

M.H. KHEDR^{*}, M.H. ABDEL-KHALIK^{**}

STUDY ON USING DOLOMITE INSTEAD OF LIMESTONE AS FLUXING MATERIAL DURING SINTERING PROCESS AND ITS EFFECT ON THE REDUCTION AND MECHANISMS

The main flux added to iron ore sinters and iron ore pellets are limestone and dolomite which are considered the source of fluxing oxides. In this investigation iron ore sinter having basicities of 0.7 and 2.1 were prepared. At each basicity two samples were prepared with either 100% limestone or 100% dolomite as fluxing material. Samples were reduced to completion in H₂ atmosphere at the temperature range from 1075 K to 1275 K. The results showed that sinter containing limestone has higher rate of reduction than that containing dolomite. Activation energy calculations together with the application of gas-solid reaction models were used to elucidate the mechanism of reduction.

INTRODUCTION

In the past decade, the annual world wide production of sinter has ranged from 530 to 586 Mt (Dawson 1993). Although alternative iron making processes are emerging, they are not expected to impact significantly the blast furnace production in the next decade and possibly beyond (Dawson 1993). In the sintering process, the temperature of a micropelletized sinter mix is raised to achieve partial fusion and produce some molten material which, on cooling, crystallizes or solidifies into mineral phases that bond the structure together. The properties of the iron ore sinter are controlled by the composition and distribution of these mineral phases. Three types of phases, i.e. oxides of iron, calcium ferrites and silicates in crystalline and glassy forms, are the major constituents of iron ore sinters. In iron-making processes, great efforts have been made to develop high basic sinter and self fluxing pellets which improve reducibility and strength to resist degradation during reduction process. The main flux added to iron ore sinter or pellets are limestone, dolomite and olivine which are considered the source of fluxing oxides such as CaO and MgO. The influence of these oxides on the rate of reduction of iron oxide was previously investigated (Shehata and Ezz 1973). It was ob-

^{*}Ironmaking Lab. Extractive Met. Dept., Central Metallurgical Research and Development Institute (CMRDI), P.O. Box: 87 Helwan, Cairo-Egypt.

^{**} Agglomeration Lab. Ore Dressing Dept., Central Metallurgical Research and Development Institute (CMRDI), P.O. Box: 87 Helwan, Cairo-Egypt

served that the presence of CaO promotes the reduction of Fe_2O_3 up to certain concentration and above which the rate decreased. The promotion effect was attributed to the increase in the porosity of CaO- Fe_2O_3 compacts while the retardation effect resulted from the formation of ferrite phase. The influence of lime addition to iron ore in the sintering process has shown that CaO greatly enhanced the rate of reduction of ores (Khalafalla and Weston 1967; Volkhenstein 1948).

EXPERIMENTAL

Raw Material

Baharia iron ore, limestone, dolomite and coke breeze were used in this investigation. The chemical analyses of these raw materials are given in tables 1 and 2.

Table 1. Chemical analysis of iron oxide

Composition	%	Composition	%
Fe total	52.76	Na_2O	0.326
SiO_2	7.58	K_2O	0.154
Al_2O_3	1.97	Cl	0.4
CaO	0.51	BaO	1.3
MgO	1.46	Zn	0.08
MnO_2	3.42	S	0.65
P_2O_5	0.39		

Table 2. Chemical analysis of dolomite, limestone and coke breeze

Element	Dolomite	Limestone	Coke breeze
Fe total	—	—	2.24
SiO_2	0.78	1.4	4.55
CaO	32.67	53.21	0.73
MgO	19.53	0.24	0.082
Al_2O_3	0.58	0.76	2.2

Sintering

Sintering experiments were carried out in down draft sinter pot of 6 kg capacity. Air flow was provided by two fans in series capable of producing suction pressure equal to 1200 mm to water gauge which equal 11.76 kPa. The upper layer of the sinter charge was ignited for 2 min. with a gas flame at 1523 K. The temperature of the

charge reached 1573 K by the action of 6% coke breeze. The produced sinter was screened with a 7 mm sieve. The + 7 mm sinter was dropped 4 times from the height of 2 m (shatter test). Then, the sinter was screened, again, with a 7 mm sieve and the percent of + 7 mm was taken as a parameter of mechanical strength.

Reduction

The apparatus used for the reduction is shown in the schematic diagram in Fig. 1. The apparatus consists of two parts: (i) gas purification system to purify N_2 (flushing gas) and H_2 (reducing gas) by passing them over hot Cu (823 K) in furnace B to remove O_2 . Towers containing silica gel (F) and anhydrous calcium chloride were used for drying gases. The second part is (ii) thermal balance which consists of vertical tube furnace with a temperature controller. The sinter was placed in a Pt basket (I) suspended by chain (S) attached to the pan and put in the hot zone.

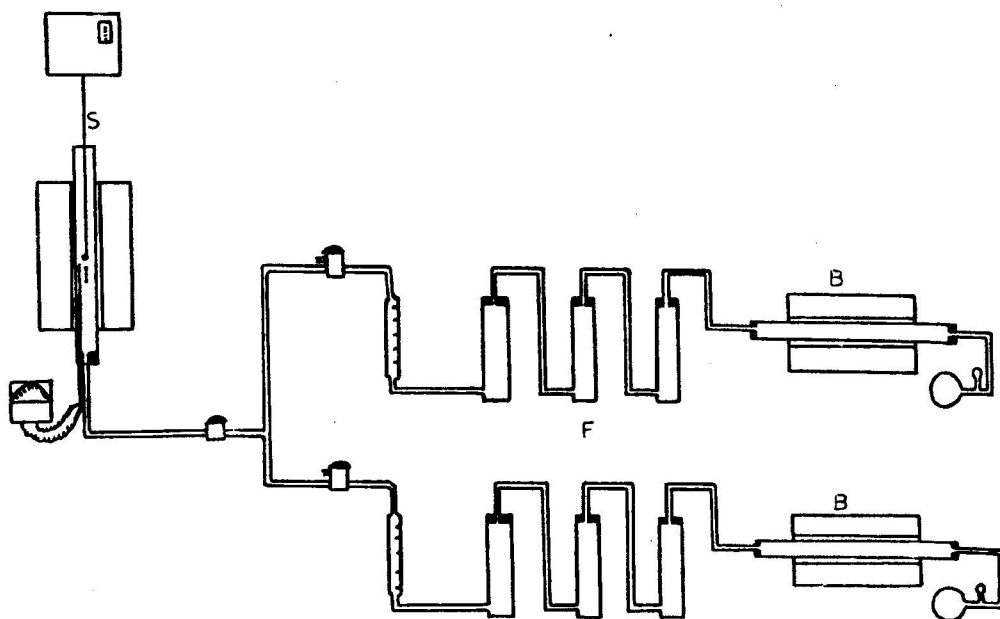


Fig. 1. Schematic diagram for the reduction system

RESULTS AND DISCUSSION

Sintering

Four samples of iron ore sinters containing 100 % limestone and 100 % dolomite at 0.7 and 2.1 basicity were produced. The results of chemical analyses of the produced sinters are given in Table 3.

The strength of the produced sinters was calculated as the percent of + 7 mm sinters after shatter test and shown in Table 4.

Table 3. Chemical analysis of the produced sinter

Basicity		Fe _{total}	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO
0.7	limestone	51.40	15.00	10.90	2.10	7.52	1.50
0.7	dolomite	52.00	16.34	10.96	2.00	5.10	4.00
2.1	limestone	44.40	7.36	9.04	1.70	21.00	1.00
2.1	dolomite	44.40	9.81	8.80	1.60	12.68	9.00

Table 4. Shatter test results for limestone and dolomite-containing sinter samples

Basicity	Mineral	Strength
0.7	limestone	60.0
0.7	dolomite	52.0
2.1	limestone	75.5
2.1	dolomite	72.1

It is obvious that the replacement of CaO by MgO leads to a decrease of the cold strength of the produced sinter. This may be due to the fact that CaO can form a melt phase with other constituents of the sinter mix at comparatively lower temperature (~ 1423 K). On the other hand MgO can form a melt phase with SiO₂ and with Fe₂O₃ at temperatures higher than 1623 and 1873 K, respectively. Therefore, the replacement of CaO by MgO leads to an increase in liquidus temperature of the melt phase. The temperature of sinter mix with 6 % coke rate consumption does not exceed 1573 K, so ferrites phase decreases by using dolomite, and slag phase becomes SiO₂ rich (Panigraly 1984).

Reduction behaviour of iron ore sinter at different basicity

The produced sinters were isothermally reduced with hydrogen up to completion at the temperatures from 1073 to 1273 K. The temperature at which reduction occurs has a very pronounced effect on the rate of reduction: temperature increase led to an increase in the rate of reduction. This conforms with basic principle of chemical thermodynamics and kinetics. The corresponding relationships between the rate of reduction (dr/dt) at both the initial (10%) and final (80%) stages and reduction temperature are shown in Figs. 2 and 3, respectively. The rate of reduction at both the initial and final stages increased with the increase of temperature. For 100 % dolomite at 0.7 basicity, the rate of reduction at the initial stage is higher than the moderate and more than the final stages. At 0.7 basicity, the rate of reduction of limestone-

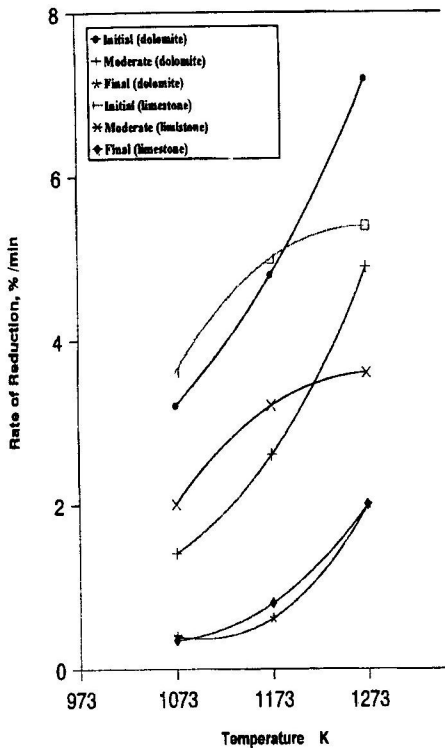


Fig. 2. Rate of reduction of 0.7 basicity sinters at various temperatures

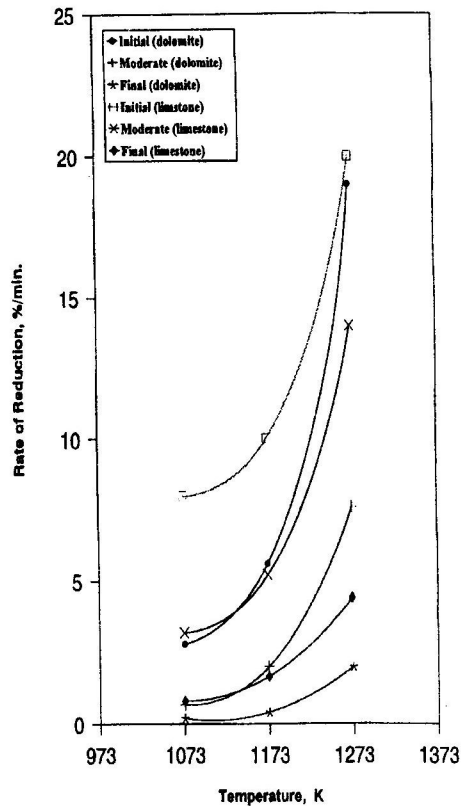


Fig. 3. Rate of reduction of 2.1 basicity sinters at various temperatures

containing sinter is higher than dolomite-containing sinter at 1073 and 1173 K while it decreased at 1273 K (Fig. 2). Figures 4–6 show the reduction curves of iron ore sinters at different basicities reduced at 1073, 1173 and 1273 K, respectively. The reduction curves at 1073 K and 1173 K show that sinters containing limestone at various basicities have higher reduction rate than those containing dolomite. This may be attributed to (i) decrease in the ferrites phase as illustrated before (Panigrahy 1984); (ii) most of the MgO migrates to the magnetite phase to form magnesiospinels rather than appearing in the slag phase and so the slag becomes SiO_2 -rich which causes a decrease in the rate of reduction; (iii) poor reactivity of dolomite is attributed to greater size of dolomite compared with limestone. The higher rate of reduction of limestone-containing sinters at basicity 2.1 than that at 0.7 is explained by the increased amount of CaO which causes the same effect as described above. On the other hand at 1273 K the trend was changed, in which dolomite-containing sinter showed higher rate than at 0.7 basicity of limestone-containing sinter. This can be attributed to the facility of reduction of magnesio-wustite phase at high temperatures.

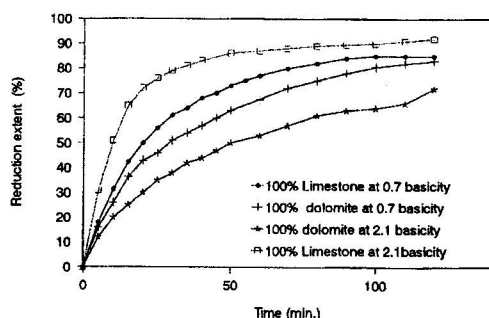


Fig. 4. Reduction curves of iron ore sinters reduced at 1073 K

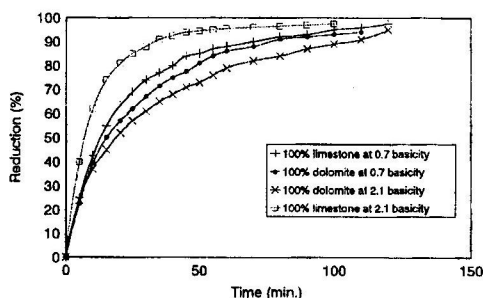


Fig. 5. Reduction curves of iron ore sinters reduced at 1173 K

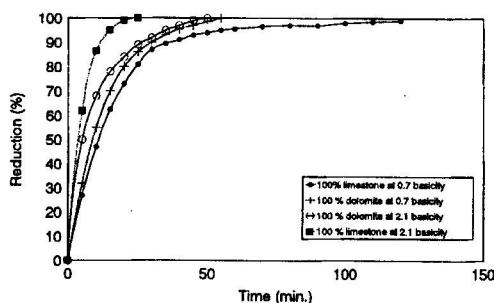


Fig. 6. Reduction curves of iron ore sinters reduced at 1273 K

KINETICS AND MECHANISMS OF REDUCTION:

The rate of reduction increases with the reduction temperature according to the Arrhenius equation

$$K_r = K_0 e^{-E_a/RT}$$

where K_r is the rate constant, T is the absolute temperature, K_0 is the frequency factor, R is the gas constant, E_a is the activation energy.

The true activation energy reflects the energy barrier associated with the rate determining steps (Tompkins 1965; Al-Kahtany 1980). The measured activation energies may be affected by the influence of temperature on the surface area of solids and on the morphology of the product, and hence, the mechanisms based merely on the magnitude of activation energy cannot be considered conclusive. The general range of values that have been obtained was summarized by Strangway (1964) as in Table 5.

The relationship between the logarithm of the rate of reduction of iron ore sinter containing limestone and dolomite at different basicity with the reciprocal of the absolute temperature were plotted at both initial and final stages and presented in Figs. 7a and 7b, respectively. The values of the apparent activation energy obtained from these

plots are given in Table 6. These values indicate that the reduction process at the initial stages for both limestone-containing sinters at various basicities and for dolomite-containing sinter at 0.7 basicity is controlled by the combined gas diffusion and interfacial chemical reaction, while for dolomite-containing sinter at 2.1 basicity, the interfacial chemical reaction is the rate controlling mechanism.

Table 5. Relationship between activation energy and the rate controlling step (Nasr 1995)

Activation energy value E_a , kJ/mole	Probable rate-controlling step
8–16	gas diffusion
29–42	combined gas diffusion and interfacial chemical reaction
60–67	interfacial chemical reaction
> 120	solid state diffusion

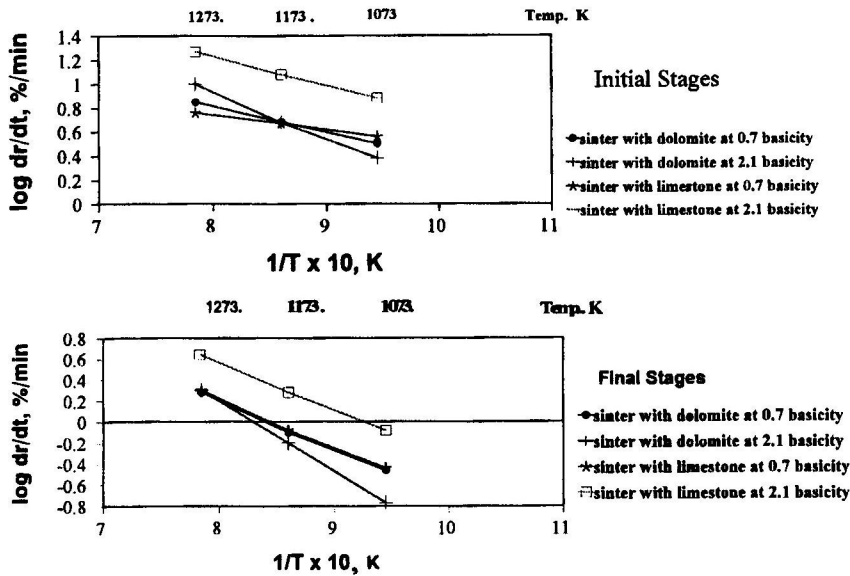


Fig. 7. Arrhenius plots for iron ore sinters at various basicities; a) initial stages (10 %), b) final stages (80%)

Gas–solid reactions, where the solid is a reactant rather than a catalyst, have been studied extensively due to their technological importance in material processing operations such as reduction of iron ores. The important non-catalytic gas–solid reactions models are unreacted-core model (Szekely 1976) volumetric model (Ishida 1968) and grain model (Levenspiel 1962). The grain model developed by Szekely was used in this work in order to confirm validity of the proposed mechanisms. The model considered the overall shapes as sphere, long cylinder and flat plate for pellets or grains. Although

the sinters examined in this work are made of fine grains, each grain is considered as a small sphere. The following formulations developed by Szekely et al. (1976, 1995) were considered:

– for chemical reaction control

$$\phi(x) = 1 - (1 - x)^{1/F_g} \quad (1)$$

– for gaseous diffusion

$$g(x) = 1 - 3(1 - x)^{2/3} + 2(1 - x) \quad (2)$$

– for combined mechanism

$$\phi(x) + g(x) = [1 - (1 - x)^{1/F_g}] + [1 - 3(1 - x)^{2/3} + 2(1 - x)] \quad (3)$$

Table 6. Apparent activation energy values (E_a) for different sinters

Content	E_a initial, kJ/mole	E_a final, kJ/mole
100 % limestone at 0.7 basicity	26.33	94.88
100 % limestone at 2.1 basicity	49.32	96.97
100 % dolomite at 0.7 basicity	43.81	93.22
100 % dolomite at 2.1 basicity	56.84	118.16

Where $\phi(x)$ and $g(x)$ are the interfacial chemical reaction and gaseous diffusion control conversion factors, respectively, x is the decimal fractional reduction and F_g is the grain shape factor. It was taken as a sphere and, therefore, F_g equaled 3 in the above formula.

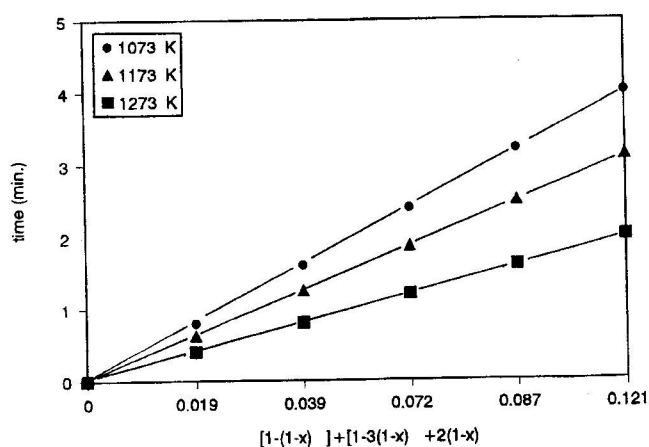


Fig. 8. Application of the combined effect equation at the initial stages for iron ore sinter containing limestone at 2.1 basicity reduced at temperature 1073–1273 K

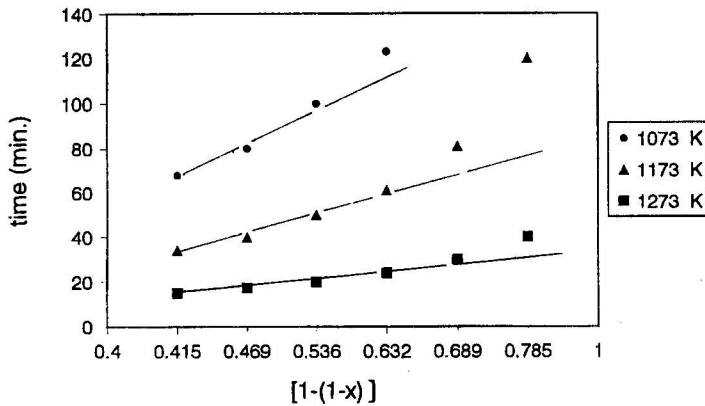


Fig. 9. Application of chemical reaction control equation at the final stages for iron ore sinter containing dolomite at 0.7 basicity reduced at temperature 1073–273 K

By applying the previous mathematical formulae at different fractional reduction, straight lines and not curves must be obtained for the proposed mechanism (Nasr 1995) which is the case in this investigation. By applying these equations to the fractional reduction of limestone-containing sinters at 2.1 basicity straight lines are obtained in equation 3 (Fig. 8) giving the evidence that the combined mechanism is the rate-controlling one at the initial stage. In the final stage equation 1 gives straight lines in accordance to the values given by the activation energy this confirms that the interfacial chemical reaction is the rate controlling mechanism for sinters containing 100 % dolomite at 0.7 basicity (Fig. 9). At the final stages the values of the activation energy indicate that the interfacial chemical reaction is the rate controlling. The values of the activation energy were shifted towards the values characteristic of the solid state diffusion mechanism indicating its contribution to the controlling process. This was confirmed by applying the mathematical formulae, in which a deviation from the straight lines took place as soon as 90 % reduction was reached (Fig. 9).

CONCLUSIONS

Four types of Baharia iron ore sinters prepared at 0.7 and 2.1 basicities with either 100% limestone or 100% dolomite. Each sample was subjected to reduction under hydrogen atmosphere at 1073–1273 K. The following results were obtained:

1. The replacement of CaO by MgO leads to a decrease of the cold strength of the produced sinter. These results were attributed to the increase of the liquidus temperature of the melt phase.
2. The rate of reduction (dr/dt) was gradually increased with the increase of reduction temperature.

3. At 1073 and 1173 K, the reduction rate of limestone containing sinter is higher than that for dolomite. This is explained by (i) the decrease in ferrite phase (ii) slag becomes SiO_2 -rich and (iii) poor reactivity of dolomite due to its greater size.

4. The trend is reversed at 1273 K. This is attributed to the case of reduction of magnesiowustite phase.

5. The values of apparent activation energy obtained from experimental results and the application of gas-solid reaction model were used to derive the reduction mechanism. At the initial stage, the reaction was controlled by interfacial chemical reaction at different basicity while at the final stage the reaction was controlled by the combined interfacial chemical reaction and gaseous diffusion mechanism.

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