Sintering of the pellets of Egyptian iron ore with lime and reduction of its via hydrogen

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Abstract— This investigation studied the effect of lime addition to the Egyptian iron ore raw material on the physicochemical properties of its pellets in green and indurate form. Also the effect of this addition on the degree of reduction was studied. The results indicated that the addition of (2-8%) lime decreases the mechanical properties of the both green and indurate pellets. Also the reduction of these pellets via hydrogen was studied and the model of reduction was put in this paper.

Index Terms: Reduction of pellets, Kinetic models, lime, cold crushing strength, drop number

1 INTRODUCTION

Dain et al. [1] indicated that the reduction of synthetic hematite samples is a multi-stage reaction with one or two intermediate oxides depending on temperature. Thermogravimetric experiments and analyses of partially reduced samples have shown that the longest step is the transformation of wustite to iron. The first two reactions, hematite to magnetite and magnetite to wustite, are successive and well separated since hematite has completely disappeared when the first grains of wustite are detected. On the contrary, the reduction of wustite into metallic iron begins before the total consumption of magnetite. In the range 550-900°C, an increase in temperature accelerates the reaction. Experiments with three types of hematite samples have shown differences in reactivity. With the sintered pieces and the nanopowder, the final iron structure can be quite dense, making the gaseous diffusion very difficult. The solid state diffusion thus probably becomes the limiting step of the kinetics and the reaction rate is lowered even if the initial specific area of the sample was high.

Ranzani et al. [2] concluded that the reduction of iron ore by H2 is faster than that with (CO)2. Decreasing the pellet size clearly accelerates the process.

FAN et al. [3], found that (1) When adding lime and light-burned-dolomite, the wet drop strength of green ball will decrease firstly, and then go up with the increase of dosage

The reason is that (Ca)2+ formed by lime and light-burned-dolomite will replace (Na)+ in the interlayer of bentonite and lower the quality of bentonite. But with high additives dosage, the binding of Ca(OH)2 can increase the wet drop strength.

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The basicity of 0.4−0.6. The reaction of CaO with Fe2O3 and SiO2 will form binding phase of calcium-ferrite, and the suitable liquid phase will improve the recrystallization of hematite, but the excessive liquid phase will destroy the structure of pellets.

Yunyun [4] found that When Butare area iron lump ores can be reduced by direct reduction method the reduced sample kept its shape without breaking into small fragments at high temperature 900°C. (2) Reduction degree of samples increases with reaction temperature. Samples reduced at high temperature 900°C shown higher reduction degree in comparison with samples reduced at 700°C - 850°C. (3) At 900°C, H2 worked as the more effective reducing gas to give higher reduction degree and faster process. (4) 0.5 L/min is the best flow rate for Butare iron lump ores compare with other flow rates. (5) Microstructure strongly influent reduction degree, smaller grain size samples reduced faster and more completely. (6) Samples reduced at high flow rate 1L/min and high temperature 900°C took longer reduction time although the sample weight was smaller.

Sarkar et al. [5] found that the addition of inorganic materials, like hydrated lime, have a slight advantage over bentonite when silica levels are the primary concern of steel makers. Addition of lime results in poor quality green balls which are fragile and easily broken, lowering production rates in iron making.

Zuo et al. [6], found that (1) Increasing hydrogen content in the reducing gas mixture or increasing reaction temperature can clearly accelerate reduction reactions, and more hydrogen can lead to a more rapid increase in reaction rate with the increase of temperature due to the endothermic reaction of hydrogen reduction partly replacing the exothermic reaction of carbon monoxide reduction. (2) The effective diffusion coefficient and the rate constant of chemical reaction are simultaneously enhanced with increasing temperature or increasing hydrogen content in the mixture. The effect of temperature on the reaction rate constant is influenced by the hydrogen content. A higher hydrogen content leads to a higher intensity of impact; the similar rules exist for the effective diffusion coefficient. Moreover, adding just a little CO into the H2 would decrease the gas effective diffusion coefficient drastically com-
pared with pure hydrogen. (3) The reduction of iron oxide pellets using an \( \text{H}_2-\text{CO} \) mixture is a compound control system; the reaction rate is dominated by chemical reaction at the very beginning, competition during reduction process subsequently, and internal gas diffusion at the end. The transition of the rate-control step varies with the reducing agent composition and reaction temperature. When lowering the hydrogen content in mixture, increasing temperature takes the transit point of the rate-control step from chemical reaction to internal gas diffusion to a high reduction degree. After gradually increasing the hydrogen content to a certain value, the effect of temperature on the transit point of the rate-control step weakens.

Mandal and Sinha [7] concluded that (1) It has been possible to use fluxed iron ore pellets using iron ore and lime fines as a raw material to minimize flux input in Blast Furnace as a limestone and avoid bentonite addition as binder in conventionally prepared pellets. (2) The preparation of fluxed iron ore pellets with high basicity (1.17) has been possible without sticking pellets up to 1300°C hardening temperature. (3) The use of lime contents up to 4 wt% (pellet basicity 1.17), in the pellets at 1300°C temperature for one hour hardening period, shown higher crushing strength (586.76 kg/pellet) and lower apparent density (2.69 gm/cc) with respect to lump ore (400 Kg/cm\(^2\) and 3.1 gm/cc). The formation of more calcium silicate in basic pellets was imparted higher strength to the pellets in comparison to acid pellet. (4) Shatter, tumbler and abrasion resistance of fluxed hardened pellets were found superior at 1300°C compared with lumpy iron ore. (5) Apparent and true porosity of hardened fluxed pellets were improved than lump ore. (6) With increasing hardening temperature, apparent porosity value was increased tremendously up to 44.61% at 1200°C. But at 1300°C, slag inside the pellets fused resulting less porosity as lower as 9.96% which enhanced crushing strength (586.76 kg/pellet) as compared to lump ore (400 Kg/cm\(^2\)).

Arup et al [8]. The preparation of fluxed iron ore pellets with high basicity (1.17) is possible without sticking at induration temperature up to 1300°C with the help of lime as an effective binder. Also the hardened pellets show higher crushing strength (586.76 kg/pellet) and lower apparent density (2.69 g/cc) than lump iron ore (400 kg/cm\(^2\) and 3.1 g/cc respectively). This is due to formation of calcium silicate in basic pellets. The values of shatter, tumbler and abrasion resistance of fluxed hardened (1300°C) pellets were superior to acid pellets and lumpy iron ore. The apparent and true porosity of hardened (1300°C) fluxed pellets were higher than lumpy ore. For example, apparent porosity 9.96 % for basic pellets is comparable with value for lump ore (i.e. 8.1%). With increasing hardening temperature, apparent porosity increased by 42.8 % at 1200°C. But at 1300°C, slag formation within the pellets resulted in less porosity (as low as 9.96 %) which enhanced the crushing strength (586.76 kg/pellet) compared to 400 kg/cm\(^2\) for lump ore.

El-Hussiny et al [9] found that (1) The reduction rates of El-Dekhila iron oxide pellets with hydrogen increased with increasing temperature of the reduction from 700 up to 950°C. (2) Also at constant reduction temperature of reduction the reduction rate increased with increased hydrogen flow. (3) The diffusion processes through the produced pellets or Avrami-Erofeev n=1 are the reduction control step.

The aim of this work is study the reduction of the indurate El-Baharia Egyptian iron ore with lime pellets by hydrogen

2. EXPERIMENTAL WORK

2.1 Materials Used

Iron ore and lime samples were supplied by the Egyptian Iron and Steel Company. The chemical composition of these raw materials is as follows:- Chemical analysis of lime: CaO= 91.48%, SiO\(_2\)= 4.41% and MgO= 4.11%. While the chemical analysis of El-Baharia iron ore: Fe total = 52.35 %, MnO= 2.92%, SiO\(_2\)= 10.84%, CaO= 0.39%, MgO= 0.18%, Al\(_2\)O\(_3\)= 1.44%, S= 0.74%, TiO\(_2\)= 0.16%, BaO= 1.17%, ZnO= 0.15%, K\(_2\)O= 0.27%, Na\(_2\)O= 0.25%, P\(_2\)O\(_5\)= 0.5 %.[10]

The X-Ray analysis of El-Baharia iron ore is illustrated in figure (1). From which it is clear that El-Baharia iron ore mainly consists of hematite and quartz. While the X-ray analysis of lime mainly consists of calcite and syn.Ca(OH)\(_2\) as shown figure (2).

2.2 Preparation of the pellets of iron ore with lime and Its Physical Properties

Iron ore and lime were grinding separately in vibrating mill to powder with size less than 75 micrometers. After which the pelletization of the iron ore with certain amount of lime were done in a disc pelletizer Fig.(3) of diameter 400 mm, collar residence time 30 min. After the materials were feed to the pelletizer the predetermined moisture amount (8.5% water + 2.5% of molasses) was then sprayed onto the rolling bed of material in the pelletizer. The green pellets in the size range 5-7 mm diameter were screened out to burning in the muffle furnace under different temperatures from 900 to 1200 °C.

The green produced pellets subjected to drop number test from 46 cm height and crushing strength tests. The crushing strength test of green and fired pellets were done by MEGA.KSC-10 hydraulic press) Fig.(4). The drop number indicates how often green pellets can be dropped from a height 46 cm before they show perceptible cracks or crumble.

Ten green pellets are individually dropped on to a steel plate. The number of drops is determined for each pellets and the arithmetical average values of the crumbing behavior of the ten pellets yield the drop number. The average crushing strength is done by compressed 10 pellets between parallel steel plates up to their breaking [11-14].
2.3 Reduction Procedures

The reduction of Pellets of El-Baharia iron ore with lime by hydrogen were done on thermo gravimetric apparatus (A schematic diagram of thermo gravimetric apparatus is shown in Fig. (5) [10, 15-20]. It consisted of a vertical furnace, electronic balance for monitoring the weight change of reacting sample and temperature controller. The sample was placed in an Ni-Cr basket which was suspended under the electronic balance by Ni-Cr wire. The furnace temperature was raised to the required temperature (700°C-950°C) and maintained constant to ± 5°C.

Then samples were placed in hot zone. The nitrogen flow rate was 0.5 L/min on all the experiments. At initial time and after the end of reduction only the weight of the sample was continuously recorded at the end of the run, the samples were withdrawn from the furnace and put in the desiccators. The amount of removable oxygen was determined by the weight loss in the sample (Wo-Wt) during the experiment of reduction with H₂ in the furnace. The percentage of reduction was calculated according to the following equations [21, 22]

\[
\text{Percentage of reduction} = \frac{(Wo-Wt) \times 100}{Wo}
\]

Where Wo: the initial mass of sample after each reduction time (t), (g).

Wt: mass of sample after each reduction time (t), (g).

Oxygen (mass) indicates the mass of oxygen percent in the sample in form Fe₂O₃, (g).

3. Result and Discussion

3.1 Effect of lime addition on physical properties of green pellets before burning

The effect of adding varying percentage of lime on the green iron ore pellets properties is shown in figures (6) and (7).

From which it is clear that increase lime addition leads to increase the drop damage resistance (drop/briquette) and compressive strength of green pellets. Increasing these properties may be due to the fact that lime increased the coagulation between particles and improved the specific area of the mix, which subsequently resulted in an increase in the growth of formed pellets thus increasing the pellets strength (15, 19, 23 and 24).
3.2 Effect of lime addition on physical properties of the fired pellets at different temperatures

The effect of adding varying percentage of lime on the iron ore pellets properties after burning in the muffle furnace under different temperatures from 900 to 1200ºC is shown in figure (8). From which it is clear that at any constant amount of lime addition the increase of firing temperature leads to an increase in the compressive strength of pellets this may be due to stronger slag bond formation inside the pellets (25, 26).

Also at any constant temperature of firing with increasing lime content, porosity was also increased subsequently the strength decreased

3.3 Effect of lime addition and firing temperature on the degree of reduction

Figure (9), illustrate the reduction percentage of iron ore contain lime pellets (sintered at (1200ºC) at 900ºC. (The weight of samples was constant and hydrogen flow rate was 1.5 L/min.). From these figure, it is clear that the percentage of reduction decreased as the percentage of lime increased.

3.4 Effect of change of temperature on the reduction percentage

In order to examine the effect of temperature on the reduc-

From these figures it is clear that the increase in temperature causes an increase in the extent of reduction. The increase of reduction percentage with temperature could be due to increase number of reacting moles having excess energy which leads to the increase of adsorption rate. Also increasing temperature leads to increase the rate of mass transfer of the diffusion and rate of chemical reaction (9, 16, 26, 27 and 28).

3.5 Kinetics reduction of reduction of pellets of indurate El-Baharia iron ore with lime

Kinetic studies for estimation of apparent activation energies were carried out for the iron ore pellets at different temperatures range from 700ºC up to 950ºC for different time
intervals in the range of 0 - 60 min.

1-Using diffusion process control equation (Jander and Anorg Equation) [27-29]

\[ 1 - (1-R)^{1/3} = kt \] (1)

Figs. (13), (15) and (17) illustrate the relation between \(1 - (1-R)^{1/3}\) against time of reduction for different reduction temperature for iron ore pellets contain zero %, 4% and 8% lime respectively, from which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for zero%, 4% and 8% lime added to iron ore. The results illustrates in Figs. (14), (16) and (18) respectively, from which it is clear that the activation energy 35.16 kJ/mole, 42.1 kJ/mole and 50.1 kJ/mole for the reduction of iron ore pellets contains zero%, 4% and 8% respectively.

Fig. 9. The reduction percentage of iron ore pellets contain lime (sintered at 1200°C) by hydrogen at 900°C

Fig. 10. The effect of temperature on the reduction of pellets of El-Baharia iron ore with zero% lime (pellets 5-7 mm, 1.5 L/min hydrogen flow rate)

Fig. 11. The effect of temperature on the reduction of pellets of El-Baharia iron ore with 4% lime (pellets 5-7 mm, 1.5 L/min hydrogen flow rate)

Fig. 12 The effect of temperature on the reduction of pellets of El-Baharia iron ore with 8% lime (pellets 5-7 mm, 1.5 L/min hydrogen flow rate).

Fig. 13 The relation between \(1 - (1-R)^{1/3}\) against time of reduction for different reduction temperature for iron ore pellets contain zero% lime.
Using geometrical contraction models (contracting volume) [30], or diffusion model [10 & 28]

\[(1-R)^{1/3} = kt\]  \hspace{1cm} (2)

Where \((R)\) is fractional reduction, \((t)\) is time of reduction and \((k)\) is the rate constant.

Figs. (19), (21) and (23), illustrated the relation between \(1 - (1-R)^{1/3}\) against time of reduction for different reduction temperatures for iron ore pellets contain zero%, 4% and 8% lime respectively, from which it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for 4% and 8% dolomite added to iron ore. The results illustrates in Figs. (20), (22) and (24) respectively, from which it is clear that the activation energy 31.993 kJ/mole, 37.02 kJ/mole, and 41.08 kJ/mole for the reduction of iron ore pellets contain zero%, 4% and 8% lime respectively.
Fig. 19: The relation between $1 - (1-R)^{1/3}$ and time of reduction for different reduction temperature for iron ore pellets contain zero% lime.

Fig. 20: The natural logarithms of $k$ against $1/T$, $k^{-1}$ for zero% lime added to iron ore.

Fig. 21: The relation between $1 - (1-R)^{1/3}$ and time of reduction for different reduction temperature for iron ore pellets contain 4% lime.

Fig. 22: The natural logarithms of $k$ against $1/T$, $k^{-1}$ for 4% lime added to iron ore.

Fig. 23: The relation between $1 - (1-R)^{1/3}$ and time of reduction for different reduction temperature for iron ore pellets contain 8% lime.

Fig. 24: The natural logarithms of $k$ against $1/T$, $k^{-1}$ for 8% lime added to iron ore.
3- Using diffusion models, Ginstling-Brounshtein equation \[ 1-\frac{2}{3}R-(1-R)^{2/3} = kt \] (3)

Where: (R) is fractional reduction, (t) is time of reduction, (k) is the rate constant of the reduction.

Figs. (25), (27) and (29), illustrate the relation between \(1-\frac{2}{3}R-(1-R)^{2/3}\) against time of reduction for different reduction temperatures for zero%, 4% and 8% lime added to iron ore respectively. From these figures it is clear that the straight line was observed.

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of reduction reaction for zero%, 4% and 8% lime added to iron ore. The results illustrate in Figs. (26), (28) and (30) respectively, from which it is clear that the activation energy 32.617 kJ/mole 37.018 kJ/mole and 54.301 kJ/mole for the reduction of iron ore pellets contains zero%, 4% and 8% lime respectively.

**Fig. 25** The relation between \(1-\frac{2}{3}R-(1-R)^{2/3}\) against time of reduction for different reduction temperatures for zero% lime added to iron ore

**Fig. 26** The natural logarithms of k against \(1/T\) for zero% lime added to iron ore

**Fig. 27** The relation between \(1-\frac{2}{3}R-(1-R)^{2/3}\) against time of reduction for different reduction temperatures for 4% lime added to iron ore

**Fig. 28** The natural logarithms of k against \(1/T\) for zero% lime added to iron ore

**Fig. 29** The relation between \(1-\frac{2}{3}R-(1-R)^{2/3}\) against time of reduction for different reduction temperatures for 8% lime added to iron ore

**Fig. 26** The natural logarithms of k against \(1/T\) for zero% lime added to iron ore

**Fig. 28** The natural logarithms of k against \(1/T\) for zero% lime added to iron ore

**Fig. 29** The relation between \(1-\frac{2}{3}R-(1-R)^{2/3}\) against time of reduction for different reduction temperatures for 8% lime added to iron ore
4 CONCLUSION

1- Addition of lime to iron ore during pelletization improve the drop number and crushing strength of green pellets.
2- Increase the firing temperature of the iron ore pellets with lime or without lime increased.
3- At any constant temperature of firing the increase of lime added to iron ore decrease the crushing strength of the pellets.

REFERENCES


