Limestone Calcined Clay Cements (LC^3)

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Laboratory of Construction Materials, EPFL

Franco Zunino
franco.zunino@epfl.ch

EPFL

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Contents

- **What is LC^3?**
- Mechanical properties and hydration of LC^3
- Assessment of calcined clay reactivity
- Phase assemblage of LC^3
- Durability
- Conclusion

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Cement fabrication

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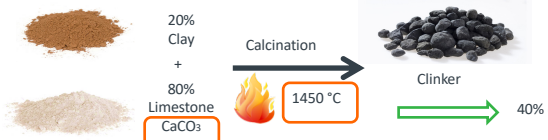
But due to the huge amount produced…



$CaCO_3 \rightarrow CaO + CO_2$

60% of CO_2 emissions

Cement and concrete production responsible for roughly 8% of man-made CO_2 emissions

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Limited supplies of common SCMs

UN environment

Karen Scrivener, EPFL, Switzerland
Vanderley John, USP, Brazil
Ellis Gartner, Imperial College, UK

Can be downloaded for free at multiple sites.

Eco-efficient cements: Potential economically viable solutions for a low-CO_2 cement-based materials industry

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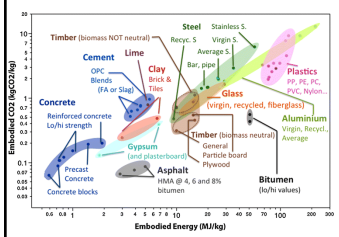
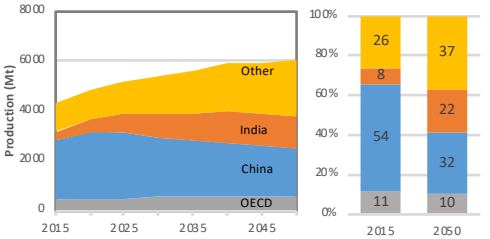
Before all…. Concrete IS an environmentally friendly material

But we use A LOT of it





The demand of cement will come from developing economies

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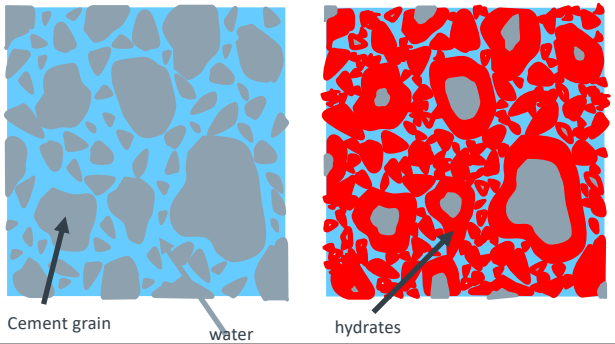
How cement works

Reaction with water increases solid volume, joins grains together



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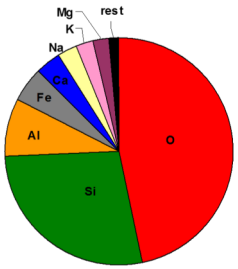
We only have (one) the Earth

Composition of Earth's crust



Only 8 elements constitute >98% or the earth's crust
Even elements we regard as common are more than 1000 times LESS abundant that the elements found in cement – cost and geographical distribution

The composition of the Earth's Crust limits the possible chemistries

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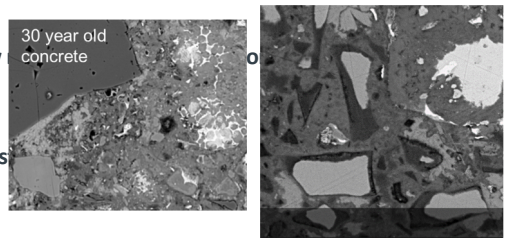
What about the different oxides we have available

Na_2O
K_2O — **Too soluble**

Fe_2O_3
MgO — **Too low**

CaO
SiO_2
Al_2O_3 — **The mos**



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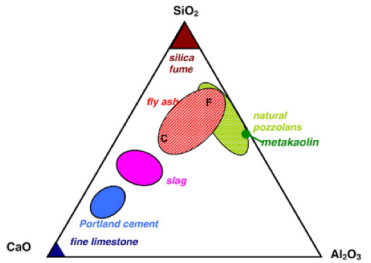
What about the different oxides we have available

Na_2O
K_2O — **Too soluble**

Fe_2O_3
MgO — **Too low mobility in alk**

CaO
SiO_2
Al_2O_3 — **The most useful**



Lothenbach et al., 2011

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Portland cement based solution will remain to be dominant

- Incredible economy of scale (clinker is produced everywhere at very low cost)
- Raw materials are abundant and widely distributed
- Easy to manipulate by low skilled workers (good solution for developing economies)
- Robust

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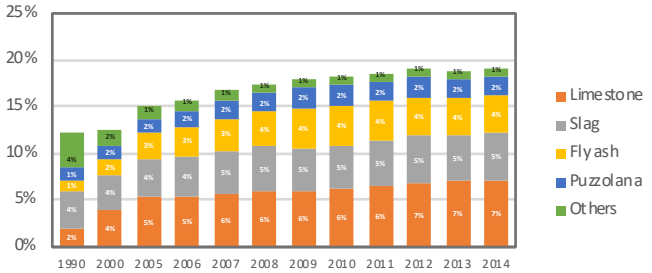
Portland cement based solution will remain to be dominant

Clinker substitution most successful strategy to reduce CO_2



- Almost no progress in last 5 years
- Only 3 substitutes used in quantity

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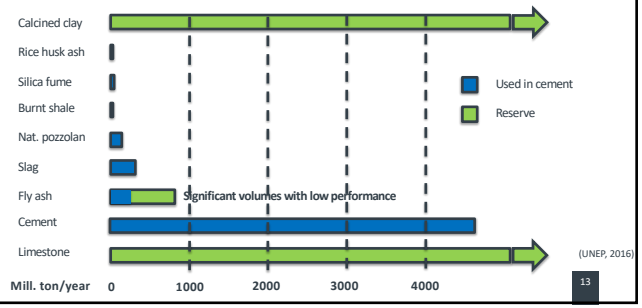
Limited supplies of common SCMs

- Clinker production: Most expansive and highest emissive step in cement production
- Reduction of these impacts using SCMs. But most of SCMs facing global shortage

4600
Million of tons of Portland cement
(CEMBUREAU, 2015)

626
Kilograms per capita per year
(UNEP, 2016)

~ 5%
Anthropogenic CO_2 emissions
(EPA)



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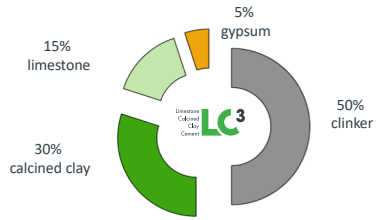
Limestone Calcined Clay Cement (LC^3)

Lower clinker content
+
Clay calcination at 800 °C
No chemical CO_2

Up to **40%** of reduction of CO_2 emissions



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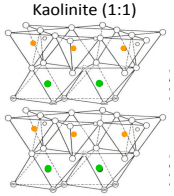
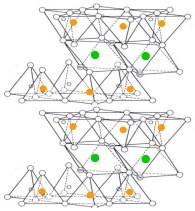
Highest pozzolanic potential for kaolinite

Antoni (2012)
Fernandez (2011)

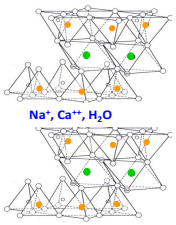
Kaolinite (1:1)

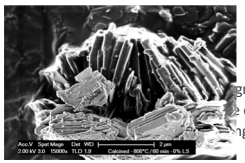


Illite (Micas) (2:1)



Montmorillonite (Smectites) (2:1)





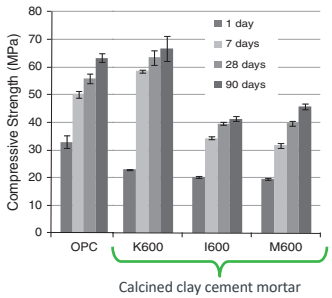
groups
of the structural layer
ng calcination

Calcination
Kaolinite → Metakaolin
AS_2H_2 → AS_2 +2**H**

Highest pozzolanic potential for kaolinite

Calcination
Kaolinite → Metakaolin
AS_2H_2 → AS_2 +2**H**

- Calcined clay cement mortars: comparison between calcined kaolinite, illite and montmorillonite
- Much higher strengths obtained for calcined kaolinite blend



Fernandez (2011)

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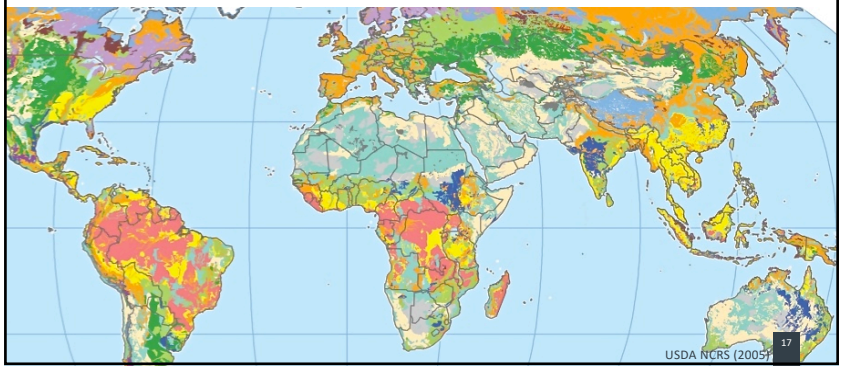
Wide availability of kaolinitic clays: yellow, red and pale green areas



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We do not need pure kaolinitic clays

» Already used by other industries

» How does the kaolinite content of clay influence the properties of LC³ blends?

Pure kaolinite / metakaolin

0% of kaolinite — 50% of kaolinite — 100% of kaolinite

Kaolinite content in clay (%)

Might not be reactive enough

Clays stockpiled as wastes. Not used by any other industries

Used by paper, ceramics, cosmetics

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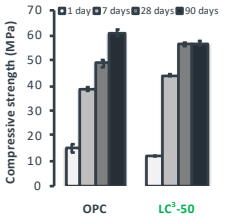
Limestone Calcined Clay Cement (LC³)

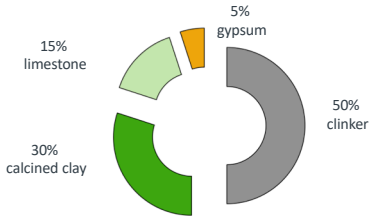
Composition

Clinker factor: **LC³-50**

Clay to limestone ratio: **2/1**



Antoni (2012)



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Limestone Calcined Clay Cement (LC³)

Reactivity

Calcined clay (metakaolin) – pozzolanic reaction

$AS_2 + 3CH + 6H \rightarrow C\text{-}A\text{-}S\text{-}H + C_2ASH_8$

metakaolin — strätlingite

Limestone reaction with clinker aluminates

$C_3A + Cc + 11H \rightarrow C_4AcH_{11}$

limestone — monocarboaluminate

$C_3A + 0.5Cc + 0.5CH + 11.5H \rightarrow C_4Ac_{0.5}H_{12}$

limestone — hemicarboaluminate

Limestone reaction with aluminates from calcined clay

Synergetic effect in LC³

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

metakaolin — hemicarboaluminate

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Typical LC³ mixture designs

Which clinker factor I will use?

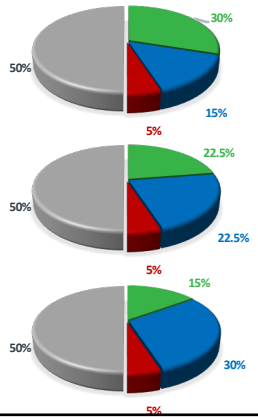
LC³-65 2/1

CEM II/B-Q-LL

LC³-50 2/1

CEM II/C-Q-LL

Clay to Limestone



2/1

1/1

1/2

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Wide range of calcined clay composition

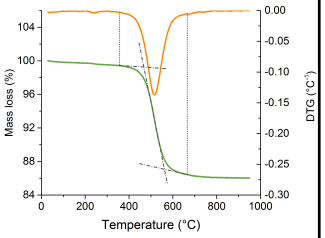
Dehydroxylation of kaolinite

$AS_2H_2 \rightarrow AS_2 + 2H$

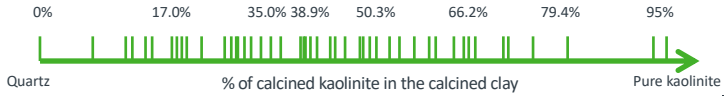
» Kaolinite content determination by TGA

Calcined kaolinite content (%)

= Kaolinite $_{raw\ clay}$ – Kaolinite $_{calcined\ clay}$



46 calcined kaolinitic clays + Quartz system



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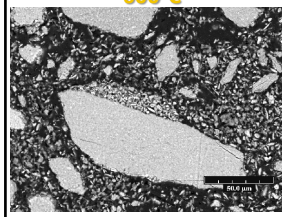
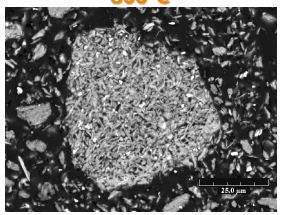
Effect of the calcination temperature

600°C

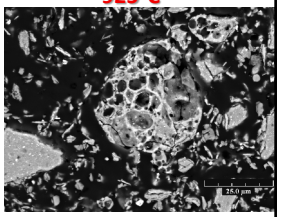


Small clay plates may agglomerate

800°C



925°C



Higher temps, some sintering, decrease of specific surface, decrease of reactivity

K. Scrivener

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Contents

» What is LC³?
» **Mechanical properties and hydration of LC³**
» Assessment of calcined clay reactivity
» Phase assemblage of LC³
» Durability
» Conclusion

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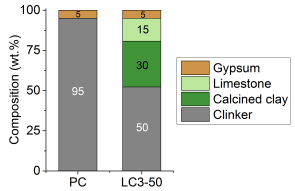
Strength development



- Influence of the grade of calcined clays on the mechanical properties ⇨ Benchmark test of clay strength
- Strengths measured at 1, 3, 7, 28 and 90 days

	Clinker	Calcined clay	Limestone	Gypsum
PC	95	0	0	5
LC^3-50	50	30	15	5

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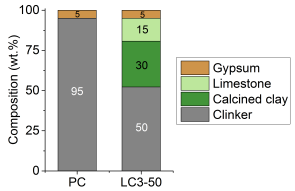
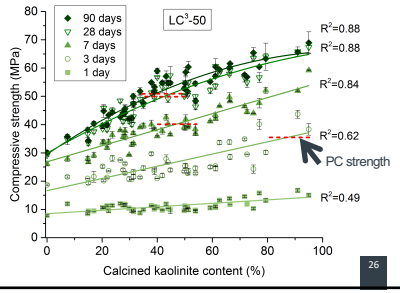
Calcined kaolinite content overwhelming parameter



- Influence of the grade of calcined clays on the mechanical properties ⇨ Benchmark test of clay strength
- Strengths measured at 1, 3, 7, 28 and 90 days



- Similar strength to PC for blends containing 40% of calcined kaolinite from 7d onwards
- At 28 and 90 days, little additional benefit >50%
- Minor impacts of fineness, specific surface and secondary phases

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LC^3-65 vs LC^3-50

LC^3-50

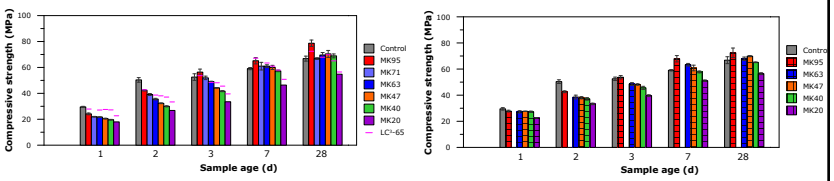
Best durability performance / Up to 30% CO_2 savings compared to OPC

Not included in current EN 197 standard

LC^3-65

Increased durability compared to OPC

Currently allowed as **CEM II/B-Q-L** in EN 197 standard



- The main difference observed between LC^3-50 and LC^3-65 formulations, for a given grade of clay, is the strength at 1 d
- From 2 d onwards, the differences in compressive strength between LC^3-50 and LC^3-65 systems disappear at ages related to the MK content of the binder

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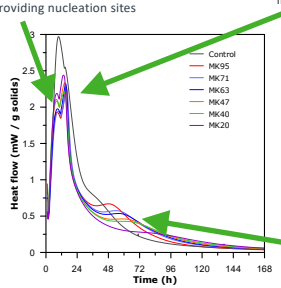
Reaction kinetics of LC^3 – Isothermal calorimetry

Silicate (first) peak inversely proportional to MK content, as more limestone is added providing nucleation sites

Increased **aluminate (second) peak** due to the inclusion high surface area additions (calcined clay and limestone)



How can we relate these peaks with the phase assemblage of the material?

Third peak linked to the formation of carboaluminates (hemicarboaluminate and monocarboaluminate) from the reaction of calcined clay and limestone

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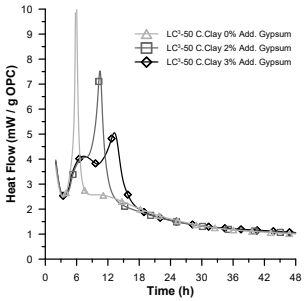
Why we have to adjust the sulfate content in LC^3?

The issue : Some LC^3 systems require further adjustment of the sulfate content



Undersulfated system (aluminate peak first, silicate peak second)

i. Aluminate reaction takes place first, consuming the sulfate ions available
ii. Lower and broader silicate peak is observed in this case

Properly sulfated system (silicate peak first, aluminate peak second)

i. Acceleration period of C_3S happens first
ii. Ettringite formation takes place afterwards with the sulfate desorbed from C-S-H

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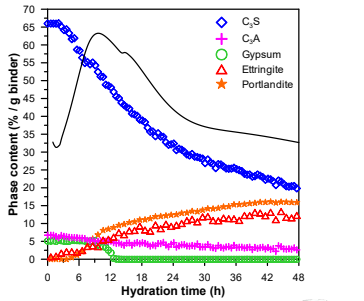
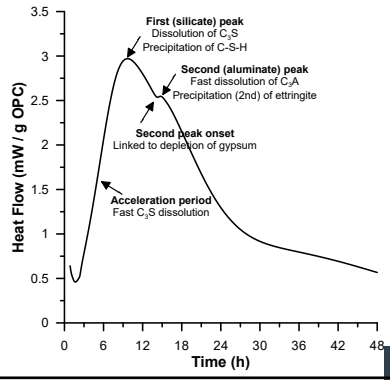
Early age (<48 h) phase assemblage in OPC



Paste sample in ring holder, covered with Kapton film



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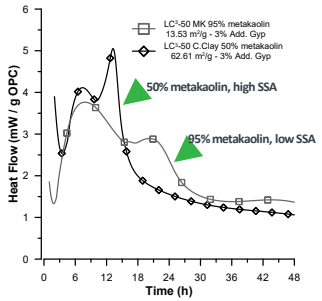
Sulfate adjustment

What is triggering the acceleration and enhancement of the aluminate peak in LC^3?



1.- Calcined clay (additional aluminate phases)

But the LC^3 with lower metakaolin content exhibits higher acceleration and enhancement

2.- Specific surface area of calcined clay (and limestone)

Contribution of SCMs through filler effect

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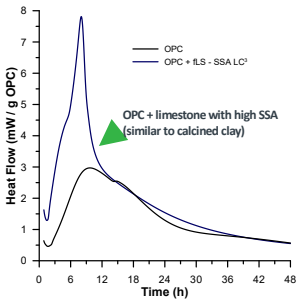
Sulfate adjustment

What is triggering the acceleration and enhancement of the aluminate peak in LC^3?

What if we remove the aluminum contribution of calcined clay but not the surface area?



1.- Calcined clay (additional aluminate phases)

However, the example presented seems to challenge this hypothesis....

2.- Specific surface area of calcined clay (and limestone)

Contribution of SCMs through filler effect

But how filler effect is linked to gypsum depletion?

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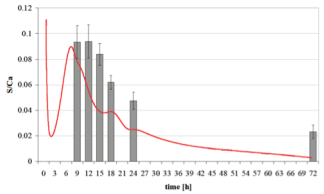
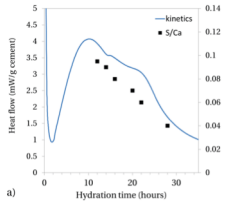
The interaction of sulfate with C-S-H

- C-S-H is the main reaction product of the hydration of cement
- It is well know that it can adsorb/incorporate different ions on its surface/structure (Al, Na, K, Cl, S)



Quennoz, PhD Thesis, 2011

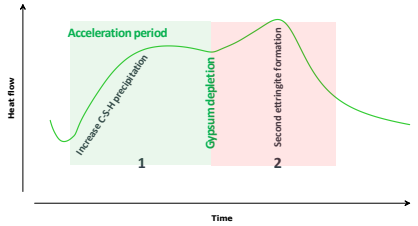


Berodier, PhD Thesis, 2015

Sulfate adsorbed on C-S-H will be desorbed at gypsum depletion

Hydration of LC^3 : role of SSA on the aluminate reaction

Proposed Mechanism



1. **Sulfate gets adsorbed in the C-S-H surface**. If the rate of C-S-H precipitation is increased, sulfate adsorption also increase
   i. Finer material hydrate quicker, consuming more sulfate per unit time
   ii. The addition of more nucleation surface (fillers) affect the C-S-H precipitation rate and therefore the sulfate balance, but the effect is independent of the chemical composition of the filler (in particular, of the Al content)
2. As hydration keeps ongoing, gypsum is depleted, triggering the **desorption of sulfate from C-S-H** which then reacts with aluminates to form ettringite (second ettringite formation)
   i. The extent and rate of the reaction is a function of how much sulfate gets desorbed from C-S-H (and maybe the space filled already at this time)

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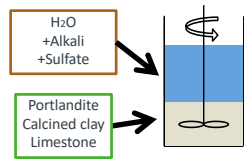
Monitoring reactivity: R^3 test

» Rapid, Relevant and Reliable (R^3)
» Other screening tests already existing, but difficult to correlate results with compressive strength

» **Focus on pozzolanic / synergetic reaction only:**
  » Adjustment of sulfate and alkali content to reproduce the reaction environment of hydrating blended cements



Two ways of measuring the reactivity

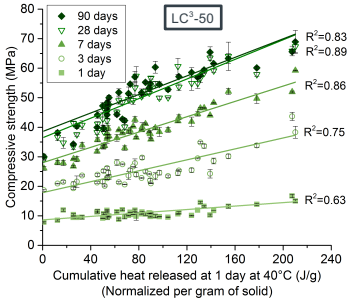
Isothermal calorimetry at 40°C
Heat release 24h

Oven thermal treatment at 400°C
Bound water 3 days

Linear correlations between strengths and heat at 1d

Isothermal calorimetry at 40°C
Heat release 24h

- Results after **24 h** ⇨ Rapid test
- Linear trends obtained for all ages ⇨ Relevant test
- Small standard deviations for the heat release ⇨ Reliable test



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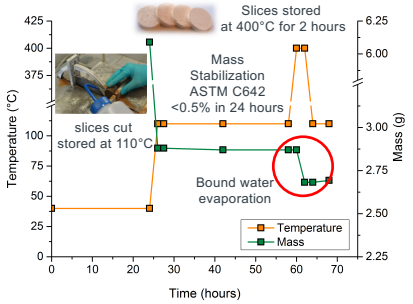
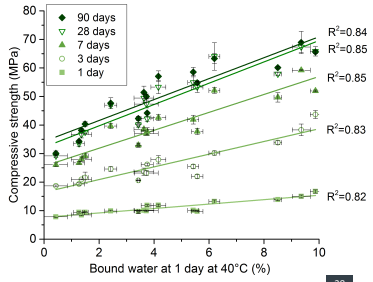
Oven method: thermal treatment at 400°C for 2 hours

- Requires an oven only!
- Very good correlation with strength results





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- What is LC³?
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Understanding of strength development

Calcined clay (metakaolin) – pozzolanic reaction

$AS_2 + 3CH + 6H \rightarrow C\text{-}A\text{-}S\text{-}H + C_2ASH_8$
(metakaolin → strätlingite)

Fernandez et al., 2011
Antoni et al., 2012
Tironi et al., 2014

Limestone reaction with clinker aluminates

$C_3A + Cc + 11H \rightarrow C_4AcH_{11}$
(limestone → monocarboaluminate)

$C_3A + 0.5Cc + 0.5CH + 11.5H \rightarrow C_4Ac_{0.5}H_{12}$
(limestone → hemicarboaluminate)

Matschei et al., 2007
Chowaniec, 2012
Bentz et al., 2016

Limestone reaction with aluminates from calcined clay

Synergetic effect in LC³

$AS_2 + 0.5Cc + 3.5CH + 8.5H \rightarrow C_4Ac_{0.5}H_{12}$
(metakaolin → hemicarboaluminate)

Antoni et al., 2012

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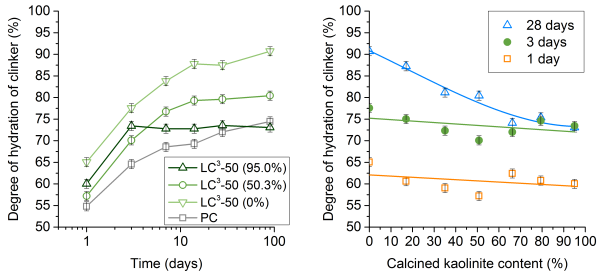
Clinker hydration degree

- Higher DoH for LC^3-50 blends due to the filler effect of calcined clay and limestone
- DoH constant for LC^3-50 (95.0%) from 3 days onwards: significant slowing down of clinker hydration
- Clinker hydration continues for LC^3-50 containing less than 65% of calcined kaolinite



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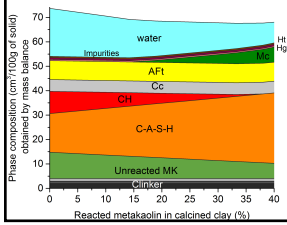
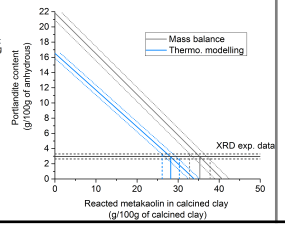
Methods for determining the amount of reacted metakaolin

- Mass balance
  - Redistribution of the reacted anhydrous phases between the hydrated phases known to form

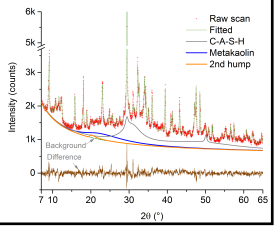
AS_2 free variable



- Thermodynamic modeling
  - Same inputs as mass balance
  - Reacted metakaolin determined from the best agreement with experimental data

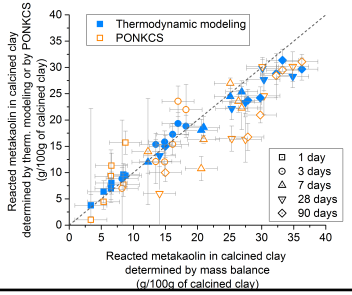


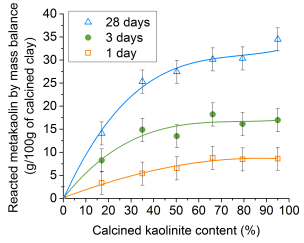
- PONKCS
  - Based on XRD-Rietveld method
  - Quantification of amorphous metakaolin phase
  - Complexity to fit the background of amorphous humps



Methods for determining the amount of reacted metakaolin

- Mass balance as most reliable method
- Increase of the amount of reacted metakaolin with the calcined kaolinite content
- This increase becomes lower with the increase of the calcined kaolinite content





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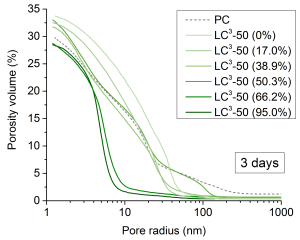
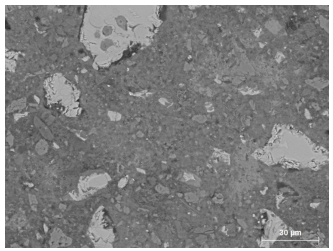
How do these reactions fill the space?

- Porosity characterization by MIP: Significant refinement of porosity already at 3 days of hydration





- Porosity already well defined at 3 days for high-grade calcined clays
- Kinetics difference depending on the grade of calcined clays

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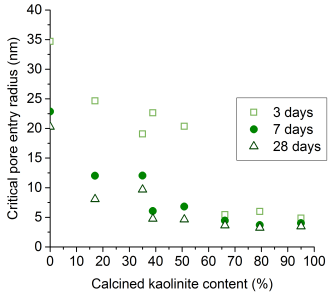
Limit of porosity refinement

- Different kinetics of refinement of porosity
- Porosity already well defined at 3 days for high-grade calcined clays
- Slower refinement for blends with lower kaolinite content
- Limit critical pore entry radius reached for blends with calcined kaolinite content ≥40%



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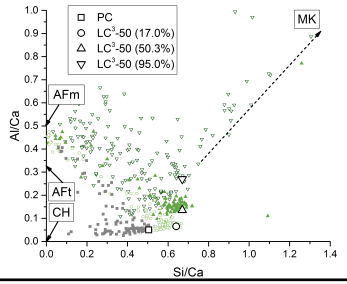
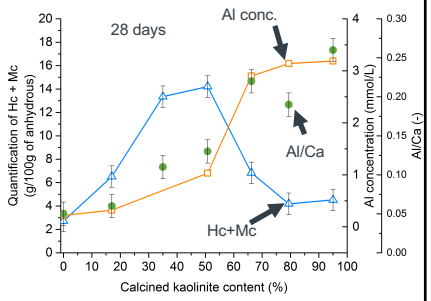
Consequence of the lack of large capillary pores

- Carboaluminate formation is limited
  - Al concentration in the pore solution goes up
    - Al incorporation in C-A-S-H increases





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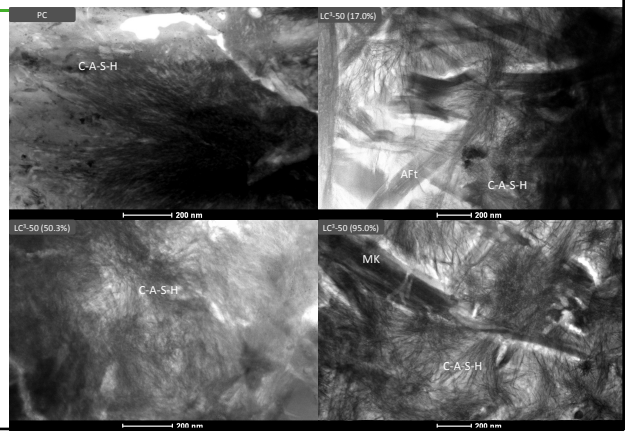
C-A-S-H morphology

- Fibrillar morphology of C-A-S-H observed for all samples
- No change of morphology with the calcined kaolinite content



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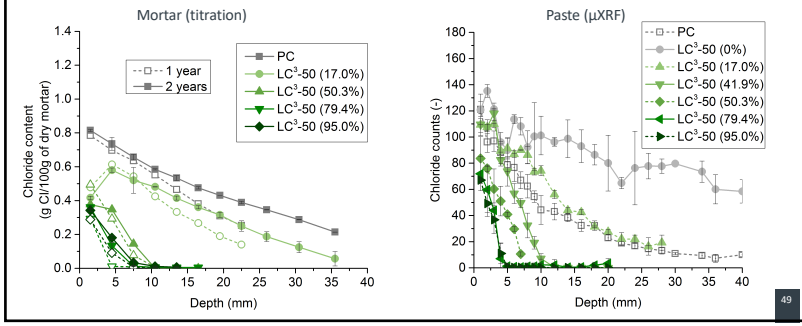
Chloride resistance (ponding in 3 %wt. NaCl solution)

» Excellent results obtained for LC^3-50 blends both on paste and mortar

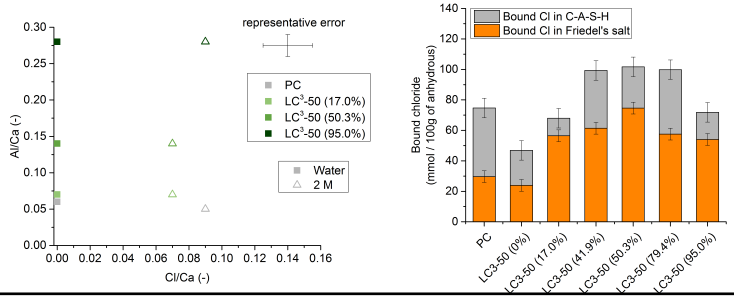


Chloride adsorption on C-A-S-H

» Chloride adsorption observed on all samples, including PC

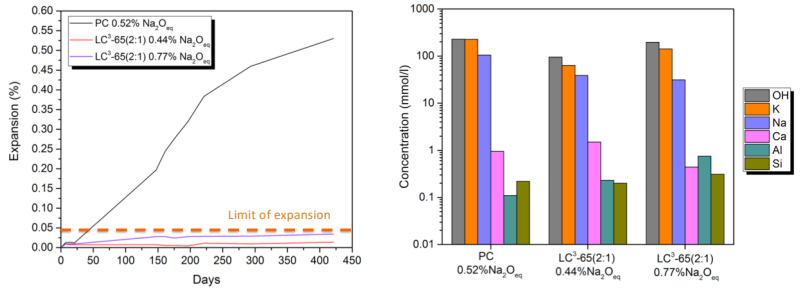
» Chloride adsorption main contributor to chloride binding for PC, Friedel's salt for LC^3-50 blends

» Good correlation between the total bound chloride measured by isotherm and by the sum of Cl in FS and C-A-S-H



Alkali Silica Reaction (ASR)

» ASR (JOBE aggregate and soaked in 0.32 M of NaOH at 38°C)



- The expansion of LC^3-65(2:1) mortars are lower than 0.04% (expansion limit) after exposure more than 1 year
- The higher presence of Al inhibits the silica dissolution from the reactive aggregate resulted in the lower ASR gel to form

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Conclusions

- LC³ is a promising alternative to reduce the carbon footprint associated with cement production
  - Widespread availability of raw materials
  - Possibility to use a variety of clays with different qualities
  - Mechanical behavior comparable with OPC
  - Refined pore structure and enhanced durability as compared to OPC
- Different methods to characterize LC³ have been developed in order to facilitate adoption
  - R^3 test to assess the reactivity of calcined clays
  - Isothermal calorimetry approach for sulfate adjustment
  - XRD diffraction and thermodynamic modelling showing that the expected phase assemblage is comparable to OPC
  - No morphological differences between the hydration products of LC³ and OPC are observed

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Conclusions

- LC³ can be used with the same tools, technologies and techniques as conventional OPC concrete
  - No special training required of the workforce, can be used even in very rough conditions
  - No investment in new machinery at the construction site required
  - No additional safety hazards as compared to normal OPC concrete

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Upscale

- Cuba
- Industrial trials
- Rotary kiln calcination
- Various applications
- Houses made of LC³
- Special interest for chloride performance

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Upscale

- India
- 2nd cement market
- Keeps growing significantly
- Bricks
- Tiles
- Pavements
- Full house
- Etc…

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Acknowledgements

Dr. François Avet, Dr. Julien Ston, Dr. Wilasinee Hanpongpun, Dr. Fabien Georget
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For expanding our knowledge on LC³ and making this technology a reality

Questions?

LC3 PROJECT
Franco Zunino
PhD Student
+41 21 69 32827
franco.zunino@epfl.ch

EPFL STI IMX LMC MXG 235
Station 12, Swiss Federal
Institute of Technology
Lausanne, 1015 Lausanne,
Switzerland

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Agency for Development and Cooperation SDC