Calcined clay limestone cements (LC³)

Karen Scrivenera,*, Fernando Martirena, Shashank Bishnoic, Soumen Maityd

a EPFL, Switzerland
b UCLV, Cuba
c IIT Delhi, India
d Development Alternatives, Delhi, India

ABSTRACT

The use of supplementary cementitious materials (SCMs) to replace part of the clinker in cement is the most successful strategy to reduce CO₂ emissions in the global cement industry. However, limited supplies of conventional SCMs make it difficult to take this strategy further unless new types of SCMs become available. The only type of material available in the quantities needed to meet demand is clay containing kaolinite, which can be calcined to produce an effective SCM. Such clays are widely available in countries where most growth in demand for cement is forecast.

Calcined clays have previously been used as pozzolans, but calcination makes the economics of substitution marginal in a conventional pozzolanic blend. The major innovation presented here is the possibility to make a coupled substitution of cement with calcined clay and limestone. This allows much higher levels of substitution. Blends where calcined clay is used as a pozzolan, typically have clinker contents around 65–70%. Combination of calcined clay with limestone allows higher levels of substitution down to clinker contents of around 50% with similar mechanical properties and improvement in some aspects of durability. The replacement of clinker with limestone in these blends lowers both the cost and the environmental impact.

1. Introduction

The use of supplementary cementitious materials (SCMs) has a huge potential to reduce carbon emissions and virgin resource consumption in cement production, especially for developing countries. However, the limited supply of SCMs in many countries or regions is an obstacle to wider use. Today > 80% of SCMs used to reduce the clinker factor in cement are either limestone, fly ash or slag [1]. Calcined clays, particularly in combination with limestone (LC³ technology) [2] have tremendous potential to extend the use of supplementary cementitious materials as a partial replacement of clinker in cement and concrete. This paper looks mainly at results emerging from the LC³ project (www.lc3.ch), which focusses on the most reactive kaolinitic clays. Other clay types may also provide raw materials for SCMs, this and other research on calcined clays is covered in the proceedings of the 1st International Conference on Calcined Clays for Sustainable Concrete [3]

The amount of slag available worldwide is around 5%–10% of the amount of cement produced (Fig. 1). This proportion is unlikely to increase as the demand for steel is increasing less rapidly than the demand for cement and, due to environmental pressures, more steel is being recycled. Furthermore the production of iron (and therefore slag) is concentrated in a relatively small number of countries so availability is even more limited in countries where demand for cement is increasing most. The amount of fly ash available is somewhat higher (around 30% compared to cement) but the quality is very variable with less than one third suitable for blending in cement [4]. Furthermore, with increasing pressure to reduce environmental emissions, the burning of coal to produce electricity is being questioned in many countries, so in the long term the availability of fly ash is also in doubt. Although limestone is abundantly available, the addition of > 10% of limestone alone to cement tends to result in increased porosity and poorer properties [5].

The problem of the lack of available conventional SCMs is seen in the marginal extra contribution of this strategy to CO₂ reduction seen in the 2009 study for the Cement Sustainability Initiative (CSI) of the World Business Council for Sustainable Development (WBCSD) [7].

To go further with the successful strategy of reducing the clinker factor it is essential to find new types and sources of SCMs. There are several sources of SCMs widely known and to a certain degree well studied, but their availability is not in the range of massive cement production. For example, ashes of agricultural wastes such as rice husk or sugar cane bagasse are considered pozzolanic, but their scattered

* Corresponding author.
E-mail addresses: karen.scrivener@epfl.ch (K. Scrivener), Fmartiena@ecosur.org (F. Martirena).

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generally be more costly than materials such as slag or limestone if calcined between about 700 and 850 °C [8]. For decades, a very reactive mineral addition known as “metakaolin” has been produced based on calcining high purity kaolinitic clays [9]. However, metakaolin is a product also used in the treatment of paper and in the ceramic and refractory industries, with stringent requirements on colour and purity. This means that it is typically sold at around 3 times the price of cement. Thus use of conventional metakaolin is not feasible for production of general purpose cement.

Studies at EPFL [10,11] have shown that a kaolinite content of only about 40% in a mixture of LC3-50 (50% ground clinker, 30% calcined clay, 15% limestone, 5% gypsum) is sufficient to give mechanical properties comparable to the reference plain Portland cement from about 7 days (EN 196-1 mortar bars w/c = 0.5, sand/cement = 3 [12]). A study of 46 clays from around the world (Fig. 2) has shown that there does not seem to be much impact of the secondary materials present, which typically include, quartz, other clay minerals and iron oxides.

Such clays are widely available in equatorial to subtropical parts of the world, which is where most rapidly developing countries are located and where the demand for cement is most likely to increase in the coming decades. The need to calcine the clays means that they will generally be more costly than materials such as slag or fly ash if such materials are locally available. However, such materials are not readily available in many countries. Furthermore, it has been demonstrated that high levels of clinker substitution are possible by a combination of calcined clay and limestone [13] for materials with similar mechanical properties to pure Portland cements. The very low cost of limestone then offsets the cost of calcination.

Industrial production of a cement having only 50% clinker, combined with a blend of calcined clay and limestone, has proven successful through industrial trials carried out in Cuba and India. The cements produced had mechanical performance similar to a CEM I Portland cement, with clinker content above 90% [14–16].

2. Technology presentation

2.1. Description

- Clay is calcined by heating to around 700–850 °C. Since the calcination temperature is low, compared to clinker production, no sophisticated equipment is necessary to produce the calcined clays. Clay may be calcined in conventional rotary kilns, flash calcination units, fluidized bed, roller hearth kilns or even by static calcination in tunnel or shuttle kilns normally used in the ceramic/refractory industry. All of these are standard equipment found commonly in the market.
- A coupled addition of calcined clay and limestone is used to substitute part of the clinker in a blended cement. We call such materials LC3 – limestone calcined clay cements. In the designation LC3-X, X refers to the clinker content of the blend in percent.
- When clay containing kaolinite is calcined, metakaolin is formed which is essentially an amorphous alumino silicate (Al2Si2O7), this can react with calcium hydroxide as a conventional pozzolan to give C-(A)-S-H and aluminate hydrates. In addition, the alumina can react with the limestone to produce carbo-aluminate hydrates [13]. All these products fill space and contribute to the development of properties (e.g. strength and durability).
- The reactivity of the calcined clay is overwhelmingly dependent on the kaolinite content of the clay (Fig. 2). Clays containing about 40% kaolinite or above give strengths comparable to plain Portland cement when used in LC3-50 (50% clinker, 30% calcined clay, 15% limestone and 5% gypsum). Such clays are widely distributed and, as clay is often one of the raw materials for cement production, may even be available in existing quarries of cement plants.
- Blended cement containing calcined clay and limestone can be used across a range of applications similar to other general use cement types.
- With this coupled substitution, it is possible to obtain good mechanical performance, particularly at early ages, at higher levels of substitution than other pozzolans. Because the clay is finely divided, it can react faster and to a higher degree than fly ash. Similar, levels of substitution are possible with slag, which is a hydraulic material rather than a pozzolan.

2.2. Robustness of the technology

Trial production runs of LC3 have been made in Cuba and India [14–16]. In both cases, the cement could be substituted one for one in standard applications by untrained workers with similar water to cement ratios and superplasticizers. Fig. 3 shows the preparation of roof tiles in India, a slightly higher water to cement ratio was used (0.5 compared to 0.475 for the fly ash blend normally used). Despite the slight increase in w/c, tiles made with all the trial blends had higher breaking strengths than the tiles made with the usual Portland fly ash cement. In Cuba, the cement was used in several applications, including blocks and pre-cast concrete culverts.

Table 1 summarises the robustness of the technology.

Calcinated clay may have high fineness, which can be exacerbated if it
is interground with the clinker. This may, but does not always, cause higher water demand, or require higher levels of superplasticizer. Therefore, the process of preparing and blending LC3 is important. Ideally the clinker should be ground first and then blended with the calcined clay and limestone. As calcined clays contain reactive alumina, it is also important that blends are properly sulfated [13]. The levels of sulfate addition needed may be checked by isothermal calorimetry, where the alumina peak should occur significantly after the silicate peak as in Fig. 4.

3. Durability aspects

An extensive testing program is underway, including both laboratory and natural exposure studies. The results (not yet published, but in preparation) so far indicate:

- Good protection of reinforcement
- Excellent resistance to chloride penetration
- Good mitigation of ASR with reactive aggregates
- Good performance in presence of sulfates
- Carbonation comparable to other blended cements

The phases present in LC3 cements are the same as those present in blended cements currently widely used in practice. However, there is a very high degree of pore refinement, Fig. 5 [17]. The pore threshold by mercury intrusion porosimetry (MIP) (for samples prepared with careful drying by solvent exchange) indicates the size of pores connected through the material. The kinetics of pore refinement depends on the original kaolinite content of the calcined clay. In LC3-50 blends, calcined clays with a high original kaolinite content (> 65%) give a low pore threshold radius of about 10 nm already at 3 days. By 28 days calcined clays with an original kaolinite content down to 40% give a well refined pore structure. In fact, at 28 days, all cement pastes made with calcined clays, even those with very low original kaolinite content, have a pore structure finer than pastes made with Portland

Table 1

<table>
<thead>
<tr>
<th>Is the technology suitable</th>
<th>Unknown</th>
<th>Proved possible</th>
<th>Needs further development</th>
<th>Not possible</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Use in poor and remote regions</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) By illiterate worker</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3) Lack or poor control of aggregates</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4) Poor control of water content</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5) Possible to use without admixtures</td>
<td>Yes, but great benefit from superplasticizers in some cases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6) Hot climates</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7) Stability of workability at high temperatures</td>
<td>Not studied in detail</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8) High strength at early ages (precast)</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9) Sensitivity to common contamination</td>
<td>Not studied in detail</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Examples of application of LC3: micro-concrete roof tiles in India (left) and precast concrete blocks in Cuba (right).
This pore refinement is especially advantageous with respect to chloride ingress. Chloride ingress is the main cause of durability problems of reinforced concrete due to the corrosion of the reinforcing steel it provokes. Chloride ion penetration for mortars of plain Portland cement (PC), and LC3-50 blends with calcined clays of different kaolinite content subjected to ponding in 3 wt% NaCl (ASTM C1543 [19]) for 1 and 2 years, is presented in Fig. 6 [20]. After 2 years, chlorides have penetrated right through the mortar cube made with plain Portland cement. For the LC3-50 systems with original kaolinite content of the calcined clay of 50% or above, which have only 50% clinker, the penetration depth is 10 mm or less. Measurements of the diffusion coefficient with an accelerated method [21] show that the diffusion coefficient for LC3-50 is 10 times lower than that for plain Portland cement [20]. Although Friedel’s salt is formed in these systems, the total binding capacity is not higher than in the OPC systems. The improved performance is mainly due to the refined pore structure.

Due to the lower overall calcium content, LC3 materials – as other blended cements – have less capacity to bind CO2 during carbonation. This is offset by the lower permeability, but this means that good curing is important. Fig. 7 shows the carbonation of mortars exposed indoors and outdoors at EPFL in Switzerland after 2 years.

4. Stage of development

Calcined clays have been used as pozzolanic materials for a number of years. For example, in Brazil calcined clays were used in dams in the 1960s to control alkali silica reaction [22]. In Brazil today several plants produce calcined clay for use in conventional pozzolanic blend (e.g. CEMII B/Q) [23]. In India a standard was adopted for the use of calcined clays as pozzolans in 1981, building on earlier standards for calcined products dating from 1959 [24]. Limestone is one of the most widely used SCMs as discussed in the introduction. LC3 builds these two separate technologies to allow much higher levels of clinker replacement to be reached while maintaining a similar performance to plain Portland cements (clinker > 90%).

LC3 is a new concept that have been proven in several industrial trials and materials used in buildings. Several companies are investigating these materials. It is already planned to start commercial production in Cuba and other countries in Latin America in 2018 or 2019.

Table 2 summarises the state of development.

5. Potential of scalability

The technology can be scaled easily to any capacity within the existing cement production system. The grinding and blending can be done in existing ball mills or other grinding facilities. Thus, the technology is widely known to producers of equipment for cement plants and can be adapted to any scale required.

5.1. Raw materials

Clays together with limestone are the most abundant materials in the earth’s crust. There is a large demand for pure kaolinite clays for the ceramic, refractory and paper industries. The cost of pure metakaolin is in the range 2–3 times the cost of Portland cement.

There are however abundant amounts of kaolinite rich clays which are not suitable for such applications. For instance, even low amounts of iron will give the clay a colour which means it may not be suitable in fields such as paper and cosmetics. Further, if accompanying minerals like quartz or feldspar are present, the industrial use of the material could be compromised in some applications. Clays containing kaolinite also occur in many tailings from mines and quarries. There are billions of tonnes of overburden material stockpiled around the world, especially in countries with long established ceramic industries (e.g. India and China), for example Fig. 8. Such stockpiles can potentially be reused in cement production, without having to open new quarries. Thus the quality and availability of kaolinitic clays are not an issue in the
6. Comparison with OPC

6.1. Production process

The manufacturing process of LC3 includes calcination and grinding. For calcination, a normal rotary kiln is needed similar in operating principle to rotary kilns for clinkerization. Depending upon the situation various other options of calcination can be adopted – for example flash calcination in dedicated equipment or in calcination tower, fluidised bed technology or static calcination. In Cuba, the old wet process cement kilns are being adapted to calcine kaolinitic clays. These kilns are especially interesting because at the chain section the clay dries, while the chains destroy the clumps, so no previous treatment for the clay is necessary. We have found that the method of calcination does not have much impact on the reactivity for similar temperatures and residence time. However, the calcination method will have a big impact on cost. The advantages of rotary kilns is the possibility to use low grade fuels such as pet coke or even biomass, which mean the cost of calcination can be less than that of clinker production.

Grinding can also be carried out with conventional equipment. Due to the multi-component nature of LC3, having ingredients with different hardness, separate grinding may be preferably. However, intergrinding with a twin chamber mill has also yielded reasonably good results [14–16].

6.2. Materials processing and application

The trials made in Cuba and India referred to above (Section 2.2) demonstrate that concrete can be produced from LC3 with exactly the same technology as Portland and other blended cements. The fineness of the clay, particularly when LC3 is produced by intergrinding, may result in somewhat shorter setting times, but still within the normal range encountered for cements and can be controlled with the same types of admixtures.

Issues like sensitivity to high temperature are currently under investigation. Proper sulfation is important as the reactivity of aluminate tends to increase more with temperature relative to silicates [25].

During calcination the layer structure of the clay persists to some production of LC3 materials.
extent. The hydroxyl bonds between the platy clay structures are driven off and there is a substantial reorganisation of the basic building units resulting in a highly amorphous material. The calcined clay platelets contribute to increased specific surface of the cementitious blend which may result in a slightly higher water demand in comparison to pure Portland systems. Specific surface measured following the air permeability Blaine protocol can be very high, but this equipment does not give reliable values above about 600 m$^2$/kg. However, as for the use of metakaolin in concrete [9], the same super plasticizers known to work well for existing cements have also been shown to work well with LC$^3$ materials.

Health and safety – clays are commonly used materials with no particular health and safety issues. If high amounts of quartz are present as secondary materials, precautions (such as classification or limitation of substitution levels) may be needed to avoid significant levels of potentially respirable crystalline silica.

7. Investment and cost of production

As outlined above, calcined clays can be produced in similar equipment to Portland cement with similar investment costs. Calcination temperatures are much lower (750–850 °C) than clinker (1450 °C) leading to lower energy costs. However, the major cost reduction is due to the high clinker substitution rates and the possibility to incorporate high quantities of limestone. Nevertheless, the issue of scale is also important. The cost of producing clinker drops dramatically when it is done in large plants and with the use of cheap fuel sources or use of waste materials as part of the fuel. Ideally, clay calcination needs to be done on the same scale and with the same fuels to realise savings. Furthermore, there may be issues if the clay is very wet and needs energy for drying.

Fig. 9 shows a study done for the return on capital expenditure in Cuba. Two LC$^3$ scenarios are foreseen; one considers retrofitting existing old kilns into clay calciners (LC$^3$ R) and the other based on setting up new flash clay calciners (LC$^3$ F). Both scenarios show better return on investment that the other two which are based on the existing cement mix in the country (67% OPC and 33% pozzolanic blend with natural pozzolan) (BAU) and on increasing the proportion of cement using natural pozzolans (TT, NCP), which is in any case not realistic due to low performance of the natural pozzolan blends [26].

The viability of any technology is dependent on four important factors:

- Technical viability
- Economic feasibility
- Low capital investment
- Easy availability of raw materials

The LC$^3$ technology developed fulfills all the above criteria. It has been technologically proven to produce a comparable quality to general purpose cement with comparable economic feasibility. It does not require any high investment in equipment and can easily be integrated into the existing cement production system. Moreover, all the required raw materials are available widely at comparable costs.

Thus the potential sustainability of the technology is well established compared to the existing cement types.

8. Simplified environmental assessment

A detailed Life Cycle Assessment study has been carried out for the Cuban cement industry, on a cradle to gate basis. LC$^3$-50 was compared with Portland cement having 5% limestone and Portland pozzolan cement having 15% natural pozzolan as clinker substitute. The evaluation was done for 3 scenarios: pilot production, foreseeable production scheme in Cuba and Best Available Technology [27]. Details are presented in Table 3.

Comparison of the CO$_2$ emissions for OPC, blended cement PPC and LC$^3$ for the three different technical levels: Pilot, Industrial and BAT – are shown in the Fig. 10. It is interesting to note that whatever the technological level, the LC$^3$ cement always produces around 30% savings in CO$_2$ emissions. Furthermore, it is noticed that the worse LC$^3$ cement made in the pilot industrial trial is better (in terms of CO$_2$ emissions) than the best OPC that can be produced with the BAT. Major emission reductions were related to energy savings and clinker substitution, although there is reported a significant decrease in electricity consumption during the grinding process due to LC$^3$ softness in comparison with OPC.

A detailed analysis has also been done by researchers at the Indian Institute of Technology (IIT) Madras based of real data from a number of cement plants [28]. This analysis also shows a 30% CO$_2$ emissions saving for LC$^3$-50 compared to OPC at the cement level and around 10% compared to a Portland Pozzolanic (fly ash) blend. Similar figures to the figures calculated in Cuba.

IIT Madras have also calculated figures for CO$_2$ emissions saving in concrete of 30 MPa grade and 50 MPa grade, shown in Figs. 11 and 12 [28]. In both cases the LC$^3$-50 concrete has the lowest emissions. In the 30 MPa grade case it is roughly the same as for a cement with fly ash,

Table 3

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Pilot level</th>
<th>Industrial level</th>
<th>BAT level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite clay distance (km)</td>
<td>150</td>
<td>60–150</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Type of fuel</td>
<td>Cuban crude oil</td>
<td>Pet-coke + Cuban crude oil</td>
<td>Gas + waste</td>
</tr>
<tr>
<td>Clinker technology</td>
<td>Wet rotary kiln</td>
<td>4 stage pre-heater + pre-calciner</td>
<td>6 stage pre-heater + pre-calciner</td>
</tr>
<tr>
<td>Calcining technology</td>
<td>Wet rotary kiln</td>
<td>Retrofitted calciner</td>
<td>Optimized flash calciner</td>
</tr>
</tbody>
</table>

Fig. 9. Analysis of the return on capital expenditures (ROCE) for the Cuban cement industry [26].

Fig. 10. Relative global warming potential impact of cement production in Cuba. All scenarios from [29].
but in the 50 MPa grade case it shows that there are significant further CO₂ savings even compared to fly ash cement.

9. Barriers and incentives

9.1. Standardization

Combinations of calcined clay and limestone are currently allowed in the European standard EN 197-1 down to a 65% clinker content (LC³-65): CEM IIB M(Q-LL). The proposed extension of this European standard with the CEM IIC class will allow down to 50% clinker, but does not include calcined clays in the list of substitute materials [29]. However, it should be possible to include calcined clays (Q) in the future.

ASTM C595 allows Pozzolan content: ≤40%, Limestone content: ≤15%, Minimum clinker content: 45% (although higher level of replacement are possible with slag) so would include LC³ blends down to LC²-45. Many other countries have more flexible standards and Cuba has recently adopted a new standard covering LC³. In general, it can be said that LC³’s are already covered in many standards, but the optimal level of clinker content for cost and CO₂ savings may be somewhat less than current standards allow. However, the existing experience of use of calcined clays, the fact the blends follow existing trends and that the hydrates are the same as in existing blends means that there should be no major obstacle to have LC³ introduced to standards in the long term.

It is also possible to add a combination of calcined clay and limestone at the concrete stage as is already often done with slag or fly ash. This is already possible under the concrete standards of many countries.

9.2. Need for investment in R&D, including for processing equipment

LC³ technology has already been used to produce concrete materials in the field. The R&D already carried out into LC³ has shown that the microstructure and chemical composition of LC³ is similar to that of existing cements. This provides a sound basis for further work.

9.3. Raw materials availability (including competing applications)

The range of clay qualities that can be used is not in competition with other applications. In fact, the extraction of purer kaolinitic clays means that there are enormous reserves of suitable materials currently lying unutilized in spoil heaps as described in Section 5.1.

9.4. Market or costs

Any alternate cement will take some time to establish in the market. However the similarity of LC³ materials to other cements containing SCMs means there should be no major barrier to acceptance.

Preliminary studies have indicated that the cost of LC³ production can be lower than those for currently produced alternatives (clearly lower than plain Portland materials and perhaps lower for other SCM blends depending on the local availability and price of these materials) [30]. Lower cost will be a major incentive for the introduction of LC³. LC⁴ is expected to be a general use cement, suitable for most applications where Portland Cement and Pozzolanic Cements are currently used.

The materials seem to have particular advantages with respect to limiting chloride ingress and alkali silica reaction.

10. Further research priorities

One of the main research priorities is to better understand the best parameters for grinding and mixing blends. For example, if clinker is interground with calcined clay, limestone and gypsum, then clinker, which is by far the hardest material, will tend to be underground and the other materials dominate the fine fraction. This may lead to problems of workability due to an excessive fineness and low early strength due to coarse clinker. Ideally, the clinker would be ground first with gypsum and then mixed with the calcined clay and limestone. If separate grinding facilities are not available, then the problems of differential hardness may be minimized by adding the calcined clay and limestone at the entry to the air separator so that fine particles are further ground. LC³ materials are also likely to benefit from the use of adapted grinding aids to help the comminution of the clinker and minimize superplasticizer demand.

As with all new materials further research is also needed to verify performance over longer time scales. Including study of the corrosion of reinforcing steel, for example.

In addition to the priority areas above there is also a wide range of research needed to optimize blends according to the materials available locally and adapt formulations to applications. Here we have focused on the LC²-50 blend – 50% clinker, 30% calcined clay, 15% limestone and 5% gypsum. According to the local materials and applications, blends higher of lower amounts of clinker may be of interest. It may also be of interest to vary the clay to limestone ratio, particularly for clay with a high kaolinite content. There is also an interest to consider using a blend of calcined clay and limestone as a mineral addition at the concrete stage for enhancing durability especially in situation where resistance to chloride ions or alkali silica reaction are important.

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References
