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LIMESTONE CALCINED CLAY CEMENT FOR A SUSTAINABLE DEVELOPMENT

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Abstract

With cement production forecast to double by 2050, it is bound to increase pressure on the already fragile environment and the natural resource base. Critical analysis shows that the most viable option to improve the sustainability of cementitious materials are blends of Portland cement clinker with, so called, supplementary cementitious materials, SCMs.

Based on previous experience we have shown that cements with good strengths at early ages may be obtained by substituting clinker with a combination of calcined clay and limestone. Such blends offer a very promising solution for cements with a lower environmental footprint, particularly in terms of associated CO_2 emissions. In this paper, some initial results on chemistry, strength development and durability are presented.

The calcination of clays was known to give pozzolanic reactive material. The most reactive clay mineral is kaolinite, obtained after calcination between 600 and 800 °C. Therefore, the blending with calcined clays containing kaolinite provides an extra source of alumina to react with limestone. It was found that even low grade clay containing only around 40% kaolin gave good results when used in combination with limestone.

The low carbon cement developed is expected to reduce CO_2 emissions by 20-50%. Experimentation is ongoing to explore the potential of using low quality clay, which are available in large quantities in various places in many countries. These studies are expected to produce localized cement without the need to transport materials over long distances. It is envisaged that low carbon cement will be a much sought after commodity contributing to a sustainable development.

Keywords:
Limestone; calcined clay; cement; CO_2 emissions

1 INTRODUCTION

Concrete and Portland cement are essential building materials for society's infrastructure around the world. Although concrete based on Portland cement is a material with an intrinsically low environmental impact, the huge volume produced means it is responsible for large emissions of greenhouse gases (such as carbon dioxide) [1].

How can we reduce the environmental impact of the cement manufacture? The long term approach to lower the environmental impact of any material is to reduce its consumption. For several reasons, including population growth, the rate of concrete consumption probably cannot be reduced for some decades. In the short term, several solutions have emerged, such as blended cements in which Supplementary Cementitious Materials (SCMs) substitute a part of the Portland cement. Table 1 presents the most common blending materials and their estimated annual production level.

SCMs	Estimated annual production level	Availability
Ground blast furnace slag	200 million tonnes (2006)	Future iron and steel production difficult to predict
Fly ash	500 million tonnes (2006)	Future capacity of coal- fired

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		power plant difficult to predict
Natural pozzolans, silica fume	300 million tonnes (2003) but only 50% used	Depends on local situation
Artificial pozzolans (calcined clay)	Unknown	Depends on local situation
Limestone	Unknown	Readily available

Table 1: Production level and availability of the most common supplementary cementitious materials adapted from CSI/ECRA technical reports [2].

In spite of the successful development of blended cements, the increase in the level of SCM substitution is slowing down because of a slow strength development at an early age and the limited supply of well-established SCMs such as fly ashes or slags. It is why we must move towards the use of other SCMs with extensive reserves worldwide.

Clays, especially low grade clays seem to be a good alternative SCM. In India, our experience [3] has shown important widespread availability of low grade clays in existing quarries. To be reactive, these clays must be calcined at around 700°C to 800°C [4].However, this range of temperature is much lower than 1450°C needed for clinkerization, hence consuming less fuel. Furthermore, recently, it has been shown that by making a coupled substitution of calcined clay with limestone, 50% of clinker can be replaced by limestone and similar mechanical performance to Portland cement maintained, so the extra saving of clinker can offset the cost of calcination. Further important advantages of LC^3 technology are:

- Cheaper or similar production costs [5]
- Low investments costs [5]

The potential for ternary blends of limestone, calcined clay and clinker, which we call LC^3 (limestone calcined clay cement) has been demonstrated in the collaborative research between the Laboratory of Construction Materials (LMC) at EPFL, Switzerland, and CIDEM in Cuba [6].

2 RESEARCH AND DEVELOPMENT OF L^{C3}

2.1 How LC^3 works?

Portland cement is essentially composed of clinker, gypsum and additions. Clinker is very reactive in the presence of water; it reacts according to the equation below (1):

$$C_3S + 5.3H \rightarrow C_{1.7}SH_4 + 1.3CH \quad (1)$$

(C: calcium oxide, S: silicon oxide, A: aluminium oxide, CH: calcium hydroxide, H=water)

This reaction (1) is the main, but not exclusive reaction that occurs during the hydration of cement. It produces the calcium hydroxide, which reacts with pozzolans such as calcined clays. Pozzolans are usually rich in silica in the presence of calcium hydroxide and water reacts according to the following equation (2):

$$S + 1.5CH + 2.8H \rightarrow C_{1.5}SH_{2.8} \quad (2)$$

On the other hand, the calcium carbonate (Cc = limestone) reacts differently. Several studies [7,8] have established that limestone additions up to 5% can react with cement. Indeed, limestone reacts with alumina to form hemi-carboaluminate and mono-carboaluminate phases as in equation (3):

$$A + Cc + 3CH \rightarrow C_3A.Cc.H_{11} \quad (3)$$

This reaction (3) is enhanced by the presence of extra alumina coming from calcined clays. This synergetic effect was demonstrated in the past with fly ashes[9] and also verified by Antoni *et al* [6] in the case of calcined clays.

2.2 Performance of LC3

The interactions between the three different components previously described have been studied in depth at the lab scale.

It was shown [10] that the level of sulphate addition has an important effect on the early strengths of the LC^3.

Further investigations were done to assess the potential of LC^3, blends incorporating calcined clays from several countries were analysed. Fig. *1* shows the strengths obtained as a function of kaolinite content. It can be observed that kaolinite content is the main parameter determining compressive strength development. Moreover, all LC^3 mixes with kaolinite content up to 40% showed higher strength than normal Portland cement 42.5 grade (dotted lines in Fig. *2*).

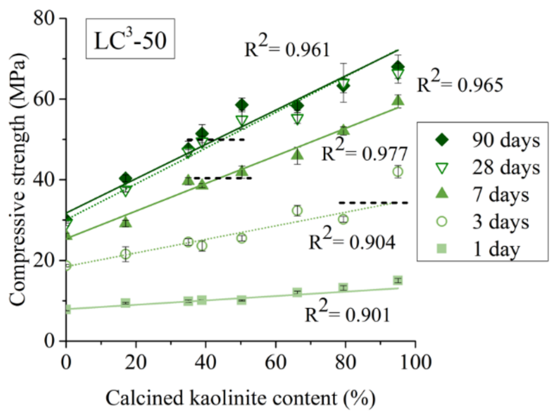

Fig. 1: Relation between kaolinite content which is calcined and the compressive strength from [11]. *The dotted lines represent the strength of pure Portland cement at 3 days, 7 days and 28 days.*

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In practice, the very early strength (1-3 days) can be improved by a better optimization of process parameters such as grinding; using finer clinker can permit an important increase in early strength.

The same experiment was carried out for different grades of limestone and showed that the quality of limestone does not play an important role in the development of strength.

Durability remains a key question when considering a new cement formulation. A large range and detailed studies were carried out in EPFL, Cuba and India. These studies can help us better understand the involved physical and chemical mechanisms from the cement paste to the full scale structure. Although, it is early days and research is ongoing, preliminary results indicate that these materials have an equivalent or even better durability than Portland cement.

First, the phases present are the same as found in Portland cement or other blended cements, already widely used worldwide.

Second, as other blended systems [12–14], this material presents a refinement of porosity[10]. The pores are smaller even though the overall porosity may be similar or slightly higher (Fig. *2*).

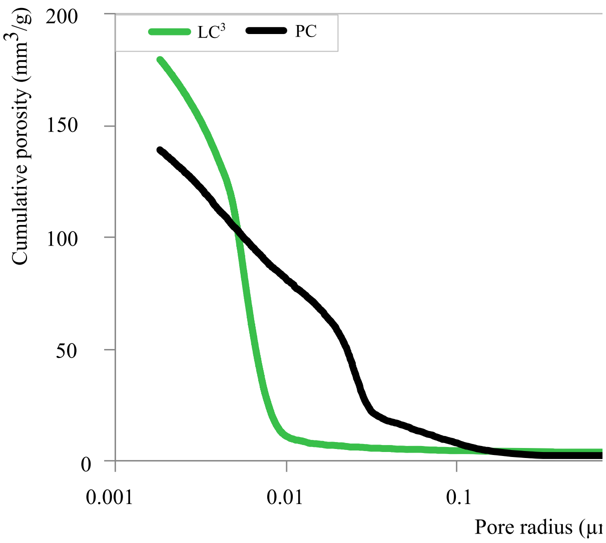

Fig. 2: Mercury Intrusion Porosity results for LC^3 (with 80% calcined kaolinite) blend and reference Portland cement PC.

Third, the work in progress on the resistance to sulphate penetration, chloride penetration or alkali silica reaction is encouraging. For example, preliminary results on resistance to chloride ions penetration shown in Fig. *3* are extremely good.

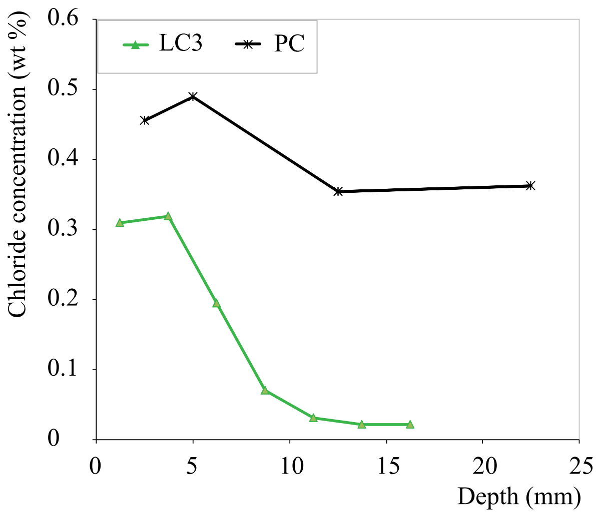

Fig. 3: Chloride profiles after 2 years ponding in 0.5M NaCl.

First results on carbonation tests tend to demonstrate that a longer curing of materials can be needed to assure the same resistance to carbonation than PC. However, performance was good for most applications.

3 FROM LAB SCALE TO INDUSTRIAL SCALE

To position itself as a potential large scale solution, the ternary blend material LC^3 must compete with materials already on the market.

After successful laboratory results, the technical feasibility was assessed using existing equipment in a cement plant.

In 2013, in Cuba, an industrial trial of 130 tons proved the feasibility of this cement with current technology. This cement was then distributed to companies of prefabricated construction materials. These companies have been able to make the same elements as with Portland cement (see *Fig. 4*).

a)

b)

Fig. 4: Prefabricated elements with LC3 cement produced in Cuba, Siguaney a) hollow concretes blocks b) hydraulic tiles (courtesy of F. Martirena)

More recently in India, a collaborative work by Technology and Action for Rural Advancement (TARA) and Indian Institute of Technology Delhi[3] showed that the ternary blend cement LC^3 could be produced in large quantities. Several tons of four different LC^3 cements containing two limestones and two clays with different quality have thus been produced. These cements have been used for producing premanufactured elements such as concrete roofing tiles, hollow concrete blocks, door and window frames and paving blocks. These elements composed a demonstration house in Madhya Pradesh (India) presented in *Fig. 5*.

Fig. 5: Demonstration house made with ternary blend cement LC3 in Madhya Pradesh, India.

4 CONCLUSION

Housing shortage is a critical issue in most developing countries and concrete is the only well suited building material to face this challenge. However, due to this huge demand, the environmental impact of concrete is not negligible. For many years now, researchers and industrial studied and developed new cements to reduce its CO_2 footprint.

To be viable, the new solutions must be abundant, affordable and adapted to local requirements in developing countries.

The Limestone - Calcined clays - Cement LC^3 attempts to answer these three criteria. Today, this material can be produced using current technology in large scale in a usual cement plant. The components of this system especially low-grade clay and limestone are largely affordable and available everywhere. Moreover, the ternary blend promises to compete with other commercial solutions in terms of performance and durability.

Research on this technology is already been undertaken by several cement producers around the world.

Of course, more work on the scientific and engineering basis is required. A network of researchers from India, Cuba and Switzerland funded by the Swiss Agency for development and Collaboration makes this possible. We hope to expand this network to improve and complement the knowledge on this material to see it appear on the market as quickly as possible.

5 ACKNOWLEDGMENTS

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