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PRODUCTION OF LAB SCALE LIMESTONE CALCINED CLAY CEMENTS USING LOW GRADE LIMESTONE

Satya Medepalli*, **Vineet Shah and Shashank Bishnoi**

Indian Institute of Delhi, New Delhi, India
**E-Mail: satya.medepalli@gmail.com, TP: +919990009680*

Abstract: In developing countries, such as India, cement production is expected to rise exponentially in the coming decades with the increasing infrastructure demand. Sustainable alternatives are being looked into to account for the growing demand and to reduce the CO2 emissions. Limestone calcined clay cement (LC3) with clinker factor of 0.5 is one of the sustainable ways to reduce the carbon footprint and meet the growing demand. In this study, clay from a particular source having a kaolinite content of 65% is selected and calcined at ~800° C in a laboratory scale rotary kiln. The calcination parameters are fixed to obtain a uniform flow in the kiln. Three different qualities of limestone with low calcium carbonate content are selected from rejected limestone dumps. LC3 blends are prepared by blending calcined clay, limestone and clinker in a lab scale ball mill using different limestone grades. The tests on physical properties of the blends were carried out and compared with the properties of fly ash based Porltand pozzolana cement. The properties of the blends are found satisfactory. The phases formed in the hydrated specimens are found using X-ray diffraction. Compressive strength and formation of phases in the hydrated paste are monitored till 90 days.

Keywords: limestone calcined clay cement; sustainable cements; clinker factor

1. Introduction

The main focus in the present era is concentrated on reducing the carbon emissions and utilization of low energy alternatives. It is generally accepted globally as a sustainable practice to blend supplementary cementitious materials to reduce the clinker content and thereby reducing carbon emissions. Supplementary cementitious materials such as fly ashes, slag and metakaolin have been in use to reduce the clinker factor in cements from a long time. Reference standards to include these materials are already in place [1–4].

In the Indian standards, replacement of cement with calcined clay as a pozzolan is limited to 25% [4] and limestone as performance improver is limited to 5% [5]. The current study is focussed on the combined use of these two materials in the production of limestone calcined clay cement (LC^3) and to study the synergic effect during the hydration of such blended cements.

Limestone is added to the cement in small quantities to improve the performance of cement and concrete. Unitl the 1940's these type of fillers were considered as inert and were added to cement only as an economical measure. It is now clear from the literature that limestone also participates in the hydration reactions apart from acting as a filler [6–8]. Different studies are carried out to find the effect of limestone additions on Portland cement[6,9,10]. It is shown that 3-5% addition has a positive effect on cement properties having high alumina content [9]. Instead of monosuphate which usually forms in ordinary Portland cements, monocarboaluminate and hemicarboaluminate are formed with limestone additions.

The term calcined clay refers to thermally activated kaolin also called metakaolin. These clays are abundant in the earth's crust. The advantages of using calcined clay in cement and concrete have been listed in different works [11,12]. Thermal activation of kaolinite clays at a temperature of ~800°C leads to dehydroxylation and formation of an amorphous material metakaolinte as per the Eq 1.

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O \qquad (1)$$

Different calcination temperatures in the range 550-850 °C are used by researchers[13,14] to find the optimal temperature required to achieve a good quality pozzolan. As undesirous crystalline phases such as mullite and spinel form above 900ºC [15,16], an optimal temperature of 800ºC is maintained in this research for the complete de-hydroxylation of kaolinite.

The present work is concentrated on the combined use of both limestone and calcined clay as a high volume replacement in cement. Earlier studies which focused on limestone calcined clay have used high purity limestone in their work [17]. As high purity limestone is anyways used in cement production, this study concentrates to use low grade limestone which is unused by the cement manufacturers and dumped in large quantities.

2. Materials and Methods

The materials used in this work include clinker from JK Lakshmi Cement plant, gypsum, three different grades of limestone and calcined clay.

LC^3 blends are prepared using three types of limestone. All these blends are prepared in a laboratory ball mill by inter-grinding for a fixed duration. The proportions for all these blends are kept constant as shown in Table 01 .

Table 01: Proportions of LC3 blends

Material	Weight fraction	Source
Clinker	50%	JK Lakshmi Cement Ltd
Calcined clay	30%	Datiya, TARAgram
Limestone	15%	JK Lakshmi Cement Ltd
Gypsum	5%	JK Lakshmi Cement Ltd

2.1 Clay

Raw clay is sourced from a clay mine in Gujarat, India which is calcined in a lab size rotary kiln (**Error! Reference source not found.**).

Fig. 01. Lab scale rotary kiln at Datiya, TARAgram

Different size fractions are used to check the retention time and material flow through the kiln. Initially pulverized clay was used but due to nature of the clay particles, material flow through the kiln was not uniform as fine particles stick to each other and to the surface of the kiln. A course fraction of maximum size 10 mm is kept as feed size (**Error! Reference source not found.**) to allow a smooth and even flow through the kiln. The length of kiln from the hopper to the outlet is 4.5m. Retention time in the kiln is maintained at 20 min. The size fraction of the raw feed clay and calcined clay from the output are also measured. The calcined clay size fraction was observed to be finer than initial

feed size of the raw clay (**Error! Reference source not found.**).

Fig. 02. Feed size of raw clay

Thermogravimetric analysis of raw and calcined clay is used to find the percentage kaolinite content and the degree of calcination of the clay. **Error! Reference source not found.** shows the TGA and DTG curves of the raw and calcined clay. The percentage of kaolinite content in the raw clay is calculated to be 65% based on the thermal decompositon of the kaolite (350-750ºC). The DTG curve of the calcined clay shows a minor fraction of uncalcined clay left.

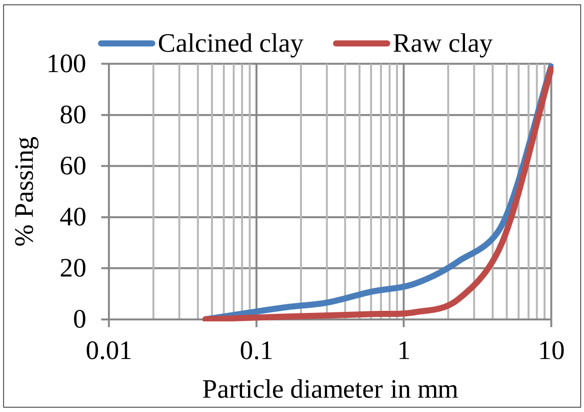


Fig. 03. Size fraction of raw feed clay and calcined clay from the outlet

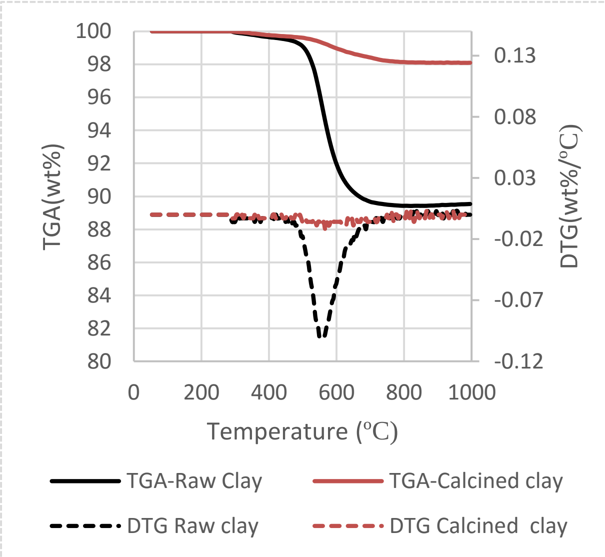


Fig. 04. TGA and DTG of raw and calcined clays

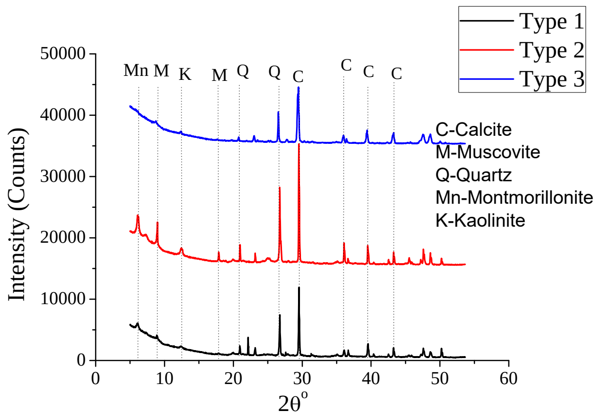
2.2 Limestone

The three types of limestone used in this work are sourced from mines of JK Lakshmi Cement near Abu Road, Rajasthan. The chemical composition is of these different grades from X-ray fluorescence is given in Table 02. Loss of ignition (LOI) for these samples is found out by heating at 1050°C for 2 hours. It is seen that these three types have less calcium oxide content and can be classified as low grade limestone. Type 1 and Type 2 limestone are similar while Type 3 has higher calcium oxide content.

Table 02: Chemical composition of limestone

Limestone	Al_2O_3	SiO_2	CaO	Fe_2O_3	LOI
Grade 1	10.12	25.84	31.95	4.805	25.9
Grade 2	9.925	27.01	31.5	5.275	26.1
Grade 3	6.44	20.61	36.72	3.68	29.1

Major minerals present in the different types of limestone used are found using XRD (X-ray diffraction). XRD analysis was conducted on a Bruker D8 Advance Eco Model with Cu Kα radiation (40KV, 25mA). The step size is 0.02 θ per second and scan range 5-65°. The total scan time was approximately 16 minutes per sample. The major peaks from the XRD in the limestone samples are calcite and quartz with muscovite, kaolinite and montmorllionite present in minor



peaks as shown in **Error! Reference source not found.**.

Fig. 05. XRD analysis of types of limestone used

2.3 LC³ blends

Three LC³ mixes are prepared as per the proportions given in Table 01 and using three types of limestone (Table 03). Only one type of Clinker, calcined clay and gypsum are used in all the mixes. The three mixes are prepared as per Table 03.

Table 03: Mixes used in current study

LC³ Mix	Limestone type
Mix 1	Type 1
Mix 2	Type 2
Mix 3	Type 3

2.4 Mortar Preparation

The three LC³ blends are used to prepare mortar cubes of size 7.06 cm with a fixed water to binder ratio of 0.45. The strength of the mortar cubes at different ages are measured using a compressive testing machine under a uniform loading rate of 35 N/mm²/min.

2.5 Hydration study

Hydration study on LC³ blends is conducted by casting paste samples in elongated cylindrical molds at fixed water-binder ratio of 0.45. Discs of 3mm size are cut from the samples to perform X-ray diffraction on wet samples so as to reduce the effect of carbonation.

3. Results

3.1 Compressive strength

The compressive strength of the blends at different ages are shown in **Error! Reference source not found.**. The strength of all the blends are comparable and even better than the minimum strength criteria specified by the standards for PPC (Portland pozzolana cement). The strengths of OPC, PPC and Low heat cement as per standard specifications are listed in Table 04 for comparison purposes.

Table 04: Specifications for standard cements

Strength at age (N/mm²)	OPC43 grade [18] IS 8112:2013	PPC IS 1489 Part-1 [1]	Low heat Cement IS 12600:1989 [19]
3 day	23	16	10
7 day	33	22	16
28 day	43	33	35

The strength development in Mix-1 was gradual though in Mix-2 and Mix-3 higher early age strengths are observed. It is interesting to note that Mix-2 developed strength almost similar to Ordinary Portland cement (Table 04). Mix-3 developed higher early age strength but the later age strength development is retarded. In all these mixes, compressive strengths are more than PPC or almost equivalent to OPC in spite of the substantial replacement of clinker (50%) with limestone and calcined clay.

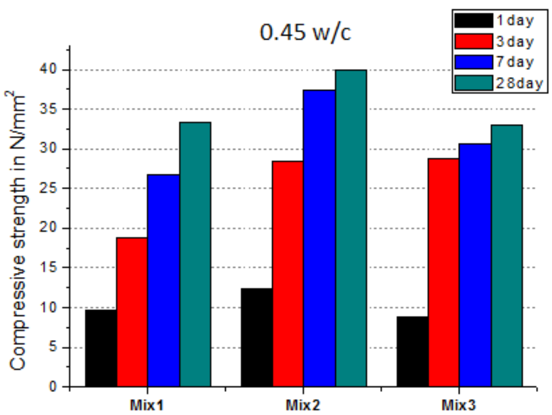


Fig. 06. Compressive strength of blends

The increase in the early age strengths in these cements even with low clinker factor is due to the pozzolanic reaction of calcined clay to form secondary C-S-H. Also, the stabilization of ettringite will lead to an increase in the compressive strength as ettringite has low density and occupies more volume and hence less porosity [20].

3.2 X-ray diffraction

To find the phases formed during hydration of these LC³ blends, XRD analysis is carried out on hydrated paste samples at different ages. As metakaolin consumes lime due to its pozzolanic nature to form C-S-H phase, we could see reduced portlandite content in XRD patters with increasing age.

XRD pattern of Mix-1 (**Error! Reference source not found.**) confirms the formation of hemi-carboaluminate at all the ages and ettrigite is stabilized. Portlandite consumption can be seen at 7 days and there is very little CH peak at 28 days indicating that most of the portlandite is consumed in the pozzolanic reaction. No major reduction is seen in calcite peak as the reaction between carbonate and aluminate ions is limited and only a small fraction of calcite is involved in the reaction.

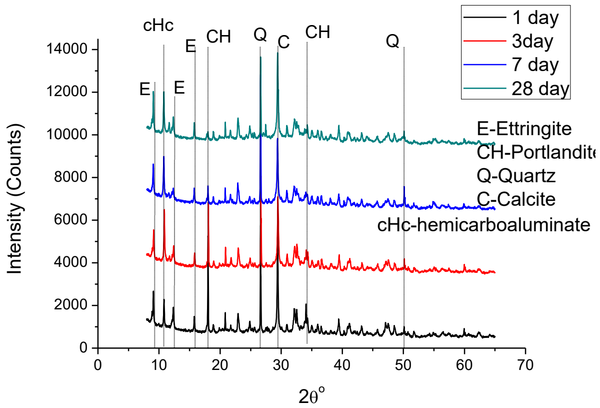
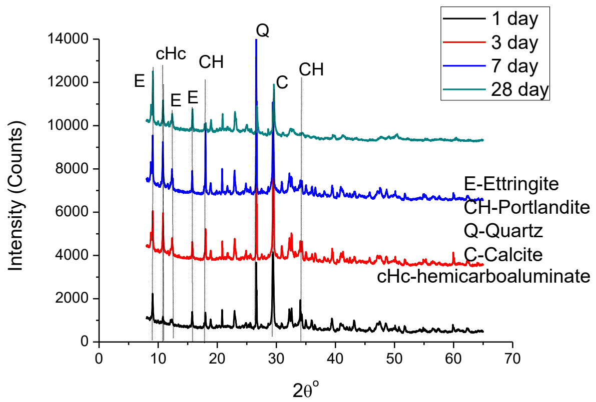


Fig. 07. XRD of hydrated samples for Mix-1

Similar observations were seen in hydrated samples of Mix 2 (**Error! Reference source not found.**). Unlike Mix 1, where CH consumption can be seen at 7 day, there is an intense CH peak in Mix-2 which has increased after 3 days. This shows that cement hydration, especially alite hydration has accelerated which explains the considerable increase in the 7 day strength. At 28 days, however the relative peak intensity has reduced considerably indicating that most of the CH has been



consumed.

Fig. 08. XRD of hydrated samples for Mix-2

Error! Reference source not found. shows the XRD pattern for hydrated samples of Mix-3 up to 28 days. In all these LC^3 blends, hemicarboaluminate (cHc) is seen as the dominant carboaluminate phase and ettringite is enhanced and stabilized confirming to other studies [17].

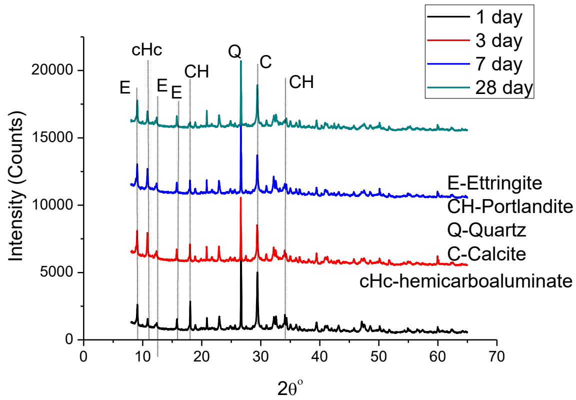


Fig. 09. XRD of hydrated samples for Mix-3

4. Conclusions

LC^3 blend which is similar to composite cement blend has been manufactured at lab scale. This study has showed that higher replacement of clinker (50%) with limestone and calcined clay yields a product whose strength development is comparable to ordinary Portland cement. This could be a viable alternative for high clinker substitutions without compromising on the strength.

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