

Variation in physico-chemical properties of iron oxide pellets using bentonite with calcium hydroxide as binder

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Bentonite and calcium hydroxide are the widely used binding materials in iron ore pelletizing plants. This investigation deals with studying the effect of using a mixture of both binders on the green, dry, and indurated iron oxide pellet properties. The binder mixtures consist of 0.4% bentonite, and varying percentage of calcium hydroxide (ranges from 0.5 to 4%). The objective is studying the possibility of partially replacing the expensive bentonite with cheap lime hydrate in pelletizing iron oxide. The results show that, on using binder mixture composed of 0.4% bentonite and 0.5% calcium hydroxide, a deterioration of the physico-chemical properties of the mill scale pellets was observed. Whereas, by increasing the percentage of calcium hydroxide in the binder mixture beyond 0.5%, a substantial enhancement in these properties was achieved.

Keywords: processes

INTRODUCTION

Mill scale (iron oxide) which is mainly magnetite, is produced during the rolling of steel sheets in the steel making process. Mill scale is considered as a valuable secondary raw material in iron and steel production due to its high iron content and low impurities, where its quantity is increasing rapidly with the current demand of increasing world steel production. The pelletization of this secondary raw material is a prerequisite for the production of high-grade iron oxide pellets. These pellets should have reasonable physico-chemical properties to be suitable for iron and steel production.

Different types of binders were applied for enhancing these physico-chemical properties (the mechanical properties, the chemical composition, the total porosity, and the reducibility of iron oxide pellets). Among all binders used for such process, bentonite and calcium hydroxide, proved to be the most effective binding materials during the different pelletization stages of iron ores and oxides. However, the effects of each one, individually, on the physico-chemical properties of iron ore pellets were the subjects of many investigators.

Callender W. (1961) suggested that small additions of bentonite promote bonding by the formation of ceramic bonds and by greater compaction of the particles during the rolling of green balls. If the proportion of slag exceeds unspecified maximum (depending on the type of slag), a weaker bond results because of the replacement of mineral – to – mineral bond by a slag – to – mineral bond.

Wynnycky J. R. and Fahidy T. Z. (1974) found that the strength index of iron oxide pellet is directly proportion with the shrinkage that takes place during firing of these pellets, and that the addition of lime increases pellet shrinkage and hence increases pellet strength. They attributed this behavior to the interaction between lime, silica and iron oxide forming calcium silicate and calcium ferrites.

Thomas C. G. et al. (1974) concluded that with increasing both temperature and lime concentration more slag was for-

med, thus consolidating the structure and lowering the accessible porosity.

Hamilton J. D. G (1976) found that with the addition of CaO the improvement in cold compressive strength of pellet at 1000 – 1200 oC, was probably due to the sintering of fine hematite particles supported by very localized secondary mineral bonding near original lime particles sites. More substantial increase in strength at 1200 – 1400 oC was correlated with the formation of slag in the porous structures and consolidation of the pellet. The decreases in pellet strength reported for pellet fired at 1400 – 1500 oC was due to the excessive formation of thermally sensitive slag and sever shrinkage cracking.

Ebrahimzadeh et al. (1964) indicated that Ca(OH)₂ has a positive influence on the drop resistance and compressive strength of green and dry pellets. Also the influence of calcium hydroxide on the final strength of fired pellets is remarkable.

Shalabi et al. (1994) reported that the addition of CaO to the iron ore charge slightly decreases the productivity of green pellets, whereas average drop number and compressive strength of green pellets increases.

There is a little information about the effect and the behaviour of using a mixture composed of the two binder types (bentonite with calcium hydroxide) as binding materials in iron oxide pelletizing process.

This investigation is devoted to study the effect of using a blend consisting of 0.4% bentonite with varying percentage of calcium hydroxide on the mechanical properties of green, dry and indurated iron oxide pellets. The effects of addition of such mixture on the chemical composition, total porosity and reducibility as well as the kinetic of reduction of mill scale pellets will also be studied. Investigation of the different phases formed during induration of mill scale pellets containing different composition of binder mixture were evaluated with the help of XRD analysis.

MATERIALS AND EXPERIMENTS

Both mill scale and calcium hydroxide samples were supplied by the Egyptian Iron and Steel Company, whereas Sinai Manganese Company supplied the bentonite sample.

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Paper sent on 23 August 2004

Chemical composition, %	Component	
	Mill scale	Bentonite
Fe _{tot}	74.2	5.46
FeO	63.9	—
Fe ₂	4	—
SiO ₂	0.36	54.01
CaO	0.18	4.18
Al ₂ O ₃	0.14	17.11
MgO	MgO	2.03
Na ₂ O	—	1.27
K ₂ O	—	1.25
Cl	—	0.01
S	0.022	1.04
C	0.65	—

Table 1 – Chemical composition of raw materials.

Tab. 1 – Composizione chimica dei materiali di base.

The total chemical composition of these raw materials is given in table 1.

A Disc pelletizer of 40 cm diameter and 10 cm depth was used for pelletizing process. The green pellets were prepared under the following constant operation conditions:

feed particle size = - 0.074 mm,

tilt angle of disc bottom = 55°,

the residence time of material in the disc = 10 min.,

and disc rotating speed = 17 r.p.m.

All measurement of physico-chemical properties of pellets were performed on pellets having the sizes ranges from 10-12 mm diameters.

Pellets were dried and indurated in electric muffle furnace type “34 X 15 X 15 cm” of model Nobertherm program controller C19.

The reduction of the indurated pellets was carried out using a thermogravimetric balance at 1000 °C in H₂ atmosphere. The type of phases formed upon firing of pellets at different firing temperature and at different Ca(OH)₂ rates was detected using XRD analysis.

RESULTS AND DISCUSSION

Effect of calcium hydroxide addition on the properties of green pellets

The effect of adding a binder mixture composed of 0.4% bentonite with varying percentage of calcium hydroxide on the green mill scale pellets properties is shown in Fig. 1. Deterioration in the mechanical properties of green pellets was observed with increasing the percentage of calcium hydroxide in the added binder mixture. This deterioration was remarkable on using binder mixture composed of 0.4% bentonite with 0.5% calcium hydroxide. Whereas, with increasing the percentage of calcium hydroxide in the added binder mixture beyond 0.5% the mechanical properties of green mill scale pellets were increased remarkably.

The first decrease in pellet properties with 0.5% Ca(OH)₂ addition may be explained as follows: Bentonite has a layer structure of octahedral alumina in between tetrahedral SiO₄, and within those layers exchange ions such as sodium, potassium and calcium exist. When water was added to the clay it surrounded the exchange ions and the layer separation increased leading to great plasticity of the clay. This plasticity was increased by replacing the calcium ions by sodium ions, thus the wet and dry strength of pellets bound by bentonite increased by the increase of the sodium ion content of the bentonite (Ball D. F. (1970)). During the addition of binder mixture, in the presence of water as a necessary liquid binder, a replacement of Na⁺ ion of the bentonite by

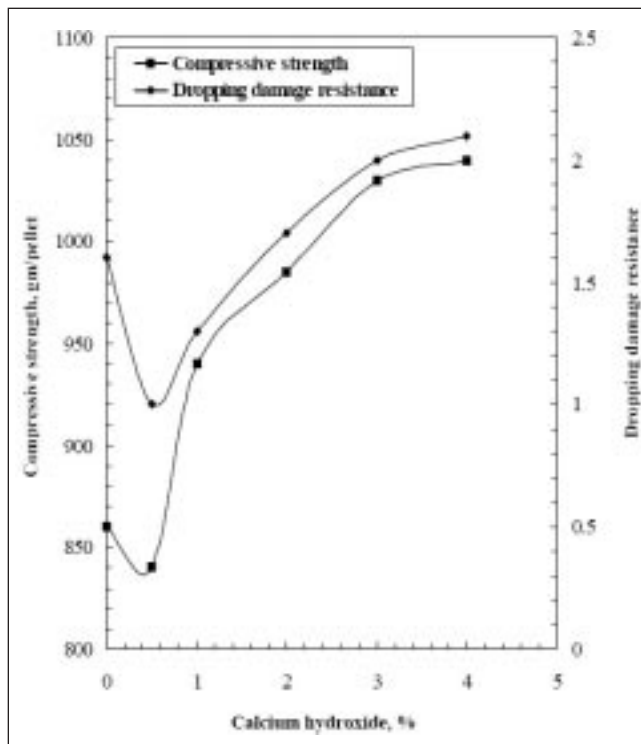


Fig. 1 – Effect of Calcium hydroxide addition on the mechanical properties of green pellets containing 0.4% bentonite.

Fig. 1 – Effetto dell'aggiunta di idrossido di calcio sulle proprietà meccaniche delle pellet a verde che contengono lo 0,4% di bentonite.

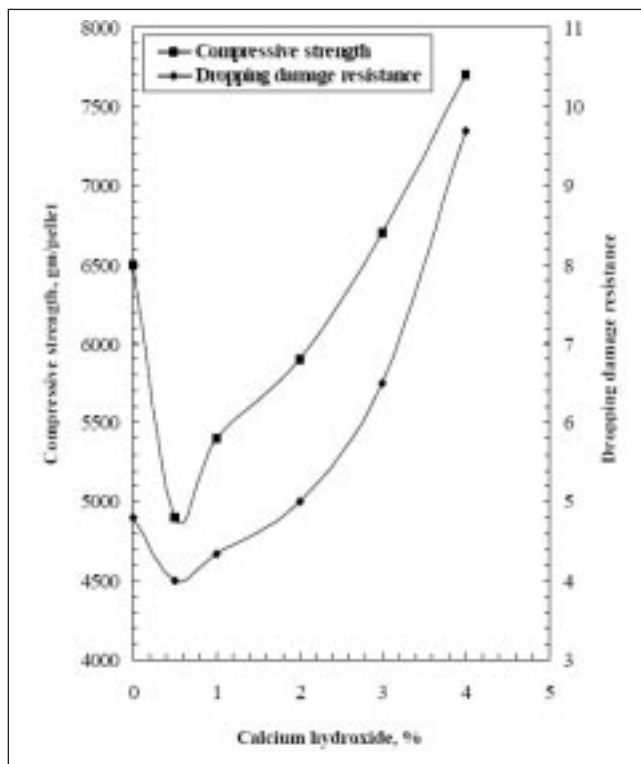


Fig. 2 – Effect of calcium hydroxide addition on the mechanical properties of dried pellets containing 0.4% bentonite.

Fig. 2 – Effetto dell'aggiunta di idrossido di calcio sulle proprietà meccaniche delle pellet essiccate contenenti lo 0,4% di bentonite.

Ca⁺ ion of Ca(OH)₂ takes place converting bentonite to more calcic in nature which is less effective as binder and leads to a decrease in the pellet properties. The increase in pellet properties with increasing calcium hy-

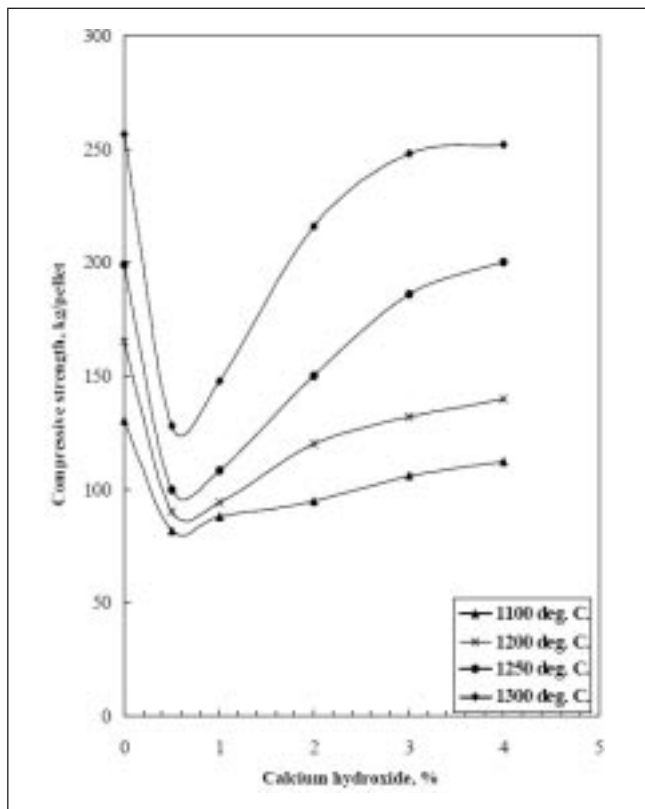


Fig. 3 – Effect of calcium hydroxide addition on the compressive strength of pellets fired at different firing temperatures and containing 0.4% bentonite.

Fig. 3 – Effetto dell'aggiunta di idrossido di calcio sulla resistenza alla compressione delle pellet sottoposte a diverse temperature e contenenti il 0,4% di bentonite.

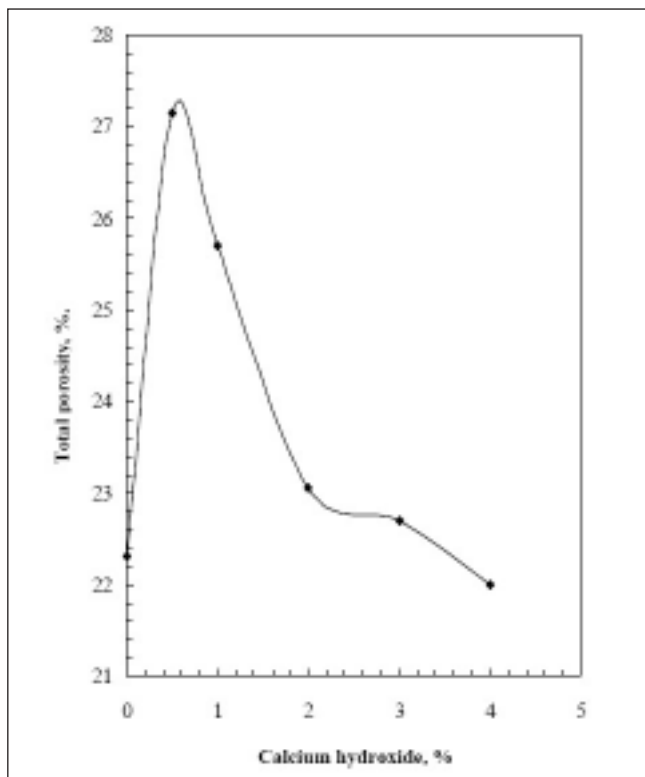


Fig. 4 – Effect of calcium hydroxide addition on the total porosity of pellets fired at 1300 °C and containing 0.4% bentonite.

Fig. 4 – Effetto dell'aggiunta di idrossido di calcio sulle porosità di pellet sottoposte alla temperatura di 1300 °C e contenenti lo 0,4% di bentonite.

dioxide addition beyond 0.5% addition may be due to the fact that calcium hydroxide increased the coagulation between particles and improved the specific area of the mix (Kurt Mayer (1980)), which subsequently resulted in an increase in the growth of formed pellets thus increasing the pellet strength (Ahmed Y. M. Z. (1996)).

Effect of calcium hydroxide addition on the properties of dried pellets

Figure 2 illustrates the relation between the dry pellet properties (pellets dried at 400 °C for 10 min.) and amount of calcium hydroxide added with 0.4% bentonite.

Increasing the percentage of calcium hydroxide in the added binder mixture (0.4% bentonite with 0.5% calcium hydroxide) leads to a decrease in the mechanical properties of dried mill scale pellets. Any further increases in the percentage of calcium hydroxide beyond 0.5% leads to increasing the mechanical properties of dried mill scale pellets.

This may be attributed to the same reason afore mentioned. The increase in both dropping damage resistance and compressive strength of dry pellet beyond 0.5% calcium hydroxide addition may be due the high surface area of calcium which imparts the character of the hydrogel to the hydroxide, the colloidal properties of which improves the plasticity of the ore mix and above all strengthens the bonding mechanism during drying (Kurt Mayer (1980)).

Influence of calcium hydroxide addition on the compressive strength, total porosity and chemical composition of indurated pellets

Figure 3 illustrates the relation between the compressive strength of fired pellets indurated at different temperatures and the amount of Ca(OH)₂ in the added binder mixture. A decrease in pellet strength was observed at 0.5% Ca(OH)₂ addition which may be attributed to the addition of Ca(OH)₂ in the presence of 0.4% bentonite, leading to an increase in the quantity of slag formed inside the pellets. This formed a weaker bond via replacement of mineral-to-mineral bond by mineral-to-slag bond (Wynnyckyj J. R. and Fahidy T. Z. (1974)). It may be also due to the increase in the total porosity of the fired pellets as shown in Fig. 4. The increase in pellet strength beyond 0.5% calcium hydroxide addition may be attributed to the fact that with increasing calcium hydroxide percentage in the added binder mixture the formation of the stronger calcium ferrite phase via the reaction between calcium oxide and iron oxide was facilitated (Thomas C. G. et al. (1974)) (as shown in Fig. 5). Also with increasing calcium hydroxide content beyond 0.5% the total porosity of the fired pellet decreased (as shown in Fig. 4.) and a more compact pellet structure was formed which was responsible for increasing pellet strength. Also from the same figure; it was noticed that at any constant amount of calcium hydroxide addition, the increase in firing temperature leads to increase in the pellet strength. This may be due to the sintering of the matrix fines with increasing temperature, whereas the formed slag consolidates and binds the iron oxide matrix (Thomas C. G. et al. (1974)). Also it may be due to the fact that the total porosity of fired pellets decreased with increasing the firing temperature as shown in Fig. 6.

Table 2, shows the effect of different calcium hydroxide addition with 0.4% bentonite on the chemical composition of pellet indurated at 1300 °C. From this table it is clear that, with increasing Ca(OH)₂ addition the amount of FeO increased which may be due to Fe₂O₃ which was formed by oxidation of Fe₃O₄ reacts with CaO and forms ferrites, in a solid – solid exothermic reaction. The heat produced from this reaction helps the dissociation of higher oxides to lower ones (Ferreira S. et al (1994)).

Table 3, shows the effect of different firing temperatures on the chemical composition of pellets containing 4% Ca(OH)₂

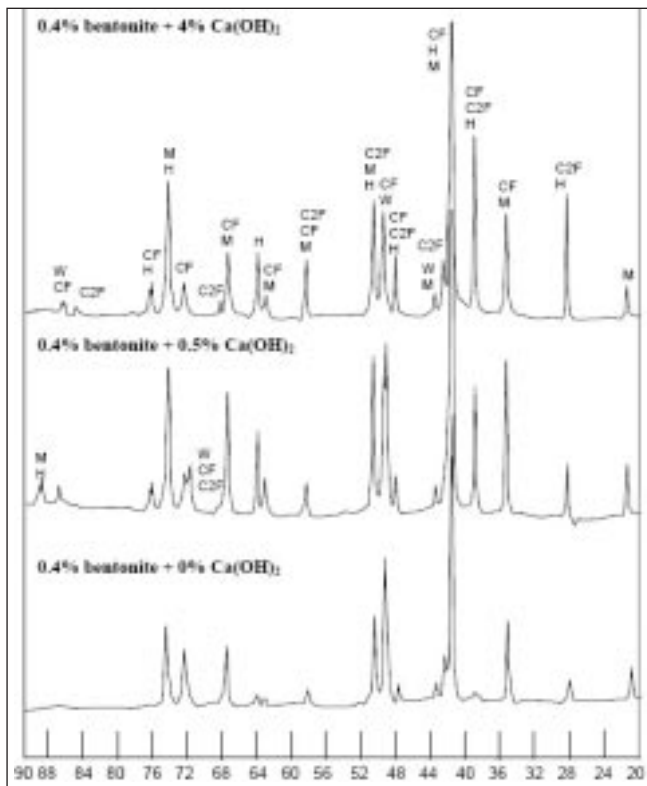


Fig. 5 – XRD of pellets containing different contents of calcium hydroxide with 0.4% bentonite and fired at 1300 °C.

Fig. 5 – XRD di pellet contenenti diverse percentuali di idrossido di calcio e lo 0,4% di bentonite sottoposte alla temperatura di 1300 °C.

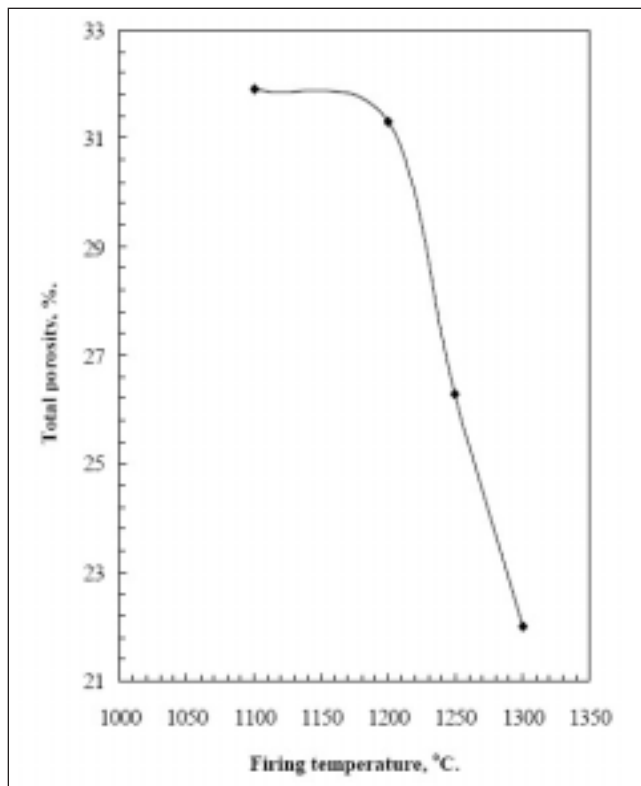


Fig. 6 – Effect of firing temperature on the total porosity of pellets containing 0.4% bentonite and 4% calcium hydroxide.

Fig. 6 – Effetto della temperatura sulla porosità di pellet contenenti lo 0,4% di bentonite e il 4% di idrossido di calcio.

and 0.4% bentonite. From this table it is clear that with increasing firing temperature the amount of FeO increased which may be due to the tendency of higher oxides to dissociate to the lower ones with increasing the firing temperature (Ferreira S. et al (1994)).

Effect of calcium hydroxide addition on the reducibility of indurated pellets

Figure 7, shows the relation between the amount of calcium hydroxide content in the added binder mixture and the degree of reduction of pellets indurated at 1300 °C. It was found that the reducibility increased in case of pellets formed with the addition of binder mixture composed of 0.4%

bentonite and 0.5% calcium hydroxide. Whereas, beyond 0.5% calcium hydroxide contents a remarkable decrease in the pellet reducibility was observed. The increase in the pellet reducibility at 0.5% Ca(OH)₂ addition may be due to the formation of a binding phase which consists of dicalcium ferrite (2CaO·Fe₂O₃), (as shown in Fig. 5). This phase which is highly reducible, can constitute a relatively high volumetric fraction of the fired pellets even at low CaO content (Rager Selin (1988)). Also the increase in the reducibility at 0.5% Ca(OH)₂ addition may be attributed to the increase in the total porosity as shown in Fig. 4. The decrease in reducibility beyond 0.5% Ca(OH)₂ addition may be attributed to the increase in the divalent oxides which are more difficult

Calcium hydroxide, %	Chemical composition, %								
	Fe _{total}	FeO	Fe _{metal}	SiO ₂	Al ₂ O ₃	MgO	CaO	S	C
0	70.6	16.12	0.8	0.6	0.131	0.12	0.22	0.01	0.08
0.5	70.3	10.0	0.8	0.55	0.14	0.13	0.29	0.01	0.07
1	70.5	19.5	1.0	0.52	0.14	0.13	0.55	0.01	0.07
2	71.1	30.0	1.0	0.54	0.13	0.13	1.29	0.012	0.07
3	72.1	38.1	1.0	0.53	0.14	0.12	1.85	0.012	0.07
4	72.7	55.0	1.0	0.54	0.14	0.13	2.25	0.013	0.07

Table 2 – Effect of the content of Ca(OH)₂ in the added binder mixture on the chemical composition of fired pellets.

Tab. 2 – Effetto del contenuto di Ca(OH)₂ nella miscela di binder aggiunta sulla composizione chimica pellet.

Firing temperature, °C	Chemical composition, %								
	Fe _{total}	FeO	Fe _{metal}	SiO ₂	Al ₂ O ₃	MgO	CaO	S	C
1100	70.3	30.2	0.9	0.55	0.15	0.14	3.17	0.018	0.07
1200	71.5	40.6	1.0	0.53	0.13	0.13	2.7	0.016	0.07
1250	71.9	50.8	1.0	0.52	0.14	0.12	2.5	0.015	0.07
1300	72.7	55.0	1.0	0.54	0.14	0.13	2.25	0.013	0.07

Table 3 – Effect of firing temperature on the chemical composition of pellets Containing 4% Ca(OH)₂ and 0.4% bentonite.

Tab. 3 – Effetto della temperatura sulla composizione chimica delle pellet che contengono il 4% di Ca(OH)₂ e lo 0,4% di bentonite.

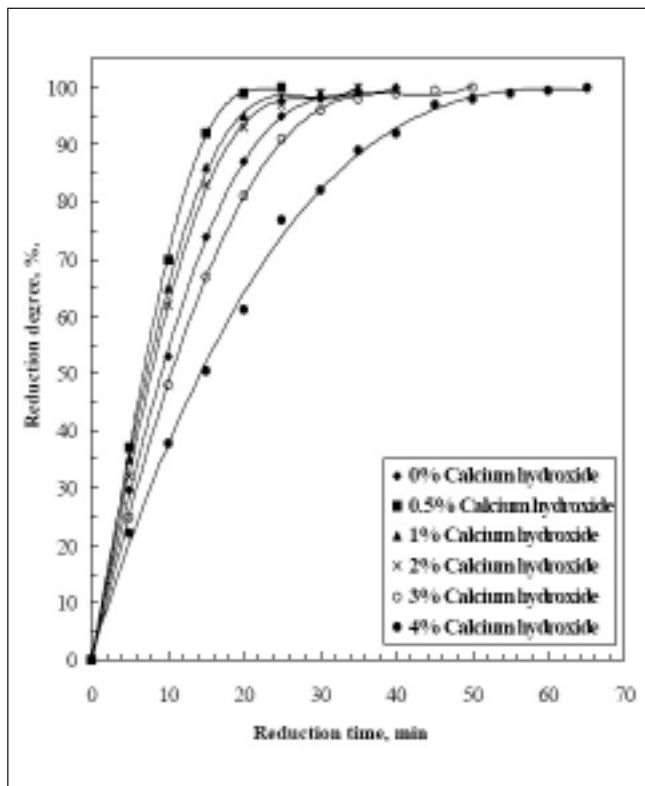


Fig. 7 – Effect of calcium hydroxide addition on the reducibility of pellets fired at 1300 °C and containing 0.4% bentonite.

Fig. 7 – Effetto dell'aggiunta di idrossido di calcio sulla riducibilità di pellet sottoposte alla temperatura di 1300 °C e contenenti lo 0,4% di bentonite.

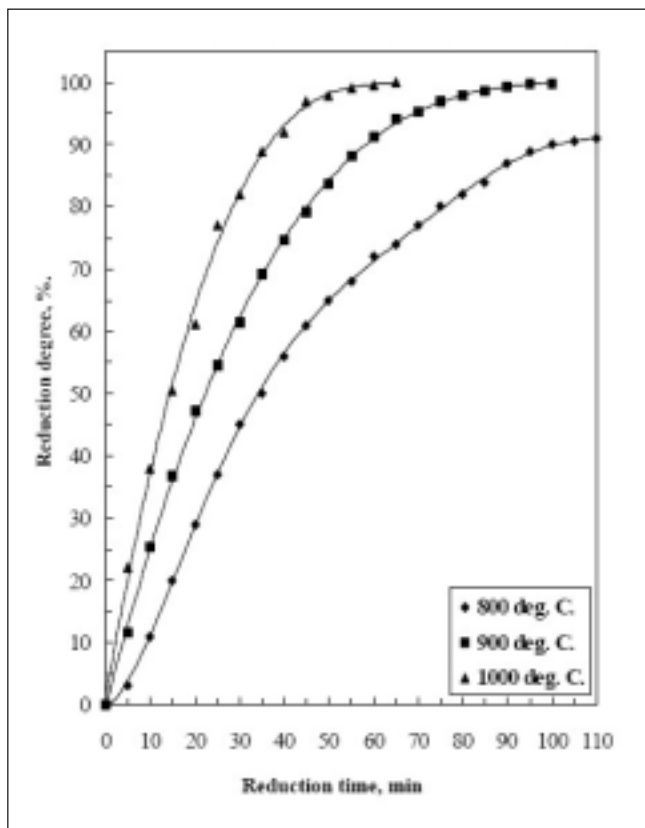


Fig. 8 – Effect of reduction temperature on the reduction degree of pellets containing 0.4% bentonite with 4% calcium hydroxide.

Fig. 8 – Effetto della riduzione della temperatura sulla riducibilità di pellet contenenti lo 0,4% di bentonite e il 4% di idrossido di calcio.

to reduce (Efimenko Yu. G. et al (1986) and Yasushi Ishikawa et al. (1981)). Also it may be due to the increase in the total porosity as shown in Fig. 4.

Kinetic of reduction of pellets containing 0.4% bentonite and 4% calcium hydroxide and fired at 1300 °C

The pellets containing 0.4% bentonite with 4% calcium hydroxide shows the highest physico-chemical properties among all other pellets containing various amounts of binder mixture. It is very well known that time is the main factor in studying reaction kinetics and driving reaction kinetic equation. Therefore, a series of experiments were conducted to study how far reduction degree changes by temperature. Based on the data obtained, a kinetic model was proposed.

A series of experiments were carried out to study the relationship between the degree of reduction and reduction time at different temperatures. The experiments were conducted at time intervals from 5 min to 65 min for temperatures range from 800 to 1000 °C on pellet size 10-12 mm. Figure 8, shows the effect of different reduction times on the degree of reduction at different temperatures, from which it can be concluded that the reduction efficiency increases with elapse of time in a parabolic fashion and at rate depending on the working temperature. Thus, the rate of reduction diminishes with increasing time.

There are different models had been proposed for the reduction involving topochemical reaction (gas-solid reaction). These models had been proposed for the different rate controlling mechanism that could took place in the reaction involving gas-solid reaction (e.g. the gaseous diffusion mechanism, chemical reaction controlling mechanism, combined mechanism, solid state diffusion mechanism). To determine the rate-controlling mechanism for the reduction process of such pellets, different models had been applied. In the mean time the model, which gives a straight line up on plotting the relation between the time of reduction and the value of the parameter in the left side of the equation of the proposed model, will indicate the controlling mechanism.

In this process the equation of the chemical controlling mechanism proposed by Masanori Tokuda, et al. (1973), is

$$kt = 1 - (1 - x)^{0.3333}$$

Application of the above equation to results in time-dependent study by plotting $1 - (1 - x)^{0.3333}$ vs. reduction time, show that this model is applicable since data gives a straight line passing with origin (as swon in Fig. 9). The slope of the straight line represents the reaction rate constant (k). Activation energy for this reaction was calculated by application of Arrhenius's equation

$$k = k_0 e^{-E/RT}$$

$$\ln k = \ln k_0 - (E / RT)$$

Plot $\ln k$ (obtained from the slope of the straight lines obtained from Fig. 9) against $1/T$ gives a straight line as shown Fig. 10. The calculated activation energy was found to be 13.9 kcal/mole. This value of activation energy falls in the region of interfacial chemical reaction controlling mechanism. Consequently, the reduction of mille scale pellets containing 0.4% bentonite and 4% calcium hydroxide and fired at 1300 °C could be modeled according to interfacial chemical reaction controlling mechanism.

CONCLUSION

The results obtained from this study showed that, in some cases it is not recommended to add more than one binder at the same time during iron oxide pelletization process. This is because instead of enhancement of pellets properties

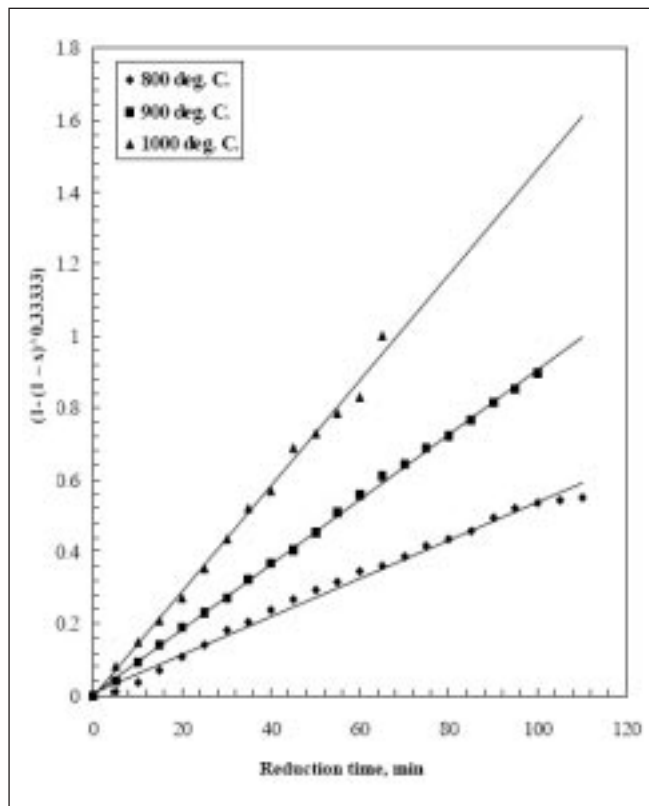


Fig. 9 – Relation between the time of reduction and $(1 - (1-R)^{0.3333})$.

Fig. 9 – Rapporto fra il periodo di riduzione e $(1 - (1-R)^{0.3333})$.

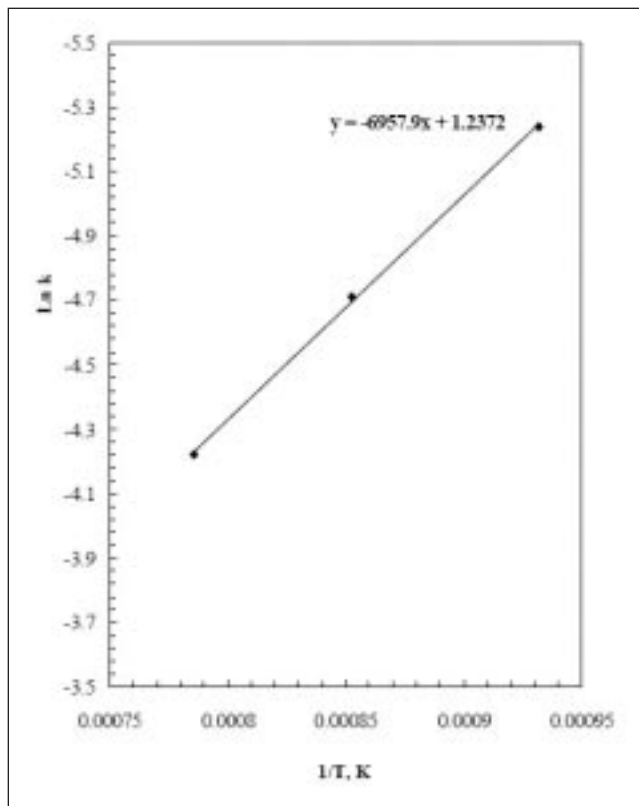


Fig. 10 – Arrhenius plot for the reduction of pellets containing 0.4 bentonite with 4% calcium hydroxide.

Fig. 10 – Diagramma di Arrhenius per la riduzione di pellet contenenti lo 0,4% di bentonite e il 4% di idrossido di calcio.

a deterioration of it might happen. This case study proves the last statement. The addition of calcium hydroxide results in a decrease the efficiency of bentonite as a binder by replacing of the more efficient sodium ion with calcium ion, converting it to the more calcic and less efficient one, leading to deterioration of the pellet properties. After a certain amount of calcium hydroxide added, some enhancement in pellet properties was achieved which could be attributed to the effect of calcium hydroxide as binder during the pelletization process. The kinetics of reduction of the pellets containing 0.4% bentonite and 4% calcium hydroxide, of the highest physico-chemical properties, revealed that the reduction of these pellets is controlled by interfacial chemical reaction.

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**VARIAZIONI NELLE PROPRIETÀ FISICO-CHIMICHE
DI UN PELLET DI OSSIDO DI FERRO
MEDIANTE UTILIZZO DI BENTONITE
CON IDROSSIDO DI CALCIO COME BINDER**

Parole chiave:
processi

Idrossido di calcio e bentonite sono materiali largamente impiegati come binder negli impianti di pelletizzazione di minerali di ferro. Questa ricerca mira a studiare l'effetto dell'utilizzo di una miscela di questi due materiali sulle proprietà

di pellet di ossido di ferro a verde, essiccate e indurite. Le miscele di binder contengono il 0,4% di bentonite e varie percentuali di idrossido di calcio (dal 0,5 al 4%). L'obiettivo è lo studio della possibilità di sostituire parzialmente la costosa bentonite con il meno costoso idrossido di calce.

I risultati ottenuti indicano che, se si utilizza come binder una miscela composta di bentoniti al 0,4% e di idrossidi di calcio al 0,5%, vi è un deterioramento delle proprietà fisico-chimiche delle pellet mill scale. Mentre aumentando la percentuale di idrossido di calcio nella miscela del binder in percentuale superiore al 0,5%, si è riscontrato un notevole miglioramento di queste proprietà.