.e. the variation of the reducing gas composition as it passes through a bigger sample with a considerable height. Also this standard size of the sample was verified to lie exactly in the centre of temperature gradient of the furnace i.e. where the temperature level was practically constant.

ii) Particle size of the sample

This has been kept in the range from 6–10 mms as this range constitutes a considerable per cent in the constitution of the actual blast furnace burden. Particle size ranges lower than this is of no importance nowadays in the blast-furnace technology especially with the outcome of the agglomeration processes. Higher ranges

of particle size (10–2) mms) might have been of more interest for study, but the main restriction in this respect during this work was the size of reduction crucible (50 mm.). It is to be noted that keeping a reasonable ratio between the crucible diameter and the mean grain diameter of the reduced sinter (about 8) is highly desirable in order to exclude some aero-dynamic problems connected with preferential flow of the reducing gas along the circumference of the grain if such a ratio was smaller.

iii) Gas flow rate

The reducing gas flow has a considerable effect on the reducibility. Increase in the supply results in a linear increase in reduction up to a certain value after which further increase in the flow rate has no effect. It was necessary therefore to determine this critical value experimentally and to fix this parameter in the standard test at a value beyond it. This is of utmost necessity in order to avoid any erroneous reduction values as a result of slight fluctuations in the flow rate in the reducing gas line. Moreover, the chosen value of flow rate throughout this work of 1000 litres/hr. (S.T.P.) corresponds to a gas velocity along the cross section of the reducing crucible of about .5m/sec., a value which is very near to the actual ascending gas column velocity in the blast furnace.

iv) Oxidation—reduction potential

Keeping the amount of reduced oxygen contained in the reduced sample constant and fixed by 10 g. oxygen throughout the reduction experiments, and having a constant gas flow as well of 1000 litres/hr; therefore a constant 'Redox' potential results and is denoted in the standard test by 100 litres of reducing gas/1 g. oxygen in the sample/hr.

v) Type of the reducing gas

Pure dry hydrogen gas was chosen throughout the experiments. Although the kinetics of reduction would have been more representative to actual industrial conditions if a mixture of Co, N₂ & H₂ gases were used, but as far as comparative study is concerned the use of H₂ gas was found to be more adequate.

vi) Test temperature

A test temperature of 950°C plus or minus 5°C have been selected and verified to be maintained in the central part of the furnace gradient. This temperature level corresponds quite reasonably to the conditions in the lower part of the blast furnace stack where most part of the gaseous reduction takes place.

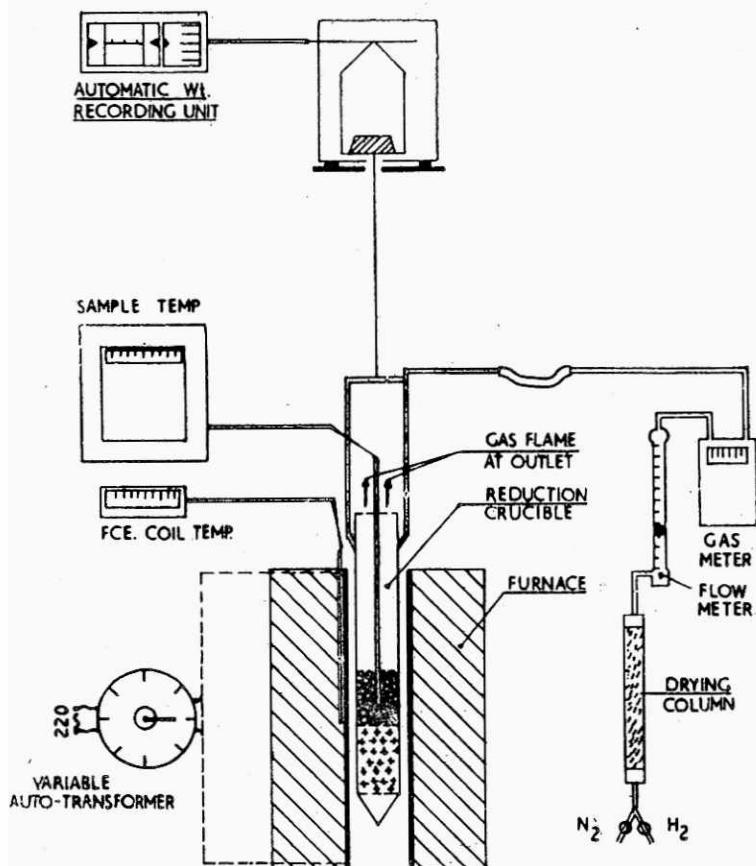


Fig. 3 Apparatus used for study of Kinetics of Reduction.

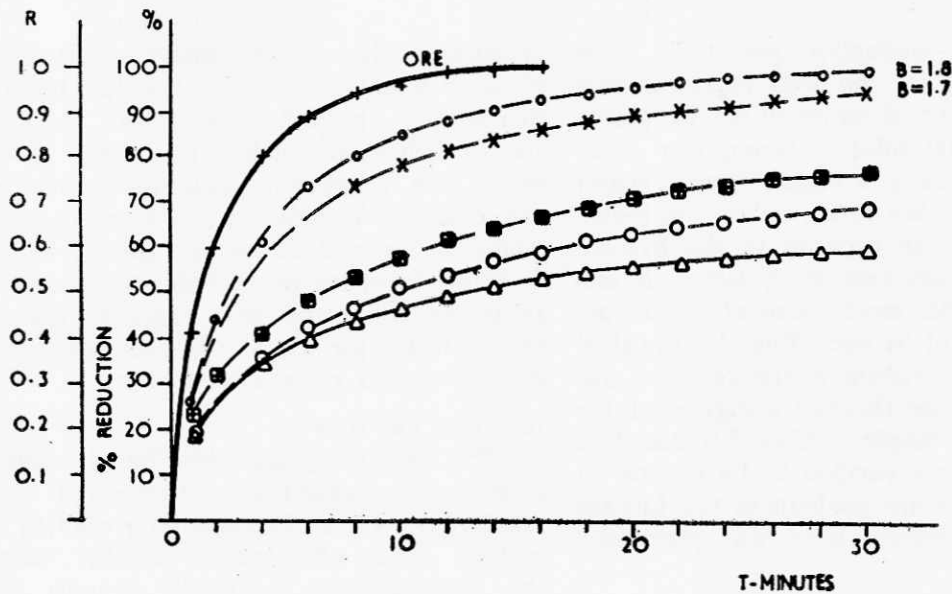


Fig. 4. Reducibility Test Results for Aswan Ore & Sinters on Time Minute Scale.

RESULTS

The results of the study of the reduction kinetics of sinters of different basicity ratios (0.2—2.0) as well as of Aswan ore normally known in Iron Technology as "Reducibility Tests" are shown in (Fig 4) It shows clearly that Aswan ore is far more reducible than any of the other different kinds of studied fluxed on unfluxed sinters. From (Table III) which lists the percentage of reduction of sinters against time it is

also clear that the reducibility increases with the increase of the basicity within the range investigated.

The parabola—exponential functions of six selected different basicities have been analysed by modern computing techniques using an "IBM" electronic computer type 1620. A program was planned (4) to examine the fitness of each of these functions for the different particular cases derived from the general reduction equation according to Jeschar (5).

$$\frac{C_u}{K_o} \cdot P_o = -\frac{1}{3} R \left(1 - \frac{1}{B_1} \right) + \frac{1}{2} \left\{ 1 - \left(1 - R \right) \frac{2}{3} \right\} + \frac{1}{D_a} \left\{ 1 - \left(1 - R \right) \frac{1}{3} \right\}$$

when $R = 1$; i.e. at complete reduction

$$\frac{C_u}{K_o} \cdot P_o (R=1) = \frac{1}{6} + \frac{1}{3B_1} + \frac{1}{D_a}$$

where :-

C_o = concentration of the reducing gas above the equilibrium value at the surface of the particles.

C_u = concentration of the reducing gas above the equilibrium value at the boundary.

K = chemical reaction velocity constant

K_o = concentration of O_2 atoms in the reduced particle.

r_o = radius of the original particle (unreduced)

t = time

R = degree of reduction = $\frac{\text{Reduced } O_2}{\text{Original } O_2 \text{ in sample}}$

Tr & Traustel Number = $\left(\frac{D_a}{B_1} \right) = \left(\frac{K}{B} \right)$

B = Transport Number

B_1 = Biot Number = $\left(\frac{B r_o}{D} \right)$

D_a = Damkohler Number = $\left(\frac{K r_o}{D} \right)$

P_o = Fourier Number = $\left(\frac{D t}{r_o^2} \right)$

These particular cases examined have, however, nearly covered all the reported rate equations of reduction kinetics published in the last two decades, since the all-over rate of a complex reaction is dependent only on its slowest stage (the controlling stage) and these cases are as follows :

Case I : (k,D) controlled reduction mechanism

$$B_1 = \infty \quad \& \quad C_u = C_o$$

$$\therefore \frac{1}{D_a} \left\{ 1 - \left(1 - R \right) \frac{1}{3} \right\} + \frac{1}{2} \left\{ 1 - \left(1 - R \right) \frac{2}{3} \right\} - \frac{1}{3} R = \frac{C_u}{K_o} \cdot P_o$$

& at complete reduction $\frac{C_u}{K_o} \cdot P_o (R=1) = \frac{1}{6} + \frac{1}{D_a}$

Under this case may be mentioned the rate equation derived by Wei - Kao - Lu (6)

Case II : (D)- controlled reduction mechanism

$$D_a = \infty, \quad B_1 = \infty \quad \& \quad C_u = C_o$$

$$\therefore \frac{1}{2} \left\{ 1 - \left(1 - R \right) \frac{2}{3} \right\} - \frac{1}{3} R = \frac{C_u}{K_o} \cdot P_o$$

& at complete reduction $\frac{C_u}{K_o} \cdot P_o (R=1) = \frac{1}{6}$

Under this case falls the rate equation determined by Jank & Von Bogdandy (7)

Case III : (k,B) controlled reduction mechanism

$$D_a = 0, \quad B_1 = \infty \quad \& \quad P_o = \infty$$

$$\therefore \left\{ 1 - \left(1 - R \right) \frac{1}{3} \right\} + \frac{1}{3} Tr \cdot R = \frac{C_u}{K_o} \cdot \frac{K t}{r_o}$$

& $\frac{C_u}{K_o} \left(\frac{K t}{r_o} \right) (R=1) = \frac{1}{3} Tr + 1$

EXPERIMENTAL RESULTS

Table (III) Reducibility of Aswan Ore and Sinters : % Reduction

| Time Minutes | Basicity B | | | | | ORE |
|-----------------|------------|----|-----|-----|-----|-----|
| | 0.2 | 1 | 1.4 | 1.7 | 1.8 | |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 18 | 18 | 23 | 30 | 30 | 41 |
| 2 | 26 | 26 | 32 | 42 | 44 | 60 |
| 4 | 35 | 36 | 41 | 58 | 61 | 81 |
| 6 | 40 | 42 | 49 | 67 | 74 | 89 |
| 8 | 44 | 47 | 54 | 74 | 80 | 94 |
| 10 | 47 | 51 | 58 | 78 | 85 | 97 |
| 12 | 50 | 54 | 62 | 81 | 88 | 98 |
| 14 | 52 | 57 | 64 | 84 | 90 | 99 |
| 16 | 53 | 59 | 67 | 86 | 93 | 100 |
| 18 | 55 | 61 | 69 | 88 | 94 | |
| 20 | 56 | 63 | 71 | 90 | 96 | |
| 22 | 57 | 65 | 73 | 91 | 97 | |
| 24 | 58 | 66 | 74 | 92 | 98 | |
| 26 | 59 | 67 | 75 | 93 | 98 | |
| 28 | 60 | 69 | 76 | 94 | 99 | |
| 30 | 60 | 70 | 77 | 95 | 100 | |

Case IV : k controlled reduction mechanism

$$B = \infty, Tr = 0, Da = 0 \text{ \& } Cu = Co$$

$$\therefore \left\{ 1 - (1-R)^{\frac{1}{3}} \right\} = \frac{Co}{K_0} \cdot \frac{kt}{r_0}$$

$$\& \frac{Co}{K_0} \left(\frac{kt}{r_0} \right) (R=1) = 1$$

This is the case recorded by McKewan (8), T.B. Beaton (9) using his plant sinters of medium sizes & porosity & recently Basu & Ghosh (10)

Case V : (D,B) controlled reduction mechanism

$$Da = \infty$$

$$\therefore \frac{1}{3} \left\{ 1 - (1-R)^{\frac{2}{3}} \right\} - \frac{1}{3} \left(1 - \frac{1}{Bi} \right) R = \frac{Cu}{K_0} \cdot Fo$$

$$\text{at } R=1 \frac{Cu}{K_0} \cdot Fo (R=1) = \frac{1}{3} + \frac{1}{3Bi}$$

Case VI : (B) controlled reduction mechanism

$$D = \infty, Bi = 0$$

$$\therefore \frac{1}{3} R = \frac{Cu}{K_0} \cdot \frac{Bt}{r_0} \text{ \& } \text{at } R=1 \frac{Cu}{K_0} \left(\frac{Bt}{r_0} \right) (R=1) = \frac{1}{3}$$

The computer analysis of the six examined parabolic shaped functions obtained in this work (fig. 4) has shown that all of them are in good agreement to the particular case (No. 1) i.e. (K,D) controlled type rate equation, while they are more or less deviating than the other particular cases. Maximum degree of deviation was observed by applying the B controlled or transport controlled mechanism.

Discussion

The (k,D) or topochemically diffusion controlled reduction mechanism deduced within this work and proposed for the reduction of Aswan Iron Ore and different basicity sinters made from it, agrees quite well with the results obtained by T.B. Beaton (9) when he used plant sinters of different grain size consist lying between (12—25 mm.). He came to the conclusion that although the estimated error in the reduction period of 1600s after the start of the test (corresponding to 34.5% actual reduction) is a minimum (+ 0.3%) if a surface reaction rate equation is applied to the mechanism, nevertheless diffusion controlled mechanism cannot be ruled out specifically if the grain size of the sinter were bigger and more dense. The difference between his deductions and these results lies in our opinion due to differences in the nature of the sinters used in both cases; Aswan ore sinters are lean and hence more dense in character as they contain more slaggy silicate constituents. Also it must be noted that his deductions concerning the more or less (K) controlled mechanism within this range was only restricted to only one third of the reduction course of the

sinters i.e. limited to surface layers adjacent to the interfaces. This has been also verified by Basu & Ghosh (10) when they noticed that the surface chemically controlled rate equation for the reduction of hematite pellets prepared with different porosities was only linear with time up to certain percentage of the reduction test (90%). Also they noticed that the increase of (K) with porosity at different temperatures was only marginal and they deduced therefore that in the case of dense pellets, the reduction of hematite falls more into the category of reactions where the interfacial reaction rates are not slow compared to the rates of diffusion through the pores, later investigation by McKewan and Olason(1) also revealed that the interfacial reaction was not the only controlling step. To our opinion therefore it is the non-uniformity of pore texture and distribution especially encountered in natural ore-bodies and prepared sinters on which rate reduction equations have been variably deduced by Joseph (12), Saunders and Tress (13), Dickie (14) and El-Mehairy (15) is the reason for such controversy in ideas.

In this work it was also possible to calculate the parameter which expresses the ratio of the two controlling factors to each other for each basicity. This parameter denoted by (Da) is therefore the ratio between the chemical reaction rate constant to the diffusion coefficient of gases into the pores multiplied by the average particle size of the sinters Kr_0/D and hence it is a dimensionless value. Other physical, data as visualised by Jeschar's treatment of the reduction mechanism, have also been calculated and listed in table (IV). The two physical values D & K are the products of simpler coefficients and values as $D = \epsilon \cdot \theta \quad Dth.$

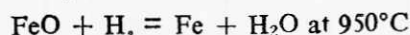
$$\text{and } K = \frac{K}{h} \frac{RT}{e^{-H/RT}} e^{S/R}$$

where $K =$ transmission coefficient usually taken as unity

$K, h, R =$ Boltzman, Plank and Gas constants respectively.

H.S. = Activation Enthalpy & Entropy

The value Co/K_0 was determined by estimating concentration of the hydrogen reducing gas above the equilibrium value of the reaction.



in all experiments. This estimation was based on calculating the actual oxygen reduced from the sample after one minute of the beginning of the reduction test and this being wholly transformed to water vapour, the latter amount was taken arbitra-

Table IV : Physico-Chemical Constant of Reduction with Hydrogen Gas at 950° C for Sinters & Ore

| Eq. No. | CaO SiO ₂ | R | T | $\frac{c}{K_0} F_0$ | $\frac{c}{K_0}$ | $F_0 \left(\frac{DT}{2} \right) r_0$ | $\frac{D}{r_0^2}$ | $2 r_0$ | D | $\frac{kr}{D} = \frac{a}{D}$ | $K = \frac{Da \cdot D}{r_0}$ |
|---------|-------------------------|-----|--------|---------------------|-----------------|---------------------------------------|-------------------|---------|----------|------------------------------|------------------------------|
| 1 | 0.22 | 10 | .55 | .1169063 | 1.80 | .0649479 | .1180871 | .65 | .0767566 | .31 | 0.029 |
| | | 50 | 9.30 | .6838355 | | .3799086 | .0408504 | | .0265528 | | |
| | | 100 | 402.33 | 3.3924732 | | 1.8847073 | .0046845 | | .0030449 | | |
| 2 | 1.09 | 10 | .55 | .1169063 | 1.85 | .0631926 | .1148956 | " | .0746821 | .31 | 0.027 |
| | | 50 | 9.00 | .6838355 | | .3696408 | .0410712 | | .0266963 | | |
| | | 100 | 229.56 | 3.3924732 | | 1.8337693 | .0079802 | | .0051923 | | |
| 3 | 1.37 | 10 | .40 | .1134274 | 1.80 | .0630152 | .1575380 | " | .1023997 | .32 | 0.040 |
| | | 50 | 6.11 | .6630391 | | .3683551 | .0602873 | | .0391867 | | |
| | | 100 | 166.89 | 3.2916667 | | 1.8287037 | .0109575 | | .0071224 | | |
| 4 | 1.63 | 10 | .30 | .1070836 | 1.70 | .0629904 | .2099680 | " | .1364792 | .34 | 0.055 |
| | | 50 | 2.75 | .6251164 | | .3677155 | .1337147 | | .0869146 | | |
| | | 100 | 66.35 | 3.1078432 | | 1.8281431 | .0275530 | | .0179094 | | |
| 5 | 1.81 | 10 | .25 | .1799180 | 1.60 | .1061988 | .4247952 | " | .2761169 | .21 | 0.070 |
| | | 50 | 2.60 | 1.0007318 | | .6254574 | .2405605 | | .1563643 | | |
| | | 100 | 34.94 | 4.9285715 | | 3.0803572 | .0881613 | | .0573048 | | |
| 6 | As. Ore | 10 | .25 | .1493760 | .50 | .2987520 | 1.1950080 | " | .7767552 | .24 | 0.240 |
| | | 50 | 1.40 | .8779344 | | 1.7558688 | 1.2541920 | | .8152248 | | |
| | | 100 | 17.31 | 4.333333 | | 8.6666666 | .5006740 | | .3254381 | | |

rily as function of the concentration of the reducing gas at the boundary conditions of the reduced sinter. The calculation of C_0/K_0 rendered it possible to calculate the other physical constants as (F_0), from which (D) was deduced. (K) was

calculated from (Da) and D , taking the average grain size of the reduced sinter sample as 8.0 mm. It is to be noted that the calculation of the different physical values of the reduction process according to this method can be considered of a reasonable degree of accuracy only within the range of the first minute of reduction for which the C_0/K_0 values were estimated. This period covers the 10 per cent reduction range for all sinters as well as the Aswan ore. Nevertheless the calculation of the data was continued for 50 and 100% R values as in table (IV) only for comparably purposes between the different sinters.

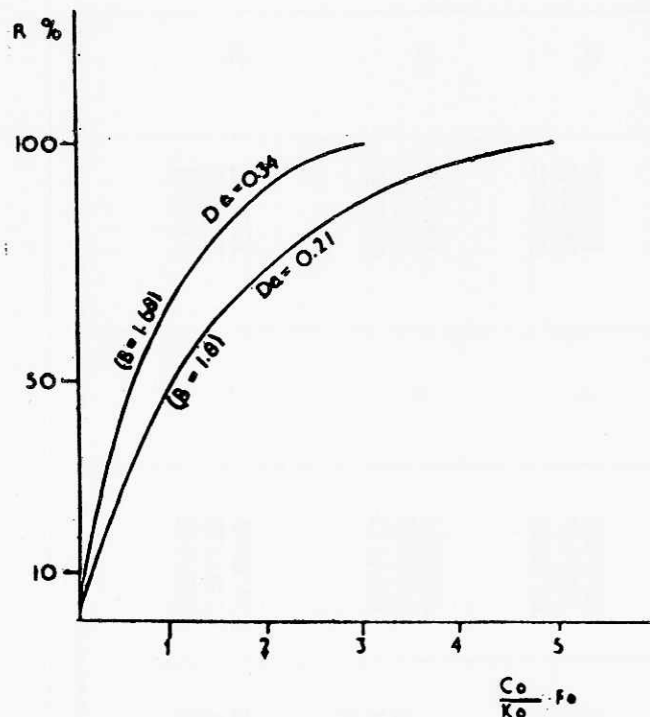


Fig. 5. Reducibility Test results on Dimensionless Time Scale

The main conclusion that can be drawn from this mathematical analysis is that both diffusion and reaction rate constants are highest for Aswan ore and are decreasing by decreasing the basicity of the sinter (table IV). This explains why the reduction is slowed down by passing from fluxed to unfluxed sinters as shown by their relevant reducibility curves. Also the reduction mechanism is not identical throughout the sinters and the ore although they all fall within the combined (K, D) controlled case. The mechanism is more diffusion controlled in the unfluxed sinters ($Da = .31$) than the more basic fluxed sinters having $Da = .21$. As the unfluxed sinters are less reducible (fig. 4) it follows that increasing the Da parameter would have an op-

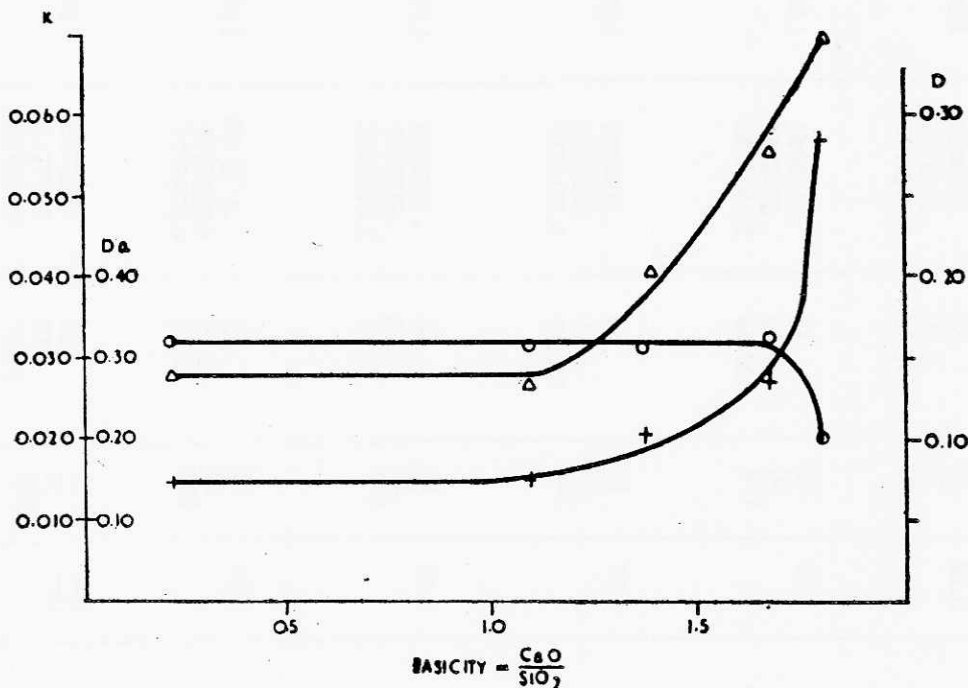


Fig. 6 Physico-Chemical constants of the Reduction process as a function of Basicity.

posite effect on reducibility to that of increasing the basicity. This might look like as contradicting the illustration of the (K,D) controlled functions deduced by R. Jeschar who attributed higher (Da) values for more reducible cases on a dimensionless time scale $CO/K\alpha-F_0$

To prove this non-contradiction between the experimental reducibility results obtained in this work on the basis of minutes time scale and the theory of Jeschar, the two functions having the extreme values of Da parameter, .21 (basicity 1.8) and .34 (basicity 1.68) were redrawn on a dimensionless scale CO/F_0-K_0 (fig. 5). The relative positions of the two functions have been reversed to those on the usual reducibility curves having minutes as time scale (fig. 4).

The opposing effect of (Da) parameter and basicity on the reducibility of sinters can also be deduced from the data obtained in table (IV). As it is clear that the rate of increase of K is less than the rate of increase of D by increase of basicity or dK/dB dD/dB therefore it follows that $Da = K/D$ or must vary proportional to the reciprocal of the basicity (fig.6).

This discussion throws much light on the major role of the pores and consequently of the diffusion phenomenon played in the reducibility of sinters. This has been verified recently by G. Subat & H. Engell (16) who determined the micro-pore distribution functions in sinters of different basicities. They found that the abundance of micropores in the range of $10-103A^\circ$ in the more basic sinters than those less basic ones is the most decisive factor for the kinetic of the reduction of the sinters at $900^\circ C$. The more the micropores in the sinters, the more the reduction process is enhanced following a combined (K,D) controlled mechanism. If the size of the pores is above this critical range ($10-103A^\circ$) the reaction controlled reduction (K controlled) will take over the (K,D) mechanism.

In the present work the evidence of increasing microporosity as the basicity of the sinters increases was left to the judgement of the mineralogical investigation of thin and polished sections, this study briefly shows that glass formation is less in the fluxed than non-fluxed sinters and disappears completely at higher basicities. Less glass formation is accompanied by the tendency of formation of micropores among the different crystalline components constituting the general texture of the more basic sinters.

Conclusions

From the experiments done within this work and the discussions that followed, the following conclusions are considered to throw some lights on the reducibility and reduction kinetics of fluxed sinter made from Aswan Ore for the feed of the blast furnaces of The Egyptian Iron & Steel Co. at Helwan:

- 1) Aswan Ore is far more reducible than any fluxed or non-fluxed sinter.
- 2) Among sinters, fluxed sinters are more reducible than nonfluxed and the more the basicity ratio $CaO: SiO_2$ (within the investigated range) the more is the reducibility.
- 3) The reduction mechanism follows a combined topochemical (surface chemical reaction) and diffusion complex physico-chemical change (k,D) controlled mechanism and agrees exactly with the rate equation derived for this particular case by Jeschar(5).

4) Micropores proved to have a pronounced effect contributing to the reduction kinetics of fluxed sinters as the basicity increases above 1.6 $CaO: SiO_2$ ratio. Beyond this range, both the reaction velocity constant (k) and the diffusion coefficient (D) are markedly increasing but the latter increases with a faster rate leading to a more reaction controlled mechanism in highly basic sinters $Da = .21$ compared to less basic ones $Da = .31$.

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DISCUSSION

M. S. Dharanipalan (Bhilai Steel Plant, Bhilai). I would like to know whether any study has been done in the addition of magnesium oxide for stabilisation on sinter of high basicity ratio? The author referred to the practice of heat-treatment of sinter in U.S.S.R. As far as I understand heat treatment is done to impart additional strength to sinter and has nothing to do with reducibility characteristics of sinter. Can the author clarify these aspects?

Dr. Eng. M.W. Salem (Author) I confirm that within our research program at Helwan, nothing has been done concerning the addition of magnesium oxide for stabilization of high basicity sinter; but I rather refer to the tremendous work has been done in this respect by Professor E. Mazanek et. al. and published in series in the Journal of I.S.I. Also I would like to stress the intimate relation between the mineralogical constitution, matrix structure, strength and reducibility of the sinter material.

That is why I might understand the reason for the heat treatment practice of sinter carried in USSR as a method for improving its reducibility by creating micro-cracks of the order of several A° in a totally crystalline matrix instead of partially glassy one, and same structure

would also improve the strength of sinter at the same time.

Dr. A.B. Chatterjea (National Metallurgical Laboratory, Jamshedpur). First of all, I would like to compliment Dr. Salem for the excellent presentation of his paper. I have got one or two minor points. The first one is whether the Helwan blast furnaces have been operated exclusively with lumpy Aswan iron ore and the fluxed sinters of the different basicities proposed by him?

If the Helwan blast furnaces have been operated exclusively with Aswan iron ore and the fluxed sinters of the different basicity degrees, how did such ferrous burden reflect on the coke rate and the productivity?

My third point is as you increased the basicity degree of the sinter, did it affect the sinter strength? If so, what was the optimum basicity degree for satisfactory strength?

Dr. Eng. M. W. Salem (Author). I would like to thank Dr. Chatterjea for his compliment about the presentation of the paper, and concerning his first question about whether Helwan blast furnaces are operated exclusively with lumpy Aswan Ore and fluxed sinter of optimum basicities as proposed by me. I would like to answer that this has proved to be unpractical due to local deficit in the production capacity of some installations within the existing sintering plant, which cannot facilitate the crushing of required limestone for the required optimum basicities around 1.3 CaO/SiO_2 . Moreover, mixed blast furnace charge containing Aswan ore and sinters proved also to cause some hanging in the blast furnaces due in my opinion to sharp differences in the softening points of Aswan ore and moderately basic sinters currently produced. Also the capacity of the sinter plant available is only parallel to the production of one of the two existing furnaces. My idea, the optimum solution would be as Mr. Astier has previously demonstrated that is waiting until the second sintering plant would be erected in the near future parallel to the second blast furnace and working one strand with ultra-basic sinter and the other with nonfluxed, and mixing the two sinters before feeding them in the blast furnaces.

Concerning the second point, I would like to say that the common practice now is working on B.F. exclusively with Aswan ore and the second

with moderately basic sinter 0.8 CaO/SiO_2 and the result is that the furnace operated with 100% sinter realizes not less than 20% decrease in coke rate than the other operated with lump ore, due to the less thermal load and slag volume associated with moderately basic sinters.

Concerning the third point is that a trough in the sinter strength curve has been noticed as correlated with basicity. This trough (minimum) coincides with basicities from 0.8—1.0 CaO/SiO_2 and the best strength was found in the range of 1.6—2.0 CaO/SiO_2 and it must be noted that higher basicities have not been tried. Mr. J.E. Astier (IRSID, France) The conclusion of the research and development studies made at one French plant in Normandy (Societe Metallurgique de Normandie) using iron ores which have some similarities with Aswan iron ores (Soumont iron ores in Normandy) checks quite well with the results given by Dr. Salem:

1. The reducibility of the sized ores is excellent, for the crude sized ore and, furthermore, for the roasted sized ore, so the sized roasted ore is an important part of the blast furnace burden.
2. The fines are used in the sinter plant with the total amount of limestone needed as flux for the total blast furnace burden.
3. In this way, we produce a very basic sinter with a basicity index (lime silica ratio) over 2.0 and, very often even upto 3.0.
4. Such basic sinters are very reducible
5. Combination of this sized acid roasted ores with ultra basic sinter gives best results in the blast furnace.

Dr. Eng. M.W. Salem (Author) I agree totally with Mr. Astier's comments.

Mr. K.N. Gupta (National Metallurgical Laboratory, Jamshedpur). (i) You have referred in your paper about standard reducibility test maintaining experimental conditions as iron ore particle size 6-10 mm, temperature 900°C and reductant flow rate 100 lit/gm of oxygen removal. Is this one of the standard reducibility test followed in Egypt and/ or it follows one of the well known reducibility test e.g. Linder, Midrex-Linder, VDEH, Gakushin etc. and if so, the basis of this adoption?

(ii) Very high rate of reductant flow rate about 100 lit/gm of oxygen removal, reduces iron ores at a very fast rate which is clear from the fact of 80% reduction in 20 minutes. Is it not deviating from the aim of obtaining some reliable reducibility data, compatible to actual practice.

iii) We have some experience of reducibility tests conducted with Oolitic iron ores from Egypt and we found that rate of reduction upto about 92-94% reduction is very high, while to obtain reducibility beyond 94-100%, it takes very very long time. Can you throw some light on this, if you have done some microscopic study, with these reduced samples of Aswan iron ores.

iv) What is the effect of increasing the basicity i.e. 1.8 and above (in the range of super fluxed sinters) on the reducibility of the Aswan iron ore sinters?

Dr. Eng. M.W. Salem (Author) (i) Concerning the question about the basis of the adoption of the standard reducibility test maintained through my experiments is that it gives under my conditions a linear velocity of about 0.5 meter/second which can be compared well with the actual linear velocity of the gases on the shaft of the blast furnace which has a prevailing temperature zone of about 900°C

ii) As previously mentioned under (i) it was aimed purposely to approach as much as possible to the conditions prevailing on the stack of the blast furnace and very high rate of reductant flow was the only means to approach that. To my idea less flow rates would lie on the unstable area of the sensitive affection of reduction due to minor fluctuations of flow rate and secondly slow flow rates as themselves deviations to actual practice within the blast furnace.

iii) Concerning the impedece of the reduction of the Aswan iron ores after 94% reduction, has been explained by me by analysing the mathematical function of the reduction as due to diffusion controlled mechanism coupled with a topo-chemical reaction mechanism and rather than proved by microscopic studies. The deviation of the shape of the experimental curve is very slight from the theoretically derived function.

iv) Concerning ultra basic sinters i.e. more than 2 CaO/SiO_2 , have not been done within my experiments.