



# **Calcination Characteristics of Limestone in relation with the reactivity of Quick Lime**

Tapas Kumar Bhattacharya<sup>1</sup> and Kaushik Maity<sup>2</sup>

<sup>1</sup>*Department of Ceramic Technology,  
Government College of Engineering & Ceramic Technology, Kolkata - 700010, WB, India  
E-mail: tkb\_ceramics@yahoo.co.in*

<sup>2</sup>*Department of Ceramic Technology,  
Government College of Engineering & Ceramic Technology, Kolkata - 700010, WB, India  
E-mail: kaushikjordan24@gmail.com*

**Abstract:** The present work is focused on the calcination characteristics of limestone at the temperature range of 750°C to 900°C with one hour soaking followed by the derived quick lime is fully hydrated to slaked lime. The carbonate derived and hydroxide derived nascent lime differ reactivity in a significant extent. The carbonate derived lime in single stage process is less susceptible to hydration than hydroxide derived lime in double stage process. Limestone when calcined at 950°C, the derived lime shows 1.2 percent weight gain but hydroxide when calcined at 570°C, the derived lime shows hydration affinity of 5.2 percent weight gain. The surface area of born lime decreases with Calcination temperature of both carbonate and hydroxide. The high reactivity of hydroxide derived lime is due to higher surface area of newly born CaO than from carbonate as well as hydroxide derived lime form at comparatively lower temperature than carbonate. The hydration affinity increases with increasing surface area.

**Keywords:** Calcination; Limestone; Quick Lime

## **1. Introduction**

Lime in the various form as quicklime obtained by light calcination of limestone and slaked lime obtained by hydration of calcined product of limestone. It is an attractive material and has extensively industrial application as a binder for the production of hydraulic mortars, plasters, filler in plastic, manufacture of cement as well as fluxing material in metallurgical process to remove the gangue present in naturally occurring ores [1-4]. The decomposition of  $\text{CaCO}_3$  is highly endothermic process with  $\Delta H = +178$  kJ/mole and the rate of calcination increases at higher temperatures, as well as at higher partial pressures of carbon dioxide and steam vapour [5]. The reactivity of quick lime depends on various factors like characteristics of the limestone, calcination temperature, pressure acquired in kilns, rate of calcination, fuel quality and presence of associated impurities like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  in limestone [6,7].

The presence of impurities in limestone increases the sintering rate which changes the pore shape, increase pore shrinkage and grain size that CaO particles undergo during heating. Densification increases at higher temperatures, as well as at higher partial pressures of carbon dioxide and steam vapour [8]. The reactivity of lime produce by calcination of limestone differ mainly due to surface area of nascent CaO. Beruto

et al. [9] found that coarser grain limestone resulted in surface areas of CaO only 2 to 5 m<sup>2</sup>/g when calcined in a rotary kiln at 980°C whereas Chan et al. [10] attained a surface area of 24.6 m<sup>2</sup>/g by calcining limestone particles in a TGA at 745°C. The surface area of born CaO by the calcination of limestone depends on so many factors like the characteristics of the limestone, calcination temperature, pressure acquired inside the kilns, rate of calcination, and fuel quality [11,12]. Lime has also been used as a hydraulic binder for the production of mortars, plasters and a pure binder to get aerial mortar or mixed with natural or artificial pozzolana for the manufacture of hydraulic mortars [13].

The present study is focused on the nature and reactivity of lime derived directly by calcination of limestone or limestone derived slaked lime. The carbonate derived or hydroxide derived lime and their reactivity towards hydration in relation with calcination characteristics of limestone is also studied in this investigation.

## **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. 1gm. powder limestone sample of -300 mesh was first dissolved in 1:1 HCl solution followed by makeup volume to 250 ml. The chemical analysis was carried out from this stock solution as per standard ASTM C25 – 19 and the analysis report was expressed in terms of oxide basis.

The reactivity of lime was varied by changing the calcinations of parent materials. The carbonate derived lime was prepared by calcinations of limestone at about 900°C followed by 1hour soaking but hydroxide derived lime 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 hydroxide powder was then calcined to oxide powder.

### **2.2 Characterisation of Materials**

The phase analysis of limestone was characterised was carried out by X-ray diffraction techniques using a Rigaku (Japan) Ultimal III diffractometer with monochromatic Cu-K $\alpha$  radiation (1.54059Å) at 40 kV and 30 mA. The scanning span (2 $\theta$ ) is ranged from 10° to 80° at a scanning speed of 1°/min. The surface morphology of limestone was characterised by thin section optical microscopy techniques. The decomposition behaviour of limestone was characterised by DTA techniques at the heating rate of 10°C/min by using  $\alpha$ -alumina as an inert material. The hydration of different reactive lime was carried out by taking weight gain of CaO powder taken in a Petridis at 70°C and 90 percent relative humidity for 2 hours in a steam humidity cabinet. After hydration the Petridis was dried at 110°C in an air oven to remove the adhering moisture from the powder surface. The percent weight gain was calculated on the basis of initial weight of CaO powder.

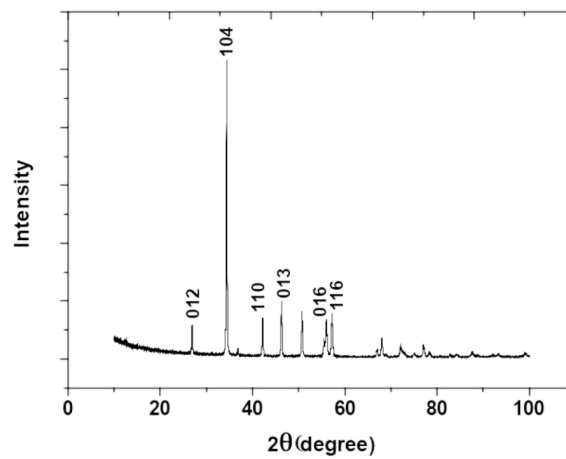
## **3. Results and Discussion**

The natural carbonate material limestone from Madhyapradesh region of India, selected in this study is relatively pure with a very low amount of impurities around 2 weight percent. The chemical analysis of raw limestone on oxide basis is shown in Table 1.

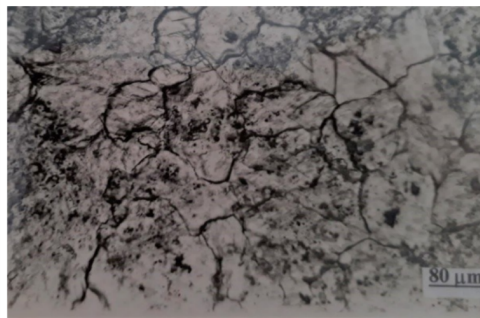
**Table 1: Chemical Analysis of raw limestone**

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	LOI
1.48	0.20	0.11	54.56	Traces	0.11	0.33	42.888

X-ray diffraction pattern of limestone in Fig. 1 shows that diffraction peaks corresponding to calcite only at (012), (104), (110), (113), (202), (108) and (116) and no aragonite and vaterite was present. These results supported by other researchers [4,6,9].

**Fig. 1: X-ray diffraction pattern of limestone**

The surface morphology of raw limestone rock in Fig. 2 shows that it consists of rounded to subrounded calcite grain with a granular texture contact situated with uniaxially negative. The grains are mostly colourless in plane polarised light but in crossed polarised light it shows higher order interference colour. One set of parallel cleavage and rhombic cleavage are clearly visible in some grains [10,12]. The average grain size was 125  $\mu\text{m}$ .

**Fig. 2: The surface morphology of raw limestone rock**

The differential thermal analysis of limestone is shown in Fig. 3. There is a highest endothermic peak at around 916°C for limestone which is very much comparable with the literature, the dissociation occur at 825°C to as high 923°C depending upon the nature, quality and largely on heating rate (14-17). The hydroxide derived from limestone decomposes earlier at 515°C than carbonate.

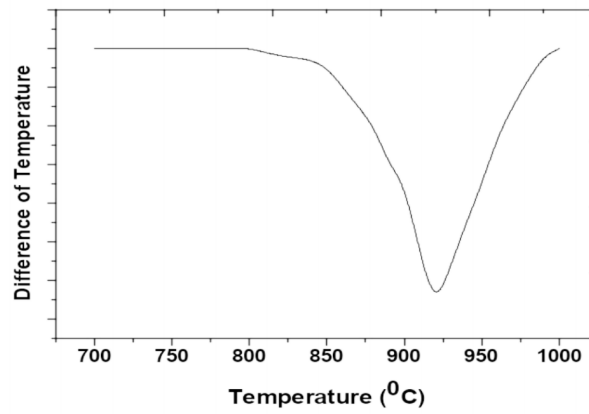


Fig. 3: The differential thermal analysis of limestone

The surface area of nascent lime derived from carbonate and hydroxide in relation with calcination temperature is shown in Figs. 4(a) & 4(b).

The surface area gradually decreases with increasing calcination temperature both in carbonate and hydroxide derived lime. The hydroxide derived lime shows higher surface area than carbonate derived lime. This is due to hydroxide decomposes comparatively lower temperature than carbonate which create more immune and less reactive surface of carbonate derived lime [17-19].

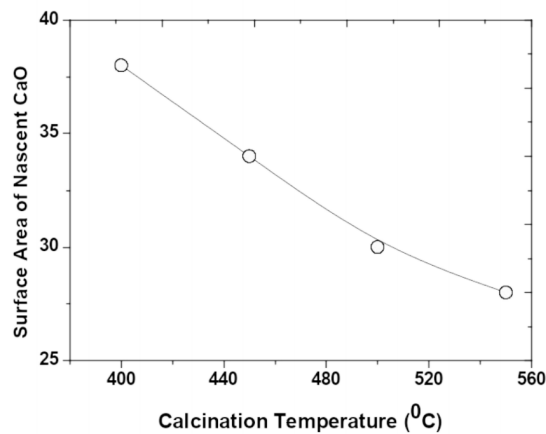


Fig. 4(a): The surface area of nascent lime derived from hydroxide in relation with calcination temperature



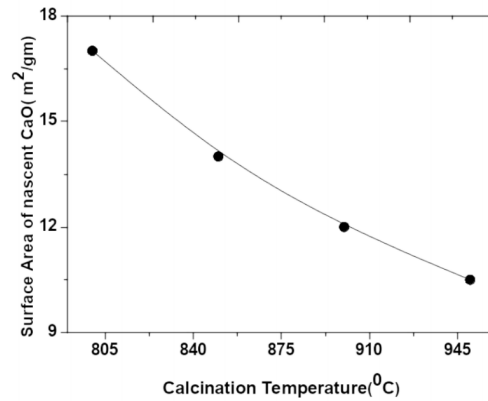


Fig. 4(b): The surface area of nascent lime derived from carbonate in relation with calcination temperature

Hydration is the chemical combination of CaO with water to form  $\text{Ca(OH)}_2$ , an importance characteristics of lime. The structural openness and thermodynamics instability causes the lime to hydrate even when CaO comes in contact with atmospheric moisture. The hydration mechanism is believed to occur in two stages (i) reversibly adsorbed water on the surface of CaO particle to form  $\text{Ca(OH)}_2$  which initially cover the oxide surface and (ii) secondary adsorbed water diffuse through hydroxide layer subsequently hydrate oxide grains. This diffusion is much slower process which controls the rate of hydration of CaO [20,21]. The hydration affinity of CaO depends on the reactivity of lime.

Figs. 5 & 6 showed that Percent weight gain of CaO decreases with calcination temperature of parent carbonate or hydroxide. This is because with increasing calcination temperature the born lime becomes more immune to hydrate. Dehydration of hydroxide occur at lower temperature than decarbonation of carbonate and hydroxide derived oxide has an enormous surface area and free energy than those of carbonate derived oxide which causes the more reactivity of hydroxide derived lime [16].

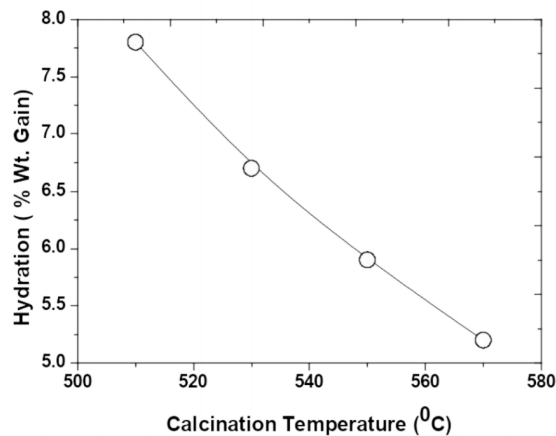


Fig. 5: Hydration (% Wt. Gain ) vs. Calcination Temperature of lime derived from hydroxide

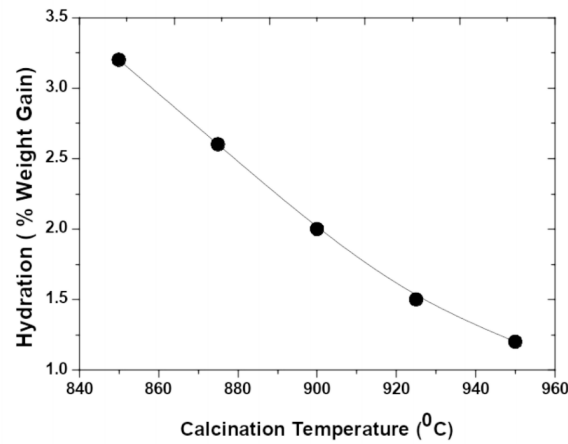


Fig. 6: Hydration (% Wt. Gain ) vs. Calcination Temperature of lime derived from Carbonate

Fig. 7 showed that hydration of CaO is a strong function of its surface area. With increasing surface area of CaO the percent weight gain increases due to enhancement of rate of chemisorptions of water on the grain boundary surface. More the surface area diffusion of water is more causes more hydration [19-21].

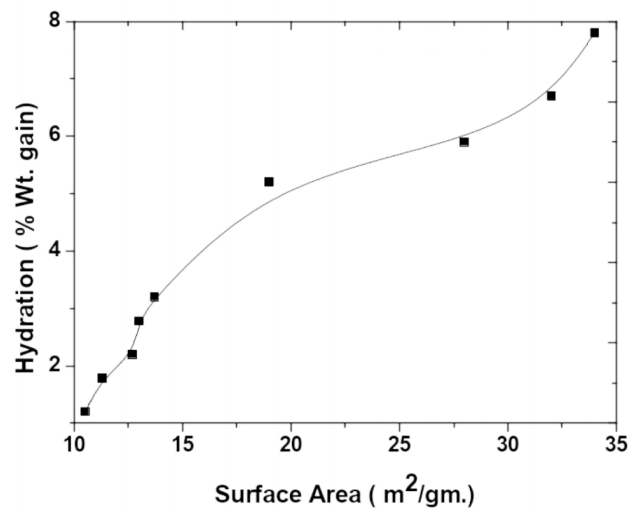


Fig. 7: Hydration (% Wt. Gain ) vs. Surface area of CaO

#### 4. Conclusion

The reactivity of born lime from limestone towards hydration is less than hydroxide derived lime due to high surface area of born CaO from hydroxide. Hydration gain of born CaO decreases with calcinations temperature of both carbonate and hydroxide. The chemisorptions of hydration process depends mainly on the

surface area of born CaO. Hydration gain decreases with surface area due to enhancement of chemisorptions which increases hydration gain.

### REFERENCE

- [1] R. Malinowsky and Y. Grafinkel, *Concr. Int.*, **62** (1991) 13.
- [2] M. Wingate, *Inter. Tech. Pub.*, London (1985).
- [3] D. Beruto, L. Barco and A.W. Searcy, *J. Am. Ceram. Soc.*, **66** (1983) 893.
- [4] R.H. Borgwardt et al., *Indust. Engg. Chem. Res.*, **26** (1987) 1993.
- [5] E.K. Powell and A.W. Searcy *J. Am. Ceram. Soc.*, **65** (1982) 219.
- [6] L. Yang and W. Zhang, *Inorg. Chem. Ind.*, **44** (2012) 16.
- [7] R.M. German and Z.A. Munir, *J. Am. Ceram. Soc.*, **59** (1976) 379.
- [8] L. Barco, et al. (1980) *J. Am. Ceram. Soc.*, **63** (1980) 439.
- [9] R.H. Borgwardt, *Chem. Engg. Sc.* **44** (1989) 53.
- [10] R.K. Chan, K.S Murthi and D. Harrison. *J. Chem.*, **48** (1970) 2972.
- [11] R. Pacciani et al., *Energy Fuels*, **21** (2007) 2072.
- [12] R.H. Borgwardt, *AIChE J.*, **31** (1985) 103.
- [13] P. Sun et al., *AIChE J.*, **53** (2007) 2432.
- [14] P.J. Anderson et al., *Proc. Br. Ceram. Soc.*, **3** (1965) 33.
- [15] V. Manovic et al., *Energy Fuels*, **22** (2008) 3258.
- [16] R.H. Borgwardt, *Indust. Engg. Chem. Res.*, **28** (1989) 493.
- [17] D. Beruto and A.W. Searcy, *J. Chem. Soc. Faraday Trans.*, **170** (1974) 2145.
- [18] S.J. Bortz et al., "Precalcination and Its Effect on Sorbent Utilization during Upper Furnace Injection," in Proceedings: 1986 Joint EPRI/EPA Symposium on Dry SO<sub>2</sub> and Simultaneous SO<sub>2</sub>/N<sub>2</sub>O<sub>x</sub> Technologies, Volume 1, EPRI CS4966, December 1986.
- [19] C.R. Milne and G.D. Silcox, *Indust. Engg. Chem. Res.*, **29** (1990) 139.
- [20] D. Beruto et al., *J. Amer. Cer. Soc.*, **67** (1984) 512.
- [21] W. Zhang, C. Chun-Bao and D. Fu-Jun, *Bul. Chin. Ceram. Soc.*, **29** (2010) 926.

