EFFECT OF Fe_2O_3 ON THE DENSIFICATION AND PROPERTIES OF LIME

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Sintering of lime by one- and two- step calcination has been investigated. Samples obtained by double stage calcination always exhibit higher bulk density than those of single stage process. Fe_2O_3 helps in the sintering of CaO by liquid phase formation at the sintering temperature. The grain size of sintered lime is higher in the presence of Fe_2O_3 additive. Fe_2O_3 containing samples have improved hydration resistance due to their larger grain size compared to Fe_2O_3 free samples. Lime samples containing 4 wt.% Fe_2O_3 and sintered at 1600°C have CaO as the major phase with a small amount of dicalcium ferrite phase (C_2F). The maximum flexural strength at 1300°C is achieved by the samples containing 2wt.% Fe_2O_3 and sintered at 1600°C.

INTRODUCTION

Lime (CaO) due to its exceptional thermodynamic stability [1] and high melting point has long been considered as a promising refractory for steelmaking. It is more stable than MgO in contact with carbon under the operating conditions of the basic oxygen furnace. It has relatively low vapour pressure at elevated temperature [2], which is the prime requirement of a refractory for secondary steelmaking processes that uses vacuum technology. In spite of all these fundamental advantages, CaO has a serious disadvantage, which restricts its use as a refractory. It is susceptible to hydration and degradation by some ferruginous metallurgical slags [3-4]. Therefore, the most important consideration for the development of lime refractories is to increase their hydration resistance. CaO which is obtained from natural limestone often contain various impurities, including SiO_2, Al_2O_3 and Fe_2O_3 [5]. These impurities can degrade its refractoriness, slag resistance and hot strength [4, 6-8]. The slag resistance as well as hydration resistance of lime can be improved by liquid phase or solid state sintering with the aid of small amounts of additives [7, 9-10]. The addition of Fe_2O_3, Al_2O_3 and CuO has enhanced sintering of lime through liquid phase sintering and lanthanides like La_2O_3 and CeO_2 through solid state sintering of lime [11-12].

This investigation aims to study the effect of Fe_2O_3 on the sintering behaviour and some properties of the sintered lime aggregates. An attempt is also made to correlate the sintering mechanism with microstructure and hydration resistance of the sintered products.

EXPERIMENTAL

The limestone used in this investigation was obtained from the Madhyapradesh region of India. Chemical analysis of the raw limestone was done by standard wet chemical methods. In single stage calcination process, powdered limestone was used directly. In double stage process, carbonate derived hydroxide (FH) was produced by calcining raw limestone at 1000°C for 2 hrs, naturally cooling in the furnace and subsequently reacting with cold distilled water. It was then kept overnight to complete the hydration and finally dried at 110 ± 5°C for 24 hrs to obtain the carbonate derived hydroxide (FH). Both the powdered limestone and FH were passed through a 60 mesh BS sieve, mixed with 1, 2 and 4 wt.% Fe_2O_3 as additive and 6 wt.% water as binder and subsequently uniaxially pressed at 100 MPa. Green briquettes thus produced were dried at 110 ± 5°C for 24 hrs and sintered in the temperature range 1500 to

1650°C with 2 hrs soaking at peak temperature. Sintering was done in an electric furnace and the heating rate was maintained at 5°C/min upto 1100°C, followed by 3°C/min up to the final sintering temperature.

Sintered lime was characterized in terms of bulk density (BD), apparent porosity (AP), high temperature flexural strength, hydration resistance and microstructure. BD and AP of the sintered lime were determined by a liquid displacement method using Archimedes' principle in a xylene medium. Flexural strength was measured at 1300°C by three point bending method using samples having dimension of 0.5 × 0.5 × 5 cm.

Hydration resistance of sintered lime was measured on the size fraction of -5+10 BS mesh. Sinters accurately weighed near to 50 grams in a Petri dish were subjected to hydration in a humidity chamber for 3 hrs. The atmosphere of the chamber was maintained at 50°C and 95 % relative humidity. The percentage weight gain after hydration was used as the measure of hydration resistance.

Microstructural characterization of the sintered samples was done by optical microscopy using reflected light. The samples were polished and thermally etched at a temperature 50°C less than the sintering temperature followed by rapid cooling to room temperature. The grain size of the sintered lime was measured from optical photomicrographs using the linear intercept method. Phase identification sintered product was done by X-ray diffraction (XRD) study. X-ray diffraction patterns were obtained in powder diffractometer using nickel filtered Cu-Kα radiation. Diffraction pattern were recorded for the Bragg's angle (2Θ) range 20-60°.

RESULTS AND DISCUSSION

Raw materials

Chemical analysis of the limestone used as starting material in this study is shown in table 1. The CaO content of the limestone is 54.56 wt.% compared to the theoretical value of 56 wt.%. The major impurities present in the limestone are SiO_2, Al_2O_3, Fe_2O_3 and alkali. The total amount of impurity is ≤ 2 wt.%. XRD pattern indicates that the only crystalline phase present in the limestone is calcite [12].

Densification

Sintering is an important step of any ceramic forming process. Earlier investigation shows that in the absence of any additive sintered samples obtained by the double stage process exhibit higher bulk density than samples obtained by the single stage process [12]. Additives play an important role on the densification and microstructural development of the sintered product. The variation of bulk density of the sintered lime (1600°C) obtained by single stage and double stage processes with Fe_2O_3 content is shown in figure 1. It is seen that samples obtained by double calcination process always exhibit higher densification irrespective of the Fe_2O_3 content. In the single stage process bulk density increases with the Fe_2O_3 content up to 4 wt.%. Where as with the double stage process the highest density is achieved with 2 wt.% Fe_2O_3 (3.19 g/cm^3), compared to the theoretical density of 3.32 g/cm^3. Although the apparent porosity of this sample is only 0.1%, the comparative lower sintered density (3.19 g/cm^3) is due to the presence of intragranular pores, which is seen in the microstructure and will be discussed in the latter part of this paper. Since the sintered samples obtained by double stage process always have higher B.D, this process is selected for further study using the additives.

Variation of bulk density of the sintered lime samples with Fe_2O_3 content and sintering temperature is shown in figure 2. From figure 2 it is seen that Fe_2O_3 plays an important role on the densification of the lime compacts. At 1500°C, 1 wt.% Fe_2O_3 addition increases the B.D of the sintered lime from 2.94 g/cm^3 to 3.13 g/cm^3. Sintered density gradually increases with temperature for the batches containing 0-1 wt.% Fe_2O_3. Samples containing higher amounts of Fe_2O_3 (2-4 wt.%) reach their maximum density at 1600°C followed by a slight decrease in B.D value (3.16 g/cm^3) for 4 wt.% Fe_2O_3 containing samples at 1650°C. Fe_2O_3 reacts with CaO and forms dicalcium ferrite (C_2F), which melts at 1436°C and there by favours the liquid phase sintering of CaO. Other investigators have also found that Fe_2O_3 helps the sintering process by liquid phase formation [7,13]. It is to be noted that the highest density (3.20 g/cm^3) is achieved at 1600°C with 4 wt% Fe_2O_3, which is much below the theoretical density of CaO (3.32 g/cm^3) due to the presence of intragranular closed pores.

Table 1. Chemical analysis of raw limestone.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
(wt.%)	1.48	0.20	0.11	54.56	Trace	0.11	0.33	42.88

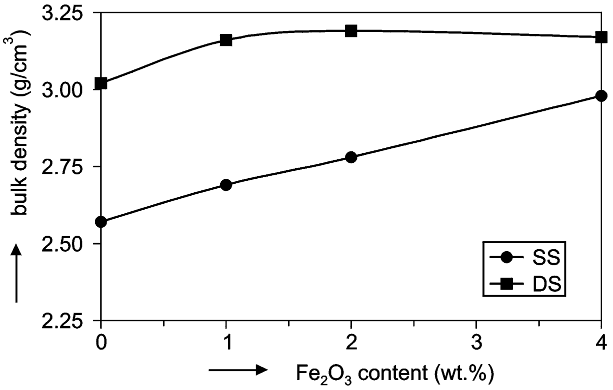


Figure 1. Effect of Fe$_2$O$_3$ content on the bulk density of lime sintered at 1600°C; SS: single stage process and DS: double stage process.

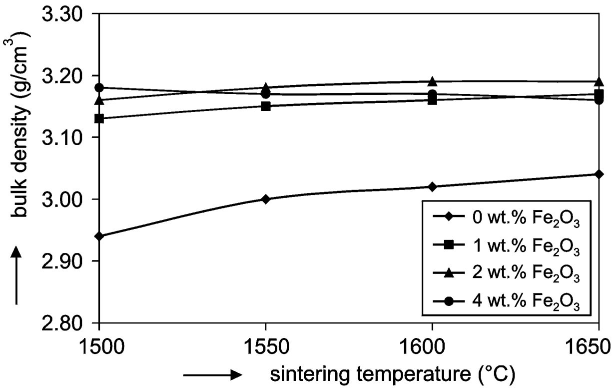


Figure 2. Variation of bulk density of the sintered lime with Fe$_2$O$_3$ content and sintering temperature.

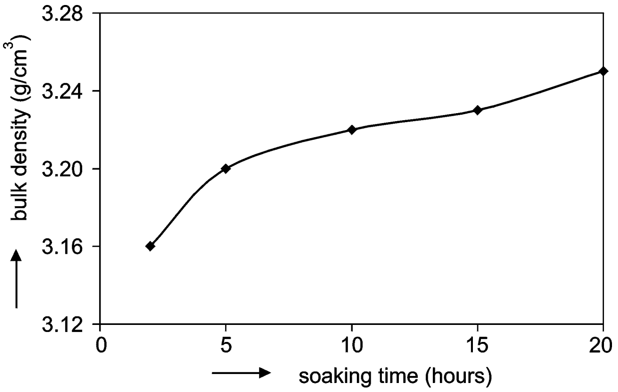
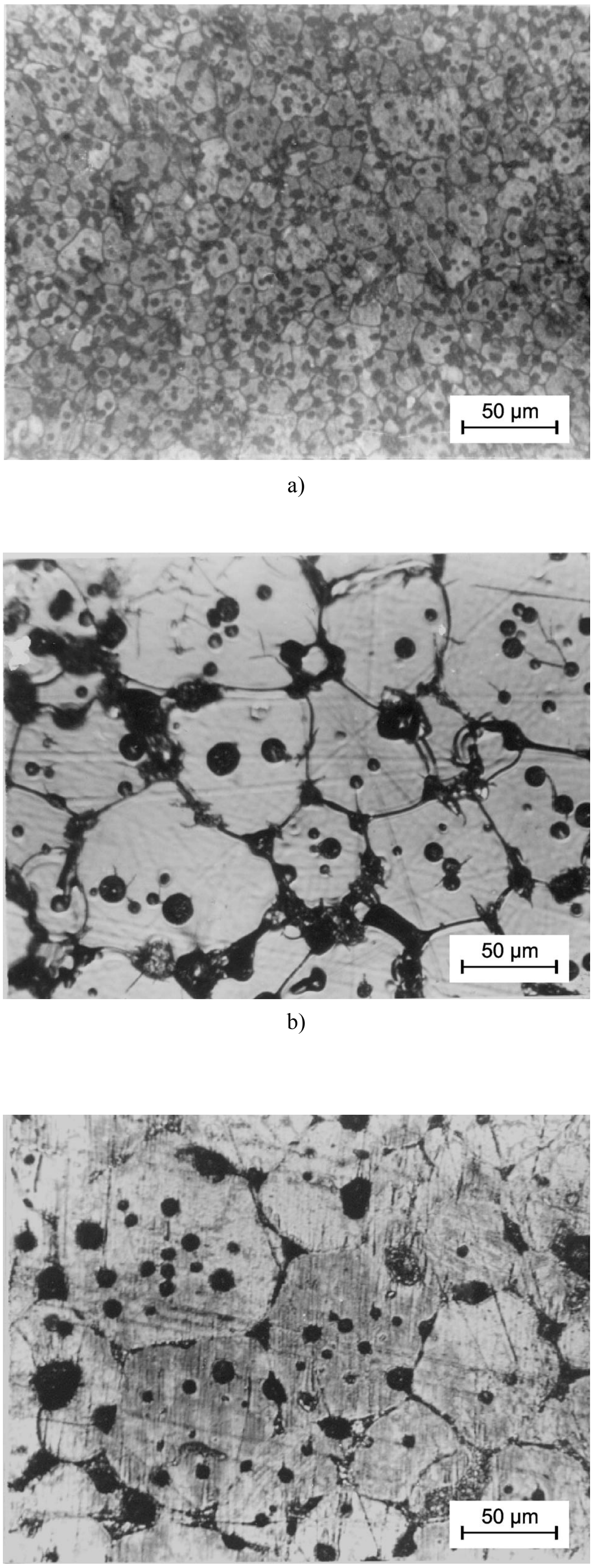


Figure 3. Effect of soaking time on the bulk density of the lime samples sintered at 1500°C.



a)

b)

c)

Figure 4. Optical photomicrographs of the lime sintered at 1600°C: a) without additive; b) with 2 wt.% Fe$_2$O$_3$; c) with 4 wt.% Fe$_2$O$_3$.

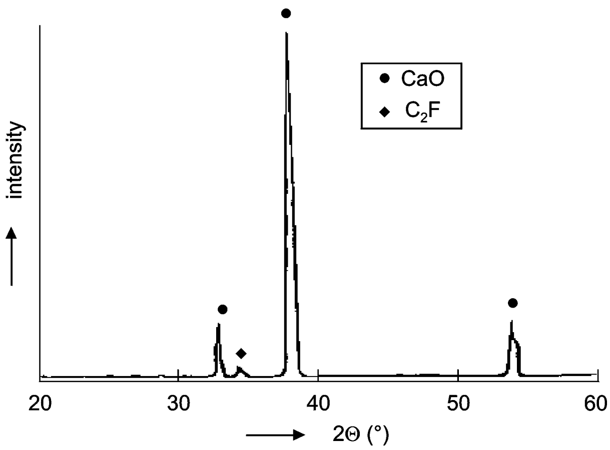


Figure 5. X-ray diffraction pattern of lime containing 4 wt.% Fe_2O_3 sintered at 1600°C showing CaO as the major phase and C_2F as minor phase.

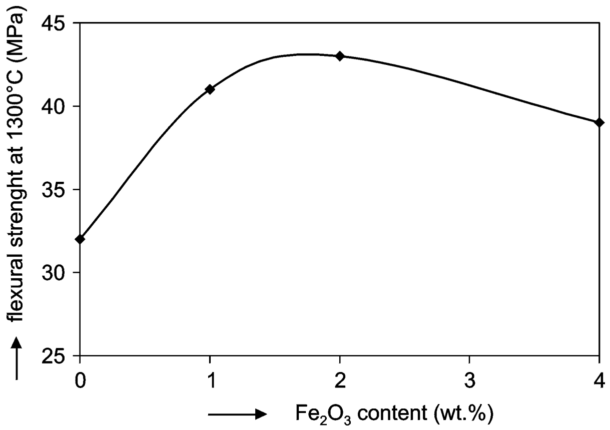


Figure 6. Variation of flexural strength at 1300°C of the lime sintered at 1600°C with Fe_2O_3 content.

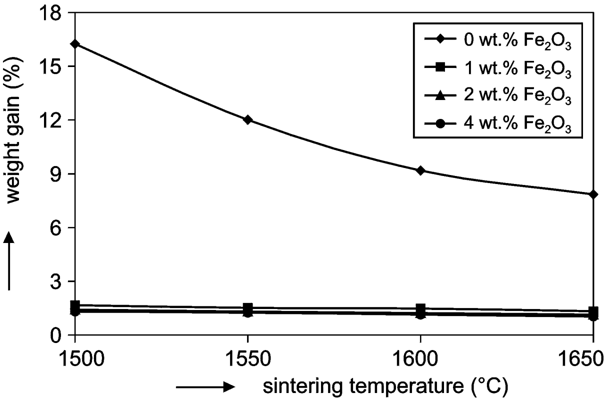


Figure 7. Hydration resistance of sintered lime with Fe_2O_3 content and sintering temperature.

Samples containing 2 wt.% Fe_2O_3 were selected to study the effect of soaking time on the bulk density of the sintered samples. Figure 3 depicts the variation of bulk density of the samples sintered at 1500°C with soaking time at peak temperature. The sintered B.D. of sample with 2 hr soaking is 3.16 g/cm^3. Density increases to 3.20 g/cm^3 at 5 hr. soaking which is equivalent to the density of samples fired at 1600°C with 2 hr. soaking. With 20 hr soaking at 1500°C the maximum density achieved is 3.25 g/cm^3. The gradual removal of intragranular pores is the main reason for this gradual steady increase in bulk density of the sintered lime samples. Microstructural observation also confirmed the same.

Microstructure

The optical photomicrographs of lime samples sintered at 1600°C are shown in figure 4a-c. CaO grains are spherical in shape. It is seen that addition of Fe_2O_3 increases the grain size of CaO. The average grain size of samples sintered at 1600°C without any additive is 17 μm. 2 wt.% Fe_2O_3 addition increases the grain size to 78 μm. Addition of Fe_2O_3 forms a liquid phase at the firing temperature and thus favours the grain growth of lime by solution-precipitation process and also by changing the dihedral angles between the grains. All the samples have closed pores, although the apparent porosity is almost zero (0.1-0.5 %). The pores are mainly present in the intragranular position. Fe_2O_3 addition reduces the intragranular porosity. Photomicrographs reveal that intragranular pores are less in 4 wt.% Fe_2O_3 containing samples (figure 4c) than that present in 2 wt.% Fe_2O_3 containing sintered lime (figure 4b). The presence of intragranular porosity is solely responsible for the lower bulk density of the sintered samples. X-ray diffraction pattern of the sintered sample containing 4 wt.% Fe_2O_3 is shown in figure 5. It indicates the presence of calcium oxide as the principal crystalline phase with small amount of dicalcium ferrite (C_2F) as the minor phase. Though the C_2F phase liquefies at 1436°C the first liquid phase is formed much below this temperature as can be seen from the pseudobinary phase diagram CaO-Fe_2O_3 (FeO). The liquid phase facilitates the sintering and grain growth of lime.

Flexural Strength at 1300°C

Since all the samples achieved their highest density on sintering at 1600°C, these samples were selected for flexural strength measurement. Figure 6 depicts the variation of flexural strength of the sintered lime samples with Fe_2O_3 content. It is evident that flexural strength increases with the increase in Fe_2O_3 content upto 2 wt.%. The highest flexural strength achieved by 2 wt.% Fe_2O_3 containing sample is 43 MPa. Higher amount of Fe_2O_3 beyond 2 wt.% deteriorates the flexural strength to 39 MPa. The initial increase in strength is due to increase in bulk density with the Fe_2O_3 content (upto 2 wt.%) and later deterioration of flexural strength with higher Fe_2O_3 content is due to excessive formation of liquid phase.

Hydration resistance

The weight gain due to hydration of sintered lime with and without Fe_2O_3 is shown in figure 7. Higher the weight gain lower is the resistance towards hydration. From figure 7, it can be seen that hydration resistance of sintered lime without any additive is increases with the sintered temperature from 1500°C to 1650°C. Weight gain of lime sintered at 1500°C is 16.25 %, whereas that of the same sample sintered at 1650°C is 7.84 %. Only 1 wt.% Fe_2O_3 addition significantly increases the hydration resistance of sintered lime irrespective of sintering temperature. Effect of Fe_2O_3 on hydration is less prominent beyond 1 wt.% Fe_2O_3. The higher hydration resistance of Fe_2O_3 containing samples is due to the higher grain size of CaO as discussed earlier. Higher the grain size lower is the grain boundary surface area and hence lower is the diffusion of water and higher hydration resistance.

CONCLUSIONS

Densification of lime is favoured by double stage calcination than single stage calcination process. Fe_2O_3 helps in the densification process by liquid phase formation at the sintering temperature. A maximum density of 3.20 g/cm^3 is achieved at 1600°C in presence of 4 wt.% Fe_2O_3. Only 1 wt.% Fe_2O_3 addition significantly enhances the hydration resistance of sintered lime irrespective of the sintering temperature. Grain growth of CaO is favoured by addition of Fe_2O_3 as well as higher sintering temperature, which ultimately increases the hydration resistance of the sintered lime. Small amount of C_2F phase is present in the 4 wt% Fe_2O_3 containing samples sintered at 1600°C. CaO grains are mostly rounded in nature. Fe_2O_3 content of 2 wt.% is optimum for improvement in high temperature flexural strength due to increased sintered density of lime and limited liquid phase formation.

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References

1. Brezny B.: J.Am.Ceram.Soc. *59*, 529 (1976).
2. Samsonov G.V.: *The oxide handbook*; 2nd ed., pp.178-206, Plenum Press, New York 1973.
3. Carr K., Evans J. L., Leonard L. A., Richardson H. M.: Trans.Br.Ceram.Soc. *64*, 473 (1965).
4. Carr K., Evans J. L., Leonard L. A., Richardson H. M.: Trans.Br.Ceram.Soc. *64*, 493 (1965).
5. Boynton R. S.: *Chemistry and Technology of Lime and Limestone*, pp.18-21, John Wiley and Sons, New York 1980.
6. Nadachowski F.: Interceram *24*, 42 (1975).
7. Shi Ying-Yi., Messing G. L., Bradt R. C.: J.Am.Ceram.Soc. *67*, C-109 (1984).
8. Williams P., Sunderlan M., Briggs G.: *Iron making and steel making 9*, 150 (1982).
9. Hubble D. H.: J.Am.Ceram.Soc.Bull. *48*, 618 (1969).
10. Nadachowski F.: Ceramurgia Int. *2*, 55 (1976).
11. Ghoneim N. H., Mandour M. A., Serry M. A.: Ceram.Int. *15*, 357 (1989)
12. Ghosh A., Bhattacharya T. K., Mukherjee B., Das S. K.: Ceram.Int. *27*, 201 (2001).
13. Wong L. L., Bradt R. C.: J.Am.Ceram.Soc. *78*, 1611 (1995).

VLIV Fe_2O_3 NA ZHUTŇOVÁNÍ A VLASTNOSTI VÁPNA

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Bylo studováno sintrování vápna jedno- a dvoustupňovou kalcinací. Vzorky získané dvoustupňovou kalcinací měly vždy vyšší objemovou hustotu než vzorky z jednostupňové kalcinace. Fe_2O_3 napomáhal sintrování tvorbou kapalné fáze. Vzorky obsahující Fe_2O_3 měly zlepšenou odolnost proti hydrataci díky větší velikosti jejich částic než vzorky bez Fe_2O_3. Vzorky vápna s obsahem 4 hmot.% Fe_2O_3 a sintrované při 1600°C se skládaly z CaO jako hlavní fáze s příměsí vápenatého feritu. Největší pevnosti v ohybu bylo dosaženo ve vzorcích s 2 hmot.% Fe_2O_3 a sintrovaných při 1600°C.