LC³: a promising alternative

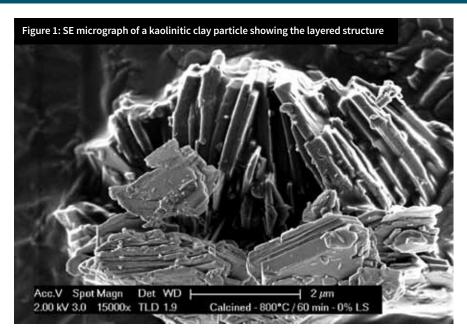
The drive for a sustainable construction industry has triggered the development of a range of building materials that serve as sustainable alternatives to Portland cement. The development of limestone calcined clay cements (LC³) offers a glimpse into the future of building materials.

■ by Karen Scrivener, Franco Zunino, François Avet and Wilasinee Hangpongpun, EPFL STI IMX LMC, Switzerland, and Anne Dekeukelaere and Laurent Grimmeissen, Cementis Consulting, Switzerland

Limestone and calcined clays are unique among supplementary cementitious materials (SCMs), as they not only offer good properties when used in combination with cement, but are also available in effectively unlimited quantities.¹ Limestone calcined clay cements (LC³) are blended cements that combine clinker, limestone, calcined clay and gypsum. They take advantage of the high reactivity of calcined clay and the synergic reaction between limestone and clay, offering equivalent mechanical performance to normal Portland cement (CEM I/OPC) with clinker factors down to 50 per cent.

LC³ constituents: limestone and calcined clay

Fine limestone is commonly used in OPC-based materials. It has also been established that limestone additions up to around five per cent can react with aluminum-rich phases in cement such as calcium aluminates.² Clay particles are made up of tens to hundreds of layers, which consequently lead to the high specific surface area (10-50m²/g) as



compared to other typical SCMs (see Figure 1). Kaolinite is the most reactive form of clay mineral for cement applications.³ Clays with different amounts of kaolinite can be found in different regions of the world, intermixed with impurities such as quartz, limestone, iron-bearing phases

and other rock-forming minerals. Calcination of kaolinitic clays between 600-800°C leads to the removal of OH⁻ groups (dehydroxylation) from the crystalline structure to give a state of more structural disorder known as metakaolin.⁴

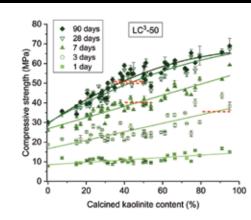
When an extra source of amorphous alumina (metakaolin) is added, limestone can further react with them. This so-called synergic effect of limestone/metakaolin leads to the formation of an increased amount of hydrates which further fills in the porosity, increasing strength and reducing permeability of LC³.

Calcination and grinding of calcined clay

Calcined clay can be produced using different thermal processes. This includes calcination in rotary kilns and flash calcination, which appear as the most promising alternatives on an industrial scale. Flash calcination exposes the material to much higher temperature gradients (103-105°C/s) over short periods of time (usually 0.2-1s,⁵ leading to a higher specific surface area as compared to calcination in a rotary kiln. Thus, flash calcination has been found to produce calcined clay with slightly higher reactivity when compared to static or rotary calcination.⁶ However, this difference is only significant at very early ages, as afterwards the kaolinite content becomes predominant.

In laboratory conditions LC³ constituents are normally ground separately in open-circuit grinding configuration. On the other hand, the most common grinding process in cement plants is the intergrinding of cement

Figure 2: compressive strength evolution over time for LC³-50 mixes with clays of varying calcined kaolinite content. Dashed horizontal lines show OPC strength at 3-90 days⁸



constituents in closed-circuit units. The main difference between separate and intergrinding is that during intergrinding the components interact with one another. These interactions are mostly due to their differences in grindability.7 In the case of LC³, calcined clay and limestone have higher grindabilities (softer particles) compared to clinker (harder particles). Thus, with intergrinding, clinker tends to remain concentrated in the coarse fraction, (reducing its reactivity), while calcined clay and limestone become much finer, which may have a detrimental effect on workability. Workability and reactivity can be improved by separate grinding and optimisation of the particle size distribution of the components.

Compressive strength

A benchmark test of compressive strength was carried out on standard mortar, using LC³-50 with a clay-to-limestone ratio of 2:1 (50 per cent clinker, 30 per cent calcined clay, 15 per cent limestone and five per cent gypsum). More than 50 clays were tested, with their calcined kaolinite content ranging from zero per cent up to 95 per cent at ages of 1, 3, 7, 28 and 90 days.8 Results are presented in Figure 2, showing the dependency of compressive strength on calcined kaolinite content. At day one, mechanical strength is only slightly affected by the clay grade. This is as expected, as the pozzolanic reaction of metakaolin in calcined clay is just starting. Between 3-28 days of hydration, the positive effect of clay grade on the compressive strength is clearly visible, as strength is almost linearly correlated to the calcined kaolinite content. This demonstrates that - for

the LC³-50 design – strength differences are primarily dependent on the calcined kaolinite content, independent of the secondary clay phases. In addition, the dashed horizontal lines represent the OPC strength at different ages - from 3 to 90 days. Interestingly, LC³ using very highgrade clays can catch up with OPC after only three days and clays having a calcined kaolinite content as low as 40 per cent are also able to reach OPC strength at 28 days.

Durability

Corrosion of steel reinforcement in concrete due to chemical attack of chloride ions (from sea water or de-icing salts) is the most important durability concern of reinforced concrete structures worldwide. Diffusion of chloride ions through concrete is governed by the pore structure as well as the phase assemblage of the binder. The chloride profile in LC³-50 blends indicates significant improvement with respect to chloride ion diffusion compared to the systems with higher clinker content (Figure 3A, using clay with 50 per cent kaolinite). A higher calcined clay to limestone ratio further reduces the penetration depth of chloride.

Normally, the use of supplementary cementing materials has an effective preventive effect against alkali silica reaction (ASR) in concrete due to the lower alkalinity in the pore solution.⁹ Figure 3 shows that LC³ is extremely promising to mitigate ASR. As for chloride resistance, even better results are obtained by increasing the clinker substitution level.

CO, savings

In addition to the technical advantages of LC³ described above, this technology also

allows significant CO, savings compared to OPC, and at the same time fulfills projected cement demand worldwide.¹⁰ A detailed assessment of the environmental benefits of the LC³-50 formulation, as compared to OPC, showed that this technology can lead to CO₂ savings of 30 per cent, independent of the technological level considered for the production of calcined clay and clinker.11

Demonstration structures and industrial trials

The different partners of the project have successfully completed industrial trials of production and implementation of LC³ under a variety of scenarios of technological development, environmental constraints and workforce specialisation. Industrial production trials of calcined clay have been successfully completed in Cuba, using a full-size clinker rotary kiln, and India, using a small rotary kiln unit. Real scale houses have been built in Cuba and India, while production of construction elements such as bricks and roof tiles has been implemented in the latter. These experiences show that LC³ enables a smooth transition from OPC without the requirement of additional training or specific equipment.

All of the above arguments in favour of LC³ will not sustain its dissemination internationally if its production is not financially attractive. However, the choice of cement in terms of financial benchmark is key. Since the cement type having the closest performance to LC³ is CEM I or OPC, this (95 per cent clinker and five per cent gypsum) should be the benchmark.

Three different implementation scenarios were analysed:

1. a cement plant willing to replace some of its CEM I/OPC production with LC³ 2. a grinding station willing to do the same using imported clinker 3. an investor willing to produce LC³ out of a greenfield project with imported clinker. A flash calciner and rotary kiln were assessed as alternatives for clav calcination. In addition, availability

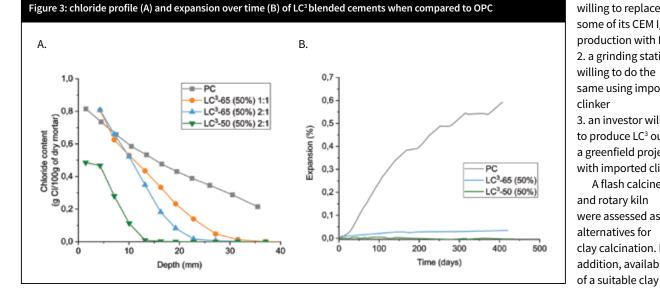


Table 1: economic feasibility scenarios for LC ³ production					
Scenario	Calciner type	Capital expenditure (US\$m)	Clay availability – distance (km)	LC3 production cost (US\$/t)	Attractiveness – IRR (%)
Scenario 1 – 1Mta LC³ in cement plant (0.3Mt calcined clay)	Flash calciner	10.3	10	23.4	63
			200	27.3	22
	Rotary kiln	6.6	10	24.2	87
			200	28.1	24
Scenario 2 – 0.413Mt LC ³ in grinding unit (0.124Mt calcined clay)	Flash calciner	8.15	10	32.1	75
			200	36.0	55
	Rotary kiln	6.1	10	32.6	98
			200	36.5	71
Scenario 3 – 0.413Mt LC³ in greenfield project (0.124Mt calcined clay)	Flash calciner	27.0	10	32.1	17
			200	36.0	9
	Rotary kiln	26.0	10	32.6	17
			200	36.5	9

close (10km) or far (200km) from the production site was considered. This difference significantly impacts the project profitability as transport cost difference is assumed at US\$13/t of clay. All scenarios use coal as the cost of fuels such as diesel will make LC³ production unviable economically unless such fuel is heavily subsidised. Cost of CEM I/OPC to be benchmarked with is estimated at US\$30/t cement if produced in a cement plant and US\$47/t if produced with imported clinker. The results are summarised in Table 1.

Assuming the sales price of LC³ is identical to CEM I, the profitability of producing LC³ when compared to CEM I/ OPC is extremely high (IRR >60 per cent) if produced in an existing cement plant and provided clay is located close to the plant. Should the clay be located 200km from the plant profitability is much less (IRR 22-24 per cent) though still acceptable. In the case of a grinding station, profitability remains high (IRR >50 per cent) even when clay is located far from the plant. In the case of a greenfield unit, profitability is rather low (IRR = 17 per cent) if clay is located close to the plant and not attractive if clay is far from the plant (IRR = nine per cent). The difference in profitability between a grinding plant and a greenfield unit is that the latter includes the impact of the grinding plant capital expenditure. If the sales price of LC³ is US\$2/t below CEM I, then the project feasibility stands only for the cases where the clay is near the production site.

These estimations are based on assumptions and costs normally found in the cement industry, and therefore they should be treated as referential. Nevertheless, in view of the above figures, production of LC³ looks attractive in most cases.

Conclusion

LC³ offers a sustainable, high-performance and cost-effective alternative for future cements. While retaining the mechanical behaviour of OPC, some relevant properties such as resistance to chloride ingress and ASR are significantly improved as compared to typical cement. Furthermore, limestone and calcined clays are some of the few raw materials available in the quantities required to constitute a technology suitable to cope with the projected cement demand worldwide.

On the other hand, some preliminary figures are presented showing that LC³ is not only a technically suitable alternative but also an economically feasible one under a variety of different implementation scenarios.

Acknowledgements

The authors would like to acknowledge financial support by the Swiss Agency of Development and Cooperation (SDC) grant 81026665.

REFERENCES

 ¹ SCRIVENER, KL, JOHN, V AND GARTNER, EM (2016) 'Eco-efficient cements: potential, economically viable solutions for a low-CO₂, cement-based materials industry' in: United Nations Environmental Programme (UNEP).
² MATSCHEI, T, LOTHENBACH, B AND GLASSER, FP (2007) 'The role of calcium carbonate in cement hydration' in: Cement & Concrete *Research*, 37, p551-558. doi:10.1016/j. cemconres.2006.10.013.

³ FERNANDEZ, R, MARTIRENA, F AND SCRIVENER, KL (2011) 'The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite' in: *Cement & Concrete Research*, 41, p113-122. doi:10.1016/j. cemconres.2010.09.013.

⁴ ALUJAS, A, FERNÁNDEZ, R, QUINTANA, R, SCRIVENER KL AND MARTIRENA, F (2015) 'Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration' in: *Applied Clay Science*, 108, p94-101. doi:10.1016/j.clay.2015.01.028.

⁵ TEKLAY, A, YIN, C AND ROSENDAHL, L (2014) 'Flash calcination of kaolinite rich clay and impact of process conditions on the quality of the calcines: A way to reduce CO₂ footprint from cement industry' in: *Applied Energy*, 162, p1218-1224. doi:10.1016/j.apenergy.2015.04.127.

⁶ SALVADOR, S (1995) 'Pozzolanic properties of flash-calcined kaolinite: A comparative study with soak-calcined products' in: *Cement & Concrete Research*, 25, p102-112. doi:10.1016/0008-8846(94)00118-I.

⁷ DE WEERDT, K (2007), Separate grinding versus intergrinding, SINTEF Report. SBF BK A. 7022. ⁸ AVET, F AND SCRIVENER, K (2018)

 'Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC³)' in: Cement & Concrete Research, p124-135. doi:10.1016/j.cemconres.2018.02.016.
⁹ SHEHATA, MH, THOMAS, MDA, BLESZYNSKI, RF (1999) 'The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes' in: Cement & Concrete Research, 29, p1915-1920.

 ¹⁰ CANCIO DÍAZ, Y, SÁNCHEZ BERRIEL, S, HEIERLI, U, FAVIER, AR, SÁNCHEZ MACHADO, IR, SCRIVENER, KL ET AL (2017) 'Limestone calcined clay cement as a low-carbon solution to meet expanding cement demand in emerging economies' in: *Development Engineering*, 2, p82–91. doi:10.1016/j.deveng.2017.06.001.
¹¹ SÁNCHEZ BERRIEL, S, FAVIER, A, ROSA DOMÍNGUEZ, E, SÁNCHEZ MACHADO, IR, HEIERLI, U, SCRIVENER, K ET AL (2016) 'Assessing the environmental and economic potential of Limestone Calcined Clay Cement in Cuba' in: *Journal of Cleaner Production*, 124, p361-369. doi:10.1016/j.jclepro.2016.02.125.

Cementreview



12 ISSUES OF INTERNATIONAL CEMENT REVIEW

"DELIVERING BUSINESS INSIGHT, MARKET KNOWLEDGE AND TECHNICAL EXPERTISE TO THE GLOBAL CEMENT INDUSTRY"

SUBSCRIPTION INCLUDES FREE HANDBOOK



2019
SUBSCRIPTIONS

SUBSCRIPTION PACKAGE INCLUDES:

- > 12 ISSUES OF INTERNATIONAL CEMENT REVIEW (ICR) – the cement industry's leading monthly publication, delivered direct to your desk by First Class Airmail with early access to the digital magazine via CemNet.com.
- > FREE HANDBOOK The Cement Plant Operations Handbook, 7th Edition (fully-revised and updated for 2019).
- > ICR SUBSCRIBER DISCOUNTS on all other reference works published by ICR.
- > BUILDING BULLETIN NEWSLETTER Monthly newsletter covering the latest developments in the building materials sector – complimentary to all ICR subscribers.

> UNLIMITED access to CemNet.com

- Full digital issues of ICR available in advance of the print edition.
- Over five years of online back issues.
- Daily news service and 15-year searchable ICR news database.
- Access to Corporate Watch and Market Reports section.
- Cement Plant Directory.
- Video presentations.

A COMBINED PRINT AND DIGITAL SUBSCRIPTION Annual subscription to ICR GBP 205 / USD 315 / EUR 260

Subscribe online at ((C) www.CemNet.com/subscribe



www.CemNet.com