1. Introduction

The reduction of iron ores has attracted special interest and trails are recently given to improve the commercially applied processes and also to develop new processes for both of reduction and smelting techniques. The reduction of iron oxide pellets or lump ores in shaft furnaces are usually undertaken under load where the upper charge layers are exerting load upon the lower layers. In the literature, scant attentions were paid to the reduction of iron oxides under load in order to simulate the shaft furnace reduction conditions.

Mourao et al. studied the reduction under load test for determining the quality control of the pellets produced for direct reduction processes. Sato et al. investigated the softening behaviour under load using cold bonded pellets produced from different iron ores. Khaki et al. studied the reduction of six types of self-fluxed pellets under load. They observed that the reducibility of each pellet was affected by its original characteristics and increased with porosity and decreased with slag former content. In pellets having the same porosity and slag former values, the reducibility increased as basicity increased from 1.27 to 1.39. Cho studied reduction of iron ore sinter under load in the temperature range from 1073 to 1188 K. He found that iron ore sinter at a basicity of 1.8 behaved fairly compared to that at a basicity of 1.6 that showed a relatively rapid shrinking. Ekpe et al. determined the reduction and strength properties of the fired compacts with different basicities by means of reducibility, reduction under load, abrasion resistance, and tumbler tests.

On the other hand, several workers studied the reduction of iron oxides under different gas pressure values. They found that at low values of total pressure of reducing gas (<0.101 MPa), the rate of reduction is directly proportional to the partial pressure of reducing gas. El-Geassy et al. studied the wüstite-iron reduction step at 1173–1373 K in CO, H₂ and their mixtures at 0.0101 up to 0.101 MPa. They concluded that the reduction rate of wüstite micropellets increased in a non-linear manner with the increase in the total pressure. At higher gas pressure, the reduction rate increased till it reached a maximum value, after which no more increase in the rate was observed. Takahashi et al. observed that the reduction of iron oxide pellets with CO, H₂ and other gas mixtures in pressurized shaft furnace proceeded topochemically at normal pressure and rather homogeneously at high pressure. The stagnation of pressure effect has been analysed by few workers from different viewpoints and the causes have been clarified. The effects of pressure and gas velocity on the reduction rate were analyzed according to the bubbling bed model, and by three interface unreacted shrinking core model with dynamic effective diffusivity. The effect of pressure on the reduction rate was found to be essentially determined by four rate parameters; effective molecular diffusivity and mass transfer coefficient, Kendsen diffusivity.
and reaction rate constant. The kinetics of reduction of commercially produced iron ore pellets by mixed gases under different gas pressure values (from 0.0101 to 1.0515 MPa) were investigated.\textsuperscript{17} The experimental results were analyzed by means of a model which accounted for the transport steps and chemical reaction. The kinetics and mechanisms of reduction of iron ore pellets under load were investigated elsewhere using three different models.\textsuperscript{18} The first depends on the calculation of activation energy values whereas the second uses the heterogeneous gas–solid mathematical formulations. A third model was developed depending on the calculation of the shrinking core reaction modulus and mixed control ratio. The developed model allows for performing a good analysis about the actual effect of temperature and applied load upon the reduction controlling mechanism.

The present work aims at highlighting and understanding the influence of load applied (0.0 up to 0.0559 MPa) on the reduction behaviour of acidic and basic fluxed iron ore pellets. The reduction was carried out isothermally at 1 023–1 273 K with reformed natural gas mixture. The influences of load values, temperature and basicity were investigated and correlated. In previous publication,\textsuperscript{18} the reduction kinetics and mechanism under load was discussed.

2. Material and Experimental Technique

The characteristics of the two types of fluxed iron ore pellets, which represent the main component of the shaft furnaces charge at Alexandria National Steel Co, ANSDK, Egypt, are given in Table 1.

- Basicity of pellets calculated from the ratio between (CaO+MgO) and (SiO$_2$+Al$_2$O$_3$) is 0.37 and 1.62 indicating that the former is acidic while the later is basic pellets. X-ray phase analysis and microscopic examination indicated that hematite (α-Fe$_2$O$_3$) is the predominant phase in these pellets. In acidic pellets, iron-aluminium silicate phases were identified while calcium and magnesium ferrites were identified in basic pellets. These phases were formed during firing of pellets at high temperature (>$1473$ K) by a solid-state reaction between Fe$_2$O$_3$ and the corresponding constituents of associated gangue minerals and fluxing materials added in the pelleting process. The photomicrographs showing the internal structure of acidic and basic pellets are shown in Figs. 1(a) and 1(b) respectively. It was observed that hematite grains were coalesced to each other forming a relatively dense structure in which macro and micro-pores were developed. The macropores are separating groups of consolidated hematite grains and the micropores were seen between incompletely coalesced hematite particles. In acidic pellets, silicates of iron and aluminium were observed whereas in basic pellets, calcium and magnesium ferrites were formed at the grain boundaries.

- Fluxed pellets were isothermally reduced at 1 023–1 273 K in a synthetic gas mixture containing 55 vol% H$_2$, 36 vol% CO, 5 vol% H$_2$O, 3 vol% CO$_2$, and 1 vol% N$_2$ at NTP. This gas mixture represents the actual composition of reformed natural gas used in ANSDK plant, Egypt, for DRI production. The reduction experiments were carried out under load values ranging from 0.0 up to 0.0559 MPa. The schematic diagram showing the gas purification system was given elsewhere.\textsuperscript{7} The reduction furnace assembly and the experimental set-up used to carry out the reduction of pellets under load are illustrated in Fig. 2. It shows that a perforated stainless steel basket (I) was vertically hanging from the balance arm inside the reaction tube (N) with reformed natural gas mixture. The temperature in the middle part of the reaction tube was controlled by a Pt–Pt/Rh thermocouple (L) attached to a control unit (M). In reduction experiment, about 50–60 g oxide pellets placed in the basket (I) were weight-ed. The predetermined load value (MPa) to be applied on

| Chemical Composition | Physical Characteristics |
|----------------------|--------------------------|
| Fe$_2$O$_3$          | 96.57 96.23              |
| SiO$_2$              | 1.46 0.96                |
| CaO                  | 0.59 1.15                |
| MgO                  | 0.30 0.80                |
| Al$_2$O$_3$          | 0.93 0.25                |
| FeO                  | 0.09 0.25                |
| S                    | 0.002 0.01               |
| P                    | 0.091 0.03               |
| TiO$_2$              | 0.020 0.30               |

Table 1. Physico-chemical characteristics of fired fluxed iron ore pellets.

Fig. 1. Internal structure of fluxed iron oxide pellets; (a) acidic pellets, (b) basic pellets.

Fig. 2. Schematic diagram showing the gas purification system.
3. Results and Discussion

Reduction of iron ore pellets was carried out isothermally at 1023–1273 K in a flow of gas mixture containing 55% H₂, 36% CO, 5% H₂O, 3% CO₂ and 1% N₂ (by volume). At a given temperature, the reduction was undertaken without applying any external weights on upper disk (Fig. 2, a) that referred herein after as 0.0 MPa load value. In another experiments, external weights were applied on upper disk (Fig. 2, a) corresponding to 0.0196, 0.0392 and 0.0559 MPa load values. The oxygen weight-loss resulted from the reduction of Fe₂O₃ was measured at interval times and the corresponding reduction extent was calculated. The influence of temperature, load value and basicity of pellets on the reduction behaviour was investigated. The internal structure was examined and correlated with the reduction kinetics in order to have a comprehensive analysis of the reduction mechanism.

3.1. Effect of Temperature and Load

The temperature at which the reduction occurs has a very pronounced effect on the rate of reduction. The typical reduction curves obtained at 1023, 1073, 1123, 1173, 1223 and 1273 K for acidic and basic pellets at 0.0 MPa load value are given in Figs. 3(a) and 4(a) respectively. For a given temperature, the reduction rate was higher at early stages and gradually decreases with time till the end of reduction process. At lower temperature (1023 K), the time required for reduction of acidic and basic pellets is 360 min and 405 min respectively, whereas, it decreased to 240 min and 225 min at 1273 K. Although the total porosity of these two types of pellets are close to each other (Table 1) the reduction of basic pellets is faster than acidic pellets at early stages up to certain extent and became slower at later stages. This is attributed to the presence of calcium and/or magnesium ferrites in basic pellets. These ferrites are more reducible than iron aluminium silicate phases developed in acidic pellets. The relatively decrease in the reduction rate of basic pellets, at later stages, is due to the formation of hardly reducible calico- and/or magnesio-wüstite phase. The influence of CaO and/or MgO on the reduction of pure Fe₂O₃ either directly to iron (one step) or to magnetite and/or wüstite (two or three steps) was given elsewhere. It was found that the presence of basic ferrites increased the reduction rate at early stages and hindered the reduction at later stages. This was greatly depending on temperature, basic oxide content and reduction extents. The relationship between the rate of reduction (dW/dt) calculated at 5, 15, 25, 50, 70 and 90% reduction extents and the corresponding reduction temperatures for acidic and basic iron oxide pellets are given in Figs. 5(a) and 6(a) respectively. They showed that the rate of reduction at early and intermediate stages (5–50% extents) gradually increases with temperature up to 1173 K, above which a significant increase in the rate was observed. The increase in the rate of reduction decreased with the increase in the reduction extent. At later stages (70–90% extents) the increase in the rate with temperature is insignificant. This is attributed to sintering of freshly formed iron developed from the reduction of lower oxides. The rate of sintering increases with the increase of metallic iron content in partially reduced
samples and with rise in temperature. Sintering of iron at the outer grain surface resulted in a dense iron layer around lower oxides which hindered gas diffusion to and from the entrapped lower oxides (magnetite and/or wüstite) giving a significant decrease in the reduction rate.

The influence of load applied (0.0–0.0559 MPa) during the reduction of fluxed pellets at 1 023–1 273 K was also studied. The typical reduction curves obtained on applying

Fig. 3. Reduction behaviour of acidic iron ore pellets at 1 023–1 273 K; (a) 0.0 MPa, (b) 0.0196 MPa, (c) 0.0392 MPa, (d) 0.0559 MPa.

Fig. 4. Reduction behaviour of basic iron ore pellets at 1 023–1 273 K; (a) 0.0 MPa, (b) 0.0196 MPa, (c) 0.0392 MPa, (d) 0.0559 MPa.

Fig. 5. Effect of temperature on the rate of reduction of acidic pellets at different reduction extents under; (a) 0.0 MPa, (b) 0.0196 MPa, (c) 0.0392 MPa, (d) 0.0559 MPa.
weights corresponding to 0.0196, 0.0392 and 0.0559 MPa load values are given in Figs. 3 and 4(b)–4(d) for acidic and basic pellets respectively. For acidic pellets (Fig. 3), it was observed that the reduction extent gradually increases with temperature upon all loads applied. Unlike in acidic pellets, the reduction of basic pellets shows two sets of reduction curves obtained depending on load and temperature. At ≤0.0392 MPa, the reduction curves obtained at 1 023 and 1 073 K are close to each other and lower than that obtained at ≥1 123 K. To clarify the effect of load on the reduction behaviour of fluxed pellets at 1 023–1 273 K, the rate of reduction (dr/dt) at 5, 15, 25, 50, 70 and 90% extents was plotted against the corresponding temperatures as shown in Figs. 5 and 6(b)–6(d) for acidic and basic pellets respectively. For acidic pellets, the rate gradually increases with temperature showing a considerable increase in the rate at lower reduction extents. On the other hand, the temperature has a great effect on the rate of reduction under ≤0.0392 MPa above which the temperature has less effect (Figs. 6(b)–6(d)). At early and intermediate stages, up to ≤50% extents, it can be seen that the rate of reduction gradually increases with temperatures up to 1 173 K and above which a considerable increase in the rate was detected. At later stages (≥70% extents), no considerable effect in the rate was observed due to the sintering of metallic iron. The sintering increases with the increase in reduction extent, load value and temperature. For a given temperature, the increase in the load value had less effect in reduction rate at early and intermediate stages. At later stages, the increase in load value showed a measurable influence on the reduction rate at later stages due to the increase in metallic iron content. In fluxed pellets, the higher the load applied, the lower the temperature effect observed. This is attributed to the increase in the rate of gas diffusion effect at higher temperature. Consequently the rate of reduction increases since no considerable amount of barley reducible wüstite grains were formed at these lower reduction extents. In previous work, it was found that the stepwise reduction of hematite compacts to magnetite and/or to wüstite was controlled by the gas diffusion mechanism at the initial reduction stages. At intermediate stages, the gaseous diffusion is still the rate determining process with less contribution of the interfacial chemical reaction mechanism. At later stages of reduction, where considerable amounts of the entrapped wüstite relics were formed, slowing down in the rate was found. This was resulted from the contribution of solid-state diffusion of anion (O^{2-}) and cations (Fe^{2+}) in the overall reduction process by a way or another depending on the shape and structure of the entrapped wüstite relics. The increase in the load value decreased the reduction rate at all
temperatures as shown in Figs. 5 and 6. The value of this decrease increased with reduction extent and temperature. The microstructure of acidic and basic pellets completely reduced at 1073 and 1273 K is shown in Figs. 7(a), 7(d) and 7(c), 7(d) respectively. Increasing the temperature to 1273 K led to densification of iron grains and subsequently, increasing the number of macropores on the expense of micropores. The internal structure of reduced pellets showed that the temperature has a considerable effect in basic than acidic pellets. At lower temperature, a large number of micropores were formed in basic pellets as observed in Figs. 7(c) and 7(a) respectively. At higher temperature, the sintering of iron is more effective in acidic than in basic pellets (Figs. 7(b) and 7(d)) resulting large macropores between iron grains.

The influence of temperature on the reduction behaviour of fluxed pellets under 0.0196, 0.0392 and 0.0559 MPa load values is given in Figs. 8(a)–8(d). It can be observed that the load applied during the reduction at 1273 K has a pronounced effect on the reduction behaviour of acidic than basic pellets. The reduction of acidic pellets on applying 0.0559 MPa load is slower than that obtained on applying ≤0.0392 MPa. The latter curves are much closer to each other and higher than that at 0.0559 MPa as shown in Fig. 8(c). Unlike in case of acidic pellets, the rate of reduction of basic pellets (Figs. 8(b), 8(d)) gradually decreased with increasing load value. This indicated that the load has a considerable influence on the reduction of acidic than basic pellets. This effect is more effective at higher temperatures. This could be due to the deficiency of reducing gas access to the outer surface of the pellets on applying higher load values which enhance sintering of the reduced products. Consequently, the gas/solid interface decreases resulting a decrease in the reduction rate. Moreover, sintering between the freshly reduced iron grains increases with temperature, which in turn, hindered gas diffusion to and from the lower oxides of iron resulting a decrease in the overall reduction rate at such conditions.

The rate-controlling step in the reduction of iron oxides with gases was previously determined from the correlation between9–21;
(a) apparent activation energy values,
(b) application of heterogeneous gas–solid mathematical formulations and,
(c) internal structure of partially and completely reduced samples.

The value of apparent activation energy (Ea) was calculated from Arrhenius equation;

$$K_r = K_{0r} \exp \left( -\frac{E_a}{RT} \right)$$..........................(1)

where $K_r$ is the reduction rate constant, $K_{0r}$ is the frequency factor, $R$ is the gas constant, and $T$ is the absolute temperature. The relationship between the rate of reduction (log dr/dt) and the corresponding values of (1/T) at early and final reduction stages of acidic and basic pellets are shown in Figs. 9(a), 9(b) and 9(c), 9(d) respectively. The computed values of $E_a$ obtained from the reduction of acidic and basic pellets are given in Table 2.

At early stages (5% reduction extent), the values of $E_a$ obtained indicated that the reduction of fluxed pellets is controlled by a combined effect of gaseous diffusion and interfacial chemical reaction (mixed reaction mechanism). The contribution of the latter in the mixed mechanism is load value dependent. At final stages (90% reduction extent) the reduction is controlled by gaseous diffusion mechanism due to sintering effect. While a mixed control mechanism is still the rate determining step in the reduction of basic pellets under 0.0196 MPa. Moreover, the mathematical formulations for gaseous diffusion, chemical and mixed control reactions derived from grain model20 were tested against experimental results. The mathematical derivation of the three formulations were given elsewhere20 and the simplest forms are as follows;

$$a = \text{for chemical reaction; } r^a = G_{0r}(X) = 1- (1-X)^{\frac{3}{2}}$$..........................(1)

$$b = \text{for gaseous diffusion; } r^b = P_{0r}(X) = 1- (1-X)^{\frac{3}{4}}$$..........................(2)

$$c = \text{for mixed reaction; } r^c = G_{0r}(X) + \delta^2 P_{0r}(X)$$..........................(3)

Where; $r^a$ is the dimensionless time, $X$=fractional reduction and $\delta^2$ is the shrinking core reaction modulus. Applying line fitting for these three formulations indicated that the mixed reaction mechanism (Eq. (3)) controlled the reduction at early stages. On the other hand, the testing of these three formulations at later reduction stages, showed that
non of them are applicable. This is due to the load applied which enhanced sintering and subsequently retarded the gas diffusion effect. For this reason, another mathematical model was derived to have a good comprehension about the effect of temperature and load. In this model, the values of \( \hat{s}^2 \) which contribute the gaseous diffusion or interfacial chemical reaction in the mixed control equation was determined under different experimental conditions. The derivation of this mathematical model was given elsewhere.18)

The developed reaction model allowed for performing a good analysis of the reduction kinetics of fluxed pellets in order to elucidate the rate controlling mechanism.

### 3.2. Inter-relating Effects of Temperature and Load

In order to highlight and follow up the influence of load applied during the reduction on the behaviour of acidic and basic pellets at different reduction stages, the time required for 20, 60 and 90% reduction extent was calculated. The relationship between the reduction time obtained and the corresponding load value applied are shown in Figs. 10(a), 10(b) and 10(c), 10(d) for acidic and basic pellets reduced at 1023 and 1273 K respectively. It can be seen that straight lines were obtained at all reduction extents. The slope of these lines decreased with the increase in the extent of reduction and temperature. At the later stages (90% reduction extent), the slope of lines obtained indicated that the reduction of basic pellets at high temperature is slower than the acidic pellets. This also confirms that the reduction of basic pellets at later stages is characterised by the presence of slowing down effect due to the formation of entrapped Ca and/or Mg–wüstite relics. The microstructure of reduced acidic and basic fluxed pellets given in Figs. 7(a)–7(d) showed the increase in the number of macropores on the expense of micropores inside the metallic iron grains due to the sintering effect that takes place during reduction at high temperatures. As the load value increases, more

| Load applied (MPa) | Acidic Pellets | Basic Pellets |
|-------------------|---------------|--------------|
|                   | Initial stages| Final stages | Initial stages| Final stages |
| 0.0000            | 39.29         | 12.96        | 34.69         | 20.91        |
| 0.0196            | 41.59         | 14.63        | 37.62         | 41.83        |
| 0.0392            | 42.64         | 22.57        | 56.85         | 12.14        |
| 0.0559            | 27.17         | 16.75        | 41.71         | 13.20        |

Table 2. Apparent activation energy values for the reduction of acidic and basic pellets under load.

![Arrhenius plots for the reduction of acidic and basic pellets at 1023–1273 K.](image)

Fig. 9. Arrhenius plots for the reduction of acidic and basic pellets at 1023–1273 K.

![Effect of load values applied and the time for the reduction of acidic and basic pellets at 1023 and 1273 K.](image)

Fig. 10. Effect of load values applied and the time for the reduction of acidic and basic pellets at 1023 and 1273 K.
bridging between the partially reduced grains is observed forming clusters a matter which renders their reduction more difficult with the increase in load values as indicated from the reduction behaviour of pellets given in Figs. 3–6. It was also noticed that the rate of reduction of basic pellets is higher than that in acidic pellets. This is attributed to the presence of easily reducible calcium and magnesium ferrites, which greatly enhanced the reduction of Fe$_2$O$_3$ compared to the barley reducible silicates of iron and aluminium developed in acidic pellets. The photomicrographs of reduced pellets showed that the iron grains were disintegrated into smaller grains, which was more pronounced at $<1173$ K rather than at higher temperatures. The disintegration phenomenon of micro-grains in compacts was previously discussed and was attributed to the carbon deposition and the subsequent reactions. This carbon resulted from the thermal cracking of CO gas (2CO=CO$_2$+C) which usually takes place at lower temperatures and catalysed by the freshly reduced metallic iron. This deposited active carbon further reacted with either metallic iron to form iron carbide (3Fe+C$\rightarrow$Fe$_3$C) or with lower oxides of iron (6FeO+5C$\rightarrow$2Fe$_3$C+3CO$_2$). X-ray and carbon analysis showed the presence of iron carbide as well as free carbon in partially and completely reduced samples. The total carbon content in partially and reduced samples (free and combined in iron carbide) was determined. It was observed that the carbon content increases with reduction extent and load value and decreases with rise in temperature. The mechanism of carbon deposition and its reactions was discussed in details elsewhere.\(^{22}\) The CO$_2$ gas bubbles formed inside the grains at the FeO/Fe interfaces, leads eventually a building up pressure, which increases by time till it reaches certain value above which the iron grains are broken down resulting large number of smaller grains.

4. Conclusion

Fluxed acidic and basic iron oxide pellets were isothermally reduced at 1023–1273 K. The reduction of pellets was carried out in a synthetic reformed natural gas mixture on applying different load values (0.0–0.0559 MPa). The reduction behaviour indicated that the value of load plays a pronounced effect in the reduction behaviour of iron oxide pellets. At early reduction stages, it was found that basic pellets are more reducible than acidic pellets due to the presence of Ca and/or Mg ferrites which promote the reduction of Fe$_2$O$_3$. At later stages, slowing down in the rate was observed in basic pellets due to the formation of barley reducible calcio- and/or magnesio-wüstite phases. Increasing temperature led to more densification of iron grains and the subsequent collapse of micropores and increase of macropores as a result of sintering. With the increase in load value, more bridging happened between the reduced particles forming clusters of connected dense large particles and consequently the reduction becomes more difficult and decreased as the value of load increased. At a given temperature, a correlation between reduction rate and applied load was obtained which greatly depends on the basicity of iron oxide pellets.

REFERENCES

1) P. M. Mourao and M. Piccole: CYRO Rev. 2 (1984), No. 3, 33.
2) K. Sato, Y. Sawamura, K. Kanbara and T. Furui: Tetsu-to-Hagané, 65 (1979), No. 12, 1673.
3) J. Khaki, Y. Kashiyawa and K. Ishii: Ironmaking Steelmaking, 21 (1994), No. 1, 56.
4) S. Cho: J. Korean Inst. Met., 30 (1992), No.9, 1087.
5) U. Eke and R. Walker: Ironmaking Steelmaking, 16 (1989), No. 4, 228.
6) W. K. McKewan: Trans. AIME, 221 (1961), 140.
7) J. M. Quests, M. E. Wadsworth and J. R. Lewis: Trans. AIME, 218 (1960), 242.
8) W. A. Hokings: Comm. Proc., 19 (1960), 545.
9) A. A. El-Geassy and V. Rajakumar: Trans. Iron Steel Inst. Jpn., 25 (1985), 449.
10) R. Takahashi, Y. Takahashi, J. Yagi and Y. Omori: Trans. Iron Steel Inst. Jpn., 26 (1986), No. 9, 765.
11) W. K. McKewan: Trans. Metall. Soc. AIME, 224 (1962), 387.
12) N. Warner: Trans. Metall. Soc. AIME, 230 (1964), 163.
13) R. Spitzer, F. Maning and W. Philbrook: Trans. Metall. Soc. AIME, 236 (1966), 163.
14) S. Kurozu, R. Takahashi and Y. Takahashi: Tetsu-to-Hagané, 66 (1980), 23.
15) K. Sato, Y. Ueda, Y. Nishikawa and T. Goto: Trans. Iron Steel Inst. Jpn., 26 (1986), No. 8, 697.
16) K. Sato, Y. Ueda and T. Goto: Trans. Iron Steel Inst. Jpn., 27 (1987), No. 1, 10.
17) L. C. B. Martins: Ph.D. Thesis, Carnegie Mellon Univ., (1981).
18) M. I. Nasr, A. A. El-Geassy, and K. S. Abdel-Halim: S5th Steelmaking and 61st Ironmaking Conf., ISS, Warrendale, PA, (2002), 597.
19) A. A. El-Geassy: ISIJ Int., 37 (1997), 884.
20) A. A. El-Geassy: Scand. J. Metall., 27 (1998), No. 5, 205.
21) A. A. El-Geassy: Ironmaking Steelmaking, 26 (1999), No. 1, 41.
22) M. I. Nasr, A. A. Omar, M. M. Hessien and A. A. El-Geassy: ISIJ Int. 36 (1996), 164.