Blended Cement Using Calcined Clay and Limestone for Sustainable Development—A Review

Ranjan Abraham, T. R. Neelakantan, Ramesh Babu Chokkalingam, and Elson John

Abstract In the cement industry, the use of pozzolanic materials is attaining paramount interest due to their beneficial effect on various properties of cement. Many type of cement have been developed in the last two decades to meet specific requirements. Ternary cement is one such type of modern cement, which consists of two pozzolanic materials with ordinary clinker. Blending reduces overall clinker content in cement. Ternary cement saves cost, resources and energy. Further, they reduce emissions & wastage of raw materials. Partially replacing clinker by calcined clay combined with limestone can be adopted to achieve blended cement with good performance. Higher levels of clinker substitution up to 50% are possible with 30% calcined clay, 15% lime stone and 5% gypsum, which contribute to reduction of CO_2 emission associated with cement production. Previous studies on such replacements and how they were beneficial for sustainable development are summarized in this review paper.

Keywords Blended cement · Supplementary cementitious materials · Sustainability · Calcined clay · Limestone · CO_2 emission

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1 Introduction

The use of Supplementary Cementitious Materials (SCM) has a large potential to reduce the emission of carbon and saving the consumption of raw materials used for cement production. This is highly beneficial, especially for developing countries like India. But the wider use of SCMs is not supported due to a limited supply of them in many countries. More than 80% of SCMs used to reduce clinker fraction in cement are limestone, fly ash or slag. Calcined clay in combination with limestone has immense potential to be used as supplementary cementitious material, in partial replacement of clinker [1].

This paper concentrates mainly on the studies on Limestone Calcined Clay Cement (LC3), which focuses on reactive kaolinitic clays. Amount of slag available worldwide is around 5–10% of the amount of cement produced, which is not likely to change, as demand for steel is increasing less rapidly than demand for cement and more steel is being recycled, due to environmental aspects. Amount of fly ash available is somewhat high, but quality is very much variable, with less than one third suitable for blending in cement [2]. Long term availability of fly ash cannot be ascertained, as burning of coal to produce electricity is not entertained in most countries, to reduce environmental emissions.

Even though limestone is available in abundance, addition of more than 10% of limestone alone to cement results in increased porosity and poorer properties [3]. To extend the strategy of reducing clinker content, identification of new types and sources of SCMs have become essential. Even though Rice husk ash, sugar cane bagasse ash and ashes of other agricultural wastes are pozzolanic, scattered distribution leads to economic viability of their use.

Clays are abundantly available worldwide. Clays having significant portion of kaolinite and calcined between 700 and 850 °C are highly pozzolanic [4]. Metakaolin, a very reactive mineral addition, has been produced by calcining high purity kaolinitic clays. Metakaolin is around 3 times costlier than cement, which makes it not feasible for production of general purpose cement.

Studies conducted at Ecole Polytechnique Fédérale de Lausanne (EPFL) [5, 6] proved that a kaolinite content of about 40% in a mixture of LC3-50 (50% ground clinker, 30% calcined clay, 15% limestone, 5% gypsum) could produce mechanical properties similar to reference plain Portland cement sample in 7 days. Clays are widely available in most developing countries where cement demand going to increase in future. The requirement of calcination makes clay costlier than slag or fly ash. But unavailability of slag and fly ash in many places makes it viable and high level of clinker substitution is possible by combination of calcined clay and limestone and exhibit similar mechanical properties of pure Portland cement [7]. Low cost of limestone balance the cost of calcination of clay. Industrial production of cement having 50% clinker, combined with a blend of calcined clay and limestone has proven successful through industrial trials carried out in Cuba and India. Cements produced had mechanical performance similar to Portland cement, with clinker content above 90% [8–10].

2 Technology

Clay is calcined by heating to around 700–850 °C. No sophisticated equipment is necessary to produce calcined clays, since calcination temperature is low, compared to clinker production. Coupled addition of calcined clay and limestone is used to substitute part of clinker in blended cement and are designated LC3—X, where X refers to the clinker content of blend in percent. Calcination of clay containing kaolinite leads to formation of metakaolin, which is an amorphous alumino silicate ($Al_2Si_2O_7$). It can react with calcium hydroxide as a conventional pozzolan to give C–(A)–S–H and aluminate hydrates. In addition, alumina can react with limestone to produce carbo-aluminate hydrates [7]. All these products fill space and contribute to development of strength and durability properties. Clays containing 40% or above kaolin give strengths comparable to plain Portland cement when used in LC3-50 (50% clinker, 30% calcined clay, 15% limestone and 5% gypsum). The coupled substitution of two materials leads to good mechanical performance than other pozzolan at early ages even under higher levels of substitution. Clay, which is a finely divided product, reacts faster and to a higher degree.

Trial production runs of LC3 have been made in Cuba and India [8–10] where cement could be substituted one for one in standard applications by untrained workers, with similar water cement ratios and super plasticizers. In India it was used for preparation of roof tiles, which showed higher breaking strengths than tiles made with the usual Portland fly ash cement. In Cuba, the cement was used in blocks and pre-cast concrete culverts. The technology proved to be robust under situations like usage in poor and remote regions, by unskilled workers, lack of control of aggregate quality, poor control of water content, use without admixtures, usage under hot climate and precast constructions where high early strength is required. Studies are yet to be done in areas of stability of workability at high temperature and sensitivity to common contamination.

Calcined clay has high fineness, which is worsened if it is inter ground with clinker, which may cause higher water demand, or require higher levels of super plasticizer. Ideally the clinker should be ground first and then blended with calcined clay and limestone. As calcined clay contains reactive alumina, it is also important that blends are properly sulfated by checking level of sulfate addition needed using isothermal calorimetry [7].

3 Strength of LC3 Blends Prepared from Low Grade Clays

Potential of blends based on limestone, calcined clay, and clinker (LC3), incorporating calcined clay from several countries (India, Brazil, Thailand and Cuba) were analyzed [1] and strengths obtained are shown in Fig. 1. Plotting these results against the kaolinite content of clays, it was seen that kaolinite content is the main parameter determining strength development and is shown in Fig. 2. In these experiments

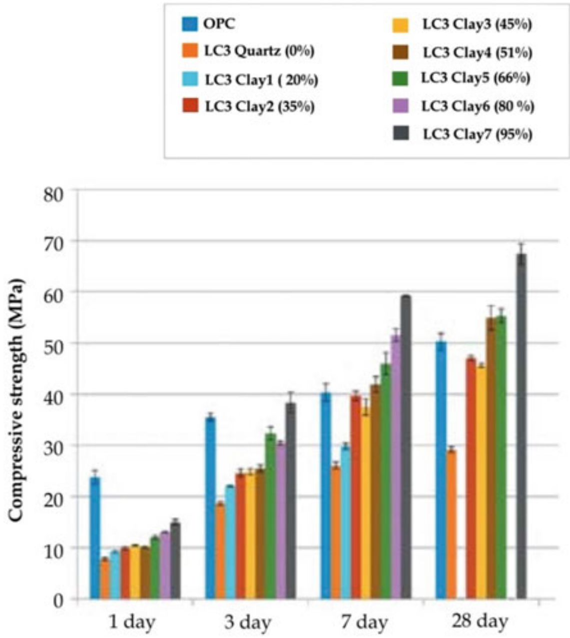

Fig. 1 Strength development for a range of blends all containing 50% clinker, 5% gypsum, 15% limestone and 30% calcined clay. (Clays originated from India, Brazil, Thailand and Cuba) [1]

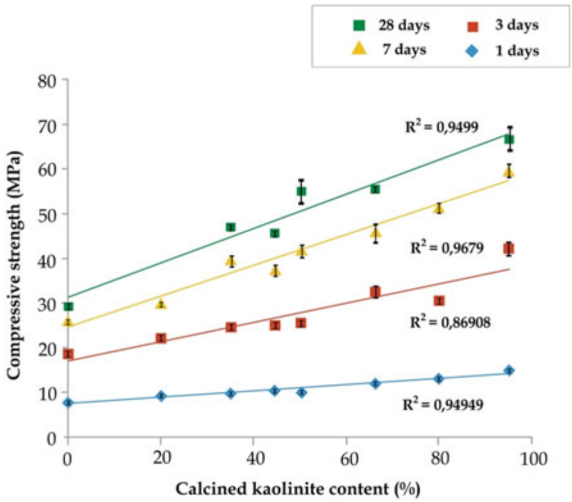

Fig. 2 Relationship between kaolinite content of calcined clay and strength [1]

cements were prepared by intermixing based on the same ground clinker. It could be seen that one day strengths are still rather low, but, for a kaolinite content of 50% or more, higher strengths than the reference were achieved by 7 days after testing Mortar cubes. One day strength could be improved by inter-grinding as is currently done for fly ash blended cements.

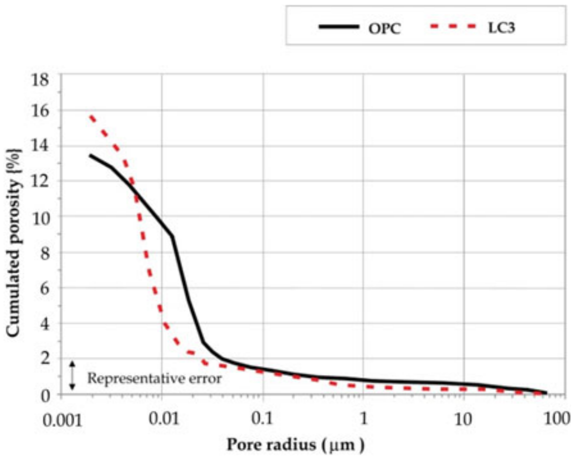

Fig. 3 Mercury intrusion porosity of results for LC3 blend and reference Portland cement [1]

4 Durability of LC3 Blends Prepared from Low Grade Clays

While considering a new cement formulation, question of durability is of prime importance. A wide-ranging and detailed study of durability of LC3 was done in Switzerland, India and Cuba. Mercury intrusion porosimetry and Chloride penetration tests were done to assess durability. Those studies looked at underlying scientific mechanisms as well as full scale exposure conditions. The material is expected to have good durability due to following reasons.

Firstly, the phase composition of materials was very similar to existing Portland and blended cements. The principal hydrate was calcium silicate hydrate, C–S–H, whose long-term behaviour is well known and understood. Other aluminate containing phases, mono and hemi carbonate and ettringite were also formed in limestone cements, widely used in Europe for many years.

Secondly, analysis of pore structure shown in Fig. 3 revealed that, pores were smaller, even though overall porosity was be slightly higher [1].

Thirdly, preliminary results on resistance to penetration of chloride ions are extremely good. Figure 4 shows chloride profiles after two years ponding in 0.5 M NaCl solution [1].

5 Environmental and Economic Potential

Developing countries demand increased need of infrastructures and production of more quantity of cement. Use of SCM is a promising solution to increase cement production without increasing negative environmental impact.

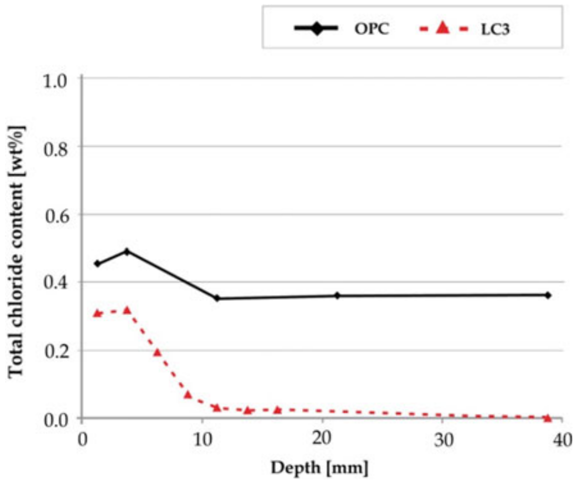

Fig. 4 Chloride profiles after 2 years ponding in 0.5 M NaCl solution [1]

A method was developed to assess details of economic and environmental potential of LC3 technology in Cuban context, in which a comparison of OPC and PPC was done. Study included a sensitivity analysis where different types of technology as well as alternative fuel types have been tested. Sensitivity of green house gas emissions savings for LC3 production was evaluated depending on level of technology, fuel and transport type [11]. Results, shown in percentages saved and tabulated in Table 1, provided data for development of LC3 technology in the Cuban market, which can be further extended to markets in other developing countries.

Technology changes induce variations from 6 to 10% depending on type of fuel used. Changes in fuel types do not provide great changes in Global Warming Potential (GWP) except when a flash calciner was used for LC3 and a preheater + pecalciner kiln was used for clinker production. Similar results were found when comparison of LC3 was made over OPC or PPC. Savings compared to OPC were around 35% while savings compared to PPC were around 25%.

Availability of suitable clay source was also a key aspect in LC3 production process. When clays were transported by truck over 350 km, economic benefits of LC3 against OPC were less. Figure 5 shows results of sensitivity of raw materials transport of LC3 compared to current OPC production costs in Cuba. If raw material transport was done by train, contribution to overall negative environmental impact of LC3 was negligible.

Comparison of environmental impact for OPC, blended cement PPC and LC3 for three different technical levels: Pilot, Industrial and Best Available Technology (BAT) are shown in Fig. 6. LC3 cement always produced 30% savings approximately. Worst LC3 cement made in pilot industrial trial was better than best OPC produced with BAT. Major emission reductions were related to energy savings and clinker substitution, although there reported a significant decrease in electricity consumption during grinding process, due to softness of LC3 in comparison with OPC.

Table 1 Economic impact sensitivity to fuels & technology [11]

GWP savings comparing PPC-LC3 (%)					GWP savings comparing OPC-LC3 (%)				
Fuels/techno	Wet (%)	Dry (%)	BAT (%)	BBAT (%)	Fuels/techno	Wet (%)	Dry (%)	BAT (%)	BBAT (%)
Crude	26	24	24	34	Crude	36	35	35	42
Petcoke	24	25	23	33	Petcoke	36	36	32	40
Gas+ Waste	26	26	25	20	Gas+ Waste	37	36	33	27

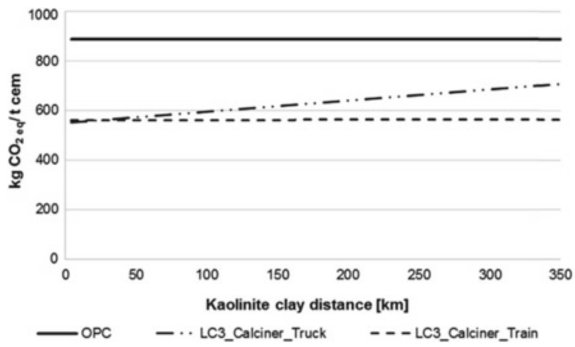

Fig. 5 GWP Comparison per transported tonne of cement [11]

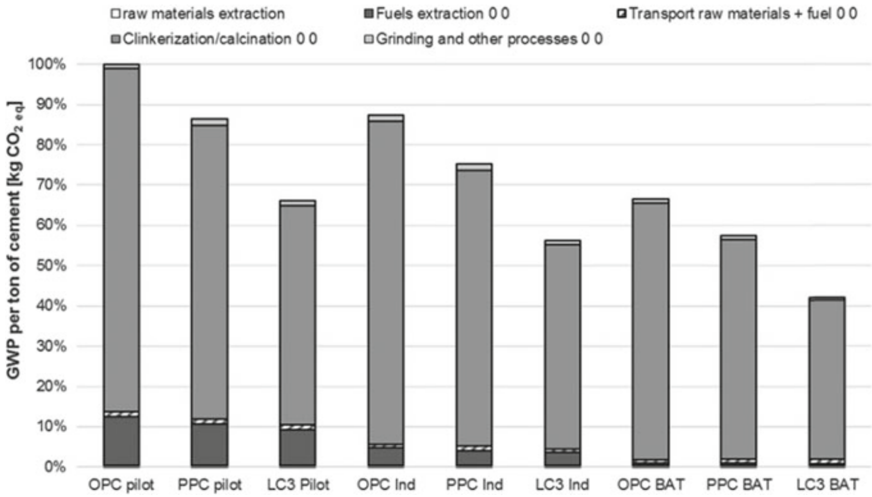

Fig. 6 Relative GWP impact of cement production in Cuba—all scenarios [11]

Concerning economic feasibility of LC3 production, an analysis was carried out and cost savings referred to OPC and PPC are presented in Fig. 7.

Sensitivity to fuel and technology showed a different pattern than environmental sensitivity. Variation in term of production costs was higher than for GWP when differences in technology were considered. It varied from 10 to 30% depending on technology and type of fuel used. Using BAT technology for clinker production as well as clay calcination (BBAT Technology) could induce higher production cost for LC3 when secondary fuels were used in the clinkerization process.

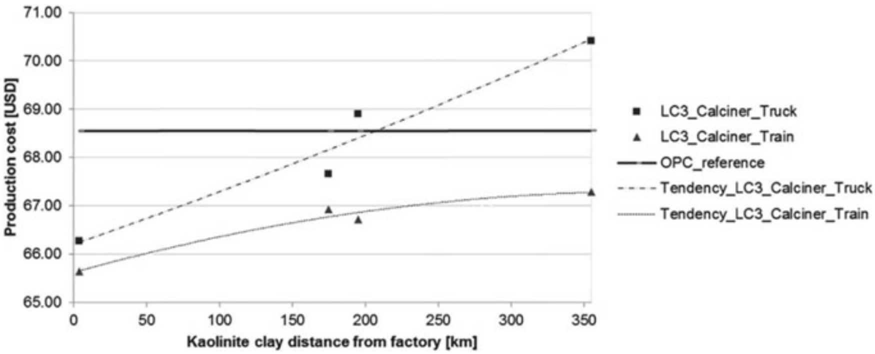

Fig. 7 Comparison depending on transport distance and cost of alternate materials [11]

6 Conclusions

- Blends with 50% clinker, 30% calcined clay, 15% unburned limestone and 5% gypsum is a promising option to achieve energy efficiency, cost efficiency and lower CO_2 emission
- Kaolinite content in clay is the main parameter determining strength development.
- The phase composition of materials was very similar to OPC and PPC.
- The size of pores was smaller compared to PPC, when LC3 was used.
- LC3 offered extremely good resistance to penetration of chloride ions.
- LC3 technology leads to reduced greenhouse gas emissions and lower global warming potential compared to OPC and PPC.

References

1. Scrivener KL (2014) Options for the future of cement. Indian Concr J 88(7):11–19
2. Snellings R (2016) Assessing understanding and unlocking supplementary cementitious materials. RILEM Tech Lett [S.l.] 1:50–55
3. Matschei T, Lothenbach B, Glasser FP (2007) The role of calcium carbonate in cement hydration. Cem Concr Res 37(4):551–558
4. Fernandez R, Martirena F, Scrivener KL (2011) The origin of pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite. Cem Concr Res 41(1):113–122
5. Alujas A, Fernández R, Quintana R, Scrivener KL, Martirena F (2015) Pozzolanic reactivity of low grade kaolinitic clays: influence of calcination temperature and impact of calcination products on OPC hydration. Appl Clay Sci 108:94–101
6. Avet F, Snellings R, Alujas Diaz A, Ben Haha M, Scrivener K (2016) Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. Cem Concr Res 85:1–11
7. Antoni M, Rossen J, Martirena F, Scrivener K (2012) Cement substitution by a combination of metakaolin and limestone. Cem Concr Res 42:1579–1589

8. Vizcaíno-Andrés L, Sánchez-Berriel S, Damas-Carrera S, Pérez-Hernández A, Scrivener K, Martirena Hernandez JF (2015) Industrial trial to produce a low clinker, low carbon cement. Mater Constr 65:(317)
9. Bishnoi S, Maity S, Mallik A, Joseph S, Krisnnan S (2014) Pilot scale manufacture of limestone calcined clay cement: the Indian experience. Indian Concr J 88(7):22–28
10. Emmanuel A, Halder P, Maity S, Bishnoi S (2016) Second pilot production of limestone calcined clay cement in India: the experience. Indian Concr J 90:57–64
11. Sanchez Berriel S, Favier A, Rosa Domínguez E, Sanchez Machado IR, Heierli U, Scrivener K, Martirena Hernandez F, Habert G (2016) Assessing the environmental and economic potential of Limestone Calcined Clay Cement in Cuba. J Clean Prod 124:361–369