

## Experimental Study of Calcination-Carbonation Process for the Production of Precipitated Calcium Carbonate

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**Summary:** The limestone of Swabi district was used to produce precipitated calcium carbonate. The optimum calcination temperature and time was found to be 1000°C-1100°C and 3 hours to 4 hours respectively. The results show that the stirrer speed of 130 rpm is the most suitable, as higher speed causes attrition of precipitates. The required particle size of precipitates of calcium carbonate can be achieved by choosing the right concentration of calcium hydroxide suspension. The impurities provide additional nucleus for precipitate formation affecting brightness and specific gravity of the product.

### Introduction

Precipitated calcium carbonate has long been recognized as versatile additive for a wide range of products such as plastics, rubber, ceramics, toothpaste, food etc. A recent boost in the production of precipitated calcium carbonate is due to switching from acidic paper making to alkaline paper manufacturing. The alkaline paper making process replaces very expensive fillers such as kaolin and wood fibre [1] with precipitated calcium carbonate. Moreover, controlled process conditions can produce high quality precipitated calcium carbonate having good light scattering quality that can replace [2] very expensive optical brightening agent TiO<sub>2</sub> used in producing special paper.

The process control requires screening of basic raw material calcium carbonate, crushing it to required size [3,4] which most researchers agree does not play much role in complete calcination of the raw material. Earlier researchers [5,6] argued that the carbon dioxide atmosphere in kiln played an important role in complete calcination of calcium carbonate. However, recent studies [4,7] show that the influence of carbon dioxide atmosphere has no effect on rate of calcination. A few investigations [3,7,8] have been made into the calcination temperature and time which showed little agreement due to the nature of ore. Therefore, no general statement may be made about the time required to burn a given sample of limestone at a given temperature. Hence, initial study in the present work was conducted at a suitable calcination temperature and time for the local ore.

Further work was carried out to evaluate the economic viability and industrial acceptability of the process for the production of precipitated calcium carbonate. The work concentrated on establishing the parameters that govern the particle size (fineness), whiteness (brightness) and chemical purity of precipitated calcium carbonate as these are basic requirements for the application of the product in various industries.

### Results and Discussion

The quick lime was hydrated to study the rate of slaking in water. Fig. 1 shows that the calcium carbonate calcined between 1000°C and 1100°C was active during hydration and raised maximum temperature of the slurry to 56°C. This peak in the curve shows the completeness of slaking of quick lime produced at 1100°C. Other lime samples calcined at 1200°C and 1300°C indicating higher temperatures affect adversely [9]. It is concluded that it may be due to vitreous formation of limestone locally causing lower hydration of the samples. The calcium carbonate samples calcined at 900°C were not soft enough to be easily crushed between the fingers showing incomplete calcinations [7,10].

Fig. 2 shows the influence of burning time of limestone at 1100°C on the slaking property of lime. The curve indicates that the excess burning time affects the quality of the lime inversely. The optimum time of calcination was found to be between 3 and 4 hours. The curve shows that lime formed in the

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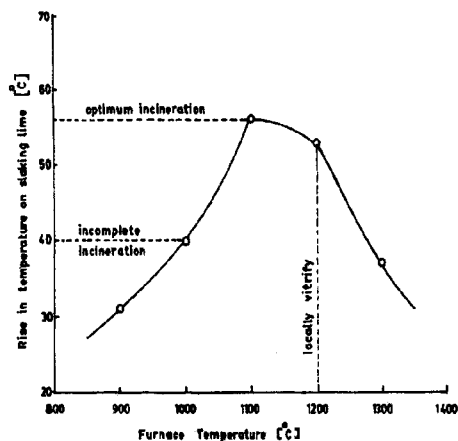


Fig. 1: Relationship between incineration temperature of limestone and slaking of lime.

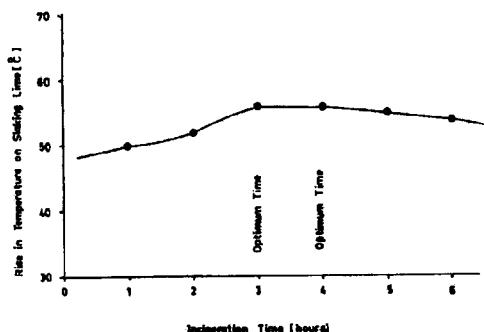


Fig. 2: Effect incineration temperature (1100°C) on the slaking of lime.

temperature range 1000°C-1100°C and 3 hours to 4 hours is very good quality as compared to the samples calcined for 6 hours.

To study the crystal growth, concentration of calcium hydroxide suspension, stirrer speed and impurities were taken into consideration for getting efficacious results.

Agitation has a considerable influence on the formation of precipitates. The precipitation rate progressively increases with vigorous agitation because of attrition of precipitates and particle - particle collision producing secondary nucleation.

The gentle agitation may not help complete mixing and hence, precipitate formation is in clumps or groups.

To quantify the above effects, a series of data using stirrer speed from 90 rpm to 150 rpm was carried out for 15% calcium hydroxide suspension. The results are given in Table-2. It can be seen from the results that precipitate formation is much lower at 150rpm. It may be due to the high stirrer speed that does not let carbon dioxide bubbles to break in the suspension and bubbles escape without reaction as the yield is found to be only 96%. The stirrer speed at 90 rpm produced classification of precipitates and caused similar concentration of precipitated calcium carbonate at various sieve analysis. The overall yield of precipitates is again low that may be caused by poor mixing of the suspension resulting in inability of carbon dioxide to react with calcium hydroxide in suspension. It was found that the stirrer speed of 130 rpm would keep the suspension in a thoroughly mixed condition, mitigate the effect of attrition on precipitates [11] and give the maximum yield (97.7%) of precipitated calcium carbonate.

It can be concluded from these results that a carefully selected stirrer speed would control the growth of precipitate size in the suspension.

Table-3 shows effect of suspension concentration and impurities on the yield of precipitated calcium carbonate. The results for 15%, 12% and 10% calcium hydroxide support the general trend reported in other studies [10-12] that with increase in concentration, the precipitate formation also increases. The maximum weight of precipitates was obtained at a range from 26.5 $\mu$  to 37 $\mu$  sieve openings indicating that the concentration of the suspension shift the formation of precipitate size to lower or higher size. Therefore, the required size too of the precipitates can be obtained by controlling the concentration of the suspension.

The presence of impurities in system also affect the precipitation process considerably. Impurities can alter the properties of suspension by changing the characteristics of the adsorption layer, crystal-solution interface or both.

The effects of the most common impurities were investigated to study their influence on the precipitate formation. Calcium nitrate (5%) was introduced in the suspension, causing maximum amount of precipitated calcium carbonate formation of 44.0  $\mu$  and also producing comparatively higher concentration at lower sieve sizes. The tap water used in the process produced almost similar sizes of product at a wide range of sieve sizes. It may be due

to the presence of magnesium and calcium salts in water providing nucleus for precipitate formation. However, the specific gravity was much higher than the specific gravity reported in the literature [13]. Moreover, these samples were not ultra bright as compared to precipitated calcium carbonate produced without impurity. It was attributed to the presence of sulphates and nitrate in the system.

### Experimental

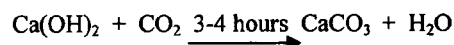
The limestone ore selected for present study was from Swabi area (N.W.F.P.) quarry. The analytical composition of the raw material was determined to design the experimental procedures. Table-1 shows the percentage composition of each constituent of limestone ore.

The limestone samples of 5-8 mesh were carefully screened and washed to remove any undesired colored impurities. The samples of 200gm each were placed in furnace at required temperature for a desired length of time. These samples were

calcined at temperatures ranging from 900°C to 1300°C for a period of 2 hours to 6 hours.

The samples were cooled, physically checked for softness and then pulverized to 100-mesh for uniformity of experiment. The samples were stored in an air-tight jar for further experimentations.

The calcined lime was hydrated with distilled water forming 10% to 15% calcium hydroxide suspension of pH between 12 and 14. The suspension was screened to remove sand and other lime impurities. The carbon dioxide from cylinder was passed through the colloidal suspension while stirring continuously to prevent settling of precipitated calcium carbonate or calcium hydroxide suspension. The carbon dioxide supplied to colloidal solution was stopped on achieving pH 7.5. The following reaction mechanism takes place during carbonation:



The concentration of suspension was measured by hydrometer and pH of the suspension determined by using Toptronic pH meter, (Italy).

Table-1: Percentage composition of each constituent of limestone ore.

CaO	SiO <sub>2</sub>	MgO	R <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	Loss of water at 110°C	Loss on ignition
53.20	0.50	0.20	1.49	2.80	2.20	39.80

Table-2: Effect of stirrer speed on precipitation of light weight calcium carbonate.

Formation is quicker	Ca(OH) <sub>2</sub> in suspension = 15% Volume of suspension = 2.0 litres								Theoretical yield	Practical yield
	19.0	22.5	26.5	31.5	37.0	44.0	53.0			
Mean Sieve Aperture (Micron)										
Mass Retained on Sieve Stirrer Speed 150 rpm	14.7	69.3	77.2	102.4	74.5	31.0	19.7	405.0	388.8	(96 %)
Mass Retained on Sieve Stirrer Speed 130 rpm	24.9	59.6	132.4	80.5	51.1	34.0	13.2	405.0	395.7	(97.7 %)
Mass Retained on Sieve Stirrer Speed 90 rpm	16.2	28.6	59.7	66.7	74.2	80.4	64.3	405.0	390.1	(96.3 %)

Table-3: The Effect of solution concentration on crystal growth.

Volume of solution = 2.0 litres

Stirrer speed = 150 rpm

Mean Sieve Aperture (Micron)	19.0	22.5	26.5	31.5	37.0	44.0	53.0	% yield	Specific gravity
Mass Retained on Sieve [15 % Ca(OH) <sub>2</sub> ]	27.9	60.6	132.4	81.5	51.1	34.0	13.2	97.0 %	2.71
Mass Retained on Sieve [12 % Ca(OH) <sub>2</sub> ]	17.7	36.2	55.6	63.3	100.9	25.0	15.2	96.8 %	2.72
Mass Retained on Sieve [10 % Ca(OH) <sub>2</sub> ]	12.9	27.1	65.2	72.3	39.5	29.6	13.2	96.2 %	2.71
Mass Retained on Sieve [15 % Ca(OH) <sub>2</sub> and 5 % Ca(NO <sub>3</sub> ) <sub>2</sub> ]	55.2	70.5	23.2	32.3	60.8	118.0	52.2	90.6 %	2.92
Mass Retained on Sieve [Tap water containing Mg and Ca Salts]	24.6	49.5	60.4	71.1	87.9	63.1	14.0	89.3 % evenly distribution	2.93

The particle size distribution [14] of precipitated calcium carbonate was carried out by employing stainless steel test sieves of 51.0 mm diameter and sieve aperture ranging from 19 $\mu$  to 53 $\mu$ . A laboratory sieve shaker was used to ensure even distribution of the sample. The samples were shaken for 25 minutes for adequate distribution of precipitates.

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