



Sintering and Properties of Calcia as a Refractory Material

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Abstract: The investigation is focused on the sintering of calcia in single stage and double stage process from natural source limestone and evaluation of its properties like bulk density, apparent porosity, hydration resistance and microstructure in relation with sintering temperature. The result showed that bulk density increases and apparent porosity decreases with sintering temperature in both single and double stage process. In single stage process, maximum densification was 79.4 percent whereas it maximised to 90.74 percent in double stage process at 1650°C. Hydration resistance of sintered calcia increases with densification as well as increase of grain size. With increasing apparent porosity hydration gain increases due to enhancement of water movement through the interconnected space followed by adsorption and chemical reaction. Double stage sintering process develops dense microstructure as compared single stage sintering process.

Keyword: Calcia; Limestone; Sintering; Hydration

1. Introduction

Calcia is considered as an attractive basic oxide refractory material in new generation due to its excellent properties like high melting point ($\sim 2570^{\circ}\text{C}$), high hot properties, excellent slag resistance and its worldwide abundance of its raw material limestone [1-4]. The thermodynamic stability of calcia, being more stable than magnesia even in contact of carbon and relatively low vapour pressure at elevated temperature, makes it suitable for steel making process using vacuum technology [5-7]. The harmful property of this material is its susceptibility to hydration, which could not be stopped even in presence of atmospheric moisture. This detrimental property can precisely be controlled by sintering of calcia to a large extent to form highly dense with large grain size [8-10]. The thermodynamically stable cubic crystal structure of CaO does not permit any polymorphic transformation and not to be dead burnt. Various attempts were made to develop highly dense with anti hydration properties of calcia by using different sintering aids, e.g. CuO, Fe₂O₃, Al₂O₃, La₂O₃, CeO₂ and other additive compounds [11]. The additives like La₂O₃, CeO₂ and Y₂O₃ have enhanced solid state sintering but CuO, Fe₂O₃, Al₂O₃ through liquid state sintering of lime. Limestone contains various impurities like SiO₂, Al₂O₃ and Fe₂O₃, play an important role in sintering by the formation of liquid coating on the CaO grains, improved hydration resistance [12]. Calcia derived from hydroxide precursor is more dense and hydration resistant than derived from carbonate [13-14].

The aim of this investigation is to study the sintering of calcia in both single and double stage process and evaluate the properties like densification and hydration resistance in relation with apparent porosity and microstructure of sinter. The performance in relation with material properties and to find out the best sintering process to develop high dense calcia sinter with improved hydration resistance.

2. Experimental

2.1 Materials

The purer variety limestone sample from Madhyapradesh region of India was selected as a basic carbonate source in this study. The lump size was crushed into $\frac{3}{4}$ to 1 inch size, properly washed and dried. The dried limestone sample was ground with a fineness of -300 BS mesh size. The hydroxide powder was prepared by calcinations of limestone first at about 900°C followed by slaking of oxide by large excess water to form calcium hydroxide. The single stage sintering was carried out from carbonate source and double stage sintering was from carbonate derived hydroxide source. Sintered calcia were abbreviated as “SSP” and “DSP” respectively for distinguishing the single and double stage process.

2.2 Materials fabrication and Sintering

Batches for “SSP” and “DSP” were prepared from limestone and limestone derived hydroxide powder respectively. The green briquette of 3.8 mm height and 12.9 mm diameter was prepared by applying uniaxial pressing with a pressure of 100 MPa with 2 minutes dwell time. The 6 weight percent water was used as a binding agent. The green briquette was dried at 110°C for 24 hours and then subjected to sintering at 1500°C to 1650°C with 2 hours soaking at peak temperature in a program controlled electrically heated muffle furnace.

2.3 Material Characterization

The densification behaviour of sintered calcia was characterized in terms of bulk density and apparent porosity by liquid displacement method in xylene under vacuum using Archimedes principle according to ASTM C-373-88. The percent densification was measured on the basis of specific gravity of pure CaO (3.35). The hydration resistance was measured by subjecting 50 gm. of -5 + 10 BS mesh sinters to 50°C and 95 percent relative humidity in a steam humidity cabinet for 3 hours as per ASTM C110-15. The microstructure of the polished surface was observed by reflected light microscopy after thermal etching at about 800°C for 45 minutes. The average grain size of the sintered lime was measured by linear intercept method as per ASTM-E112-13.

3. Results and Discussions

Limestone as a carbonate sources is collected from Madhyapradesh region of India. It is relatively pure with a very low amount of impurities around 2 weight percent. The physico-chemical properties of raw limestone is shown in Table-1 and it is already reported in my previous publication [15].

Sintering of characteristics of calcia in terms of bulk density and apparent porosity is shown in fig.1. It is seen that bulk density of calcia derived from double stage sintering process is quite high than single stage sintering process. The relative bulk density of all sintered materials increases and apparent porosity decreases with increasing sintering temperature. Bulk density in single stage sintering process at 1550°C is 2.48 gm/cc with a 24.4 % apparent porosity. With increasing sintering temperature from 1550°C to 1650°C in single stage sintering process, densification improved to 2.62 gm/cc. Double stage sintering process yield maximum density of 3.04 gm/cc with 2% apparent porosity at 1650°C.

Table-1: Physico-chemical properties of raw limestone

Chemical Analysis of raw limestone (wt.%)							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI
1.48	0.20	0.11	54.56	Trace	0.11	0.33	42.88
Physical Properties of Limestone							
DTA (endo peak, °C)				: 914			
Specific gravity				: 1.58			
Specific surface area (m ² /gm) of carbonate derived CaO				: 7			
Specific surface area(m ² /gm) of hydroxide derived CaO				: 24			

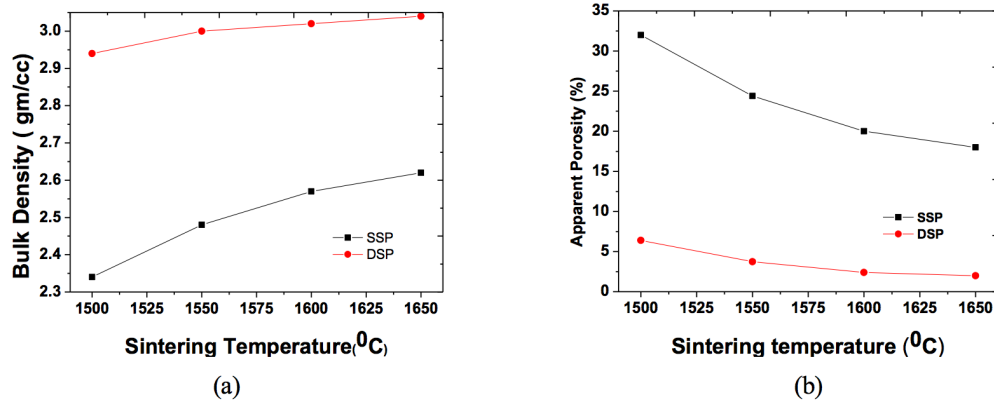


Fig. 1: (a) Bulk Density of sintered Calcia at different sintering temperature, (b) Apparent porosity (%) of sintered Calcia at different sintering temperature

Oxide formation from $\text{Ca}(\text{OH})_2$ or CaCO_3 form excess vacancies into lime lattice which appreciably increases the rate of material transport and greatly reduce activation energy of densification. These vacancies disappear at an appreciable rate above 1100°C [16]. Dehydration of hydroxide occur at 550°C, relatively lower temperature than decarbonation of carbonate. The early born oxide from hydroxide has an enormous surface area and free energy than those of carbonate derived oxide. These early born oxides undergo plastic flow and show significant sinterability at relatively low temperature. It is found that at 870°C the rate of sintering of hydroxide derived oxide should be equal to that of carbonate derived oxide at 1400°C [16,17]. Moreover, the water vapour evolves from hydroxide enhances the sintering by lowering the equilibrium value of dihedral angle between oxide grains and pores [16-18]. The inter particle space is also moistened by it and a capillary suction is generated which brings the particle together for neck growth at an early stage [19].

The most unwanted unique hydration property of calcia refractory is called hydration, the chemical combination calcia with water to form calcium hydroxide. The structural openness of CaO lattice facilitate to hydrate even at atmospheric moisture. The affinity towards hydration can be minimised by increasing bulk density, grain size of sintered as well as formation of protective layer on the surface of calcia grain. This is achieved by sintering at higher temperature. The percent hydration gain decreases with increasing sintering temperature both in single and double stage process and shown in Fig. 2(a). Calcia derived from single stage

sintering process from carbonate precursor shows lower hydration resistance than derived from hydroxide. Hydration gain of sintered calcia from carbonate precursor at 1650°C is 7.84 percent and that for hydroxide derived calcia, the hydration gain reduced to 3.20 percent. The higher hydration resistance in double stage sintering process is due to develop of dense sinter with higher grain size of calcia from hydroxide precursor[11,15]. The relative material performance of sintered calcia is also shown in fig. 2b.

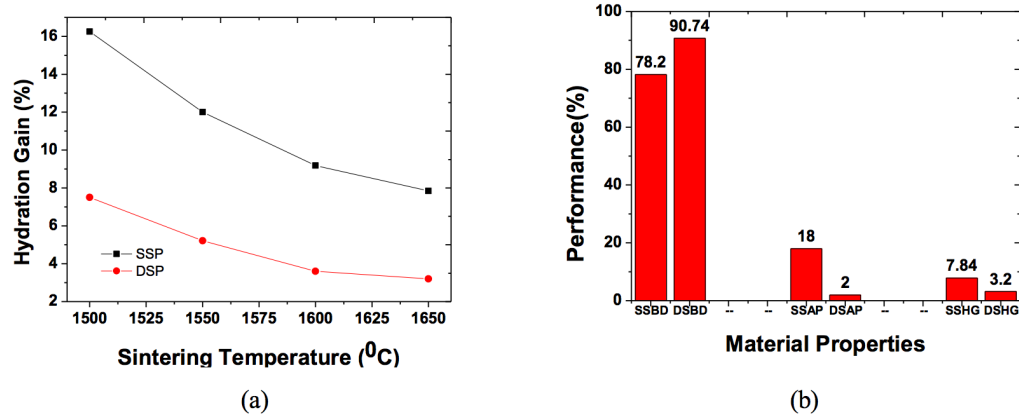


Fig. 2: (a) Hydration Gain (%) of sintered Calcia at different sintering temperature, (b) Comparative performance of Single stage & Double stage sintering process (SSBD = Highest Bulk density of Calcia in single stage process, DSBD = Highest Bulk density of Calcia in double stage process, SSAP = Lowest Apparent Porosity of Calcia in single stage process, DSAP = Lowest Apparent Porosity of Calcia in double stage process, SSHY = Highest hydration resistance of Calcia in single stage process, DSHY = Highest hydration resistance of Calcia in double stage process).

Apparent porosity part play an important role on hydration process as its presence favours the movement of water through the interconnected space followed by adsorption chemical reaction. The hydration gain in both single and double stage process increases with increasing apparent porosity and shown in Fig. 3. With increasing apparent porosity, the exposed surface area of sintered calcia increases, enhanced the formation of calcium hydroxide [15,16,18].

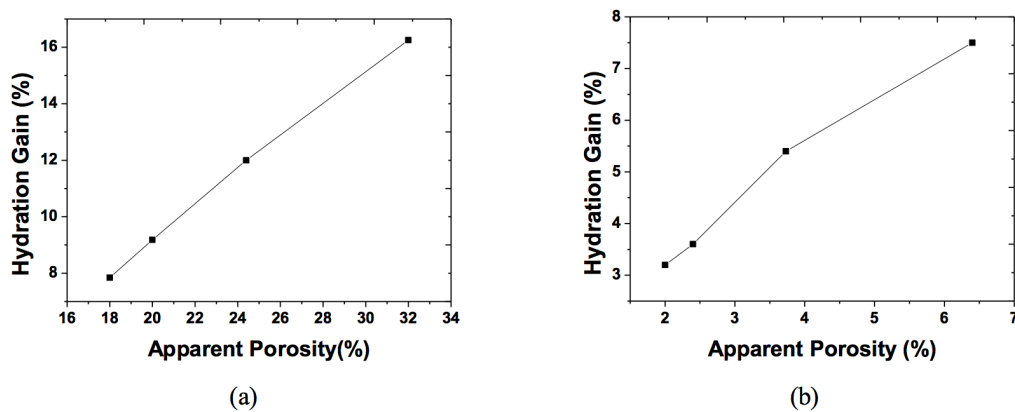


Fig. 3: (a) Hydration Gain (%) of sintered Calcia with apparent porosity (%) in single stage sintering process, (b) Hydration Gain (%) of sintered Calcia with apparent porosity (%) in double stage sintering process.

The micro structural evaluation of calcia is very much significance with densification and hydration resistance of sintered product. The optical micrograph of calcia sinter in both single and double stage sintering process are shown in Fig. 4. Carbonate derived calcia in single stage sintering process does not show significant grain growth whereas hydroxide derived calcia in double stage sintering process develop grains of irregular shape with a significant extent. The inter and intra granular pores are present in all microstructure. The microstructure of calcia in single stage sintering process is too much porous due to insignificant densification. The average grain size of sintered calcia in single stage sintering process is 10 μm whereas in double stage sintering process is 32 μm .

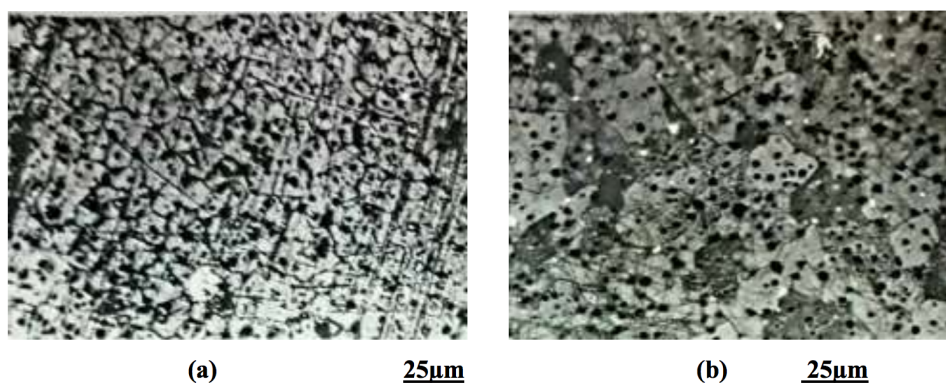


Fig. 4: Microstructure of sintered Calcia at 1600°C for (a) in single stage sintering process and (b) in double stage sintering process

4. Conclusion

The calcia sintered derived from double stage sintering process showed better performance towards densification and hydration resistance. The maximum densification in double stage process was 90.74 percent with 3.2 percent hydration gain. Hydration gain increases with apparent porosity of sintered calcia both in single and double stage process. Double stage sintering process develops dense microstructure with an average grain size of 32 μm . The intra and inter granular pores are present in both calcia microstructure derived from single and double stage sintering process.

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