Fizykochemiczne Problemy Mineralurgii, 31 (*1997*)*, 31–41*

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THE ROLE OF CALCIUM HYDROXIDE IN THE PRODUCTION OF IRON OXIDE (MILL SCALE) PELLETS

Mill scale which is a valuable secondary raw material produced from the rolling of steel sheets in steel making process, can be agglomerated by using the pelletizing technique for the production of iron oxide pellets. The physicochemical properties of iron oxide pellets produced from mill scale were found to be improved with calcium hydroxide addition. The amount of calcium hydroxide added is varied from 0.5–4%, where the green, dry and indurated mill scale pellets properties were studied and the results of the experiments can be summarised as follows: 1. As the amount of calcium hydroxide added increased the productivity, average drop number (the resistance of pellets to be broken or cracked when dropped from 30 cm hight) and compressive strength of green mill scale pellets increased. 2. The compressive strength and average drop number of dried pellets increased with the increase of both the amount of calcium hydroxide and the drying temperature. 3. The maximum value of compressive strength of indurated pellets was attained at 4% of calcium hydroxide addition followed by induration at 1300 °C. 4. The reducibility of the indurated pellets was highest with 0.5% calcium hydroxide and decreased with increasing the amount of calcium hydroxide. While on increasing the firing temperature from 1000 to 1300°C for pellets containing 4% of calcium hydroxide, the reducibility decreased. 5. The compressive strength of reduced mill scale pellets increased with increasing both the amount of calcium hydroxide and firing temperatures for pellets containing 4% of calcium hydroxide. 6. The reduction process of mill scale pellets containing 4% of calcium hydroxide was controlled by combined mechanism for both the initial and final stages of reduction.

INTRODUCTION

Lime hydrate is both binder and basic additive in many agglomerates during induration. The basic additives first react with the acidic gangue constituents whereby a natural or basic matrix between the iron oxide grains is formed. Ebrehimzedeh (1964) indicated that $Ca(OH)_2$ has positive influence on the average drop number and compressive strength of green and dry pellets. Also the influence of calcium hydrate on the final strength of fired pellets is remarkable (Ebrehimzedeh 1964, Zhuraviev, Merlia 1987). Ruchkin (1976) and Osin (1954) indicated that the strengthening effect of the quicklime is due to its ability to become dispersed into very small particles in a moist medium which is accompanied by an increase in the contact of the combined

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water, hence a growth in pellet strength is noticeable. Tatsienko et al. (1981) reported that with addition of lime to the mix the pH of moisten medium changes, which leads to a change in its phase dispersion state and influences the pelletization process favorably. Savelev et al. (1987) found that the addition of lime as a binder is better than bentonite, and the optimum content of lime components in a mix was equal to 1.5%. Shalabi et al. (1994) has reported that the addition of CaO to the iron ore charge slightly decreases the productivity of green pellets, while average drop number and compressive strength of green pellets were increased. Fedorov et al. (1985) found that the economic indices of the production and the quality of iron ore pellets were improved by replacing bentonite binder with lime in the precharge.

EXPERIMENTAL

The mill scale and calcium hydroxide used in this work were obtained from the Egyptian Iron and Steel Co. Their chemical composition are given in Table 1.

Table 1. The chemical composition of raw materials

Raw materials	Chemical composition							
	Fe_{total}	FeO	Fe_{metal}	SiO_2	MgO	Al_2O_3	CaO	C
Mill scale	74.2	63.95	4	–	–	–	0.18	0.65
Lime	–	–	–	5.00	–	2.0	91.6	0.26

Pellets were shaped in a laboratory disc pelletizer of diameter 40 cm and its rim was 10 cm only pellets with diameter from 10–12 mm were used in the determination of the average drop number and compression strength. The pellet (–12 +10 mm in diameter) were dried and indurated in a computerized muffle furnace type 34·15·15 cm of model Nabertherm program controller c19. The reduction of indurated pellet was carried out at 1000 ^{O}C in H_2 atmosphere. The metallurgical properties and microscopic examination were carried on the indurated and reduced pellets.

RESULTS AND DISCUSSIONS

Influence of calcium hydroxide on properties of green pellet

Figures 1, 2 illustrate the relation between the amount of calcium hydroxide added, the productivity of the produced pellets and its strength. From Figs. 1, 2 it is clear that as the amount of calcium hydroxide added increased, the productivity of the produced pellets, its average drop number and its compressive strength were increased. This is due to the fact that calcium hydroxide increases the coagulation between particles and improves the specific area of the mix (Mayer 1980), and it may be also due to the fact that calcium hydroxide improves the granulometric composition and configuration of the agglomerating particles (Korshikov 1974) which subsequently increases the growth of formed pellets and this in turn increases its compressive strength (Mohamed 1993). Also, calcium hydroxide is the binding material which associated with colloidisation of the $Ca(OH)_2$, which reduced the internal strength of the pellets (Savelev 1987) and also the addition of $Ca(OH)_2$ leads to the increase in the pH value of the moistening medium which leads to a change in its phase dispersion state (Tatsienko 1981).

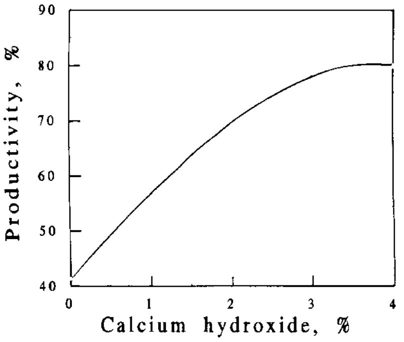


Fig. 1. Effect of calcium hydroxide on the productivity of mill scale pellets

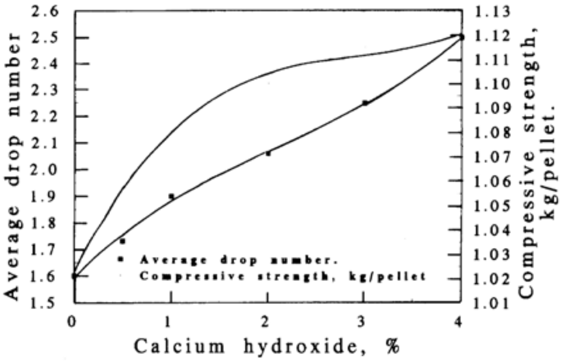


Fig. 2. Effect of calcium hydroxide addition on the average drop

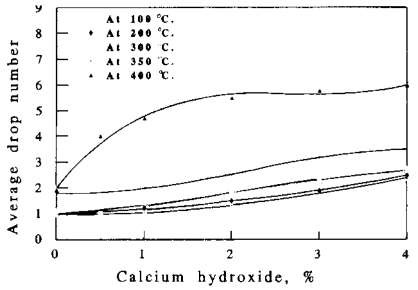


Fig. 3. Effect of calcium hydroxide addition on the average drop number of mill scale pellets at different drying temperatures

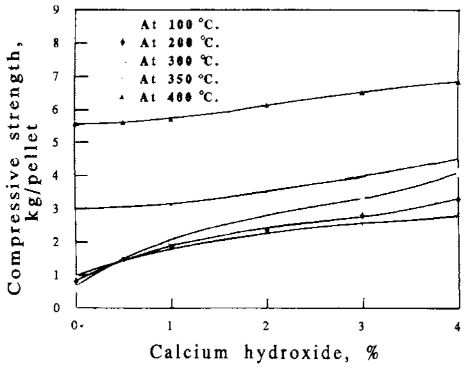


Fig. 4. Effect of calcium hydroxide addition on the compressive strength of mill scale pellets at different drying temperatures

Influence of calcium hydroxide on dry pellets strength

Figures 3, 4 show the relationship between the calcium hydroxide addition and both the average drop number and compressive strength of dried mill scale pellets which were dried at different temperatures. Inspecting experimentally the strength of dried pellets, it was concluded that at any constant amount of calcium hydroxide, as the drying temperature increased the average drop number and the compressive strength increased. Also, at any constant drying temperature, the average drop number and the compressive strength of dried pellets increased with increasing amount of calcium hydroxide added. This is due to a good bonding power of the hydrated lime in the dry pellets (Mayer 1980).

Influence of calcium hydroxide on properties of indurated pellets

Effect of calcium hydroxide addition on the compressive strength, total porosity and chemical composition of indurated pellets. The effect of hydrated lime on the compressive strength of indurated pellets was studied and the results are shown in Fig. 5, from which it is clear that at any constant amount of calcium hydroxide added (0.5–4%), the increase of the temperature leads to an increase in the compressive strength. This may be attributed to the fact that the increase in temperature leads to an increase in the amount of reaction between CaO and Fe_2O_3 with the formation of different types of calcium ferrite phases which substantially accelerates crystal growth particularly at temperature above 1250 °C. Also this is due to the fact that the melting point of these ferrites at lower temperatures speed up the diffusion of the individual crystal ions in such a way that the crystal growth proceeds free from any melting phase (Mayer 1980). On the other hand, the reaction between solid–solid constituents is exothermic reaction thus the temperatures of pellets increased more than the temperature of the furnace (Vegman 1978). Therefore, more melt is formed and subsequently the porosity of pellets decreased which subsequently increases the compressive strength. The increase of the compressive strength with increasing the amount of calcium hydrate added may be due to the increase in the slag amounts (Ball 1974).

Figure 6 shows the effect of temperature on the total porosity of pellets containing 4% of calcium hydroxide from which it is clear that as firing temperature increased the total porosity decreased. This is also clear from Photos 2–4. It is obvious that at 4% of calcium hydroxide and 1000°C firing temperature that the structure contains more micro and macropores while the increase in the temperature till 1300 °C, the porosity decreased due to the formation of more melt. Also the influence of calcium hydroxide addition on the final strength of pellets fired at 1300°C is remarkable. This may be due to the decrease in the total porosity of the pellets as shown in Photos 4–5, and Fig. 7.

Tables 2, 3 show the effect of calcium hydroxide on the chemical composition of the produced pellets.

From Table 2 it is clear that as calcium hydroxide increased the amount of FeO increased. This may be due to that the Fe_2O_3, which was formed by oxidation, reacted with CaO and forming ferrites with evolution of heat. This heat helps in the decomposition of Fe_2O_3 again to FeO, subsequently the amount of total Fe in the pellets increased (Ferreira 1994, Pashkov 1987).

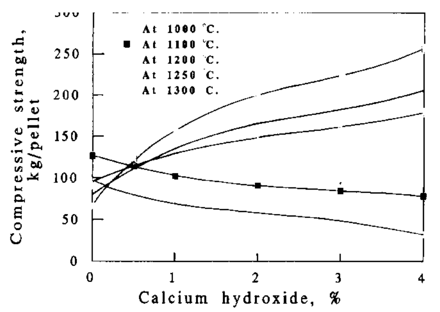


Fig. 5. Effect of calcium hydroxide addition on the compressive strength of mill scale pellets at different firing temperatures

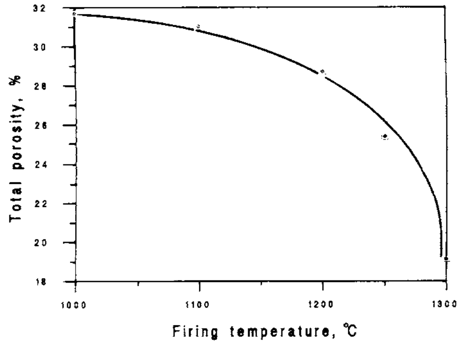
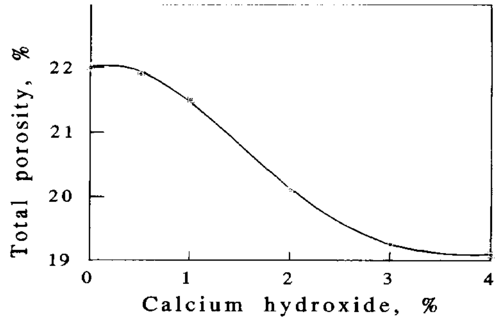


Fig. 6. Effect of firing temperatures on the total porosity of indurated mill scale pellets containing 4% of calcium hydroxide



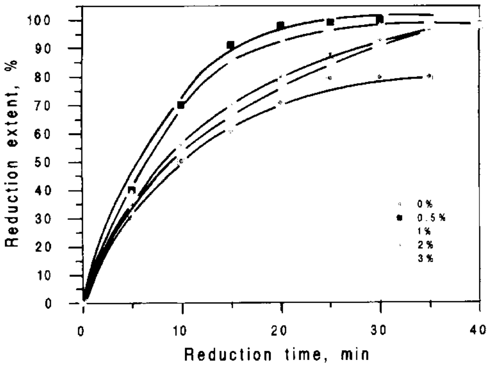


Fig. 7. Effect of calcium hydroxide addition on the total porosity of indurated mill scale pellets fired at 1300 °C

Fig. 8. Effect of calcium hydoxide addition on the reducibility of indurated mill scale pellets fired at 1300 °C

Table 2. Effect of calcium hydroxide addition on the chemical composition of indurated pellets fired at 1300°C

Calcium hydrate %	Chemical composition, %							
	Fe_{tot}	FeO	Fe_{met}	SiO_2	Al_2O_3	MgO	CaO	C
0	69.8	8.0	0	0.34	0.13	0.12	0.17	0.07
0.5	70.2	9.26	0.8	0.30	0.14	0.13	2.33	0.07
1	70.4	18.28	1.0	0.30	0.14	0.13	0.50	0.07
2	71.0	28.0	1.0	0.30	0.14	0.13	1.25	0.07

3	72.0	37.0	1.0	0.30	0.14	0.13	1.8	0.07
4	72.4	55.04	1.0	0.28	0.14	0.13	2.17	0.08

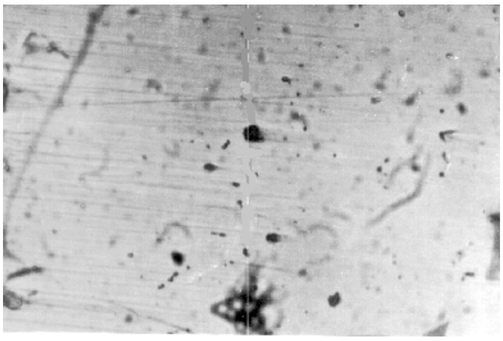


Photo 1. Photomicrograph for mill scale pellets fired at 1300 °C for 25 min. Hematite (white), pore (black) embedded in the matrix. (X1000)

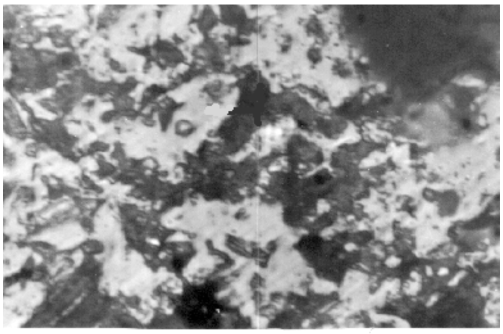


Photo 2. Photomicrograph of mill scale pellets having 4% of calcium hydroxide and fired at 1100 °C. Magnetite, hematite and pores embedded in matrix (X1000)

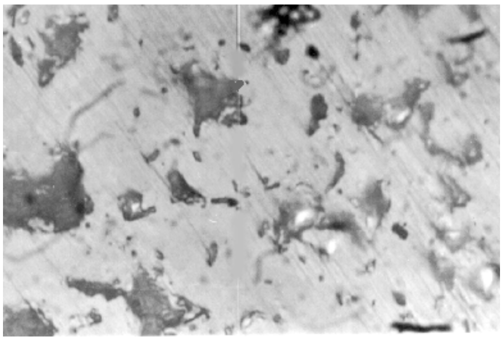


Photo. 3. Photomicrograph of mill scale pellets having 4% of calcium hydroxide and fired at 1200 °C. Magnetite, hematite and pores embedded in matrix (X1000)

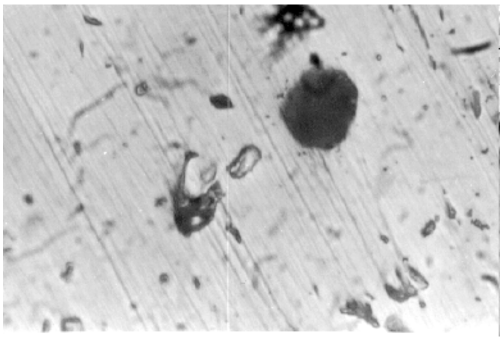


Photo 4. Photomicrograph of mill scale pellets having 4% calcium hydroxide and fired at 1300 °C for 25 min. Magnetite, hematite and pores embedded in matrix (X1000)

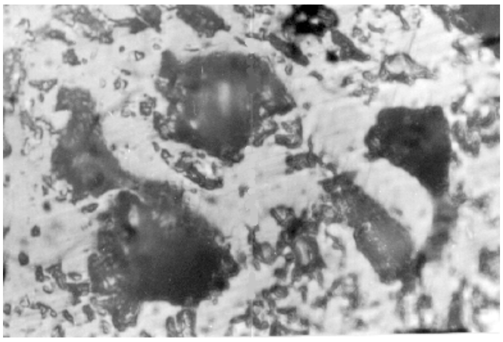


Photo 5. Photomicrograph of mill scale pellets having 0.5% calcium hydroxide and fired at 1300 °C. Magnetite, hematite and pores embedded in matrix (X1000)

Table 3. Effect of firing temperature on the chemical composition of indurated pellets containing 4% of calcium hydroxide

Firing temperature, °C	Chemical composition, %							
	Fe_{tot}	FeO	Fe_{met}	SiO_2	Al_2O_3	MgO	CaO	C
1000	69.0	19.08	0.8	0.30	0.15	0.14	2.84	0.07
1100	70.2	37.69	1.0	0.32	0.14	0.13	2.67	0.08
1200	71.0	43.0	1.0	0.34	0.14	0.13	2.67	0.07
1250	71.8	50.44	1.0	0.30	0.13	0.12	2.20	0.07
1300	72.0	55.04	1.0	0.28	0.14	0.13	2.17	0.08

From Table 3, it is evident that as the firing temperatures of pellets containing 4% of calcium hydroxide increased the amount of FeO increased. This is due to the increase of heat which led to more dissociation of pellets which contain CaO (Ferreira 1994, Pashkov 1987).

Effect of calcium hydroxide on the reducibility of indurated pellets fired at 1300 °C. A series of reduction experiments tests were carried out on the indurated mill scale pellets having different amounts of hydrated lime, (0.5–4%) in H_2 atmosphere. Figure 8 shows that the maximum reduction extent was achieved with 0.5% calcium hydroxide while the reducibility decreased with increasing the amount of calcium hydroxide from 0.5 to 4%. This might be due to the following reasons, 1) the increase of divalent oxides which is more difficult to be reduced (Shkodin 1963, Efimenko 1986, Masajikase 1981). 2) the formation of dicalcium ferrite, Fig. 9 (Srinivasan 1977, Edstrom 1958, Mazanek 1966, Takayuki 1986). 3) the decrease in the total porosity of pellets as shown in Fig. 6, Photos 4, 5. While the increase in the reducibility when 0.5% calcium hydroxide was added may be attributed to the formation of mono calcium ferrites beside the increase of micropores as shown in Photos 1–4.

Effect of firing temperature on the reducibility of indurated pellets containing 4% of calcium hydroxide. Figure 6 shows the effect of firing temperatures on the reducibility of indurated mill scale pellets having 4% of calcium hydroxide, from which it is clear that as the temperature increased the reducibility of pellets decreased. This might be attributed to the decrease in the total porosity of the indurated pellets as shown in Fig. 6 and Photos 2–4.

Effect of 4% of calcium hydroxide on phase transformation of mill scale pellets

Figure 9 shows X-ray diffractograms of the effect of calcium hydroxide addition on the phase transformation of the mill scale pellets. From Fig. 9 it is clear that the main phases are magnetite (M), wustite (FO), mono calcium ferrite (CF) and di calcium ferrite (C_2F). Also from the same figure it is clear that as the amount of calcium hydroxide increases the hematite (H) phase decreases due to the dissociation of higher oxides to lower oxides.

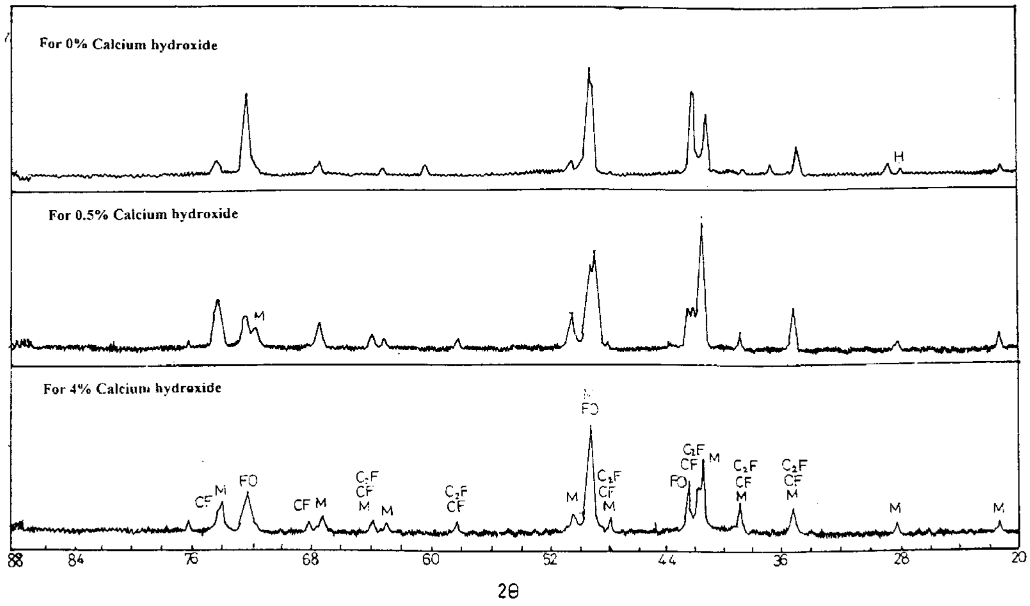


Fig. 9. X-ray diffractograms of indurated mill scale pellets having different percentage of calcium hydroxide and fired at 1300 °C for 25 min; M – magnetite, H – hematite, FO – wustite, FS – fayalite, C_2F – dicalcium ferrite, CF – monocalcium ferrite

Effect of 4% of calcium hydroxide addition on the reduction behaviour and rate controlling mechanism

Figure 10 shows that as the reduction temperature increased the time of reduction of indurated pellets containing 4% of calcium hydroxide fired at 1300 °C decreased (i.e., times for 80% reduction are 115, 85, 35 min at 800, 900 and 1000 °C, respectively).

To illustrate the rate controlling mechanism at both the initial and final stages of reduction, the apparent activation energy was calculated and were found to be 23.83 and 36.19 kJ/mole for the initial and final stages, respectively. These values reveal that the reduction processes at the initial and final stages are controlled by the combined gaseous diffusion and interfacial chemical reaction mechanism (Strangway 1964).

In order to confirm the validity of the mechanism, the mathematical formulas derived by Sohn and Szekely (1972, 1976) were applied for gaseous diffusion, chemical reaction and combined mechanism. Straight lines were only obtained for combined mechanism (Sohn 1972, Szekely 1976). Figures 12–13 show the application of the combined mechanism for pellets containing 4% of calcium hydroxide at the initial and final stages of reduction respectively.

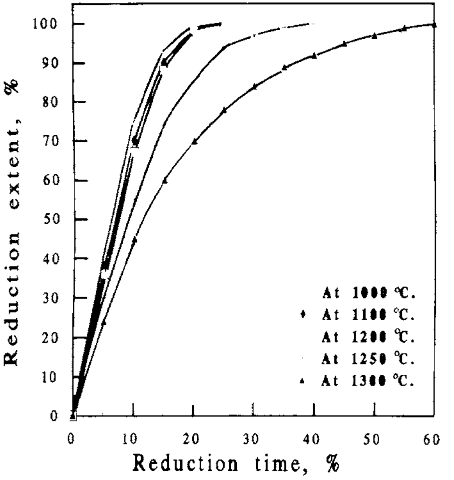


Fig. 10. Effect of firing temperatures on the reducibility of mill scale pellets containing 4% of calcium hydroxide

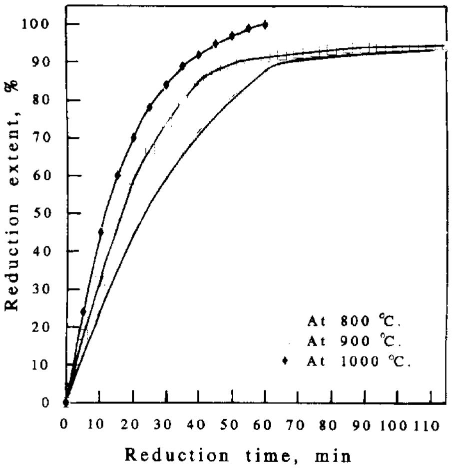


Fig. 11. Effect of reduction temperature on the reducibility of indurated mill scale pellets containing 4% of calcium hydroxide and fired at 1300 °C

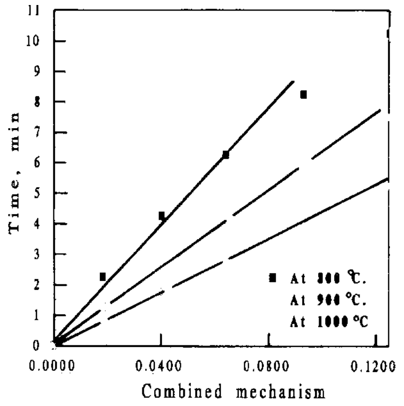


Fig. 12. Application of combined mechanism on the initial stages of mill scale pellets containing 4% of calcium hydroxide and reduced at 800–1000 °C

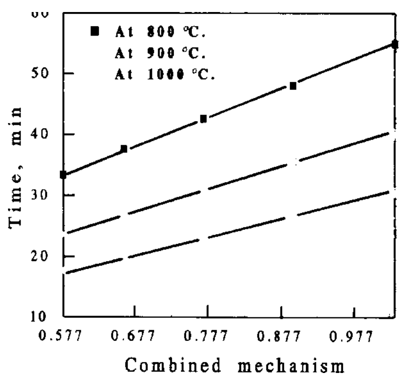


Fig. 13. Application of the combined mechanism on the final stages of mill scale pellets containing 4% of calcium hydroxide and reduced at 800–1000 °C

CONCLUSION

- As the amount of calcium hydroxide added increases the productivity, average drop number and compressive strength of green mill scale pellets increased.
- The compressive strength and average drop number of dried pellets increased with the increase of both the amount of calcium hydroxide and the drying temperature.
- The maximum value of compressive strength of indurated pellets was attained at 4% of calcium hydroxide addition followed by induration at 1300 °C.
- The reducibility of the indurated pellets was highest with 0.5% calcium hydroxide and decreased with increasing the amount of calcium hydroxide. While on increasing the firing temperature from 1000 to 1300°C for pellets containing 4% of calcium hydroxide the reducibility was decreased.
- The compressive strength of reduced mill scale pellets increased with increasing both the amount of calcium hydroxide and firing temperatures for pellets containing 4% of calcium hydroxide.
- The reduction process of mill scale pellets containing 4% of calcium hydroxide was controlled by combined mechanism for both the initial and final stages of reduction.

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Ahmed Y.M.Z., Khedr M.H., Mohamed O.A., Shalabi M.E.H., Rola wodorotlenku wapnia w procesie produkcji grudek tlenku ¿elaza – zgorzeliny. *Fizykochemiczne Problemy Mineralurgii*, 31, 31–41 (w jêz. angielskim)

Zgorzelina hutnicza, wartościowy surowiec wtórny, powstaje podczas walcowania blach stalowych i może być aglomerowana przez grudkowanie. Fizykochemiczne właściwości grudek tlenku żelaza produkowanego ze zgorzeliny są lepsze, jeżeli zastosuje się wodorotlenek wapnia jako dodatek. Uzyskane wyniki badań mogą być podsumowane następująco: 1) wzrost ilości wodorotlenku wapnia zwiększa produktywność, odporność grudek na zniszczenie lub spękanie charakteryzowaną tzw. *drop number* oraz zwiększa ich wytrzymałość na ściskanie, 2) wytrzymałość na ściskanie i średnia *drop number* dla suchych granulek wzrasta wraz ze wzrostem ilości wapna i temperatury suszenia, 3) maksymalna wytrzymałość na ściskanie utwardzonych grudek otrzymano przy 4% dodatku wapnia i temperaturze utwardzania 1300 °C, 4) podatność na redukcję utwardzonych grudek była najwyższa przy 0,5% dodatku wapna i malała wraz ze wzrastająca jego ilością, 5) wytrzymałość na ściskanie redukowanych grudek wzrasta wraz ze wzrostem ilości wapna i temperatury wypalania dla grudek zawierających 4% wapna, 6) proces redukcji grudek zgorzeliny żelaznej zawierającej 4% wapna była kontrolowana przez połączone mechanizmy początkowych i końcowych etapów redukcji.