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Densification of reactive lime from limestone

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Abstract

Sintering of lime from natural limestone was carried out by a single stage (from natural carbonate) and double stage (from limestone converted hydroxide) process in the temperature range 1500 to 1650°C. In double stage process hydroxides were activated by three different techniques through pre-calcination and hydration. Different techniques employed are air-quenching the powder after precalcination, furnace cooling and water quenching of powder. The air quenching process showed better densification. Incorporation of hydroxide into carbonate powder up to an extent of 25 wt.% showed maximum densification. Hydration resistance was related to densification and grain size of sintered lime. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; B. Microstructure; Hydration resistance; Reactivity of lime

1. Introduction

Lime has been considered to be an attractive refractory on a broad scale of applications in the metal and ceramic industries because of its good properties such as high fusion point (~2570°C) and worldwide abundance of limestone [1,2]. CaO also has a relatively low vapour pressure at elevated temperature [3], a factor that is of primary consideration for all secondary steel making processes those use vacuum technology. CaO has exceptional thermodynamic stability [4], being more stable than magnesia in presence of carbon at high temperature [1,5]. However inspite of its superior properties the manufacture and usage of lime refractories is restricted owing to its susceptibility towards hydration when exposed to atmospheric moisture. CaO refractories that are obtained from natural limestone ($CaCO_3$) often contain various impurities, including SiO_2, Al_2O_3 and Fe_2O_3 [1]. SiO_2, Al_2O_3 and MgO have little effect on hydration resistance while Fe_2O_3 is considerably effective [6]. The reactivity of CaO obtained by dehydration of $Ca(OH)_2$ at 550°C is much greater than that formed by the decomposition of $CaCO_3$ at 1000°C. This increased activity was linked with the considerable contraction that $Ca(OH)_2$ undergoes between 600 and 1000°C. It is, thus, deemed reasonable to consider that the CaO produced at low temperatures from its precursors should be better suited to sintering [7].

2. Experimental procedure

2.1. Preparation and characterisation of precursors

The starting material used was relatively pure limestone. It was originated from Madhya pradesh. The carbonate powder of 300 mesh sieve was obtained by grinding and sieving the limestone. Hydroxide precursors were made by precalcination and hydration by different ways. In the first case limestone after calcination at 1000°C and soaking for 2 h, was taken out from the furnace and poured into water when hot. This hydroxide was designated as ‘water quenched’ (WQ). In the second case after calcination the sample was allowed to cool inside the furnace and then react with cold water. This sample was designated as ‘furnace cooled’ (FH) . In the third case the sample after calcination was subjected to quench directly in air followed by hydration. This sample was designated as ‘air quenched ’(AQ). The reactivity of the precursors were characterised by specific surface area of the oxides derived from carbonate and hydroxides. The reactivities was also ascertained through the measurment of differential thermal analysis and also the hydration of derived oxides in 100% relative humidity for a period of 24 h.

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2.2. Sintering

The densification study was conducted on 35 mm diameter × 12 mm high briquettes which were formed in a uniaxial press under a pressure of 1000 kg/cm^2. Water containing 6 wt.% was used as binder. Briquettes after drying at 110°C for 24 h were subjected to firing at 1500, 1550, 1600 and 1650°C with 2 h soaking at each peak temperature in a programmer controlled super kanthal furnace. Heating rates were maintained at 5°C/min up to 1100°C followed by 3°C/min from 1100°C to selected temperature.

2.3. Properties of sintered lime

The sintered lime was characterised by bulk density, hydration resistance and microstructural analysis. Bulk density were measured by immersion method in xylene under vacuum using Archimedes' principle. The hydration resistance was measured by subjecting 50 g of −5 +10 BS mesh sinters to 50°C and 95% relative humiditity in a steam humidity cabinet for 3 h. After the experiment the percentage weight gain was calculated. The microstructure of the polished surface was observed by reflected-light microscopy. A linear intercept method was used for the determination of grain size of sintered lime from optical photomicrographs.

3. Results and discussion

The natural limestone selected for the study (Table 1) is relatively pure with an impurity content around 2 wt.%.

Table 1
Chemical analysis of raw limestone

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
1.48	0.20	0.11	54.56	Trace	0.11	0.33	42.88

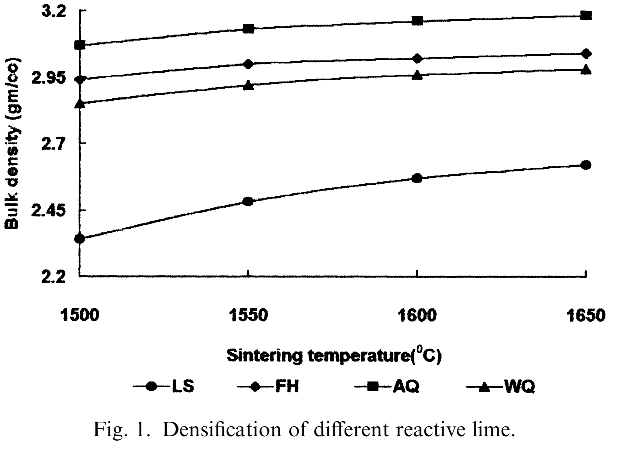


Fig. 1. Densification of different reactive lime.

3.1. Densification

The densification study of lime by single stage and double stage process has been carried out from 1500 to 1650°C. The relation between bulk density and sintering temperature is shown in Fig. 1. It is revealed that for both the process the bulk density increases with the increase in sintering temperature. The densification at 1650°C is 78% for carbonates (single stage- LS) and it is between 89 and 95% for hydroxides (double stage- AQ, FH and WQ). The hydroxide decomposes earlier than carbonate and the hydroxides (AQ, FH and WQ) derived oxides have higher surface area (Table 2) than carbonate (LS) derived oxide. These early borned oxides from hydroxide (HDO) undergo plastic flow [9] and shows significant sinterability at relatively low temperature. The sintering rate of HDO at 870°C is equivalent to that

Table 2
Characterisation of oxides derived from carbonate and hydroxides

	Oxide derived from			
Properties	LS	FH	AQ	WQ
Specific surface area (m^2/g)	7	24	28	19
DTA (endo peak, °C)	914	517	512	520
Hydration of CaO after decomposition (wt.% gain)	6.52	20.40	29.0	13.0

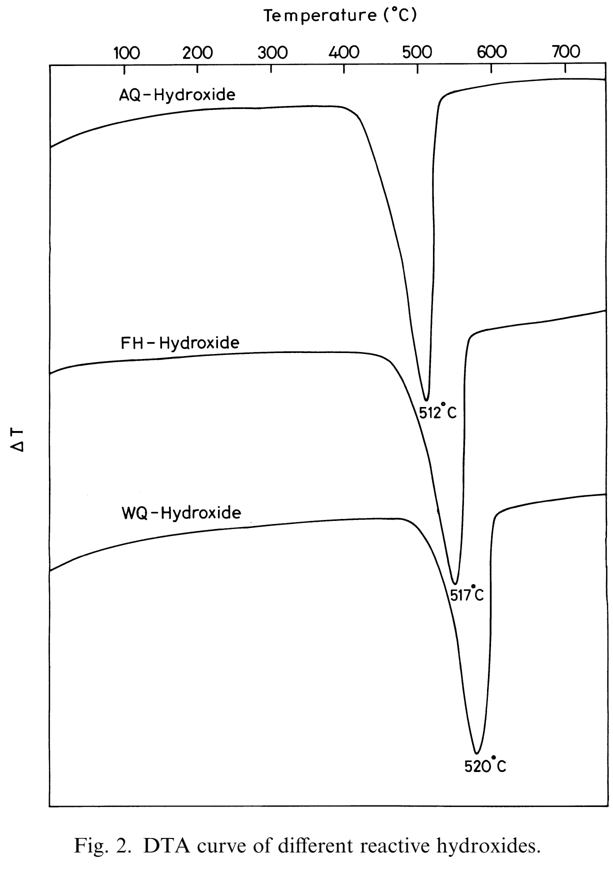


Fig. 2. DTA curve of different reactive hydroxides.

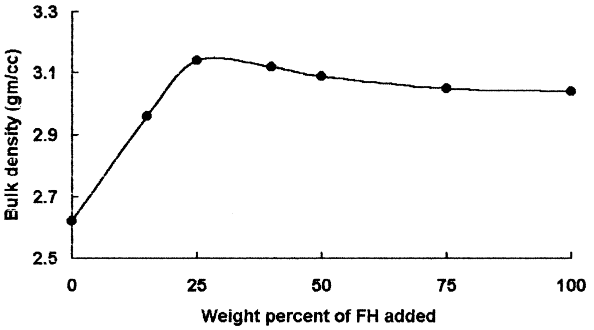


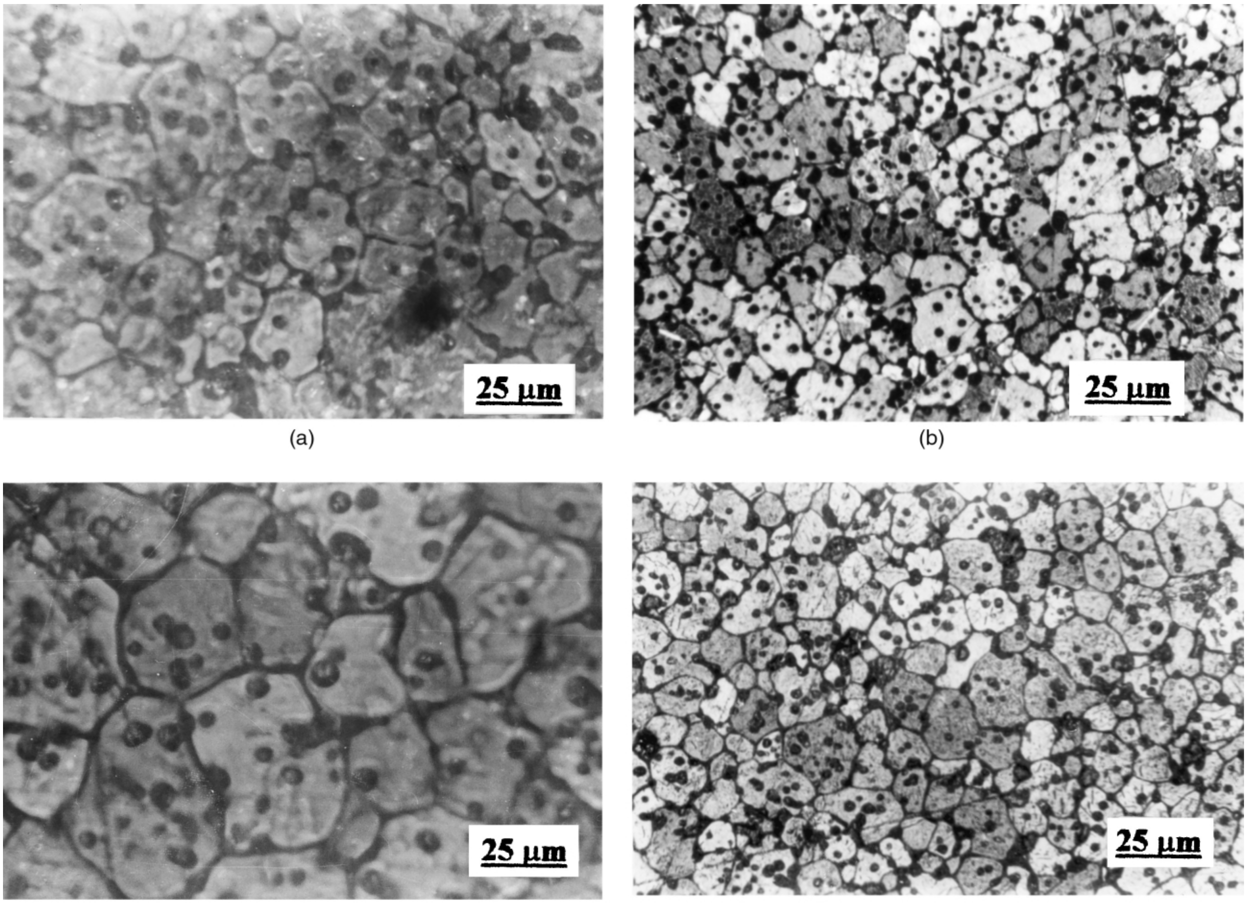
Fig. 3. Densification of lime from carbonate–hydroxide mixture.

of carbonate derived oxide at 1400°C [8]. Moreover, the water vapour evolves from hydroxides enhances the sintering by lowering the equilibrium value of dihedral angle between the oxide grains and pores [10].

In the double stage process the air-quenched samples (AQ) showed a densification of 95% (3.18 g/cc) which is highest amongst the reactive hydroxides. In this case when the high temperature oxides are air-quenched, the sample experiences thermal shock, which generates CaO grains of small particle size with creation of defects in the CaO crystals. The defects in the CaO lattice will facilitate the transport of matter by accelerating the diffusion rate of the grains [8]. The decomposed calcium oxide when cooled inside the furnace (FH) was relatively coarser and showed lower surface area than AQ. The densification of FH (90.7%) is, therefore, lower than AQ. The water quenched sample showed the lowest densification (89%) amongst the double stage lime sinter. The new borned CaO when water quenched from high temperature will spontaniously convert to hydroxide. Therefore the oxide lattice will not suffer sufficient thermal shock as it will happen in case of AQ sample. This hydroxide derived oxide produced low surface area (19 m^2/g) and resulted in low densification due to a relatively low rate of matter transport.

The reactivities of hydroxides AQ, FH and WQ were ascertained from the decomposition peaks in DTA experiment (Fig. 2) and percent weight gain in hydration test (Table 2)

The effect of hydroxide additions (FH) in carbonates on the densification of lime is shown in Fig. 3. The bulk density is increased with the incorporation of calcium hydroxide (FH). The densification reaches up to 93.7% (B.D = 3.14 gm/cc) at 25 wt.% hydroxide addition then gradually decreases. The substitution of ultrafine



(a) (b)

(c) (d)

Fig. 4(a–d). Microstructure of sintered lime.

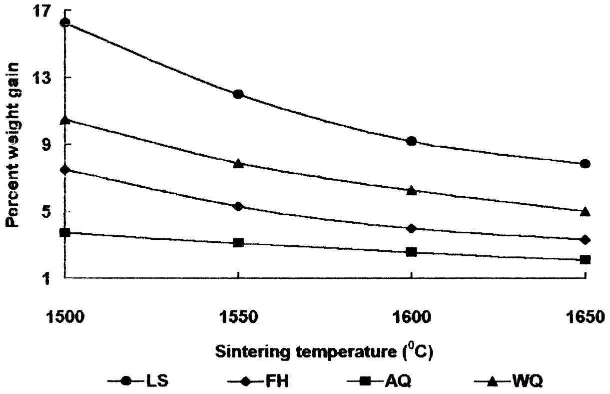


Fig. 5. Hydration resistance of sintered lime.

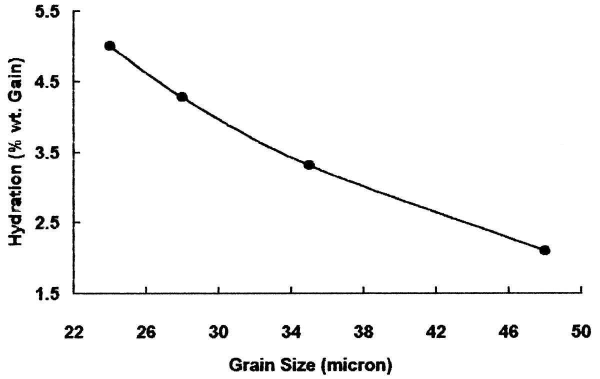


Fig. 6. Variation of hydration resistance with grain size of sintered lime.

$Ca(OH)_2$ into relatively coarser limestone powder increases the reactivity for sintering, particle-particle packing and interactions between particles which appear to be responsible for higher densification [11].

3.2. Microstructure

The microstructure of sintered lime fired at 1650°C is shown from Fig. 4a–d In most of the sinters the pores were present in intergranular and intragranular positions and very often in grain boundary triple point. The average grain size of AQ sinter is 48 μm (Fig. 4c) which is highest amongst the sinters formed by double stage process. In this sinter the pores were present mostly in intragranular position. The grain size of FH and WQ sinters are 35 and 24 μm respectively. The pores are randamly distributed throughout the microstructure of WQ sintered lime and the pore size and concentration is greater in grain boundary triple point than inside the grain. Both type of pores are uniformly distributed throughout the microstructure of FH sintered lime.

When hydroxide (FH) is added to limestone fines, grain growth occured (Fig. 4d) but the pore size decreased and it is mainly present in individual grains. The grain size (28 μm) is comparable with double stage sinter. It has been suggested elsewhere that when grain growth occurs in ceramics, pores often become isolated from the grain boundaries [12].

3.3. Hydration resistance

The relation between percent weight gain of sintered lime and sintering temperature is illustrated in Fig. 5. It is shown that for all the samples the weight gain is decreased with the increase of sintering temperature. The AQ samples showed maximum hydration resistance because of its bigger grain size. Fig. 6 depicts the effect of grain size on percentage weight gain. When the grain size is increased the percentage weight gain is decreased, so the sinter would be more resistant towards hydration with increasing grain size. The rate and degree of hydration of CaO sinter depends on the rate of chemisorption of water on the grain boundary surface [13]. The more the grain size the lesser will be the grain boundary surface area, hence, the diffusion of water will be minimised.

4. Conclusions

(I) Hydroxide derived sintered lime showed better densification than carbonate derived sintered lime.

(II) Air quenching of newly borned CaO develops maximum densification of 95% at 1650°C, by generating fine particles with lattice defects.

(III) Incorporation of 25 wt.% hydroxide to carbonate fines improves the particle packing and sintering reactivity, resulting to a densification of 93.7%.

(IV) Hydration resistance of sintered lime increases with higher densification and bigger grain gize.

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