

Carboaluminates: the overlooked key to highperformance LC³ cements

Prof. Franco Zunino

zunino@berkeley.edu





What we have achieved with calcined clays



✓ 50% clinker
 ✓ 30-40% less CO₂ compared to PC
 ✓ Equivalent performance to PC
 ✓ Enhanced durability

CEM II/C-M (Q-LL) (EN 197-5) CEM IT (P30)(L15) (ASTM C595)

Calcination

Kaolinite \rightarrow Metakaolin AS₂H₂ \rightarrow AS₂ +2H



Metakaolin



First LC³ deployment in CA (National Cement)



A: AI_2O_3 S: SiO_2 H: H_2O

- Reactive
- Abundant

Replacing part of **portland cement** by **low-carbon materials** is the most effective strategy to cut CO₂ emmisions



Availability argument Reactivity argument



Londono-Zuluaga et al., Mater. Str. 2022

(UNEP, 2016)

Reactivity of calcined clays saves clinker

LC³ versus portland pozzolanic cements (NP) from the Chilean market



Save 40-45% clinker with LC³ compared to NP



What explains this substantial difference in performance?

Reactivity overview of LC³





Calcined clay (metakaolin)

 $AS_2 + 3CH + 6H \longrightarrow C-A-S-H + C_2ASH_8$

metakaolin

Limestone reaction with clinker aluminates

Relevant for Type IL cements

Limited by A availability (5-10% replacement)

 $C_{3}A + Cc + 11H \longrightarrow C_{4}AcH_{11} Mc$ $\underset{\text{imestone}}{\text{monocarboaluminate}} Mc$ $C_{3}A + 0.5Cc + 0.5CH + 11.5H \longrightarrow C_{4}Ac_{0.5}H_{12} Hc$ $\underset{\text{hemicarboaluminate}}{\text{hemicarboaluminate}} Hc$

Limestone reaction with aluminates from calcined clay

Additional A source to sustain Hc/Mc

Synergic reaction of limestone and c. clay

 $AS_2 + 0.5Cc + 3.5CH + 8.5H \longrightarrow C_4Ac_{0.5}H_{12}$

Microstructural effects of carboaluminate precipitation



Hc, Mc CH, Cc Anhydrous 0.6 0.5 Hc/Mo 0.4 AI / Ca (-) 80 Ett 0.2 0.1 0 🤇 CH/Cc 0 0.1 0.2 0.3 C,S 0.4 0.5 0.6 0.7 0.8 0.9 Si / Ca (-)





Third peak of hydration and Hc/Mc precipitation





The third peak of hydration in LC³ corresponds to the enhancement of Hc/Mc precipitation (48-72h)

Evidence of Hc/Mc precipitation on mechanical properties





Hc/Mc precipitation can be directly associated with the increase in compressive strength between 48-72h

Equilibrium phase assemblage of LC³ as function of MK DoR



Independent of the extent of MK reaction, only Mc is predicted to form by TM



CH

Long-term stability of hemicarboaluminate (Hc)





Incorporation of SO₄²⁻ into the Hc lattice might explain the long-term stability of this phase

Long-term (3 yr) phase assemblage in LC³ cements





Strätlingite observed in systems with high MK content. Partial conversion of Hc to Mc, however Hc is still observable in all systems.

Implications for low-clinker (<50%) LC³ cements



Metakaolin reactivity in low clinker systems



20 Portlandite (g/100g of anhydrous) - PC - LC³-50-2:1 - LC3-35-2:1 - LC3-25-2:1 - LC³-35-1:1 - LC³-25-1:1 - LC3-35-1:1-CH - LC3-15-2:1 - LC3-25-1:1-CH - LC3-15-1:1 LC³-15-1:1-CH 0 100 1 100 100 10 10 10 10 100 Time (days)

> CK 50% : CH is not limiting factor CK <50% : CH is a limiting factor





Additions of CH enable and incresed degree of MK reaction

Metakaolin reactivity in low clinker systems



Precipitation of carboaluminates





Strength development enhanced by CH additions





However we do not solve the 1-2 day strength issue and $CO_{2e} CH > CO_{2e} PC$





 $LC^{3} - 25$



Concluding remarks



- LC³ cements decrease their porosity considerably between 48-72h, leading to an increase in strength that ultimately matches OPC (at 50% clinker factor).
- The decrease in porosity is associated with the precipitation of carboaluminates (hemi and mono), which effectively fill large capillary pores that remain after alite dissolution.
- From a kinetic standpoint, the precipitation of carboaluminates can be associated wit the 3rd peak of hydration. Carboaluminates only precipitate after gypsum depletion.
- Hemicarbonate incorporates sulfate in its lattice, likely explaining its long terms stability.
 Better thermodynamic data of CO₃-AFm solid solutions is urgently needed.
- In low-clinker LC³, the contribution of carboaluminate precipitation to strength development is even higher than in materials with 50+% clinker.



Thank you for your attention

Prof. Franco Zunino Assistant Professor (CEE – SEMM)

zunino@berkeley.edu



