Journal of Asian Concrete Federation
Vol. 2, No. 2, Dec. 2016, pp. 110-116
ISSN 2465-7964 / eISSN 2465-7972
http://dx.doi.org/10.18702/acf.2016.12.2.2.110

Relative evaluation of performance of limestone calcined clay cement compared with Portland pozzolana cement

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(Received: August 4, 2016; Accepted: November 6, 2016; Published online: December 31, 2016)

Abstract: Cement is most widely used binder to produce concrete and the most common construction material today. Though concrete is a material with the lowest greenhouse emission, cement has the highest. With the carbon footprint of cement accounting for over 7% of total world emissions, it becomes single most important material of environmental concern around the world. This concern has led to a search for lower carbon emitting binders and use of blended cements, incorporating large number of natural and industrial by-products. This paper describes the performance of a composite cement binder consisting of calcined clay, limestone, and Portland cement clinker as compared to a traditionally used fly ash based Portland pozzolana cement. This study reports behavior of the two cement binders with respect to strength development, hydration, porosity of hydrated pastes, normal consistency, and admixture response with ageing. This study finds that, though the clay based cement attains higher early age strength, the later age strength in mortar is lower as compared to commercial fly ash based cement. Further the clay based cement has higher water demand, but lower porosity compared to composite cement binder.

Keywords: binder, calcined clay, limestone, microstructure, hydration, porosity, water demand.

1. Introduction

Concrete is most widely used construction material in the world today with over 25 billion tons placed every year [1]. It is made from graded aggregate system, cemented together by a binder, normally called Portland cement. Often this concrete also includes various industrial by-products, which may have either pozzolanic or self-cementing properties. Modern concrete also has superplasticizers to make the concrete workable and pumpable for various applications. In spite of various developments, cement remains the only binder in concrete. The cement is highly energy intensive to produce and is responsible for about 7% of greenhouse emissions in the world today [2]. Even though carbon footprint of concrete is lowest among building materials used in construction (see Fig. 1), the same is highest due to sheer volume of concrete being used today. Researchers in academia and industry have been working on reducing the carbon footprints of cement and have been successful in reducing the same by about 20% in last one decade as reported in World Cement Sustainability Initiative Report published in 2012.

Cement production has been progressively increasing and currently over 4 billion tonnes of cement is being produced annually across the world. Realising the problems of greenhouse gases, the cement industry has undergone a lot of changes. The changes are in process engineering as well as in variety of cements being produced. Today, utilization of blended cements is usually preferred due to their economic and technical benefits and indirect advantages such as lower level of CO_2 emissions by reducing clinker production in plants. While the emerging family of cementitious materials has been expanding to a larger number, namely fly ash, silica fume, calcined clay, metakaolin etc., materials like fly ash (FA) and ground granulated blast furnace slag (GGBS) are being widely used for cement production.

The primary objective of usage of wide range of cementitious materials, both natural and artificial is to reduce the CO_2 footprint and progressively increase usage of non-bio degradable industrial waste. These major industrial wastes are fly ash and GGBS. Other minor industrial waste could be used as cementitious material. Introduction of calcined clay pozzolana as cementitious material has been

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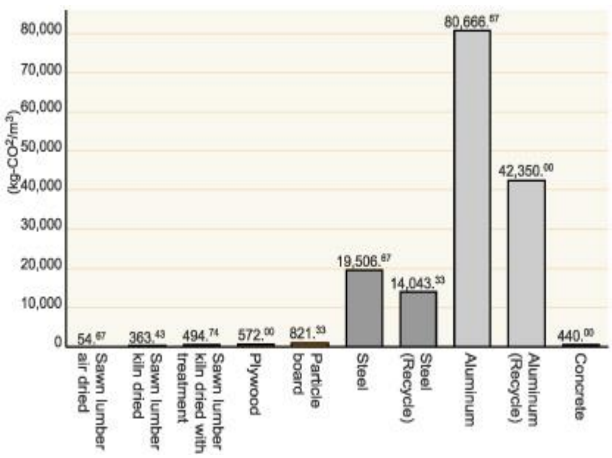

Fig. 1 – CO_2 discharge in production process of construction materials

reported long back elsewhere globally. In India, it began in late 1970s only, when BIS standard for calcined clay became available for manufacturing of Portland pozzolana cement [5]. Many publications report that performance of mortar and concrete composed with calcined clay closely compares with mortar/concrete made with fly ash and GGBS. The calcined clay is the potentially rich cementitious material and its usage would greatly contribute in reducing carbon foot print.

The objective of this study is to evaluate the performance of limestone calcine clay cement (LC3) and commercially available Portland pozzolana cement (PPC) towards understanding the products in greater details. The blended cements have been in use widely for more than two decades in reducing the CO_2 footprint in relation to conventionally used ordinary Portland cements. Most of the countries today produce and use blended cement, either binary or ternary blended for various construction applications [3-7]. Accordingly the specification of cement are becoming performance oriented rather than current one of prescription oriented [8]. In India, due to large availability of fly ash and to some extent GGBS, over 75% of cement used is blended cement. The trend is similar across the world and even in ordinary Portland cements, performance improvers or minor additional compounds such as GGBS, limestone, and fly ash are replacing clinkers to the extent of up to 5% [9]. With these efforts, clinker conversion factor, which is a measure of how much cement is produced per unit clinker, has gone to 1.6 from traditional level of 1.03 reducing carbon footprints by over 50%.

In countries, where fly ash is not abundantly available, construction industry has been using limestone powder as clinker substitute. Limestone replacement into Portland cement has been widely studied for several years [9-11]. Limestone not only works as micro filler, but also takes part in hydration process of clinker, improving workability, strength, and durability [12]. The limestone can also be used in ternary blends in combination with fly ash, calcined clay and other pozzolana.

This study compares the behavior of two blended cements, one produced at small cement production unit for this experimental study, the other one being commercially available fly ash based Portland pozzolana cement. The tests were conducted in accordance with Indian standards [13-14].

2. Production of LC3 Cement

A limestone calcined clay cement (LC3) consisting of limestone, calcined clay, and portland cement clinker was used. Cement has 15% limestone, 31% calcined clay, and about 50% portland cement clinker with remainder being gypsum. Properties of the raw materials are given in Table 1. Limestone and calcined clay were ground separately and intermixed with ground clinker. A commercially available Portland pozzolana cement (PPC), made from fly ash conforming to Indian Standard [5] were used for bench marking.

The clay was calcined in a rotary kiln at a temperature of 900 degree Celsius for optimum calcination. A weight loss of 0.3% was observed and lime reactivity of calcined clay was observed to be 7.8 MPa, which was significantly higher than the requirements of pozzolanic materials and certainly better than those of fly ash.

Table 1 – Oxide composition of raw materials

Element	Clinker, %	Lime-stone, %	Clay, %	Gypsum, %
SiO_2	21.1	11.02	54.47	2.77
Fe_2O_3	4.32	1.55	4.93	0.36
Al_2O_3	4.65	2.53	27.29	0.62
CaO	65.16	44.24	0.06	32.62
MgO	2.13	1.96	0.13	1.20
SO_3	0.77	0	0.01	38.75
Na_2O	0.38	0.5	0.12	0.06
K_2O	0.20	0.28	0.25	0.04
LOI	0.96	36.96	10.28	23.02

3. Materials and Test Methods

3.1 Cement

Cement, after proper sampling, was tested as per Indian Standards [13-14] for the following items:

- fineness, by Blaine test apparatus;
- full physical properties, including particle size distribution and retentions on different sieve

sizes like 90 micron (R90), 75 micron (R75), and 45 micron(R45);
- full chemical analysis including insoluble residue (IR), sulphate (SO_3), loss on ignition (LOI), magnesium oxide (MgO), total & soluble alkalis;
- hydration study using calorimeter (ICP) at w/c of 0.4 at 24, 72, 144, and 672 hours; and
- hydration study of LC3 by scanning electron microscopy (SEM).

3.2 Cement paste
- Workability retention study using marsh cone and mini-slump
- At w/c of 0.5 % by wt. without admixture and at 0.4 with admixture
- Fluorescent microscopy on cement paste porosity
- Mercury intrusion porosimeter Quanta chrome MIP with high pressure 60,000 psi system for porosity of paste

3.3 Cement mortar
- Cement mortar with standard stand, ratio 1:3 for compressive strength

Cement pastes were tested for admixture compatibility using a marsh cone and retention was measured using a mini slump. The mini-slump test which was originally developed by Kantro [15] and later modified by Zhor & Bremner [16], measures the consistency of cement paste and is commonly used for evaluating admixture-cement response for flow and retention across the world. The mini-slump cone is a small version of the slump cone. The mini-slump cone is placed in the centre of a piece of plane rigid and non-absorbent surface / table. The paste was prepared at a water-binder ratio (*w/b*) of 0.55 and retention of flow was measured up to 120 minutes.

4. Results and Discussions

A limestone calcined clay cement (LC3) consisting of limestone, calcined clay, and Portland cement clinker was used. Limestone and calcined clay were ground separately and intermixed with cement. A commercially available Portland pozzolana cement (PPC), fly ash based, conforming to Indian Standards [5] was used for bench marking. Properties of cements, tested as per relevant Indian standards [13-14] are given in Tables 2 and 4.

4.1 Cement properties

The chemical composition of cements is given in Table 2 whereas the physical properties of cement are listed in Tables 3 and 4. The LOI of LC3 are much higher than the PPC. The higher LOI is primarily contributed from the limestone addition. The requisite variety of limestone for the purpose of usage in LC3 are having intrinsic LOI in the range of 32–37% typically whereas typical LOI of fly ash is in the range of 0-6 %. SO_3 range is 1.87–2.83%. Crystals of tri-calcium silicate present in commercially available cement are mixed with impurities such as alkalis, sulphates, phosphorous, and host of trace minerals. The hydration process of alite or tri-calcium silicate initiates in presence of alkali sulphate or alkaline sulphate environment. Alite activates when sulphate concentration (SO_3) of the solid solution is close to 2% [17]. However PPC is having SO_3 concentration of 2.83% owing to possible usage of high sulphur bearing clinker. Insoluble residue (IR) for all the cement is ranging 22.68–24.23%. The contributory factors for IR are the percentage of fly ash addition and calcined clay.

Table 2 – Composition of cement

Cement	LOI	IR	SO_3
LC3	7.18	22.68	2.15
PPC	2.78	24.23	2.83

Table 3 – Particle size distribution of cements

Sample	d_{10} %, µm	d_{50} %, µm	d_{90} %, µm	Mean size, µm
LC3	1.26	13.11	57.48	22.25
PPC	1.70	18.09	51.80	23.04

Table 4 – Physical properties of cements

Cement	Blaine fineness, m^2/kg	Normal consistency, %	Compressive strength in mortar, MPa, at the age of			
			1 day	3 days	7 days	28 days
LC3	685	31	7.3	23.4	34.2	40.1
PPC	322	30	7.4	18.6	31.7	57.9

The Blaine fineness of LC3 is significantly higher in comparison with PPC, though mean particle size is similar (see Tables 3 and 4). The Blaine fineness of the cement is influenced by the material characteristics and the comminution system adopted. Calcined clay and the limestone are vastly different from clinker and fly ash as far as the material hardness and grinding efficiency is concerned. In general, the mean size of cements was similar, though d50 of LC3 was significantly lower as compared to PPC. The normal consistency of LC3 and PPC are in a close range of 30–31% despite the fact that LC3 Blain fineness level is more than the double of PPC.

The compressive strength of the mortar cubes of all cements are shown in Table 4. One day strength of all the cement are in a very close range. However 28 day strength of LC3 is remarkably low in relation to PPC. This may be contributed to lower clinker concentrations. The LC3 exhibited early strength development up to 7 days and the development between 7 days to 28 days was lower in comparison with PPC.

The compressive strength development from 7 to 28 days of LC3 is 15% of 28 days strength whereas, it is 46% for PPC. The hydration kinetics is closely linked with the intrinsic material characteristics. In the case of fly ash, the products of hydration closely reassembles calcium–silica hydrates produced by hydration of Portland cement. However the reaction does not start until sometimes after mixing. In the case of fly ash class F, this can be as long as one week or even more. The glass material in fly ash is broken down only when the pH value of the pore solution is at least about 13 [18]. The strength recovery of PPC from 7 days to 28 days is much higher than in relation to LC3.

The lime reactivity of calcined clay was much higher than fly ash resulting in higher demand of Portlandite (CH) availability in the hydration system. The LC3 cement exhibited higher one day strength and higher recovery of strength from 1 to 7 days in comparison with PPC. The higher rate of reactions with available pore solution resulted in total consumption of Portlandite generated in system. This could cause availability of unreacted calcined clay. Pozzolana cement resulted in lower growth or lower strength recovery from 7 to 28 days. Reaction of alumina and calcium carbonate with the progress of hydration process of LC3 is possibly contributing to improved early strength of LC3 up to 7 days in comparison with PPC.

4.2 Hydration behavior

The isothermal (heat conduction) calorimetry is an efficient tool to study the stages related to the hydration of cement pastes or mortars at constant temperature. The calorimeter continuously measures and displays the heat flow related to the hydration reactions taking place in the cement paste after mixing. The respective cement was studied for heat liberation using conduction calorimeter at a w/c ratio of 0.40. The heat flow curve and the total heat liberation curve are shown in Fig. 2 along with that of PPC. The heat liberated at different age are given in Table 5.

It has been observed that LC3 hydrated faster with heat liberation almost double when compared with PPC. However, the same tapers down after144 hours without significant gains till 28 days. PPC catches up and surpasses LC3 at 28 days. This is in agreement with compressive strength development of the two cements.

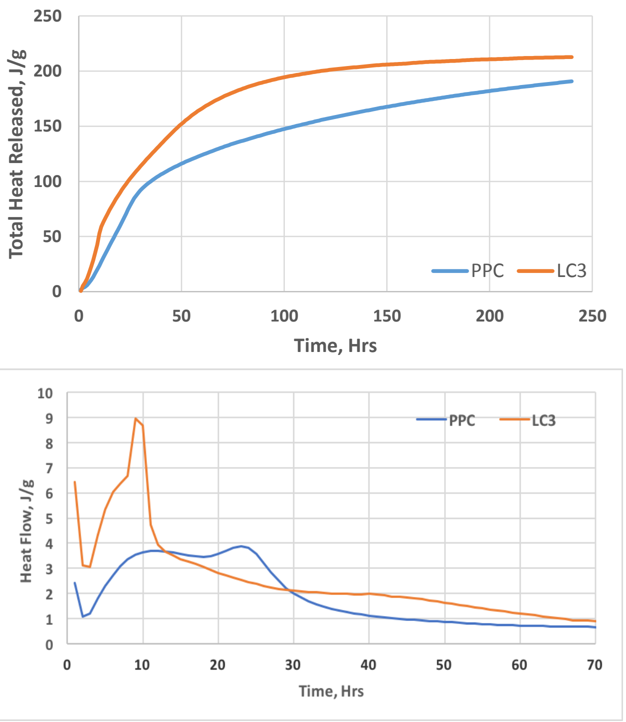

Fig. 2 – Total heat released and heat flow of LC3 compared with PPC

Table 5 – Heat liberated for LC3 and PPC at different age

Heat liberated, J/gram of cement	Time, hours			
	24	72	144	672
LC3	100.1	178.2	205.1	215
PPC	68.3	142.3	165.8	230.4

4.3 SEM analysis of hydration products

Changes with time in the morphology and nature of the hydration products of LC3 cement, at water to cement ratio of 0.5, were studied by scanning electron microscope. The microstructure was observed at different intervals of hydration: i.e. 1, 3, 7, and 28 days. The samples were studied in both fractured surface and polished section using SE and BSD at variable pressure mode. The hydration products such as calcium silicate hydrate (C-S-H), portlandite (CH), ettringite (AFt), monosulfate (AFm), C-S-A-H, limestone particles, and deleterious materials like quartz and feldspar were observed. The initial products at 1 day of hydration are amorphous looking like fibrous shape. These products mainly appear on the surface of the unhydrated grains, filling in void space as they grow. Fibrous like C-S-H having size <200 nm, CH, Aft, and AFm phases appear more at 1 day.

Interlocking structure of C-S-H and rod like ettringite appear at 3 days. During the first 7 days of

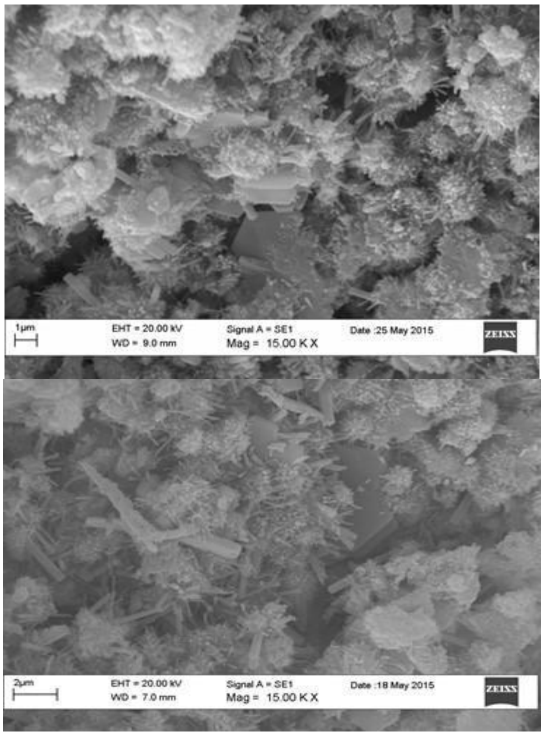

Fig. 3 – Morphology of hydration products at 1 days

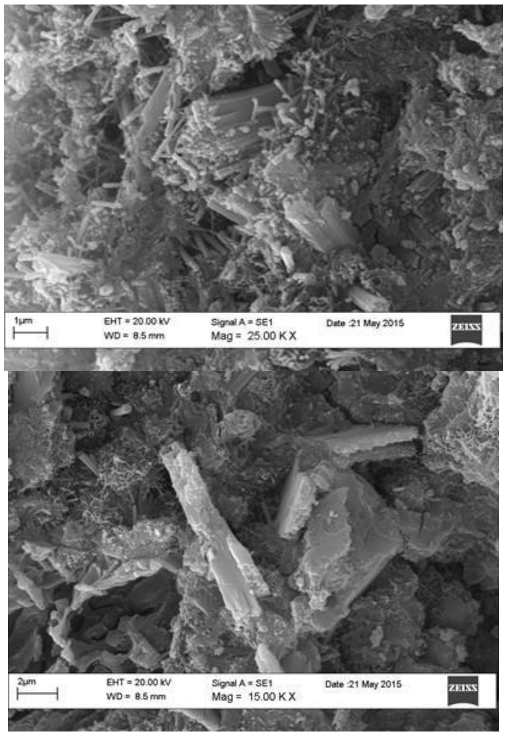

Fig. 4 – Morphology of hydration products at 3 days

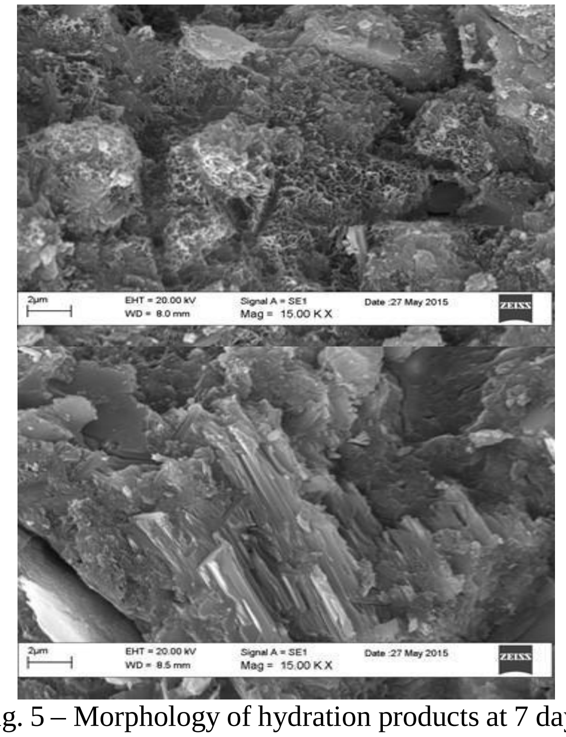

Fig. 5 – Morphology of hydration products at 7 days

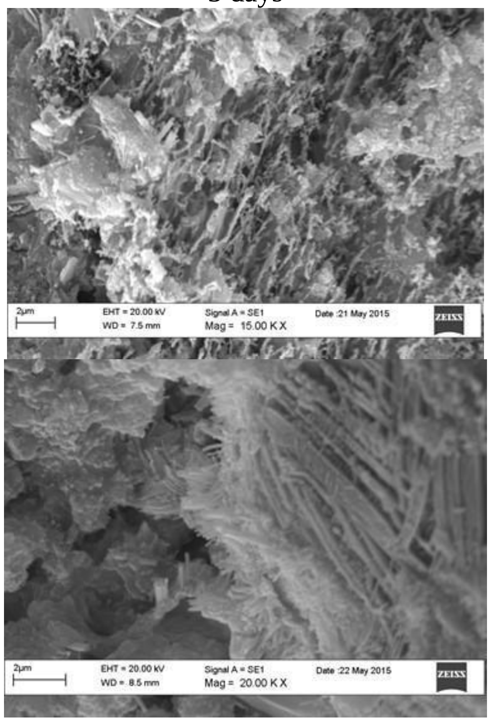

Fig. 6 – Morphology of hydration products at 28 days

hydration, the surface of the C_3S grain are covered by the radiating fibrous particles of C-S-H,honeycomb structure, and interlocking space between the grains.

As time of hydration increased, the fibrous structure developed into a needle like C-S-H at 28 days. At 28 days hydration, the paste displayed a massive tabular structure with platy with occasionally fibrous hydration products. The morphology of C-S-H is similar at 3 and 7 days.

Both type I and II C-S-H were observed in all the hydration period. The size of C-S-H increased form 200 nm to 1.5 micron as the hydration period in creased from 1 to 28 days. The morphology of ettringite also changes from needle to rod like structure as the hydration period increases. Limestone particles are frequently present at all the ages indicating incomplete reaction with cement particles. The amount of AFm and CH also decreases as hydration period increases.

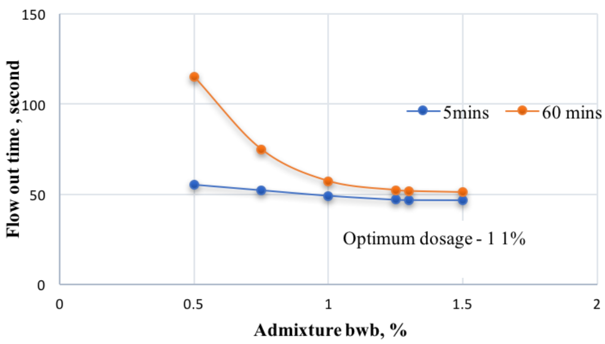

Fig. 7 – Flow behavior of LC3

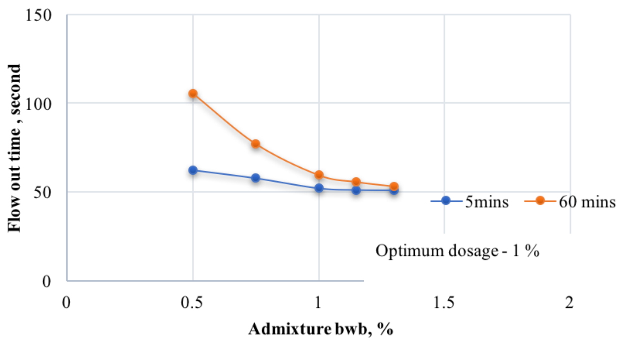

Fig. 8 – Flow behavior of PPC

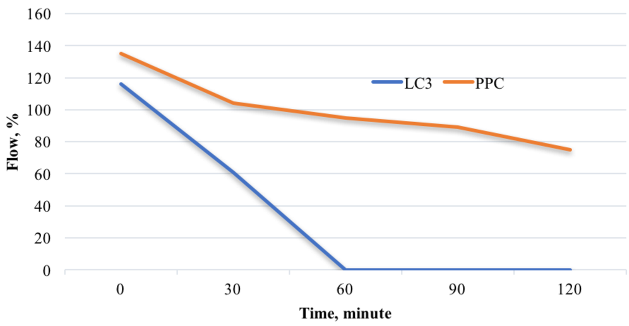

Fig. 9 – Flow retention of cement pastes

4.4 Porosity of cement pastes

The porosity of cement paste composed with LC3 and PPC with ratio of water to cementitious material 0.4 was determined using mercury intrusive porosimeter, both in terms of inter particle and intraparticle porosity [19]. The results are listed in Table 6. It is observed that hydrated LC3 paste has lower porosity in comparison with that of PPC. The total porosity of LC3 paste is 0.92% against 1.13% of PPC.

4.5 Admixture demand of cement paste

Admixture compatibility of cements, tested with common admixture showed that the optimum dosage for LC3 was 1.4%, while it was 1.0% for PPT. The flow behavior of cement paste showed that LC3 has higher admixture demand, almost 40% higher as compared to binary blend cements PPC

Table 6 – Porosity of cement paste by MIP

Cement	Porosity, %		
	Interparticle	Intraparticle	Total
LC3	0.844	0.074	0.918
PPC	1.248	0.087	1.133

(see Figs. 7 and 8), even though the water demand for normal consistency was similar. This may be due the higher fineness of LC3.

4.6 Retention of flow

Retention of flow of cement paste shows that LC3 has a low initial flow and poor retention as compared to PPC (see Fig. 9). This may be due to fine limestone powder and higher fineness of LC3.

5. Conclusions

This study observed that the limestone calcined clay cement behaves differently as compared to commercially available fly ash based blended cement. The compressive strength development of limestone calcined clay cement is also different to fly ash based blended cement in terms of low improvement at later ages. The hydration behavior shows a distinct difference in terms of high heat evolution at early age, unconventional of blended cements. Not only the cement paste has a high water demand, resulting in lower workability, but also it needs higher dosage of superplasticizers, if used. Porosity of LC3 cement paste is lower than that of PPC paste showing an improved durability.

Acknowledgements

The paper is based on the study at Central R&D of UltraTech Cement Limited at Taloja Centre, under the leadership of the authors. Acknowledgements are due to all scientist who have contributed to the study in one or another way. Dr. Suresh K., Dr. Mohan Medhe, Dr. Narendra Kumar, Manish Kuchya, Er. Sandeep Keskar, Dr. Arunachala Sadangi need special mention for analytical support.

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