Advanced cementitious materials, MSE 420

Lecture 2: SCMs and Limestone Calcined clay cement (LC3)

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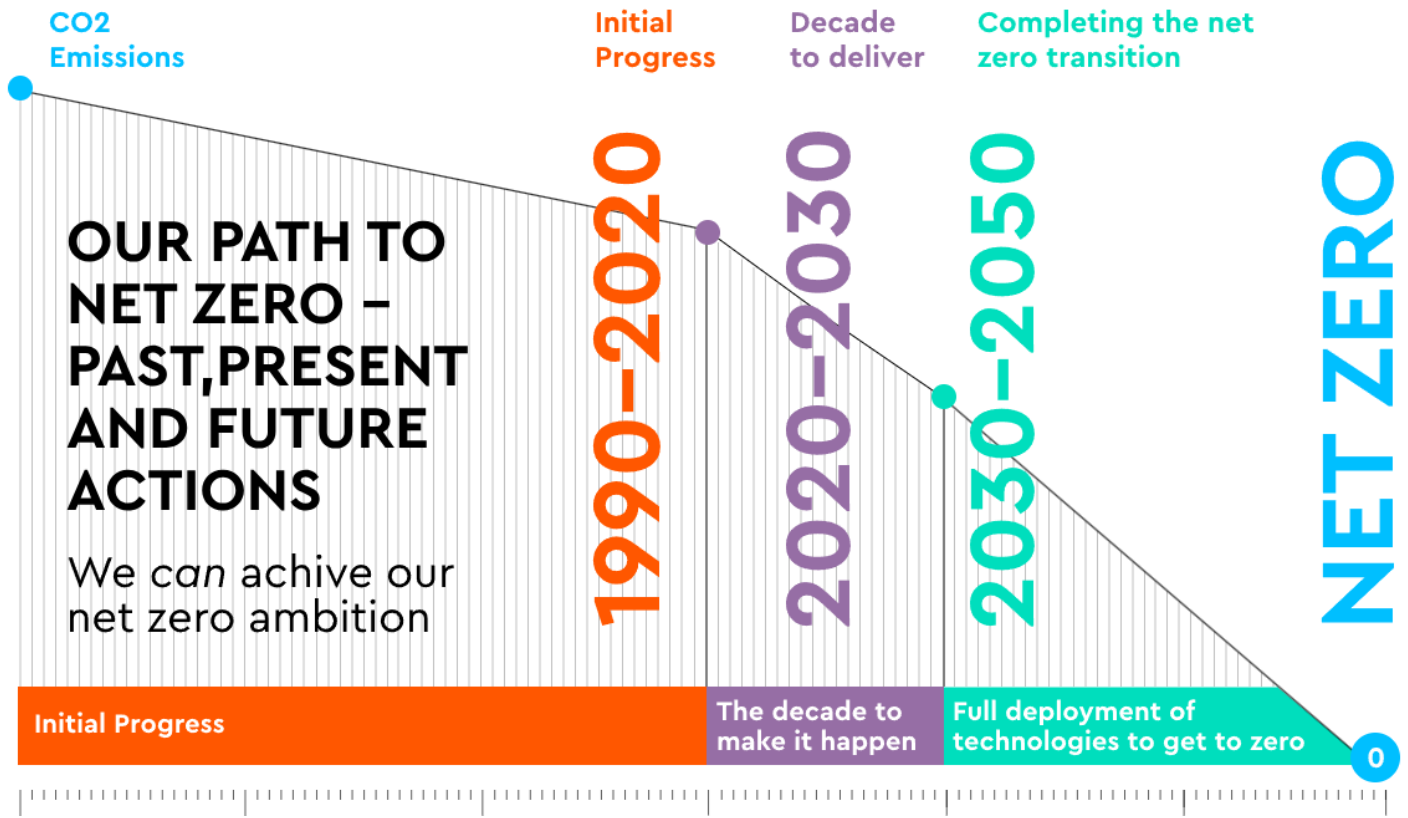
17th September 2025

Learning objectives

By the end of this class, you will be able to

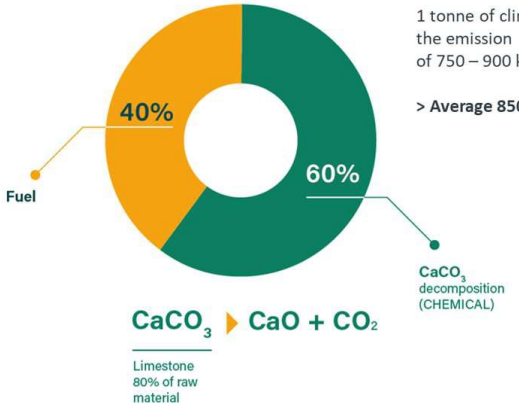
- The significance of adopting blended cements
- Distinguish between the different types of blended cements
- Test methods to assess the reactivity of SCMs and interpret their performance
- Benefits of LC^3
- Identify the key properties of LC^3

Why do we add additives in cement?


CO2
Emissions
Initial
Progress
Decade
to deliver
Completing the net
zero transition
OUR PATH TO
NET ZERO –
PAST,PRESENT
AND FUTURE
ACTIONS
We can achive our
net zero ambition
1990–2020
2020–2030
2030–2050
NET ZERO
Initial Progress
The decade to
make it happen
Full deployment of
technologies to get to zero
0

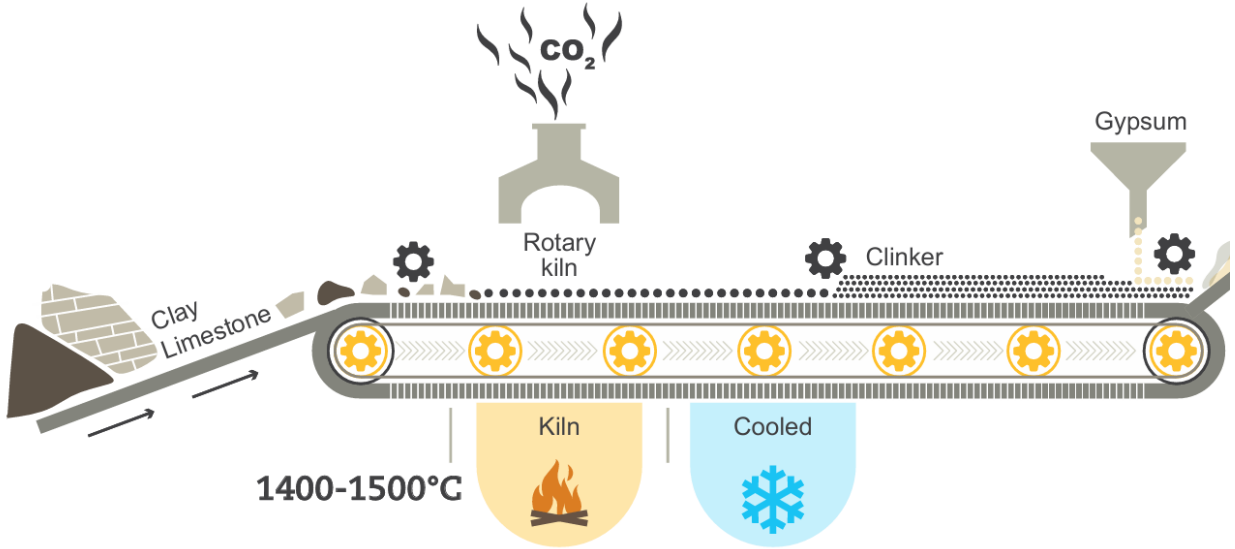
Mehnaz Dhar

Carbon emission

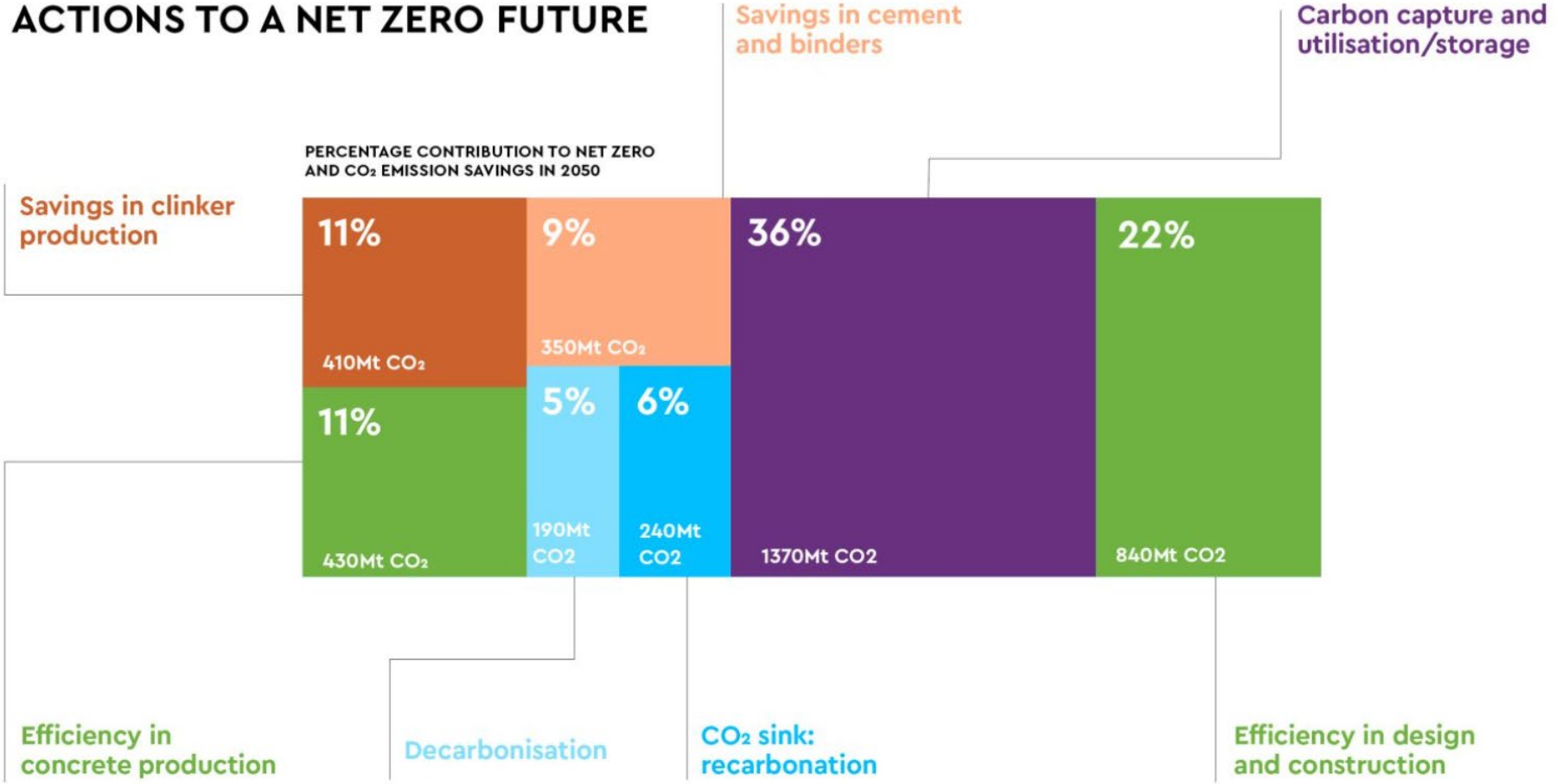


1 tonne of clinker leads to the emission of 750 – 900 kg CO_2

> Average 850kg/t



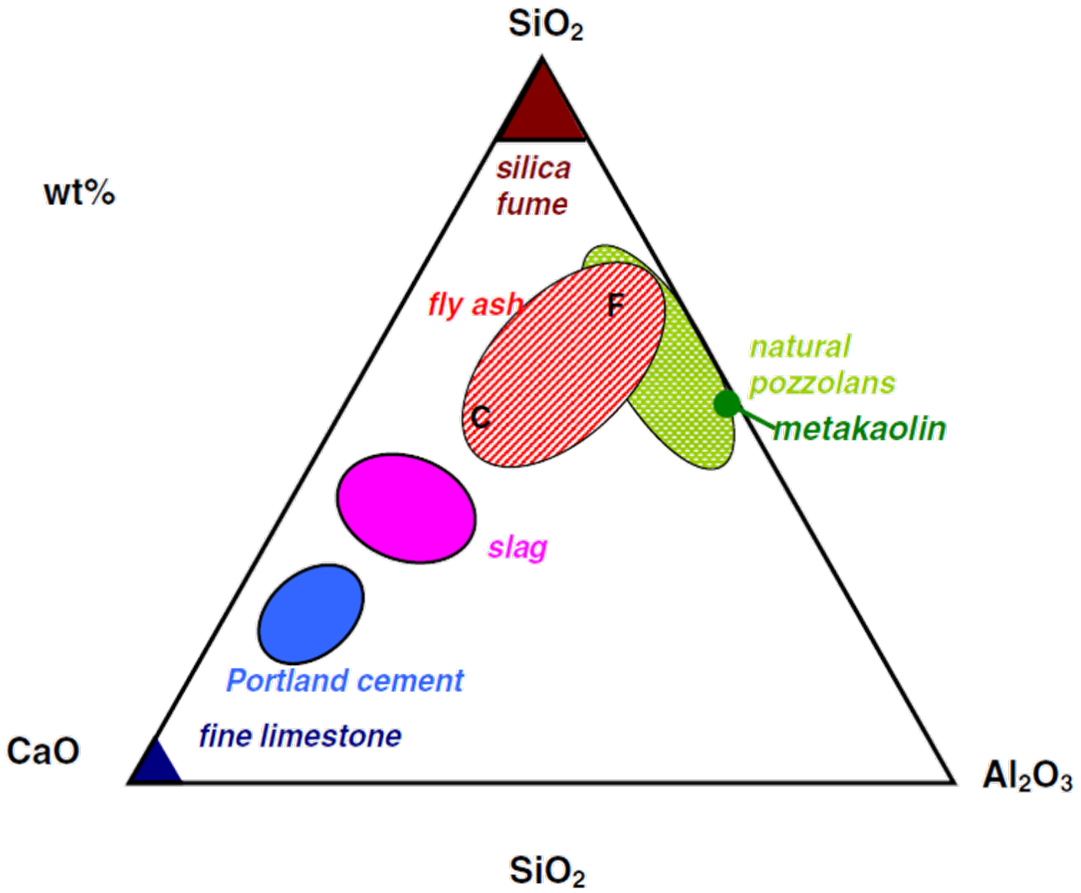
ACTIONS TO A NET ZERO FUTURE



Mineral additives

- Pozzolanic material (Defined by ASTM C618)
  - Siliceous or siliceous and aluminous material
  - Not hydraulic by themselves
  - Reacts with calcium hydroxide to form CSH
- Hydraulic material
  - Set and harden upon water
- Inert fillers
  - Fine materials and do not react in cement paste

Composition of SCMs

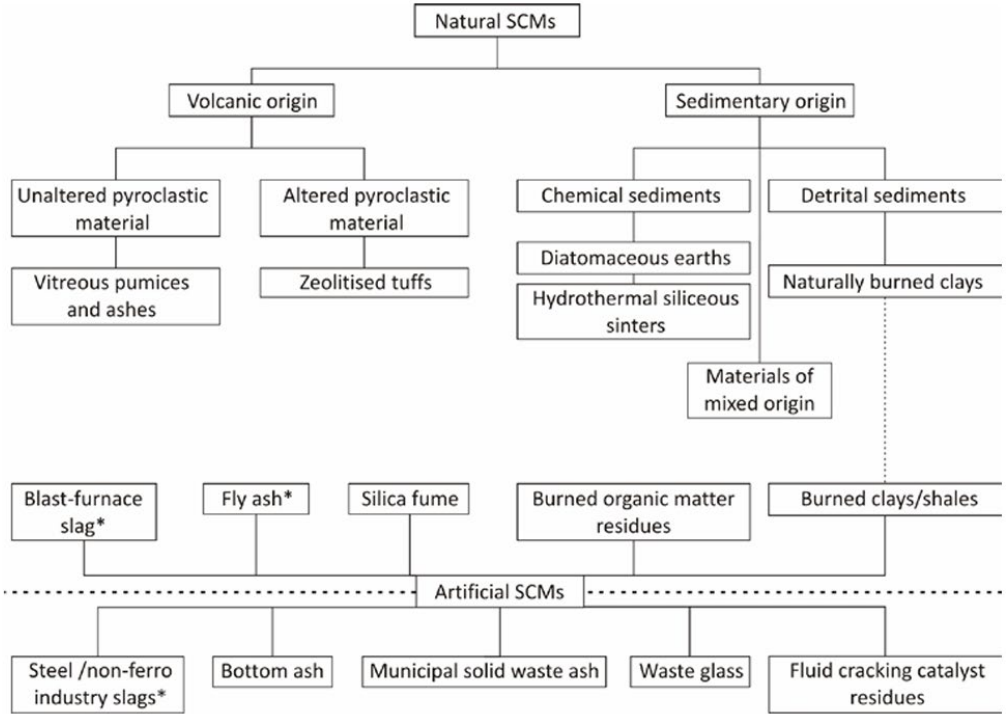


Pozzolanic reaction

- A generalized form of pozzolanic reaction is:
- S (Pozzolana) + CH+ H → C-S-H

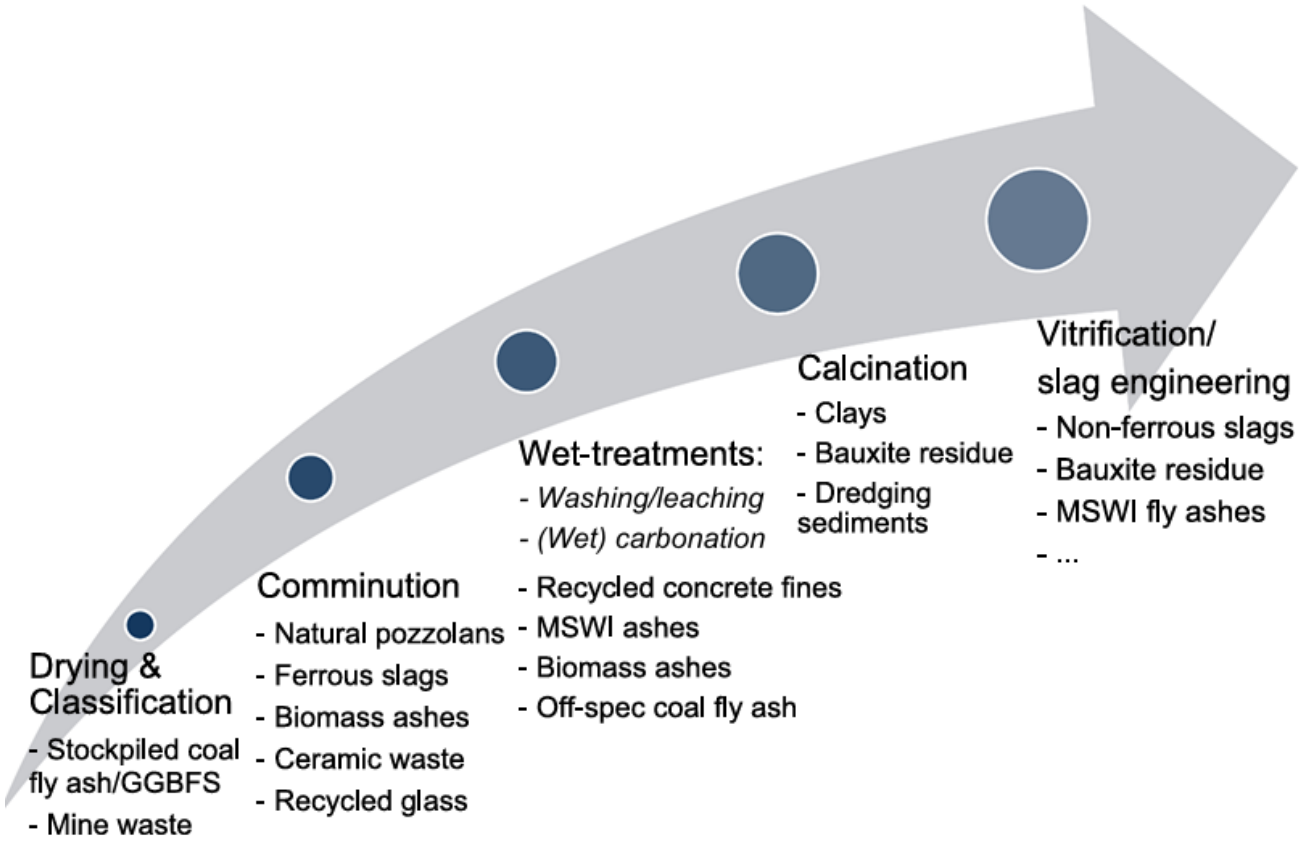
- CH comes from hydration of C_3S and C_2S
- $C_3S + 5.3\ H \rightarrow C_{1.7}\text{-}S\text{-}H_4 + 1.3\ CH$
- $C_2S + 3.3\ H \rightarrow C_{1.7}\text{-}S\text{-}H_4 + 0.3\ CH$

Types of SCMs



R. Snellings, et al. Supplementary cementitious materials. Reviews in mineralogy and geochemistry, 2012

Processing techniques



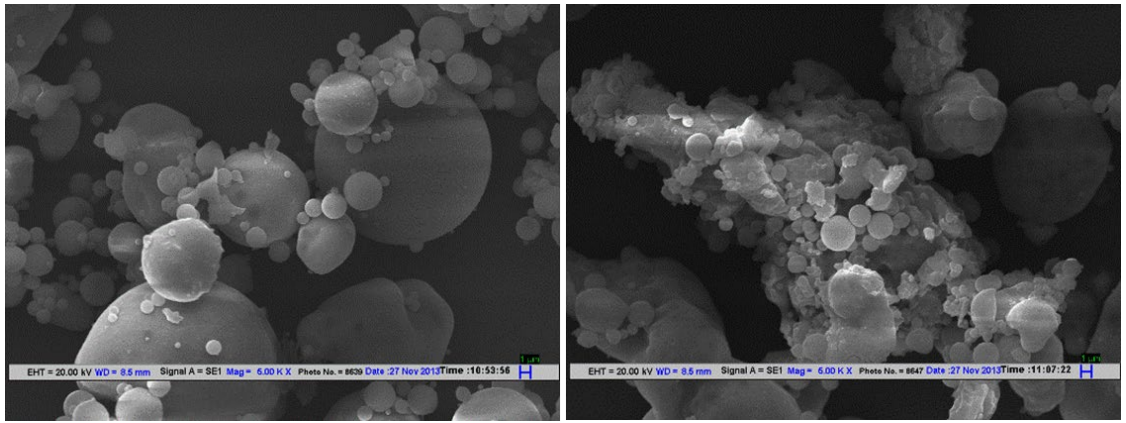
R. Snellings, et al. Future and emerging supplementary cementitious materials, CCR, 2023

Natural pozzolanic materials

- Volcanic rocks (glass, tuffs), shales
- Disordered aluminosilicates highly reactive under alkaline conditions
- Use mostly limited depending on local availability

Fly ash

- Ignition of coal in power plants
- Fine spherical particles
- SSA (usually 300-500 kg/m^2)



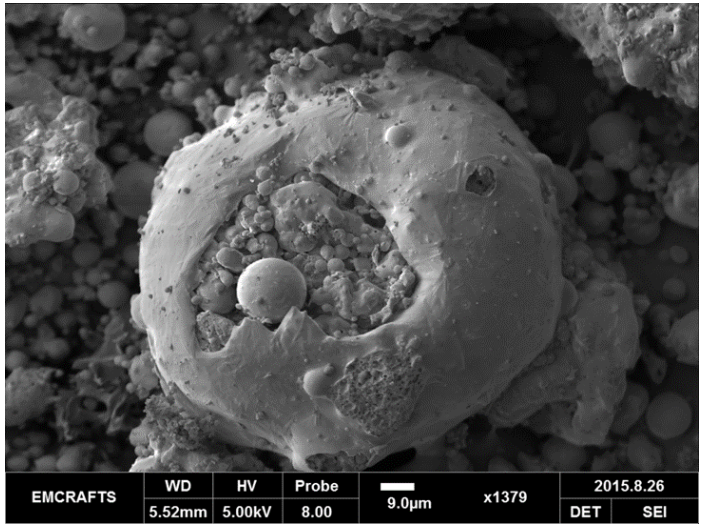
Surbak et al. 2004

Classification- ASTM C618

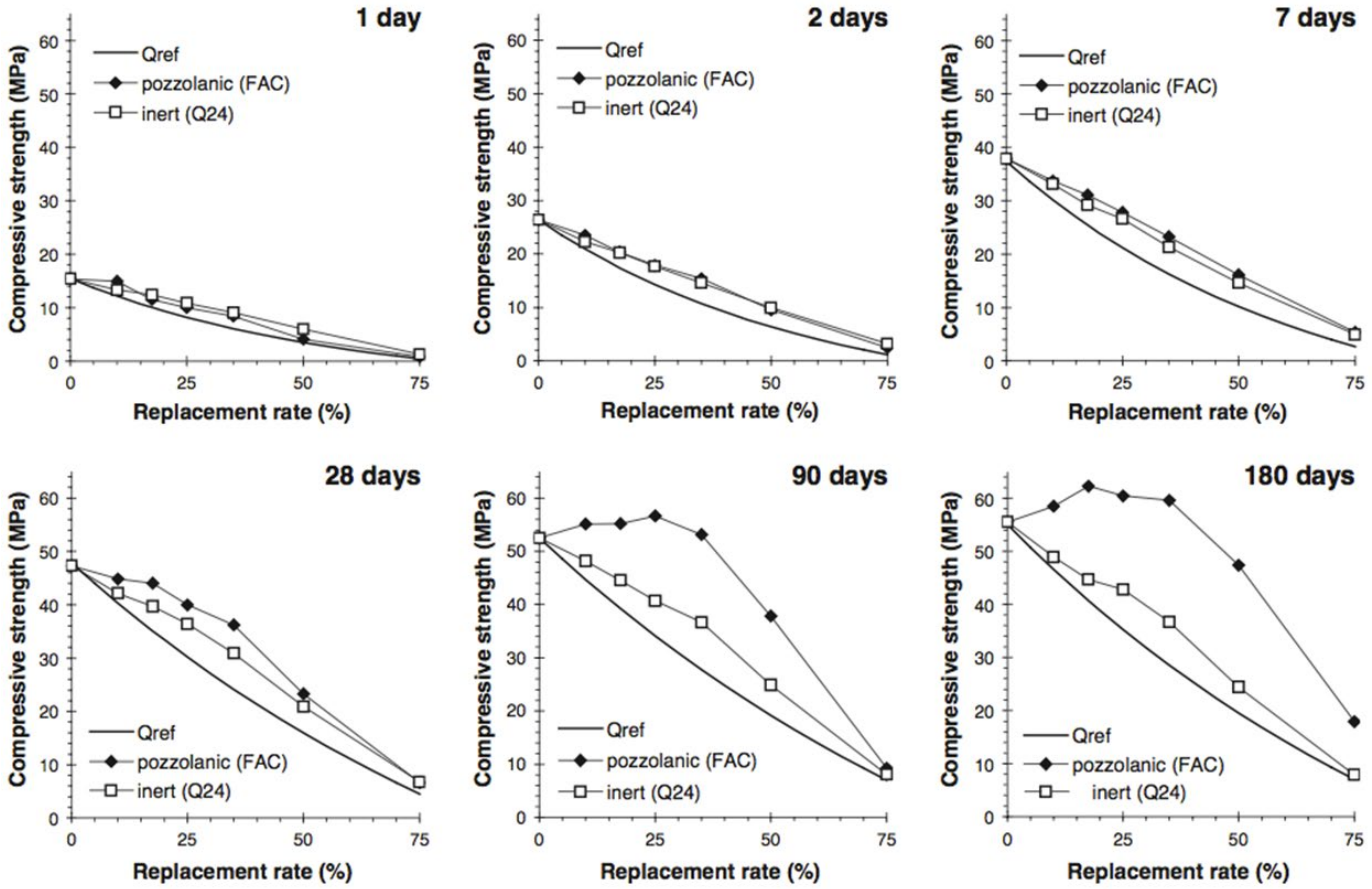
- Class F
  - With pozzolanic properties
  - Low calcium (<10%) and carbon (<5%)
- Class C
- With pozzolanic and cementitious properties
- High calcium (10-30%) and low carbon (<2%)

Fly ash types

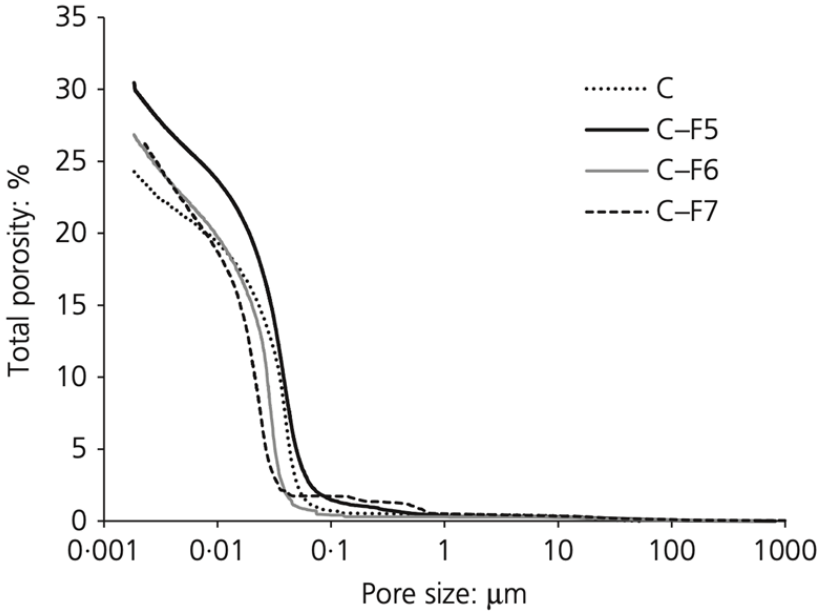
- Cenospheres – generally hollow glassy spheres
- Plerospheres – hollow spheres with particles packed inside them

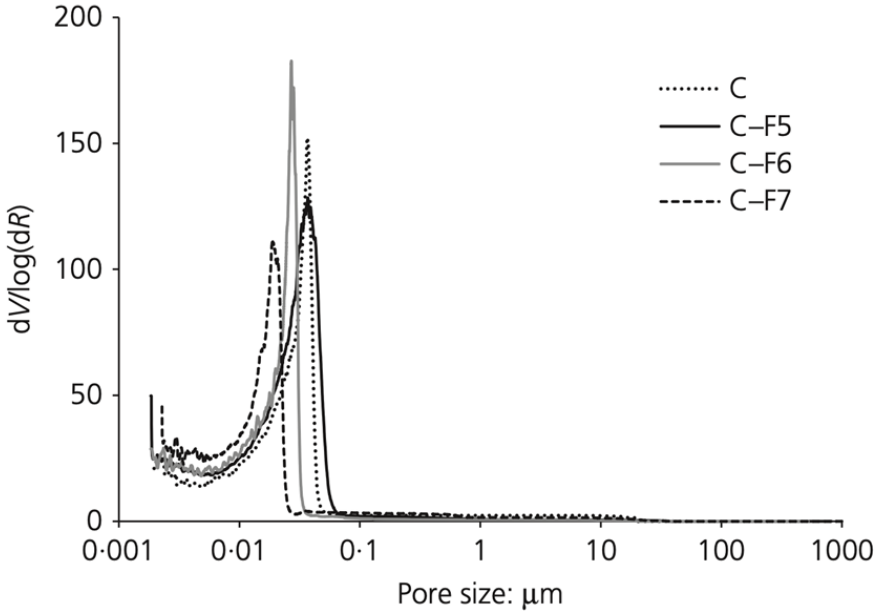


Compressive Strength

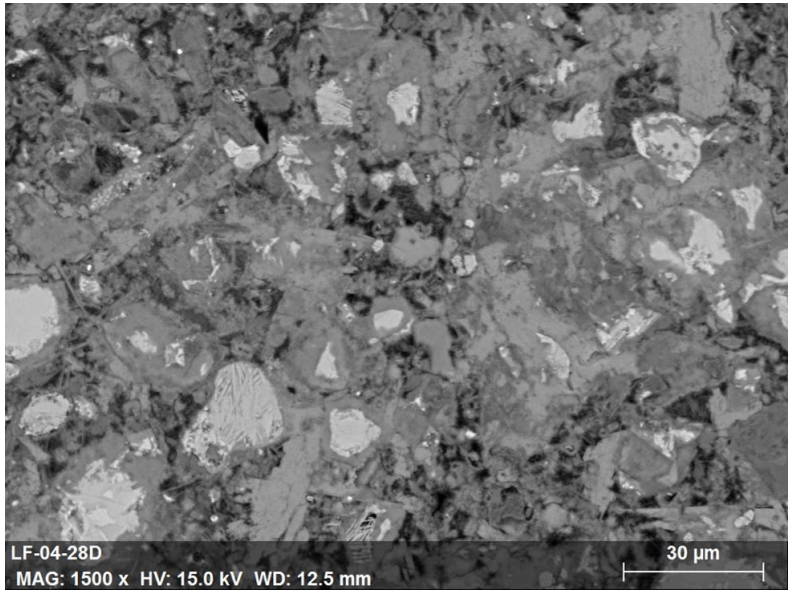


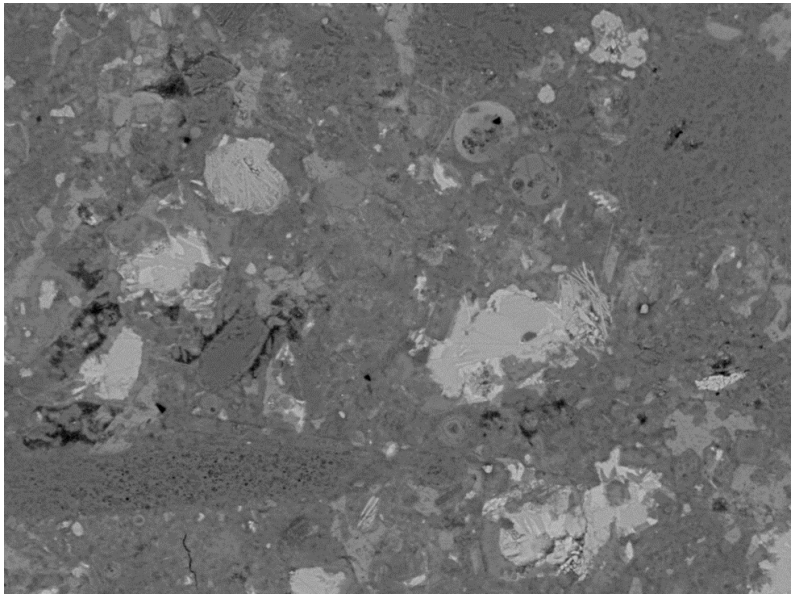
Effect on pore size





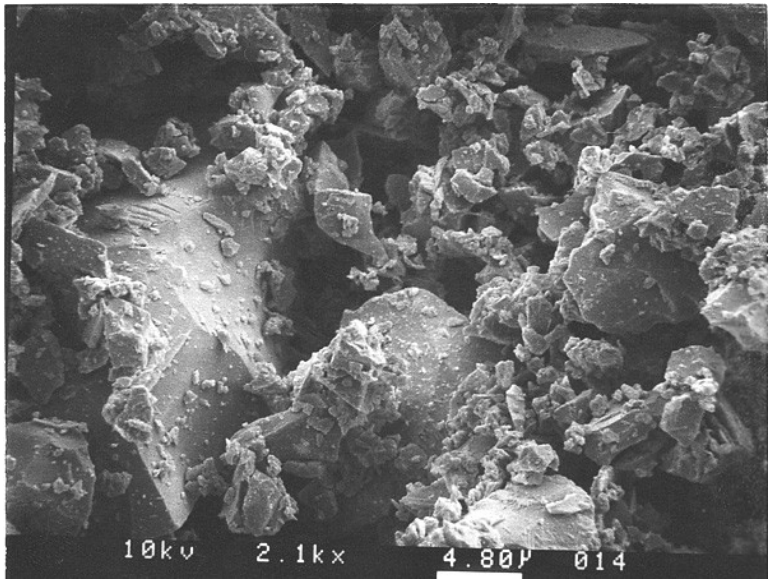
Effect on pore size





Slag

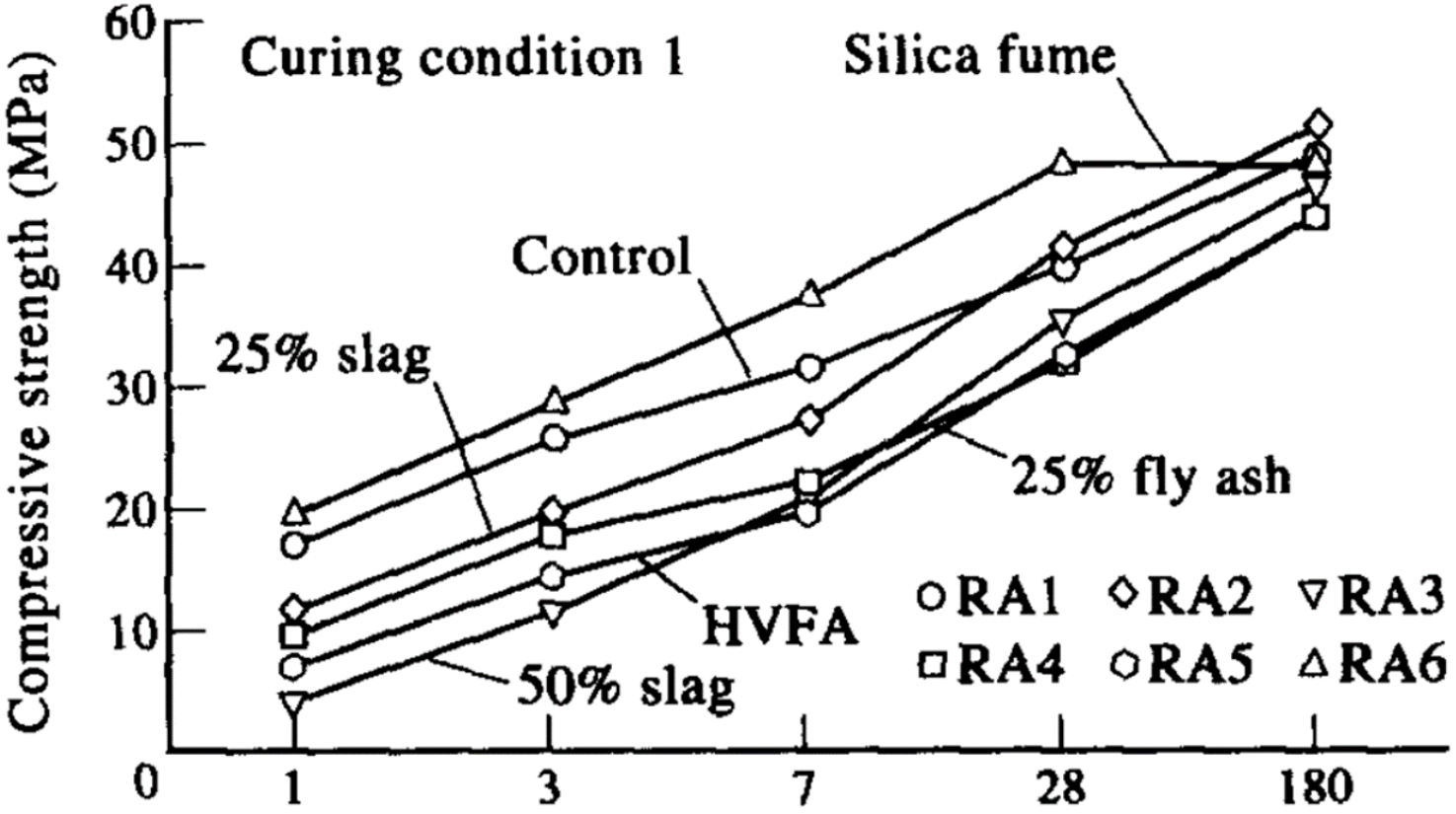
- Byproduct from the production of iron
- Silicate glass is the major phase
- Usually fineness to OPC



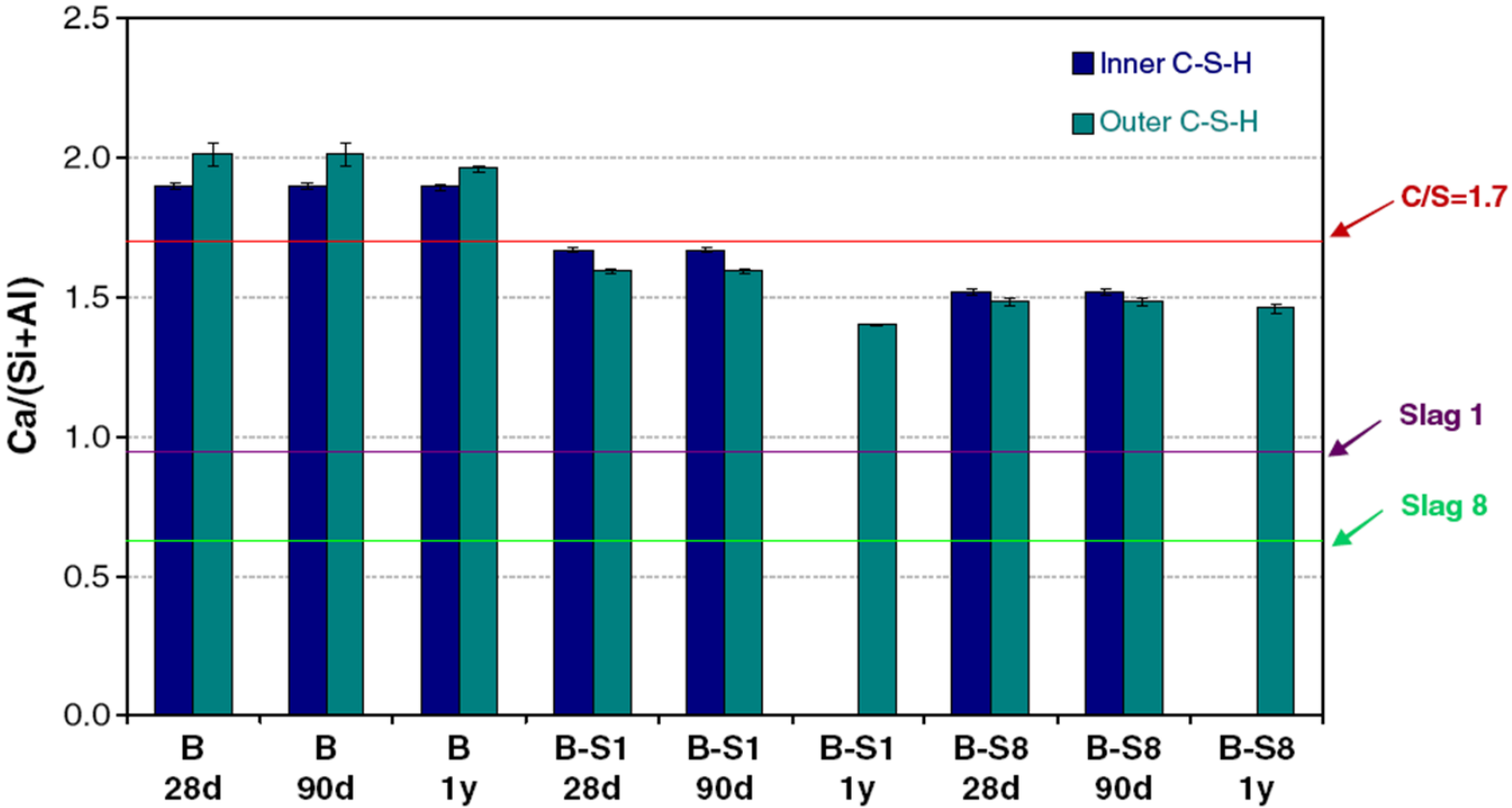
Use of slag in concrete

- As much as 70% cement replacement
- Chloride binding
- Carbonation can be improved

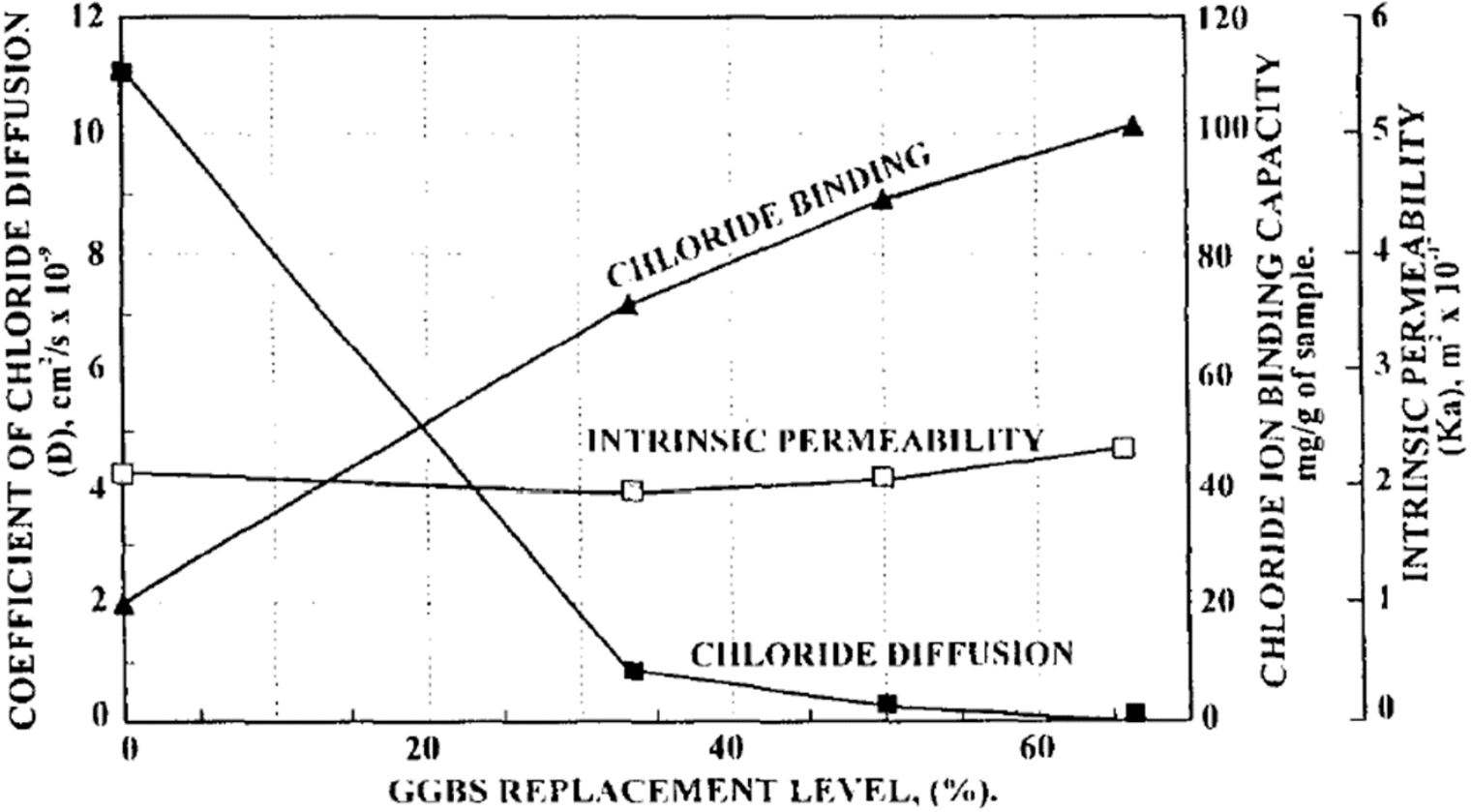
Slag- compressive strength



Slag- Ca/(Al+Si)


Ca/(Si+Al)
2.5
2.0
1.5
1.0
0.5
0.0
Inner C-S-H
Outer C-S-H
C/S=1.7
Slag 1
Slag 8
B 28d
B 90d
B 1y
B-S1 28d
B-S1 90d
B-S1 1y
B-S8 28d
B-S8 90d
B-S8 1y

Slag- Chloride ingress



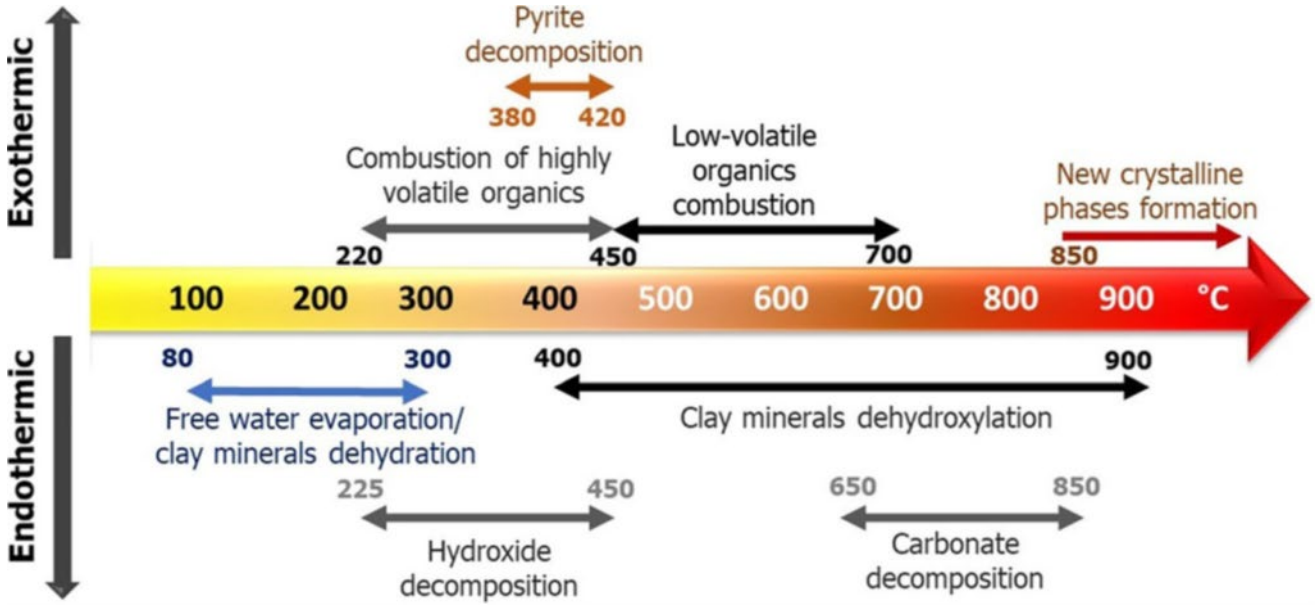
Silica Fume

- By-product of reduction of high purity quartz with coal
- >85% amorphous SiO_2
- Spherical particles

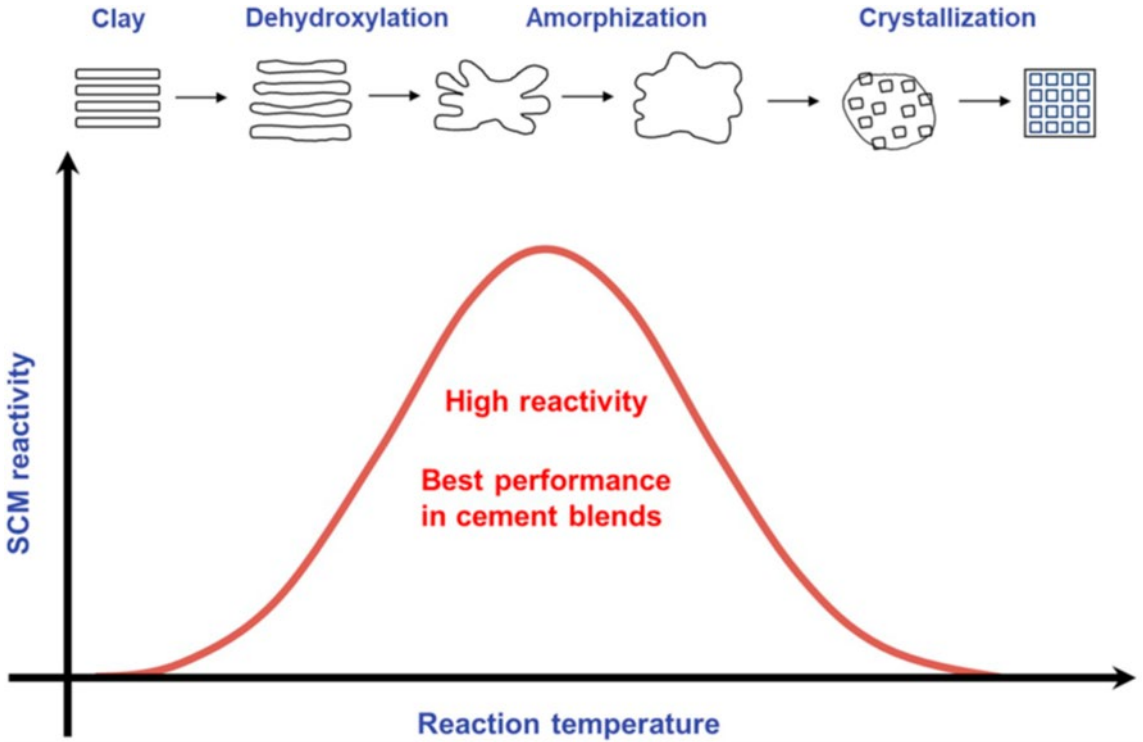
Silica Fume

- The fine particles pack into spaces between cement particles
- Improved rheology due to ball-bearing effect
- Higher cohesion – reduced segregation and bleeding
- Higher water requirement
- Use of dispersants can reduce water requirement
- SF particles allows production of very low w/c (<0.2) concretes by filling gaps

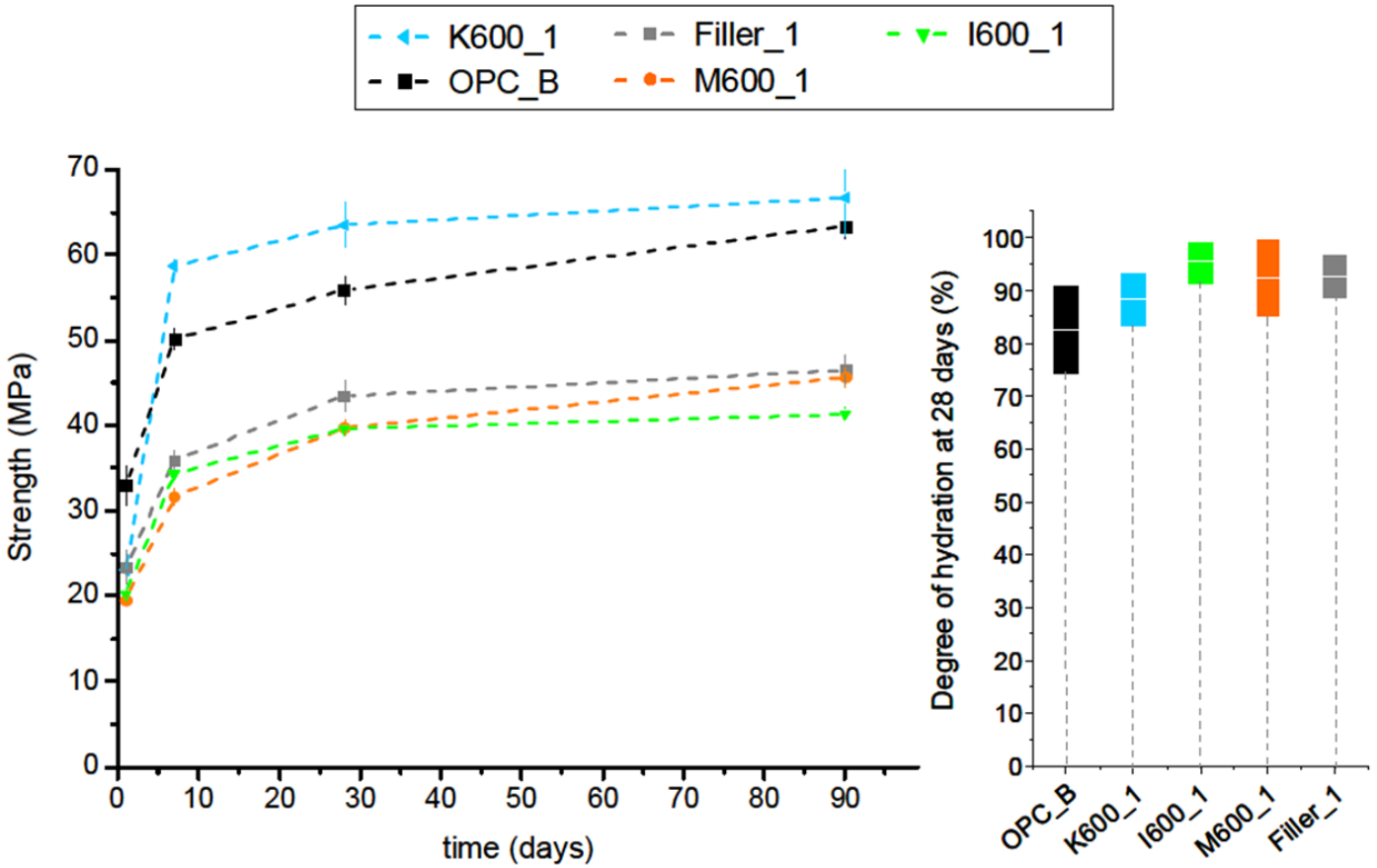
Calcined clays



Calcined clays

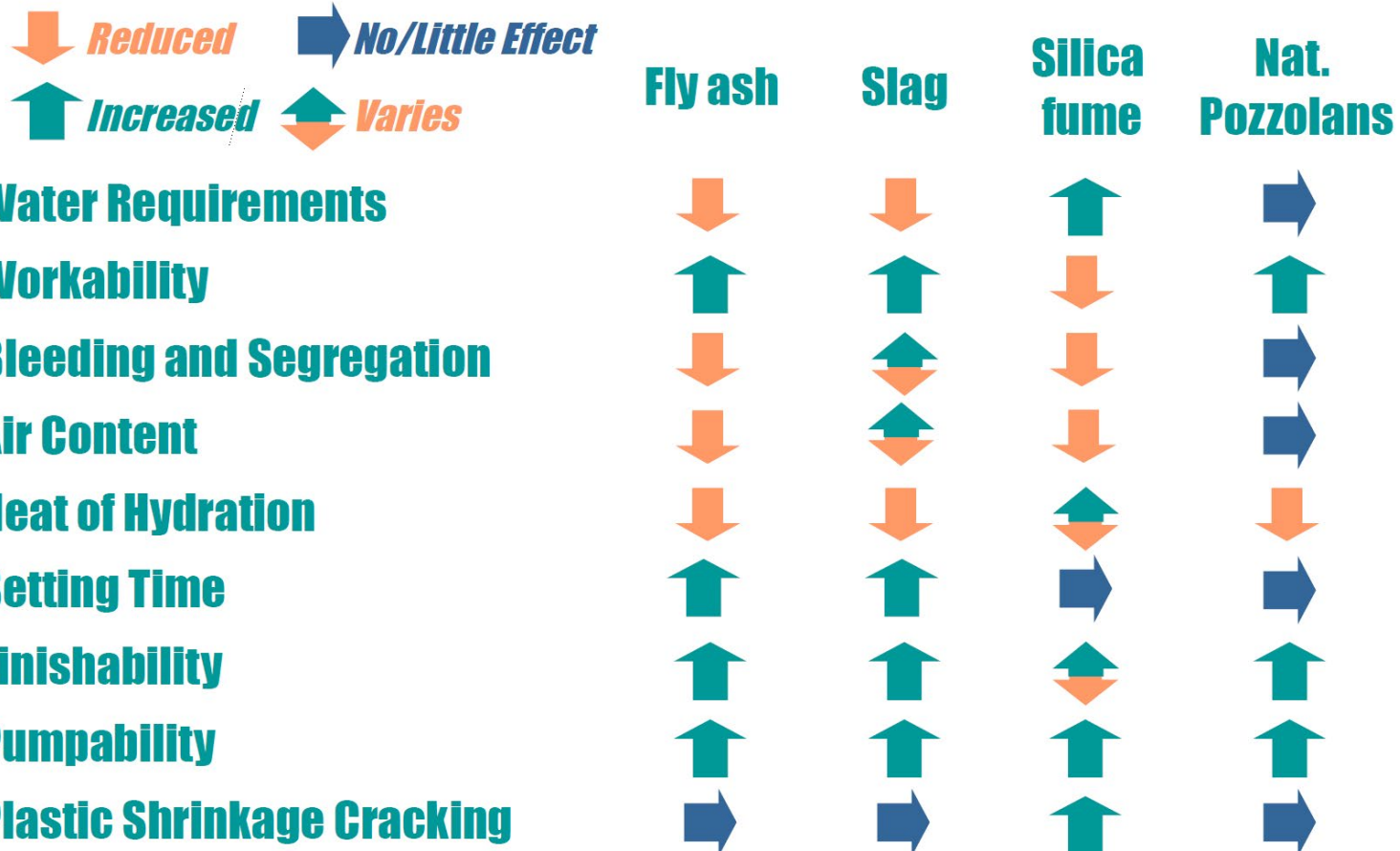


Calcined clays



Effects of Supplementary Cementing Materials on Freshly Mixed Concrete

From PCA



Inert fillers

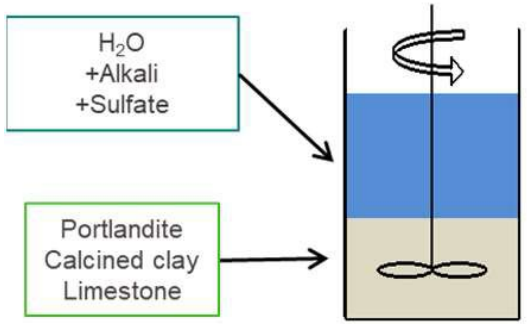
- Crushed limestone particles can be added
- Not reactive, but can improve the properties
  - Compressive strength
  - Permeability
  - Early age properties

Reactivity of SCMs

Duration	Test methods
Short Duration	Modified Chapelle test
	Amorphous content using XRD
	Dissolution solubility test
Medium Duration	Lime Reactivity
	R3 test
	Isothermal calorimetry
	Frattini test
Long Duration	Cement mortar strength test
	Strength activity Index
	Chemical shrinkage

R3 Test- Rapid, Relevant and Reliable

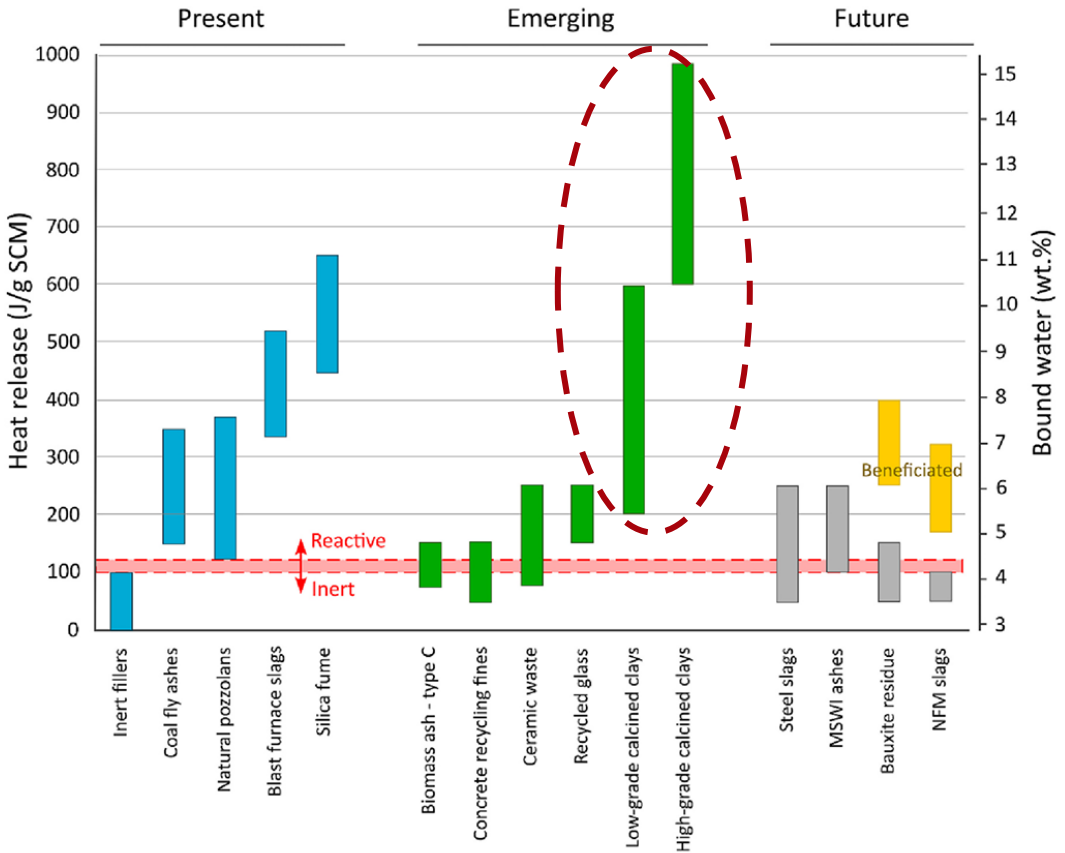
- ASTM C 1897-20



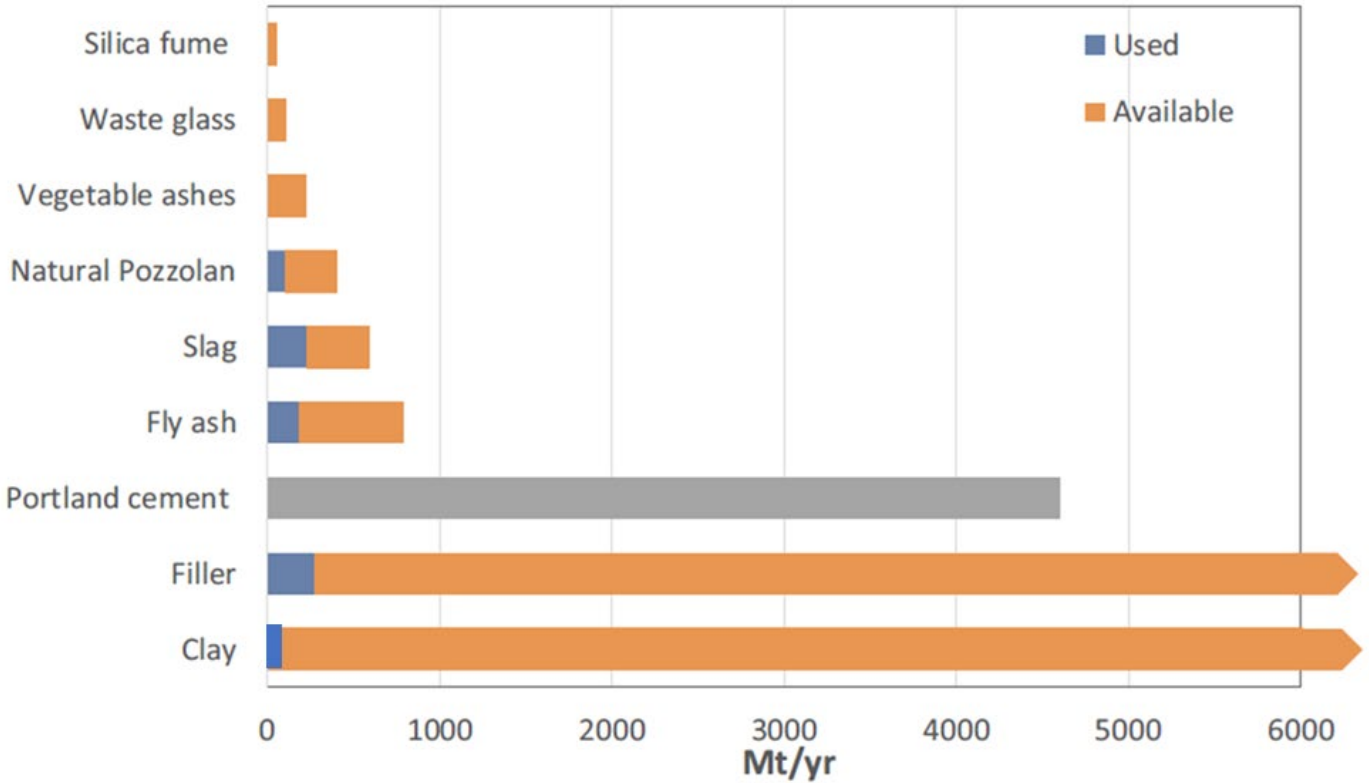
Isothermal calorimetry at 40°C

Oven thermal treatment at 400°C

Reactivity of SCMs



SCM Availability



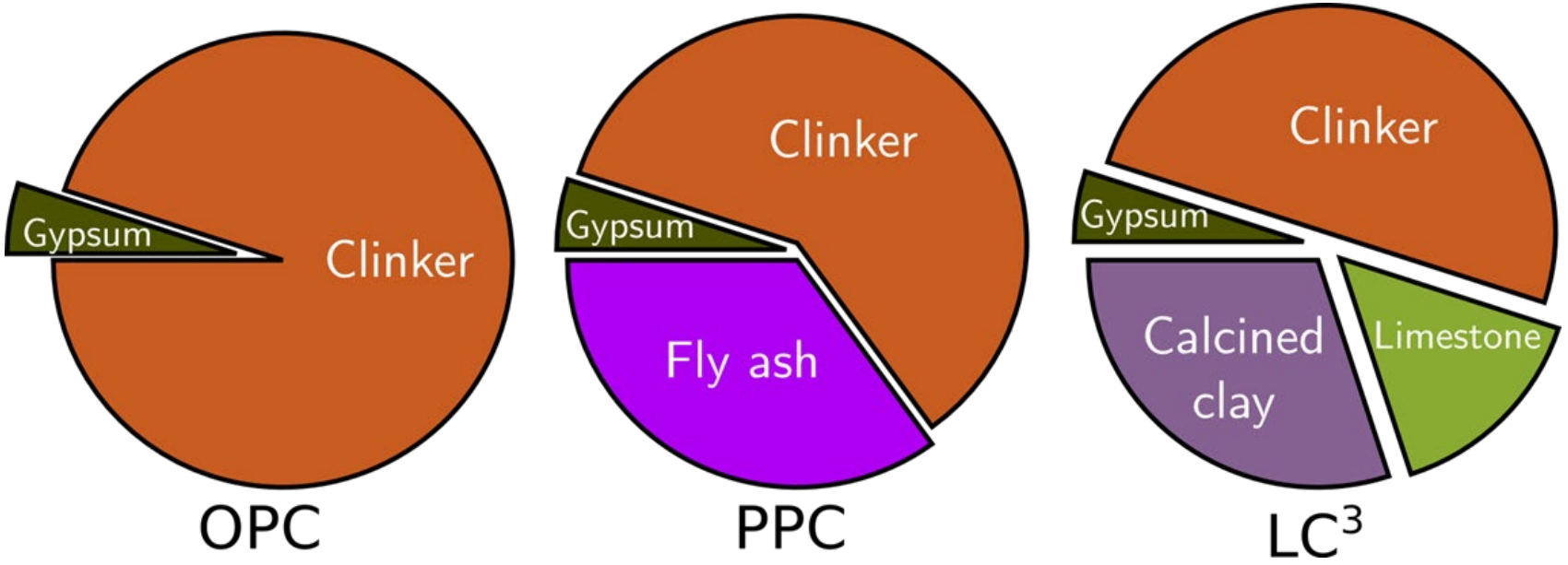
Limited supply of common SCMs

UN environment

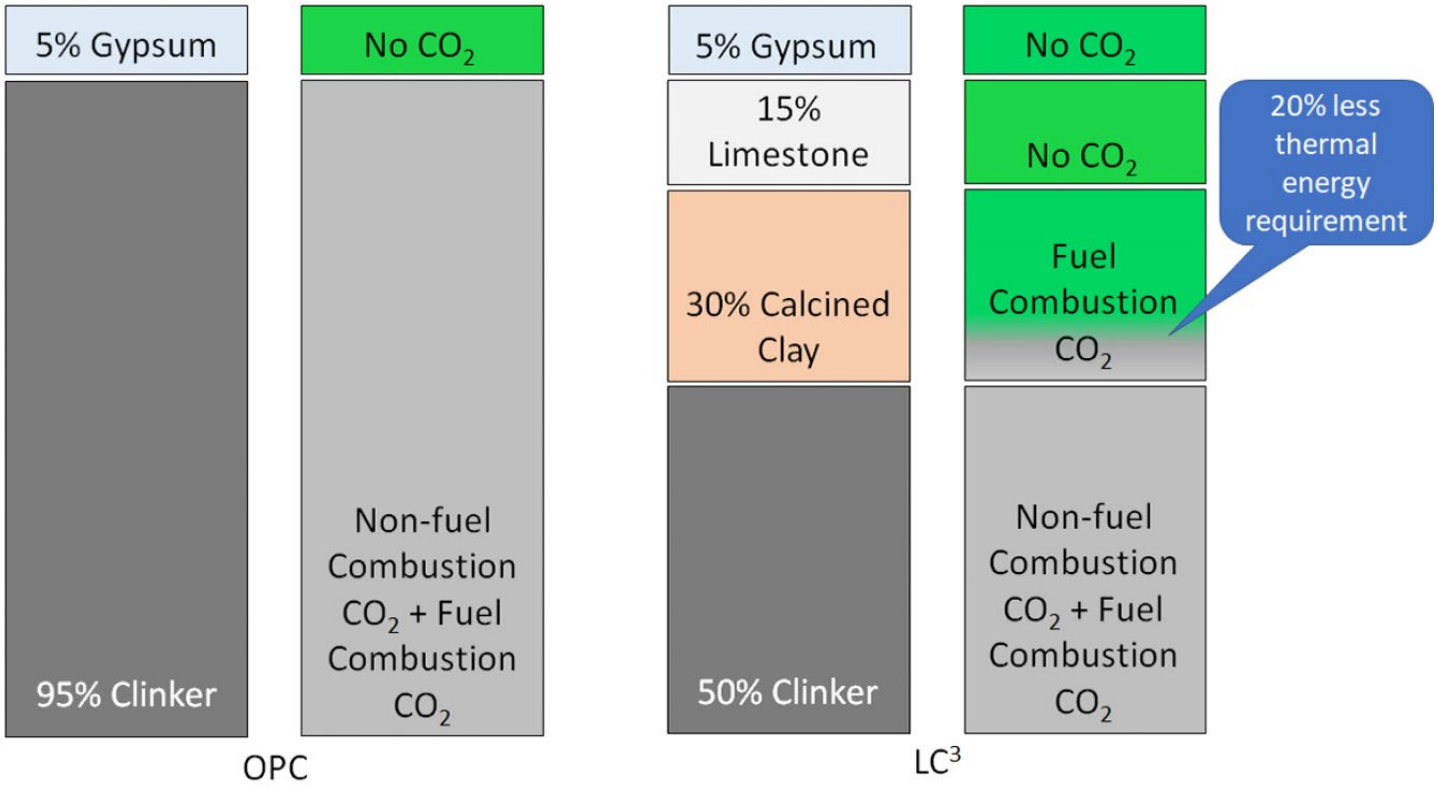
Eco-efficient cements:
Potential economically viable solutions for a low-CO_2 cement-based materials industry

Blended cements

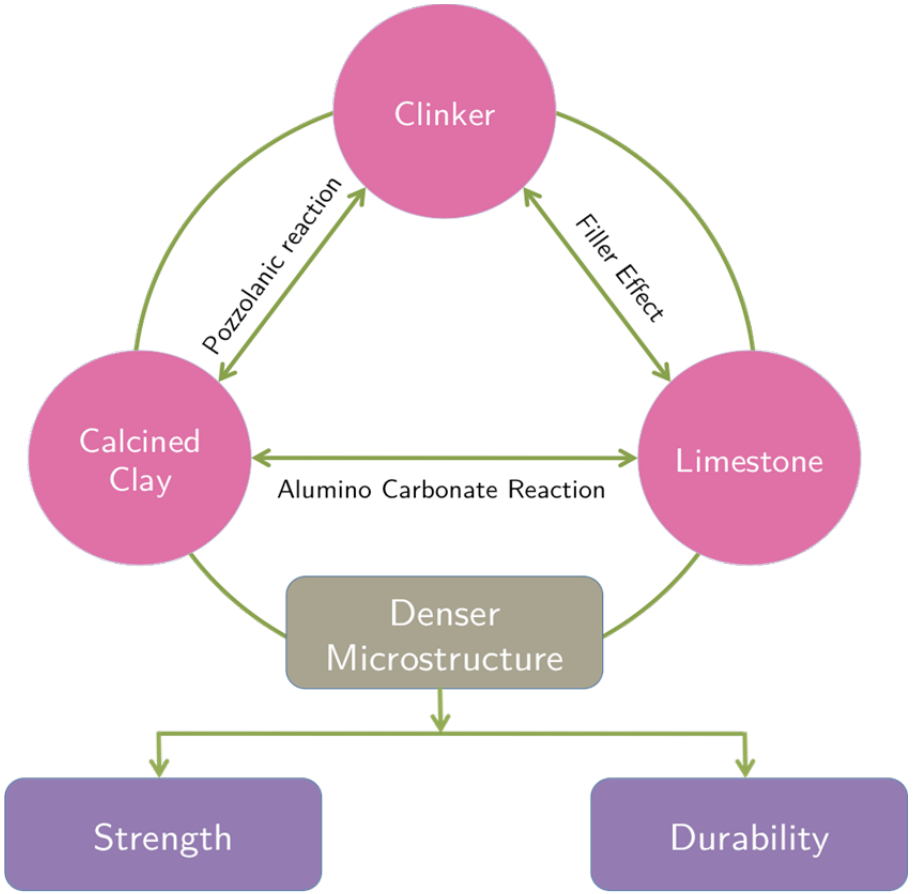
Blended cements



Advantage of LC^3 over OPC



All mechanisms occur simultaneously!!

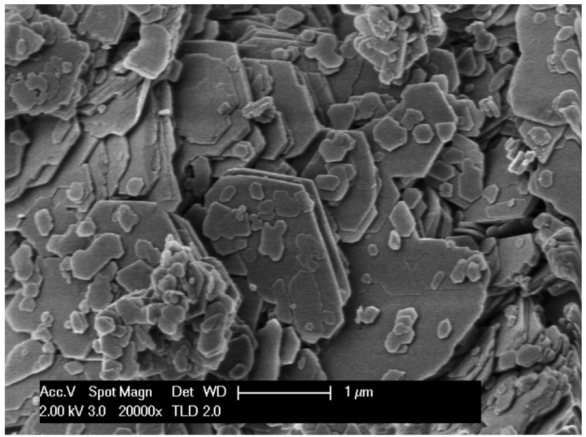


Chemistry of LC^3

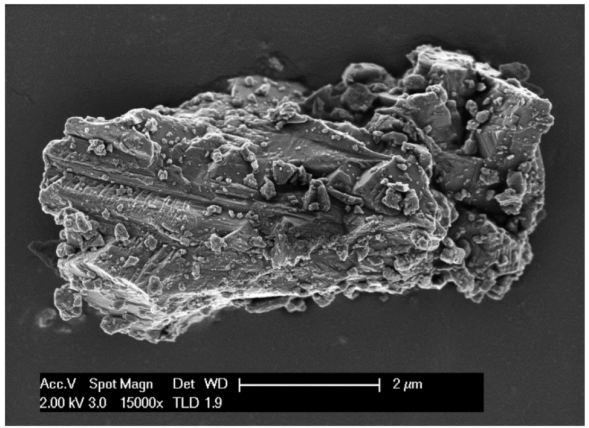
- The reaction of calcium silicates
  - C_3S + H → C-S-H + CH
  - C_2S + H → C-S-H + CH
- C-S-H is the main “glue” in the cementitious system
- The reaction of aluminates/ferrites
  - $C_3A + 3C\$ + 26H \rightarrow C_6A\$_3H_{32}$
  - $C_4AF + 10H \rightarrow C_3AH_6 + FH_3 + CH$
  - $2C_6A\$_3H_{32} + 1C_3A + 3H \rightarrow 3C_4A\$H_{12}$

Chemistry of LC^3

- Pozzolanic reaction of calcined clay
  - CH + AS_2 + H → C-A-S-H + C-A-H
- Presence of calcite modifies the pozzolanic reaction
  - CH + AS_2 + $C\bar{C}$ + H → C-A-S-H + $C_4A\bar{C}H_{11}$ + $C_4A\bar{C}_{0.5}H_{12}$



Calcined clay



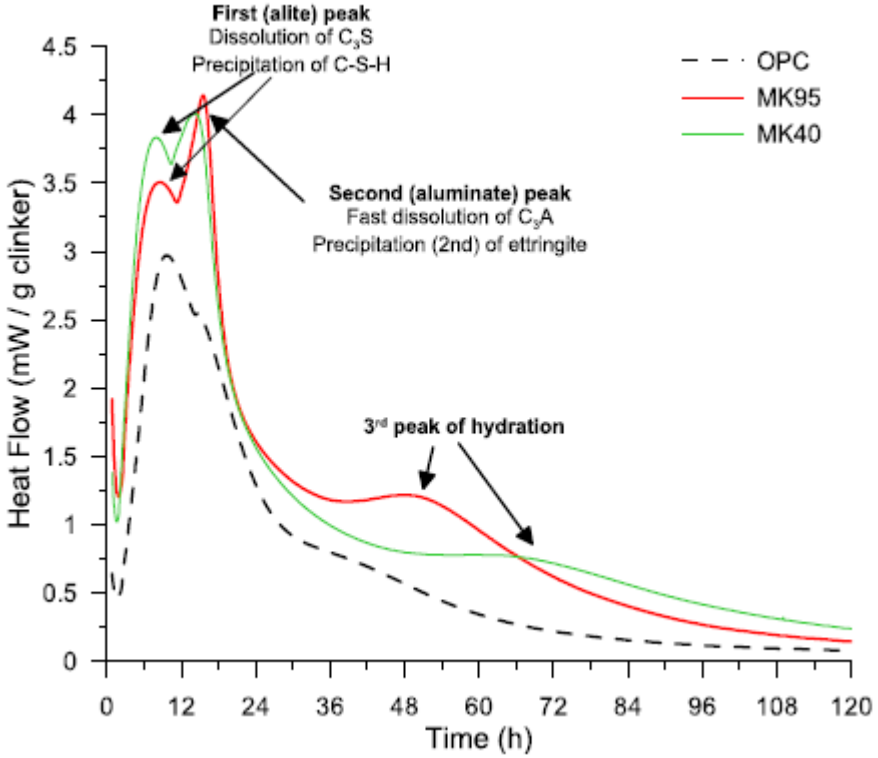
Limestone

Stabilisation of ettringite

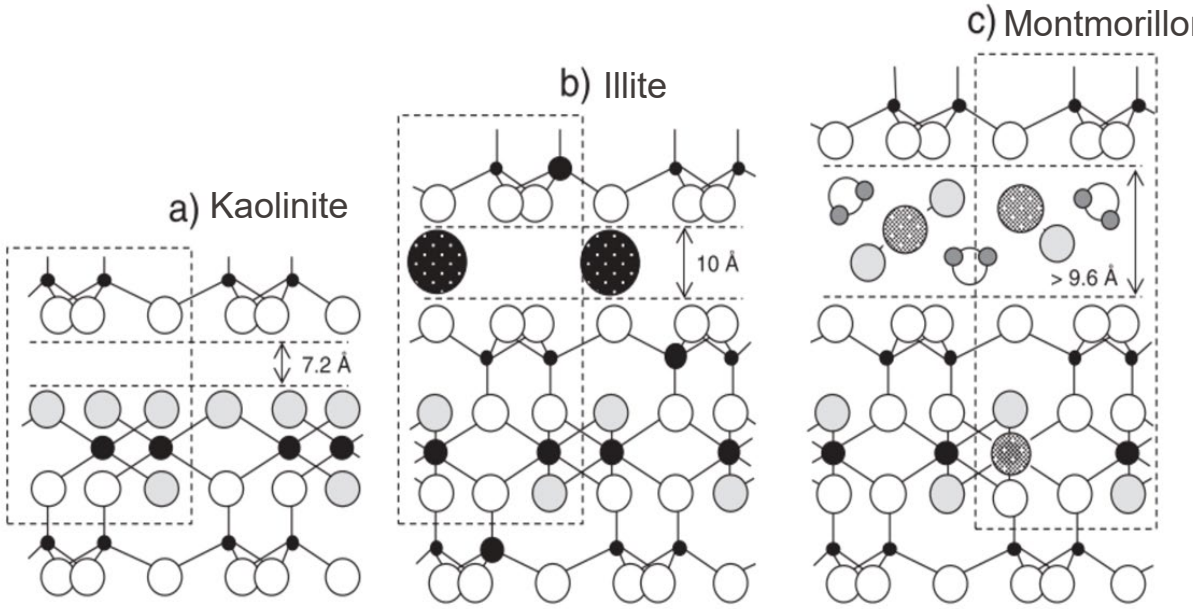
- Ettringite is the first phase to precipitate
  - $3C\$H_2 + C_3A + 26H \rightarrow C_6A\$_3H_{32}$
- If additional alumina is available, ettringite converts to monosulphate
  - $C_6A\$_3H_{32} + 2C_3A + 4H \rightarrow 3C_4A\$H_{12}$
- Presence of CO_3^{2-} ions modifies the reaction
  - $3C_4A\$H_{12} + 2C\bar{C} + 18H \rightarrow C_6A\$_3H_{32} + 2C_4A\bar{C}H_{11}$

Ettringite, being a low-density phase, occupies more volume!!!

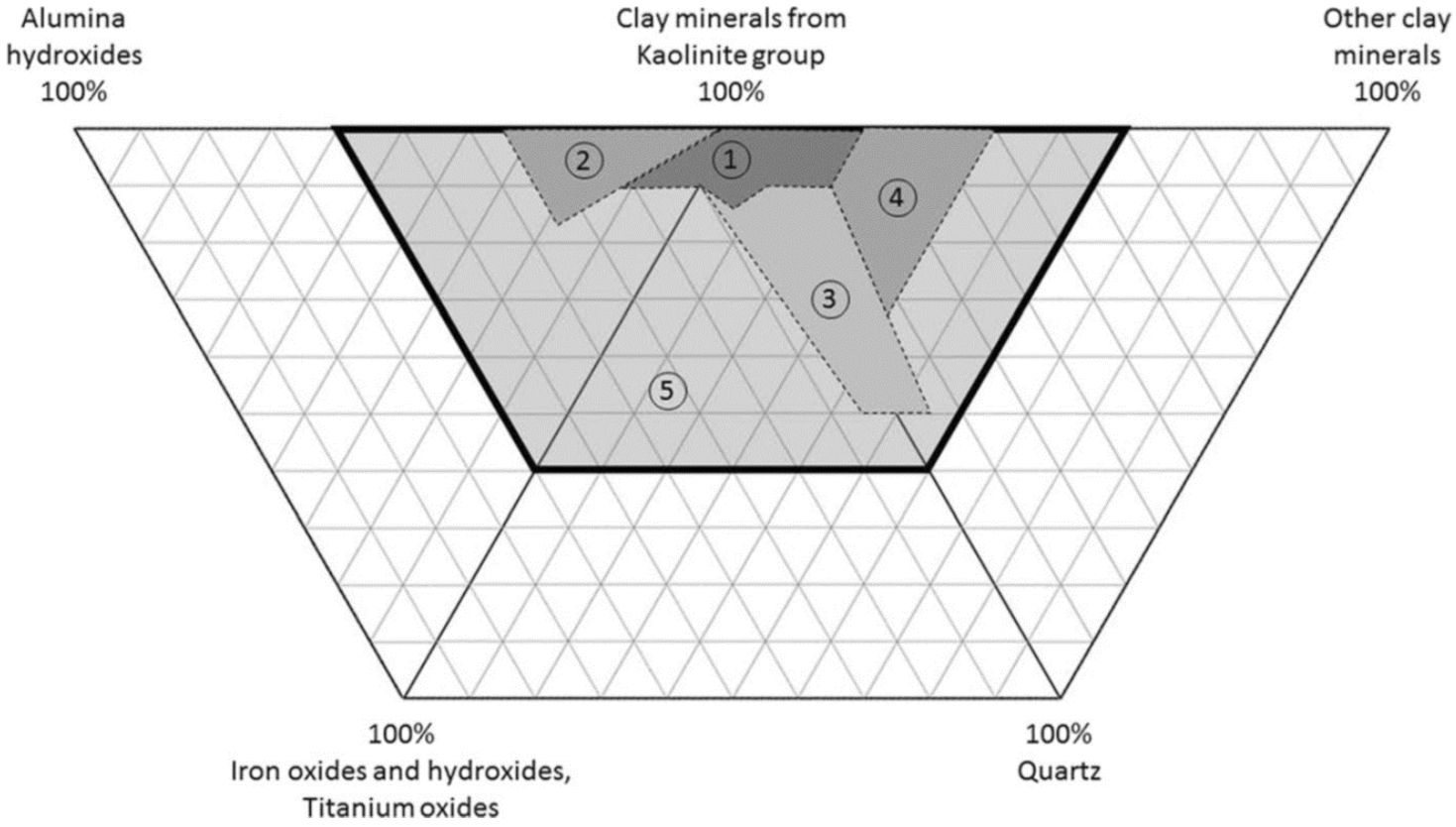
Reactivity overview of LC^3



Which clays are suitable ??



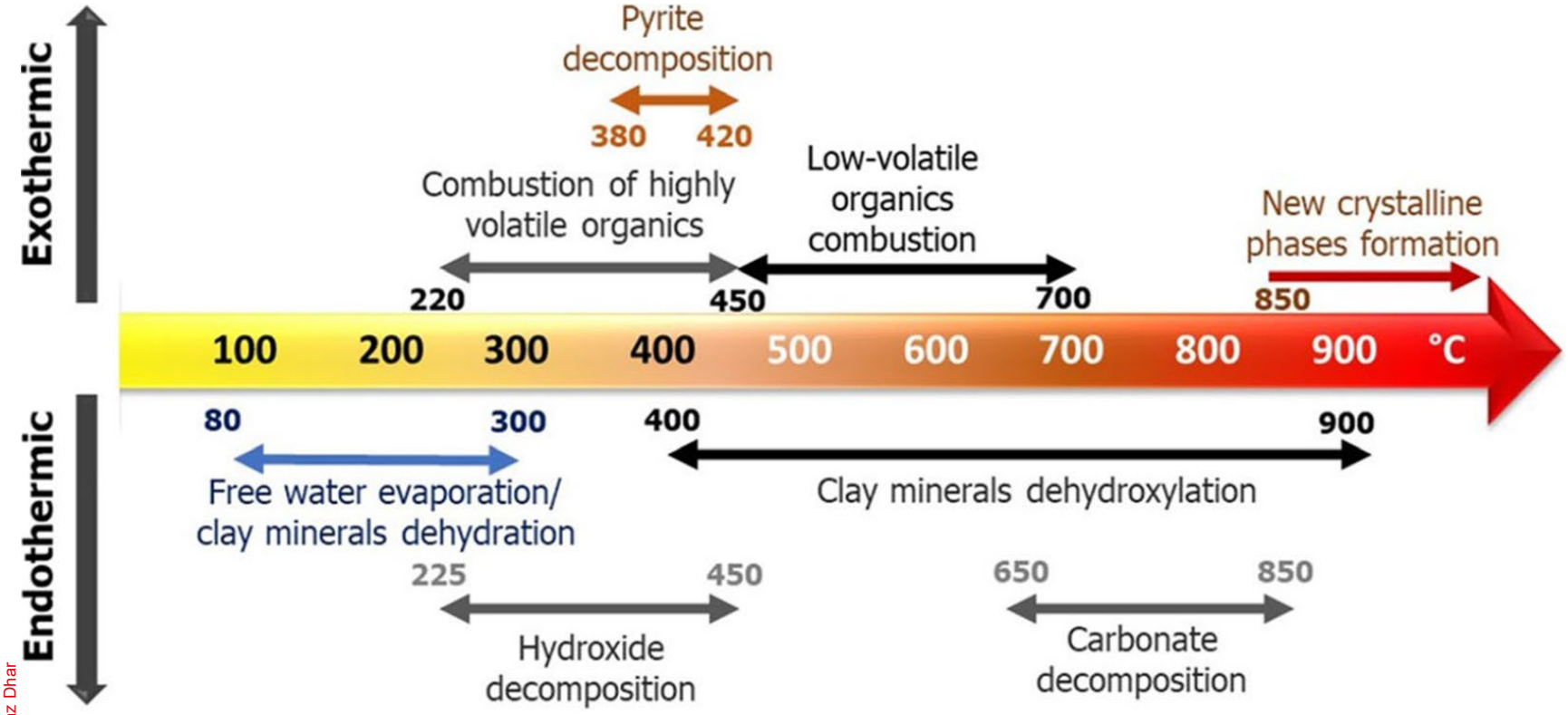
Composition of kaolinite clays



Global distribution of clay minerals

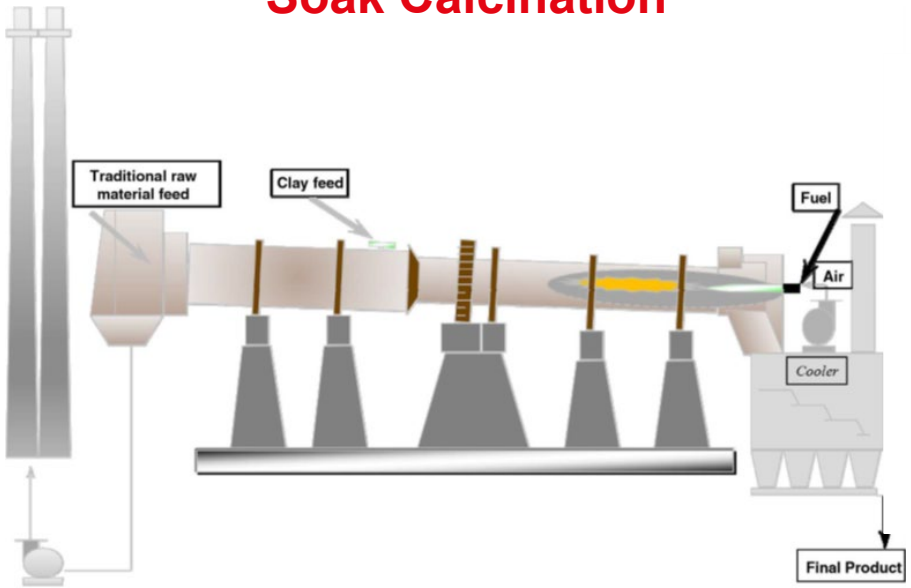
Rejected clays from clay mines

What happens when clays are heated ??

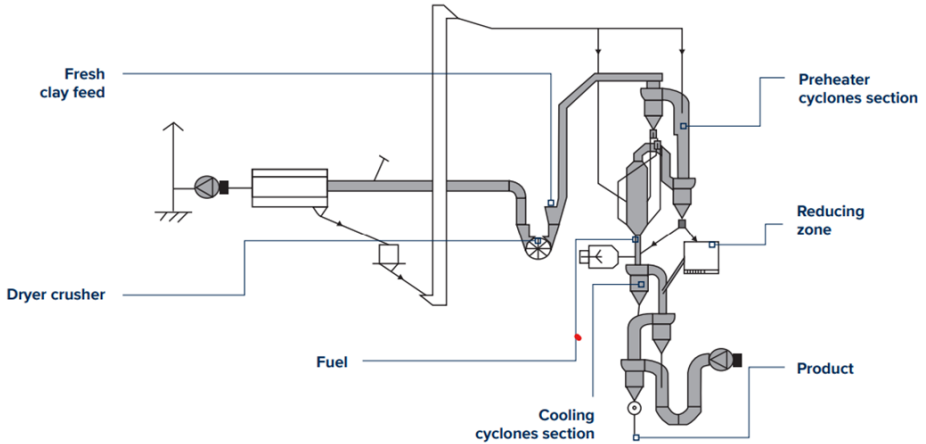


What happens when clays are heated ??

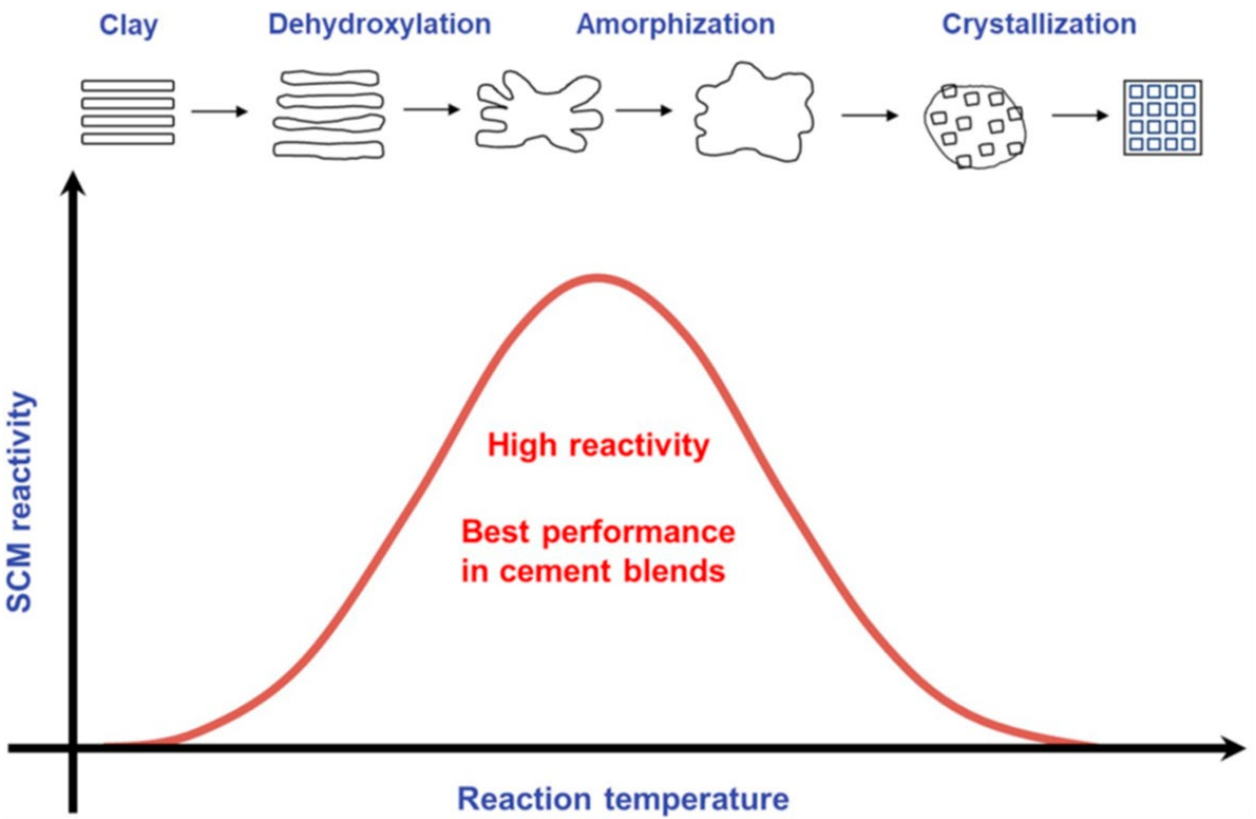
Soak Calcination



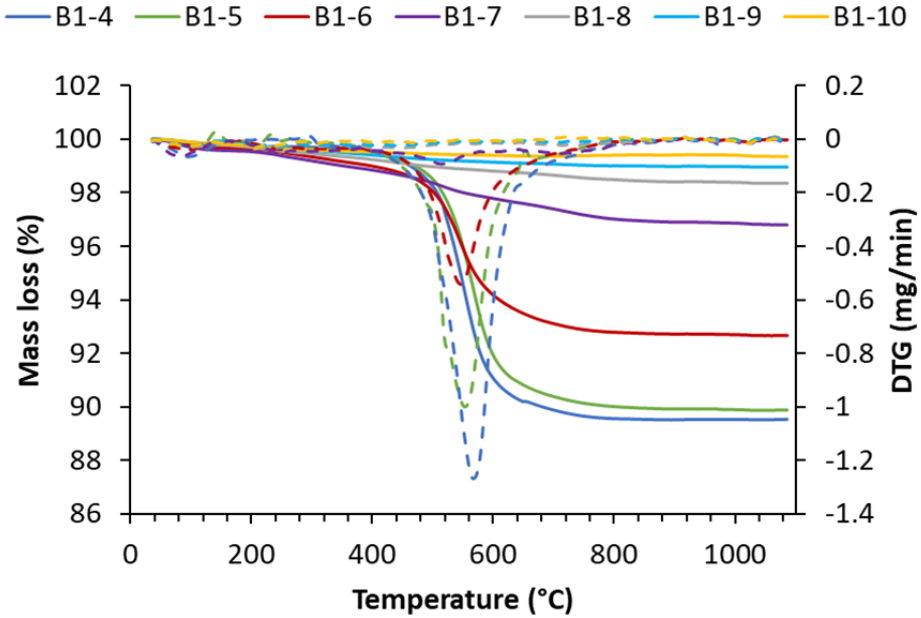
Flash Calcination

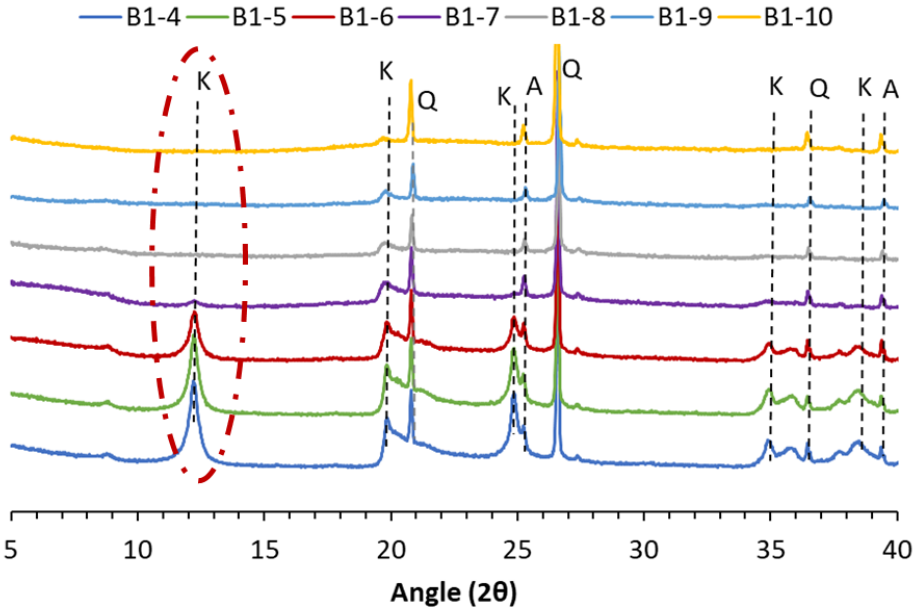


Reactivity Vs Temperature

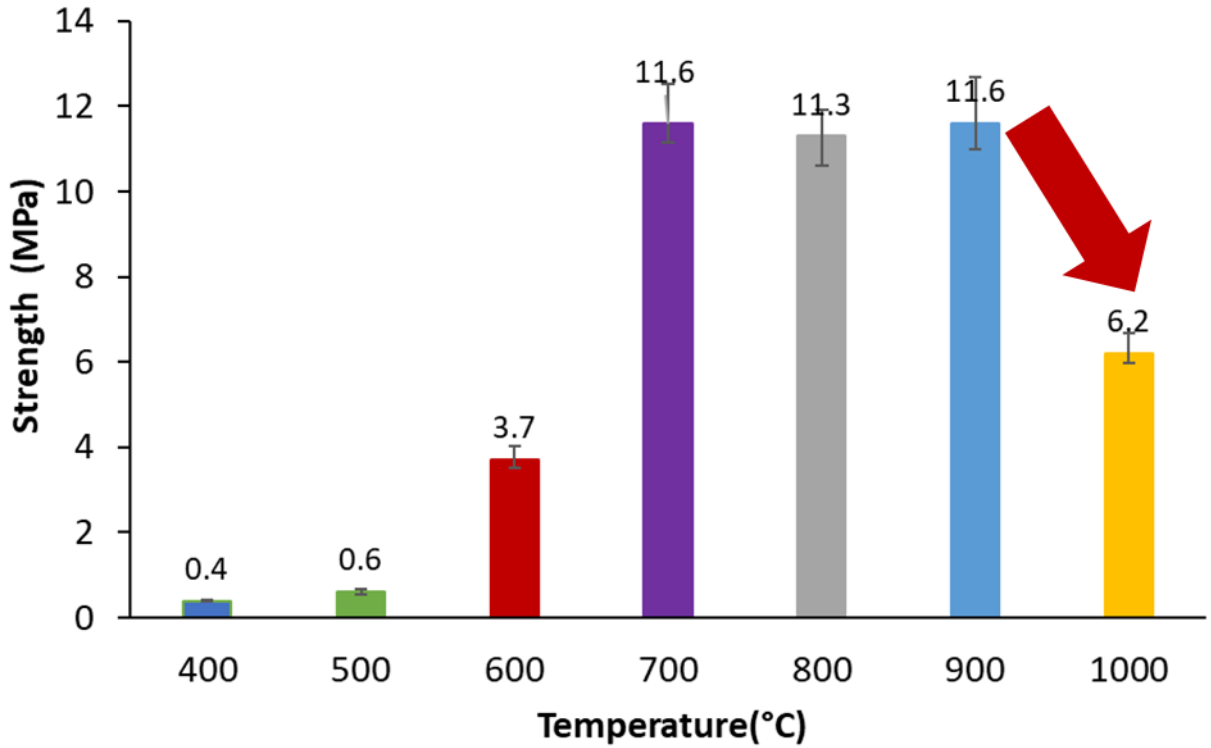


Method to check under-calcination

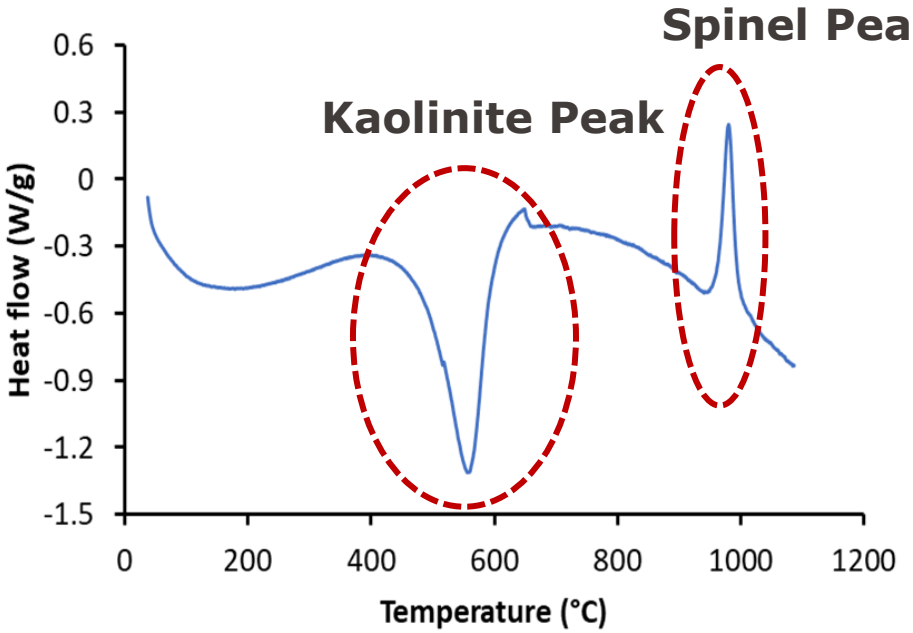


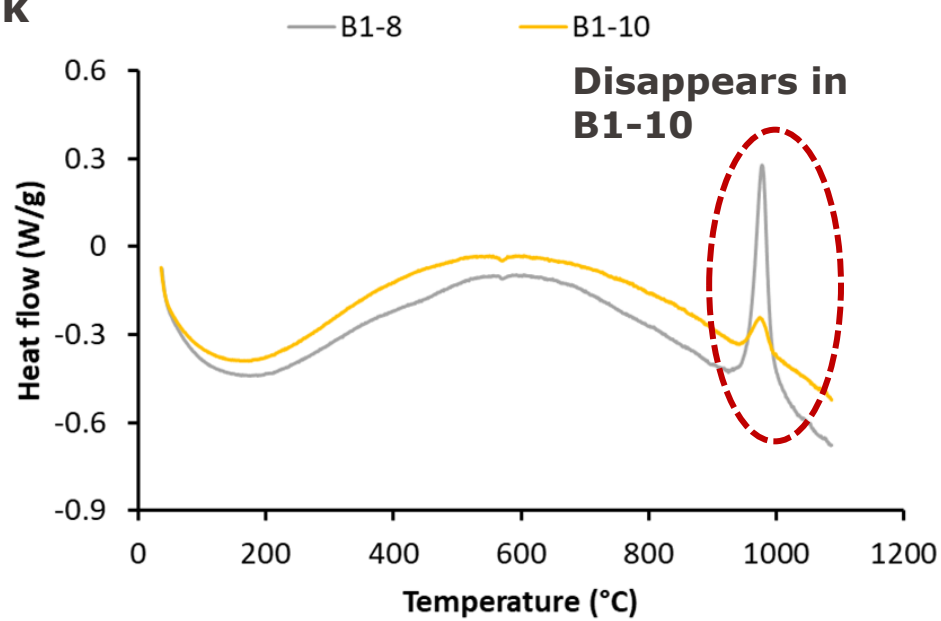


Over-calcination is also a problem



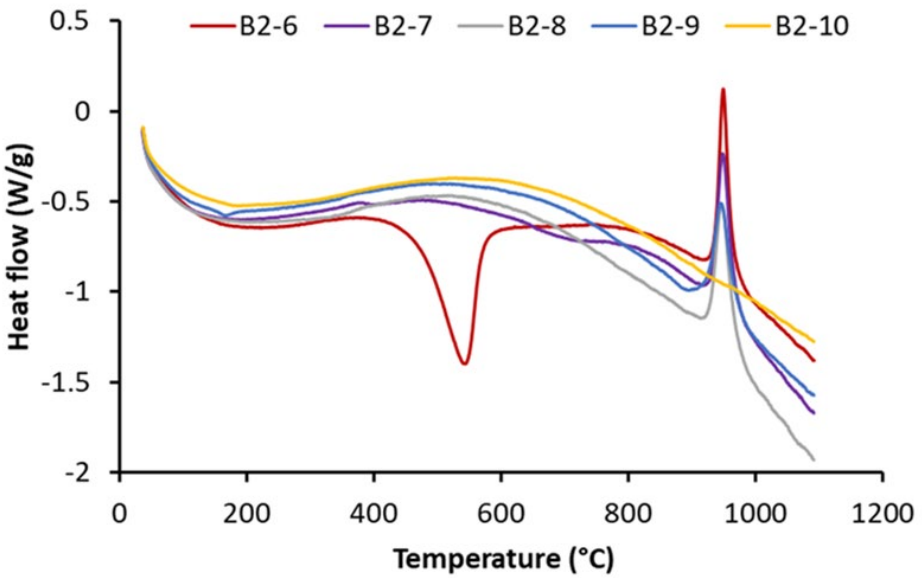
Method to check over-calcination



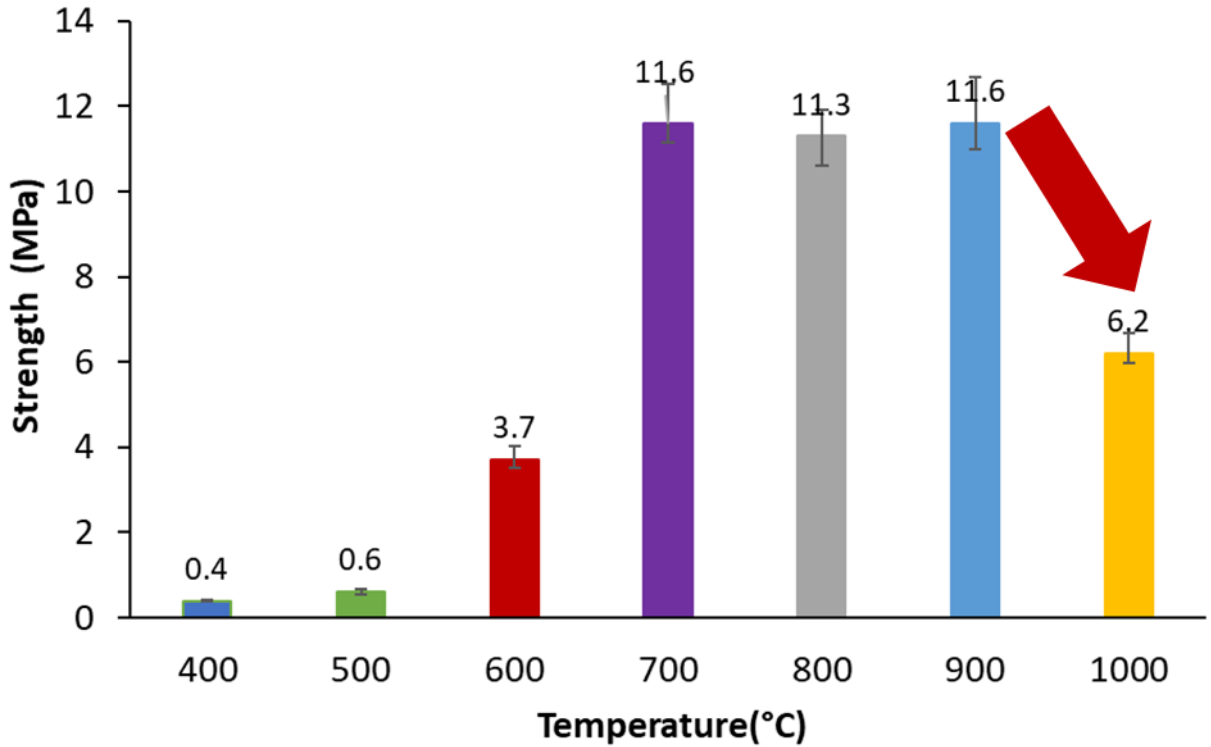


Method to check over-calcination

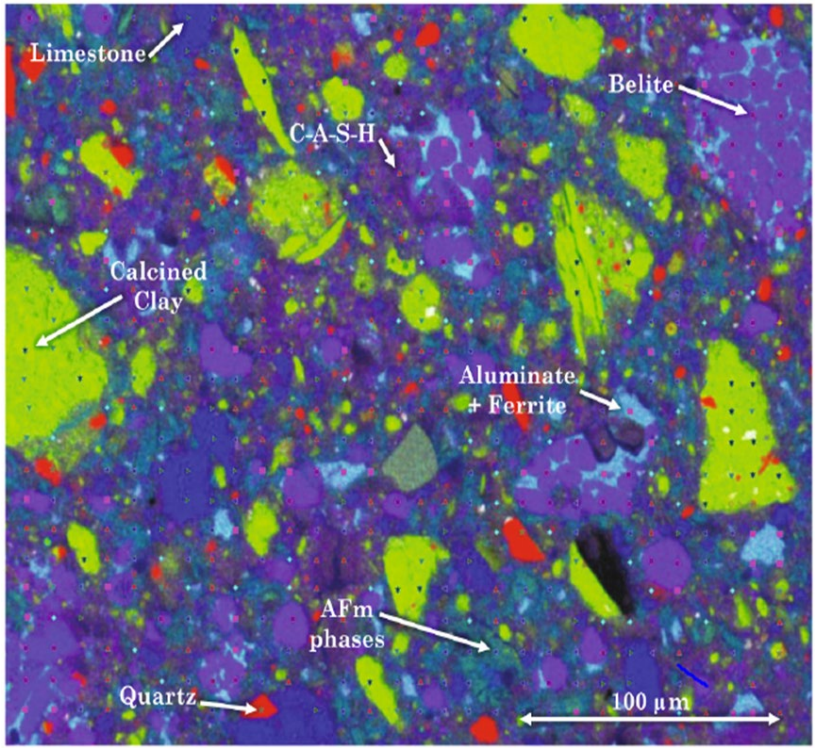
	Endo- Peak	Exo-Peak
Under calcined	Present	Present
Proper calcined	Absent	Present
Partial over calcined	Absent	Partial
Over calcined	Absent	Absent



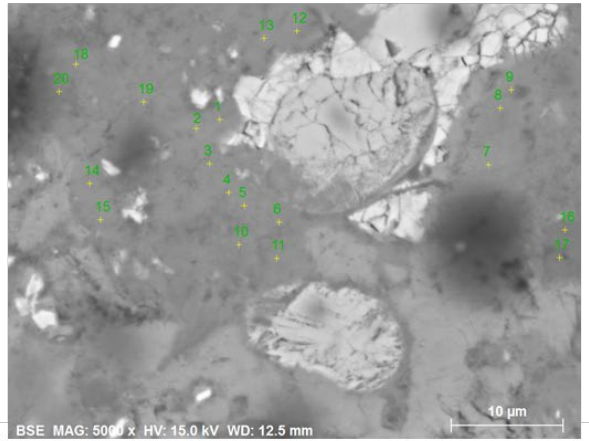
Method to check over-calcination

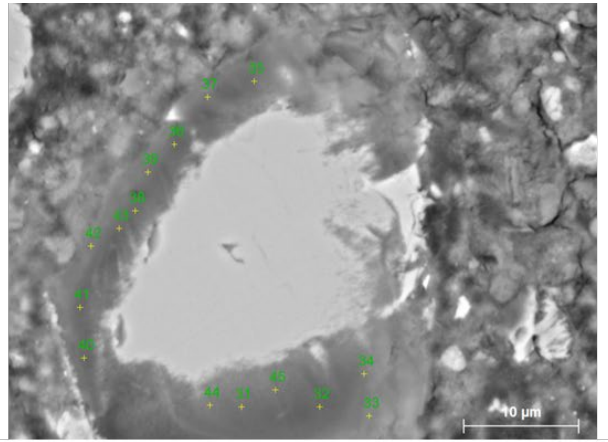


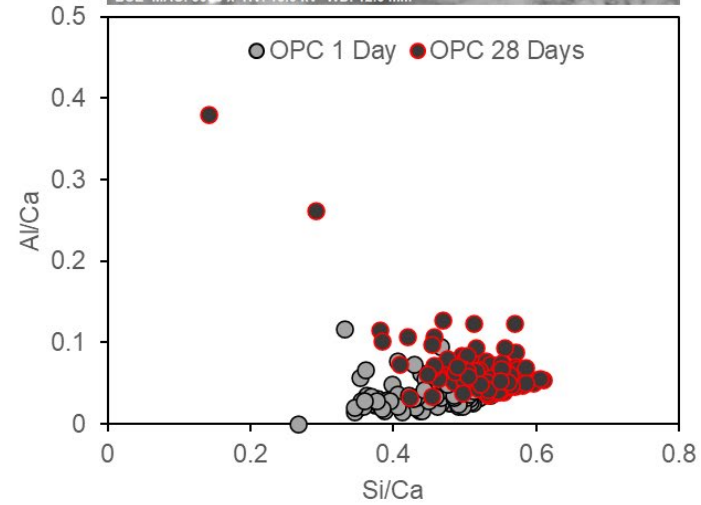
Intermixing of products

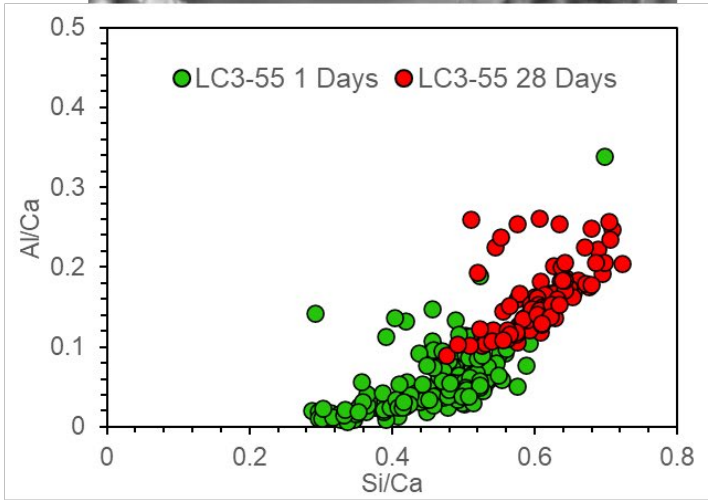


Nature of C-A-S-H

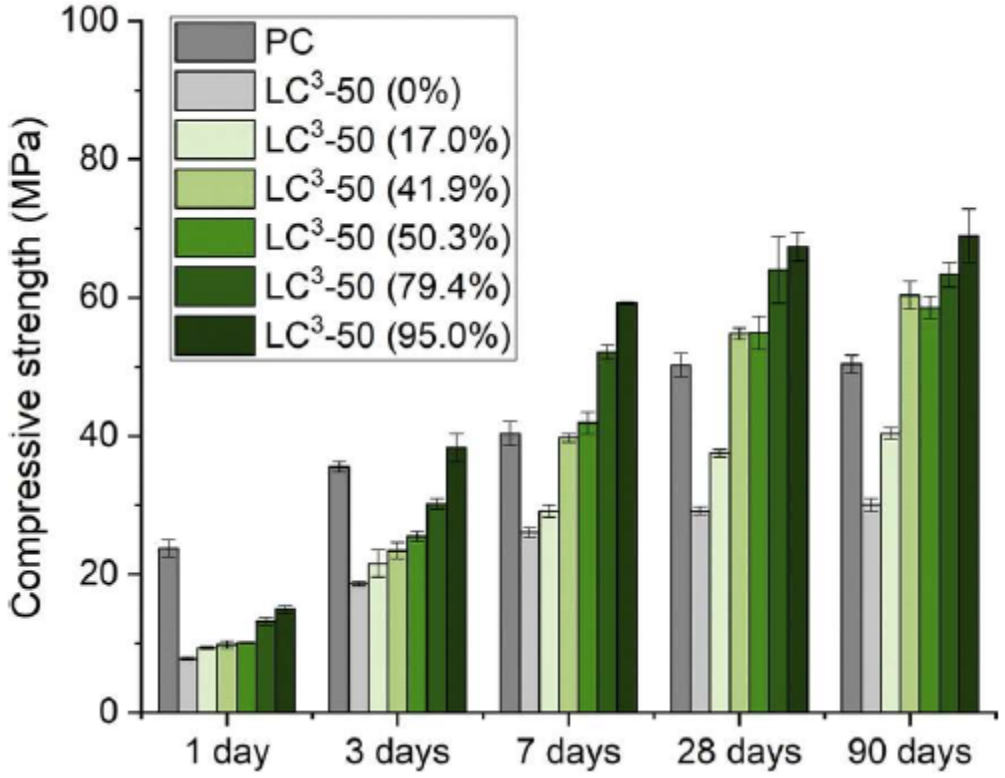








Effect of MK content in calcined clay

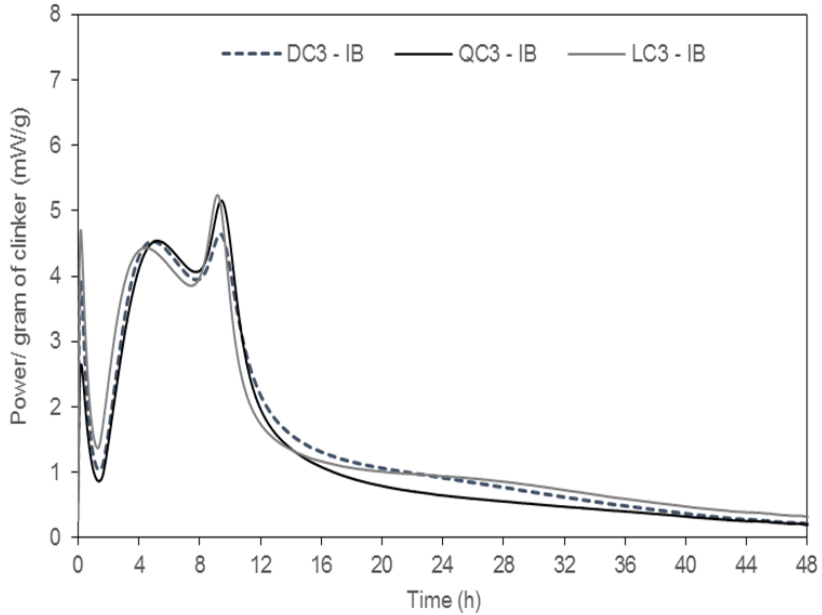


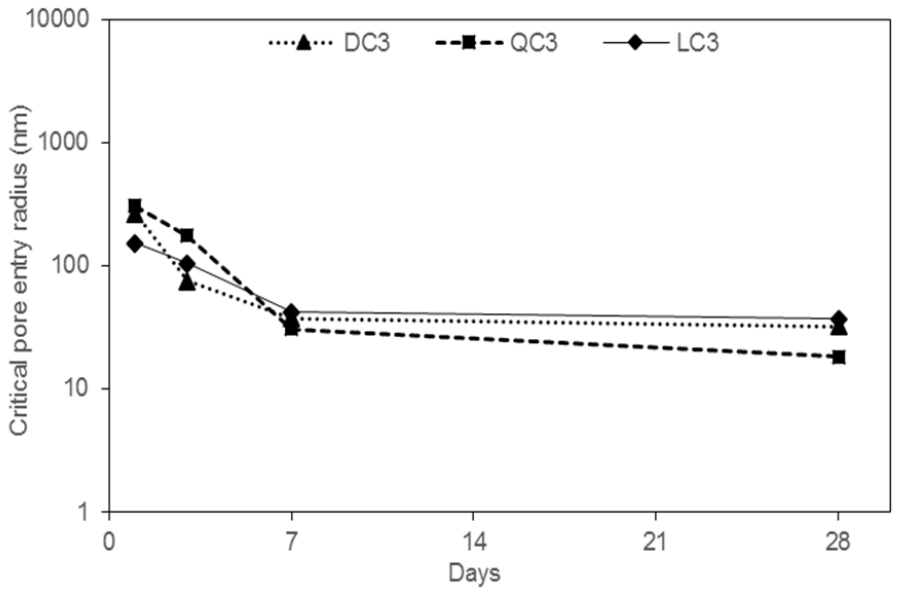
Limestone for LC^3

- Dolomitic limestones are not suitable for clinker production due to potential unsoundness
- Dolomite decomposes in the rotary kiln to form periclase
- Periclase react with water to form brucite causing an increase solid volume

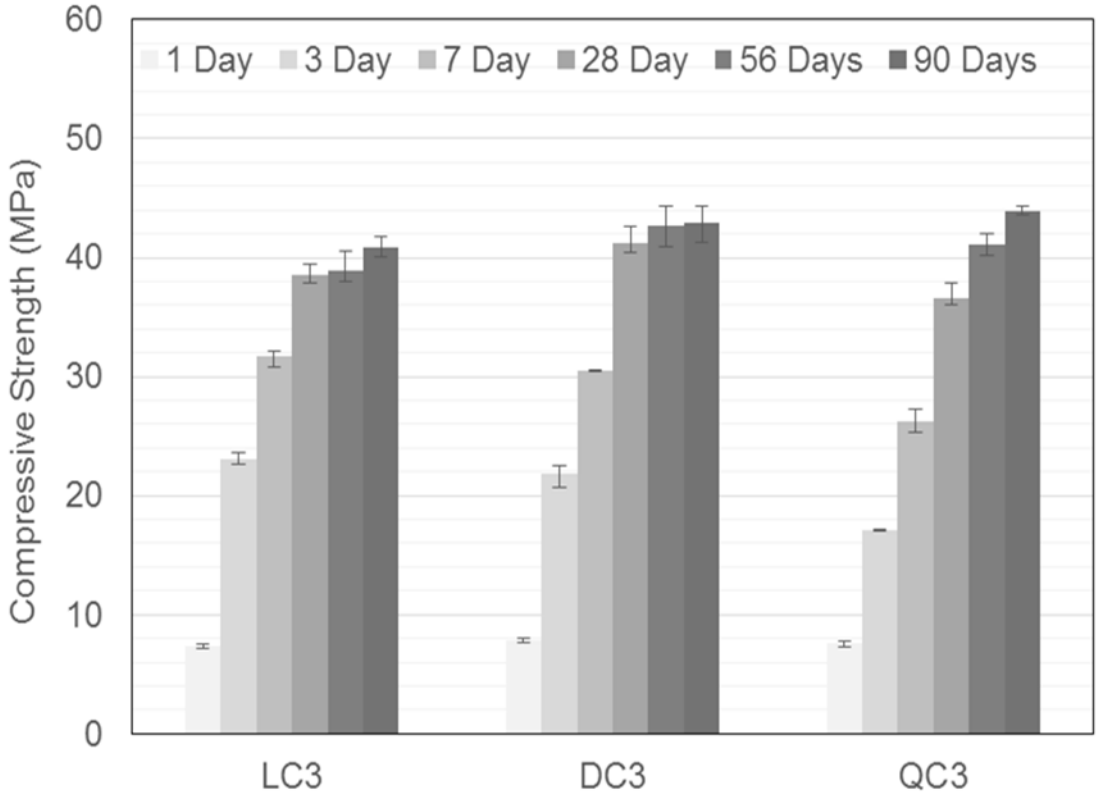
Use of dolomite as carbonate source

- Similar reaction kinetics and pore refinement in dolomite and limestone systems



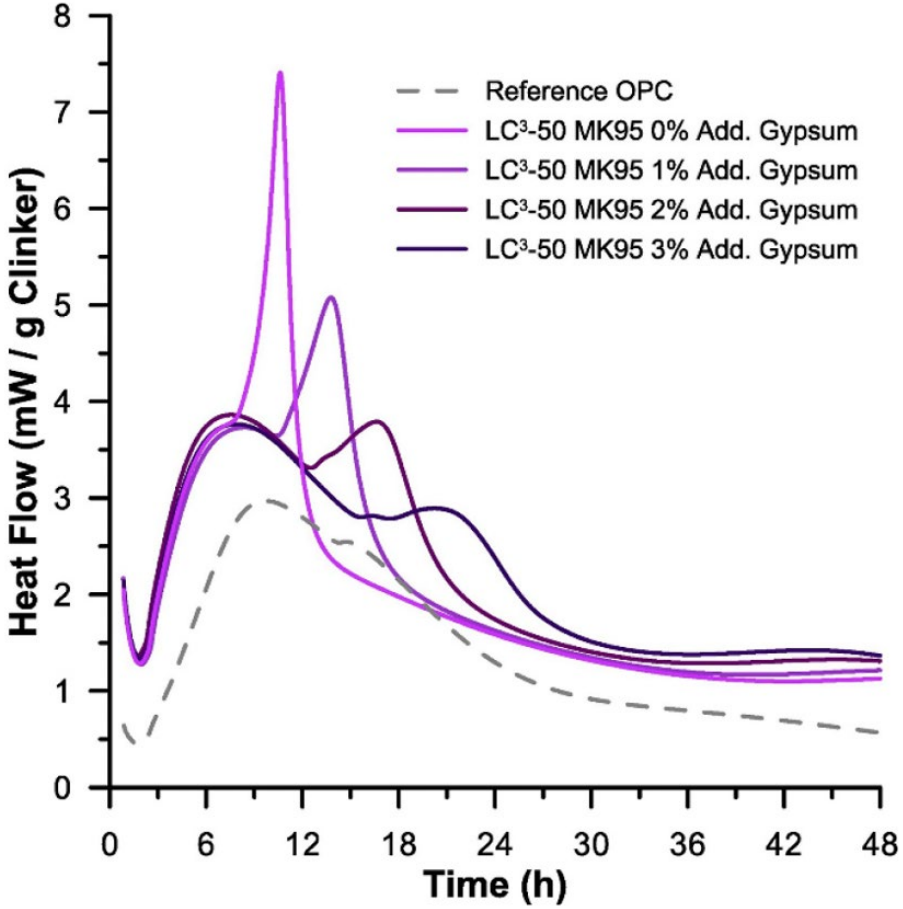


Use of dolomite as carbonate source

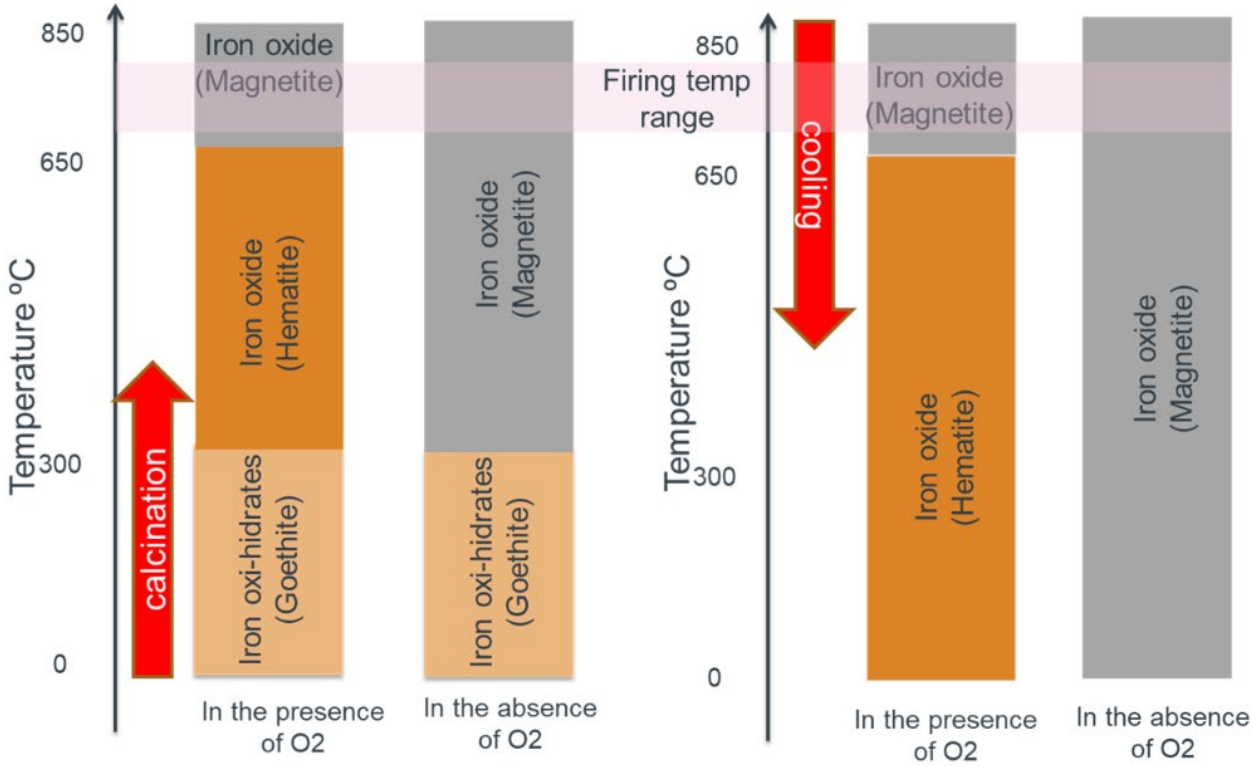


Limestone for LC^3

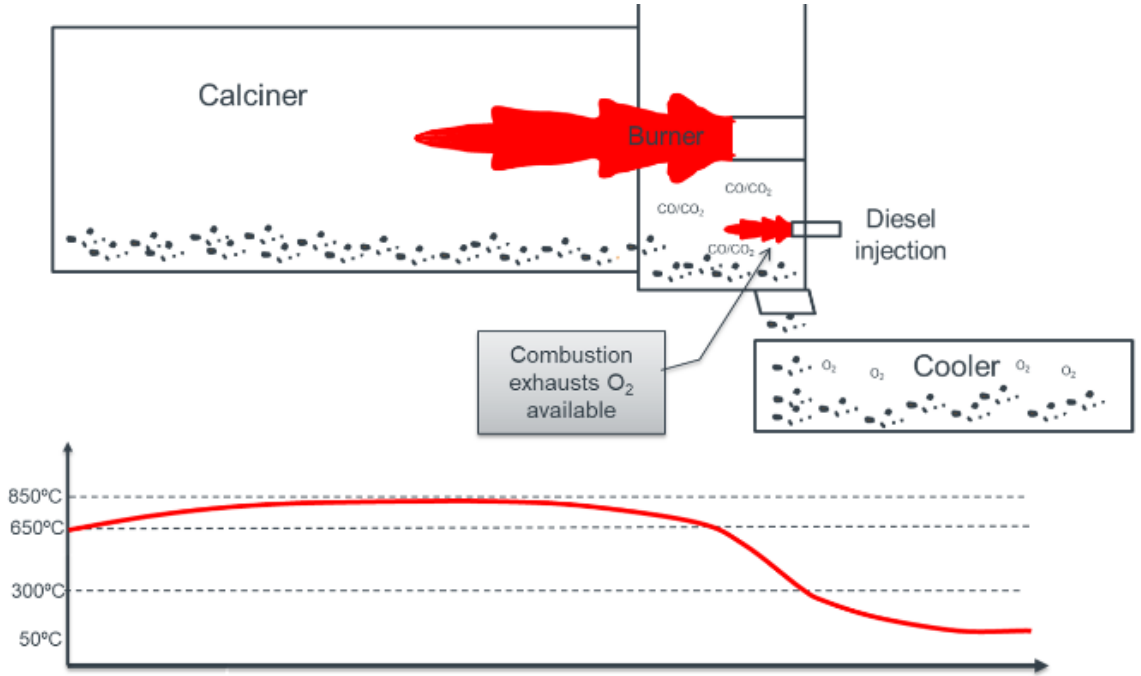
Gypsum optimization for LC^3



Colour control in clay calcination

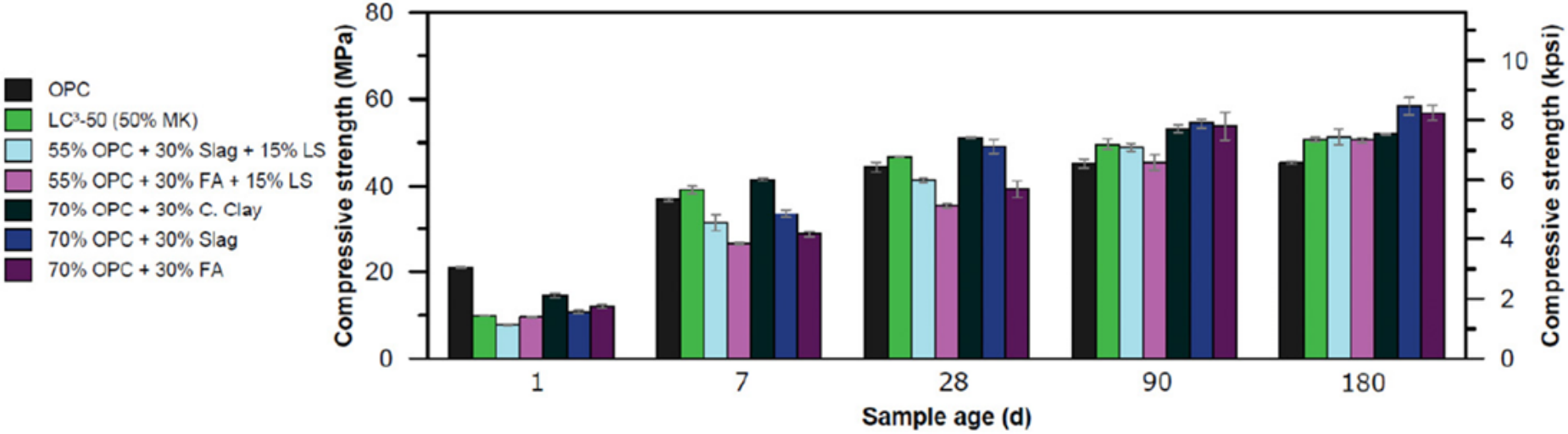


Colour control at pilot plant

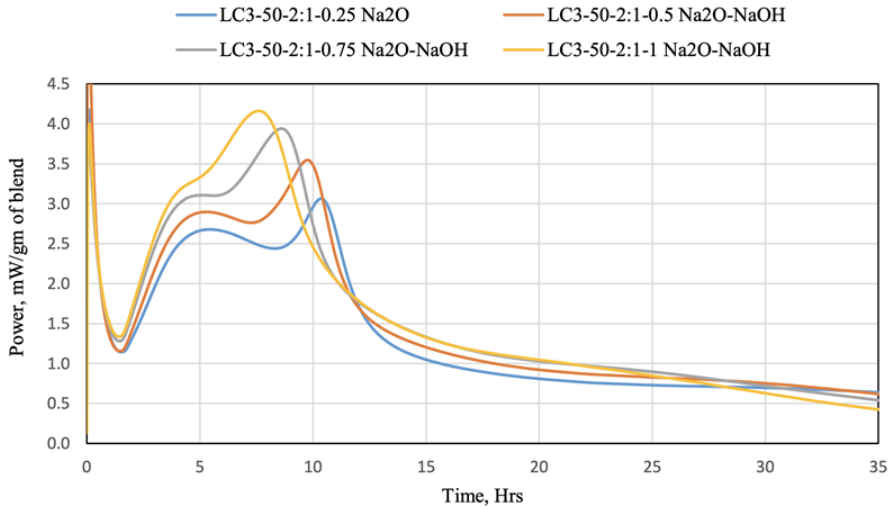


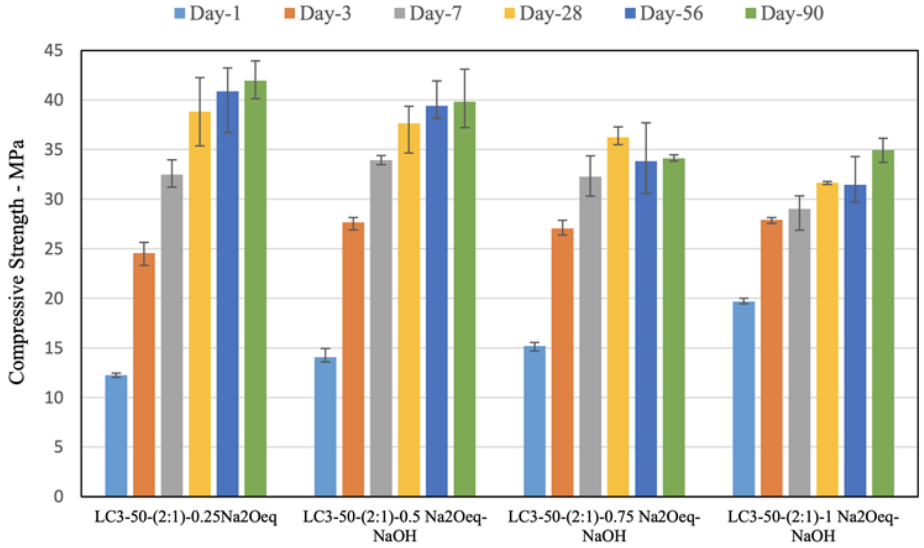
Colour control

Compressive strength

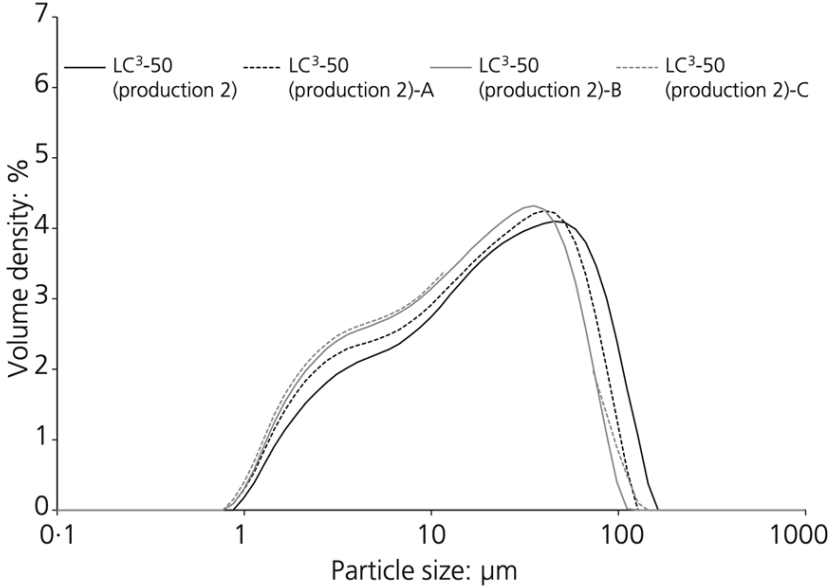


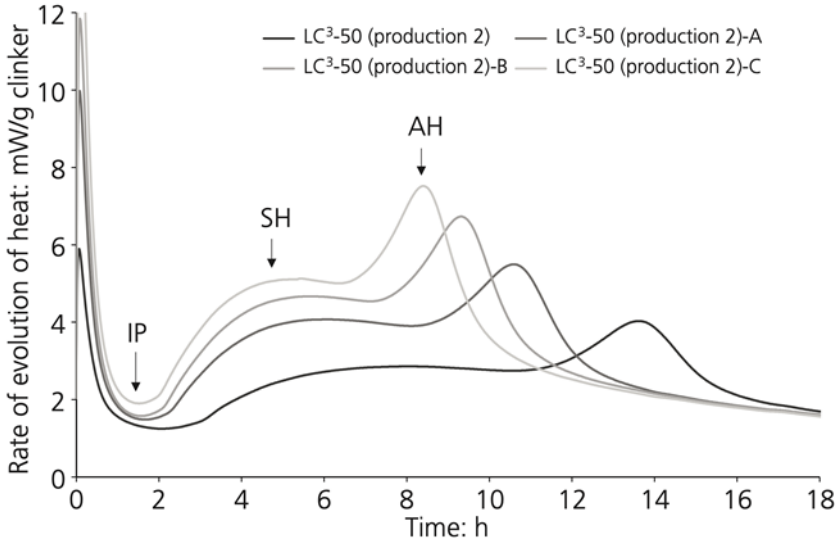
Effect of alkalis



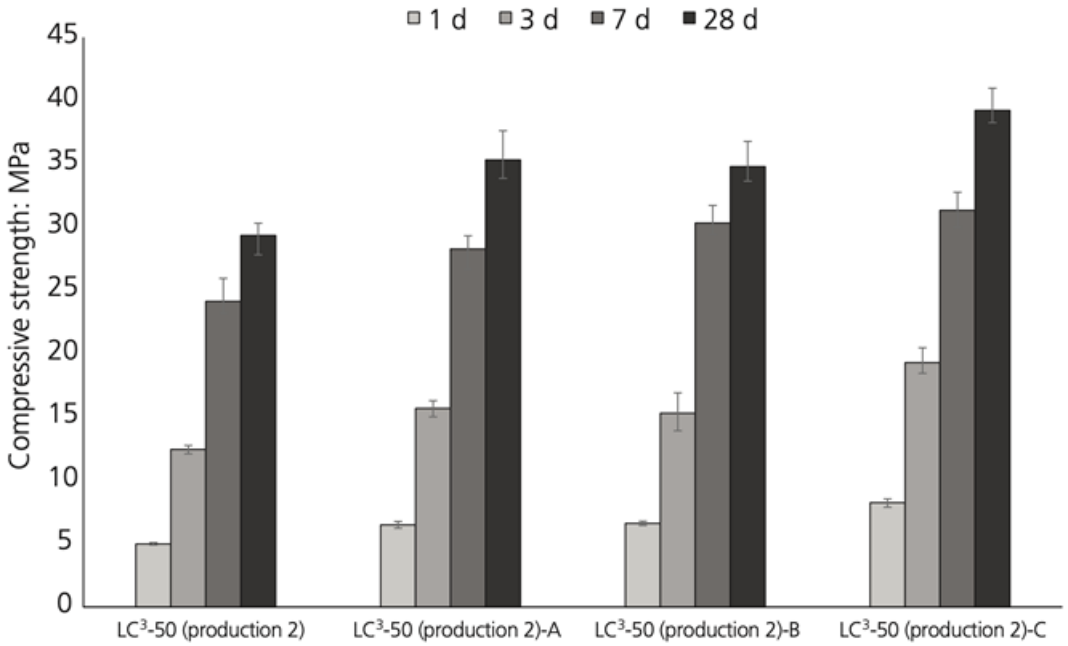


Blending of LC^3





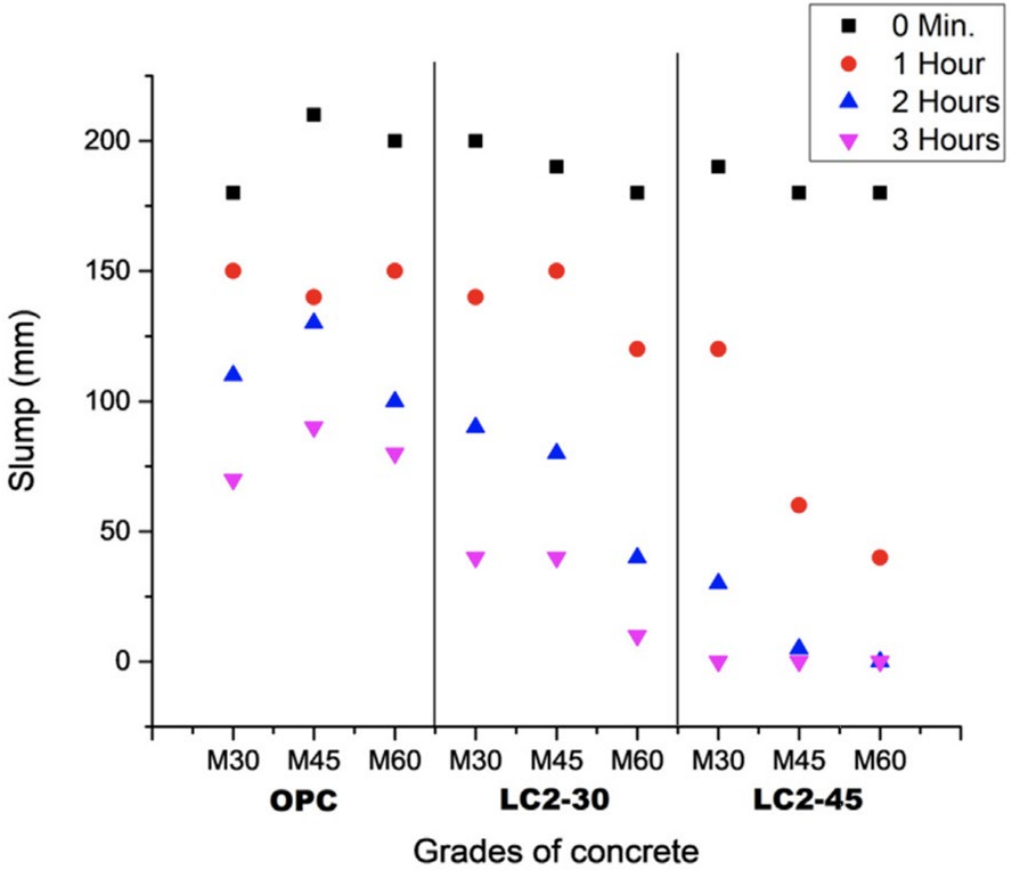
How Important is grinding



Grinding aids

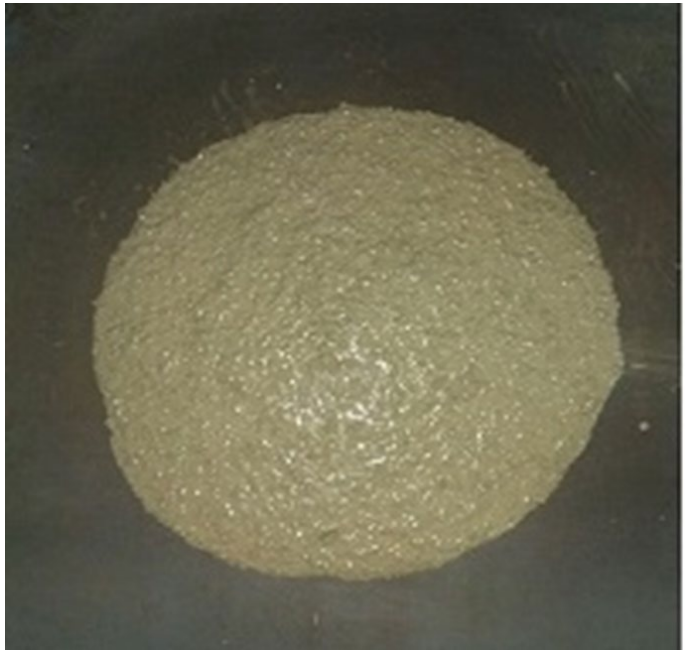
Workability of LC^3

MIX	OPC	35% FLY ASH	10% LC^2	20% LC^2	30% LC^2	40% LC^2
Admixture dosage	0.5%	0.52%	0.9%	1.1%	1.2%	1.3%

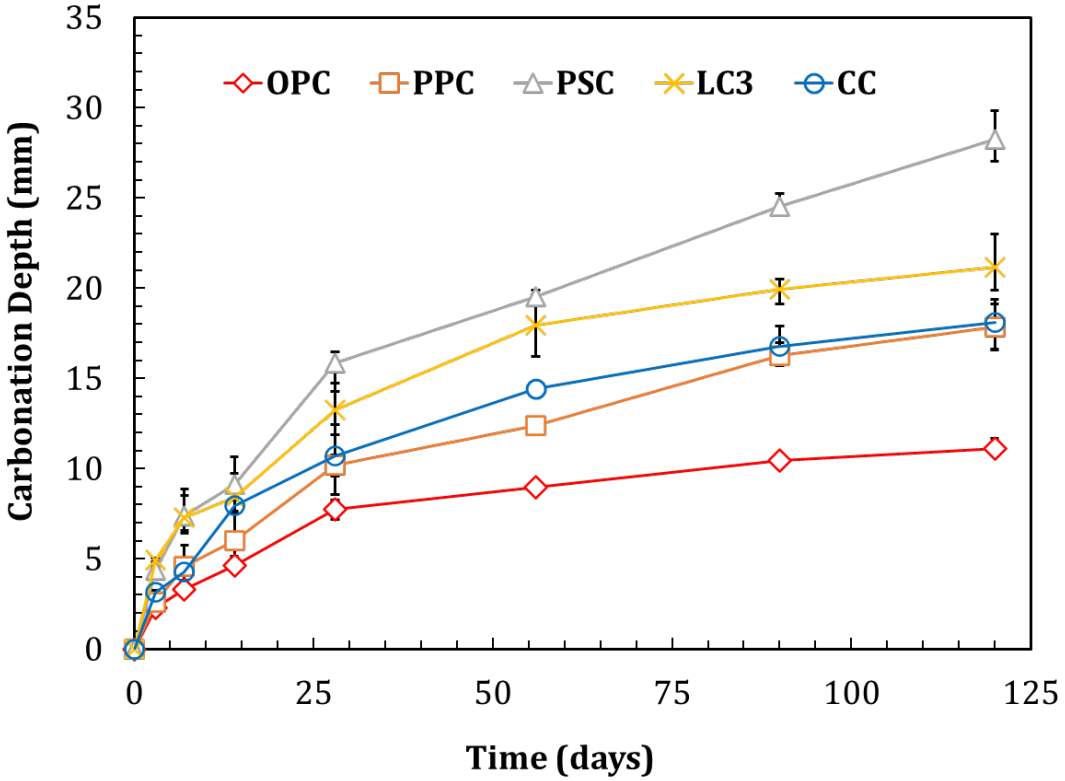


Workability of LC^3

- Water and admixture demand can be 10% to 50% higher than OPC
- PCE based admixtures work well
- Good cohesion in concrete
- Well-suited for SCC

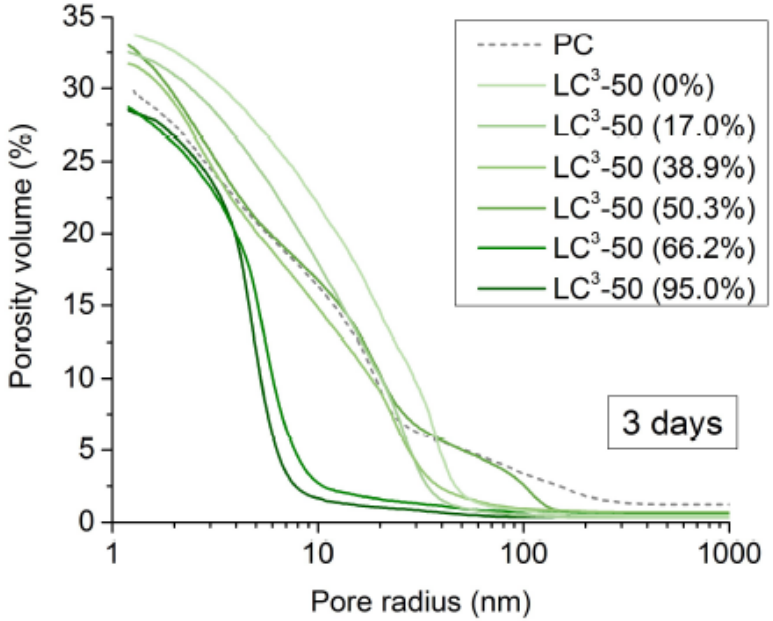


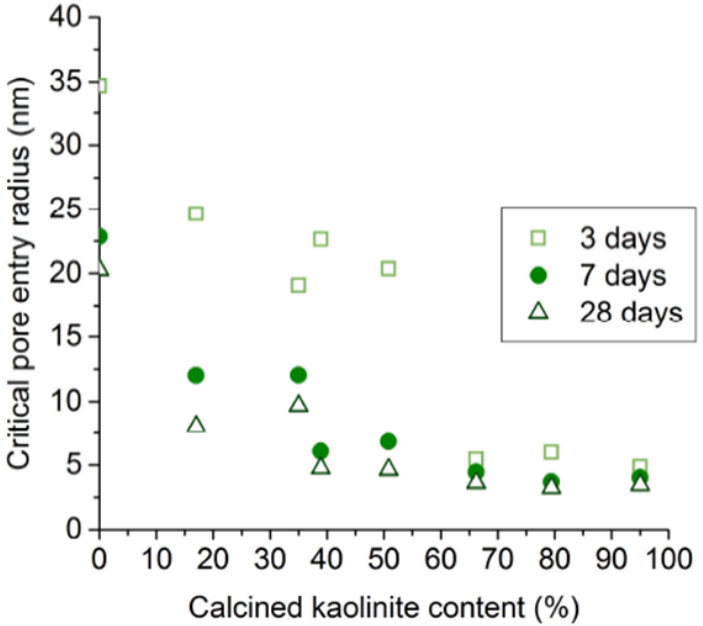
Carbonation of LC^3



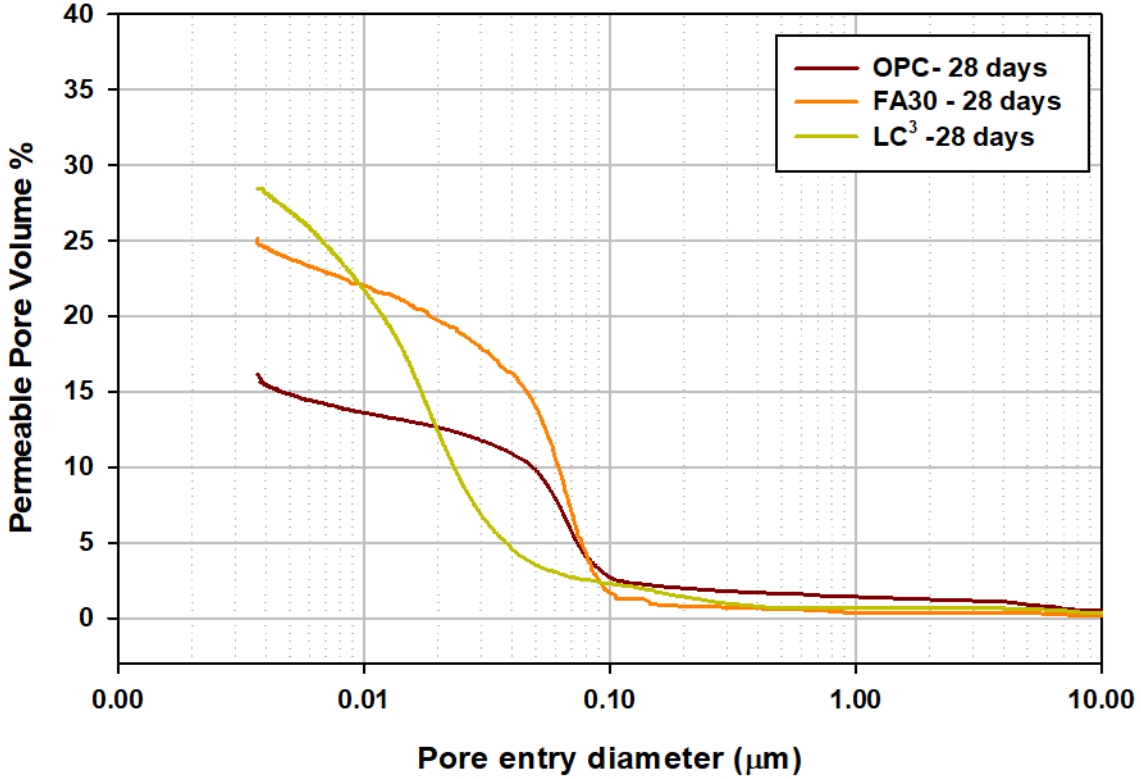
Pore refinement

Characterized by MIP: Significant refinement of porosity already at 3 days of hydration





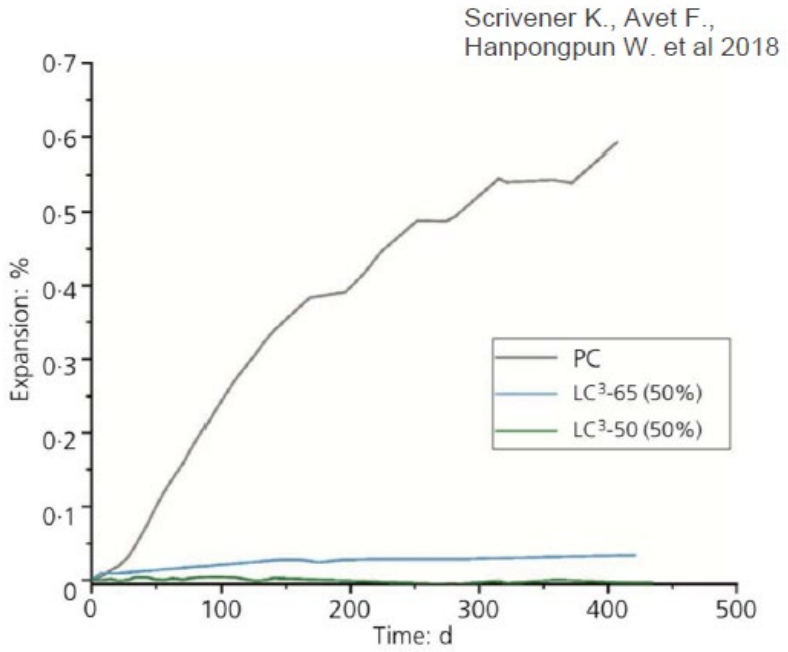
Pore refinement



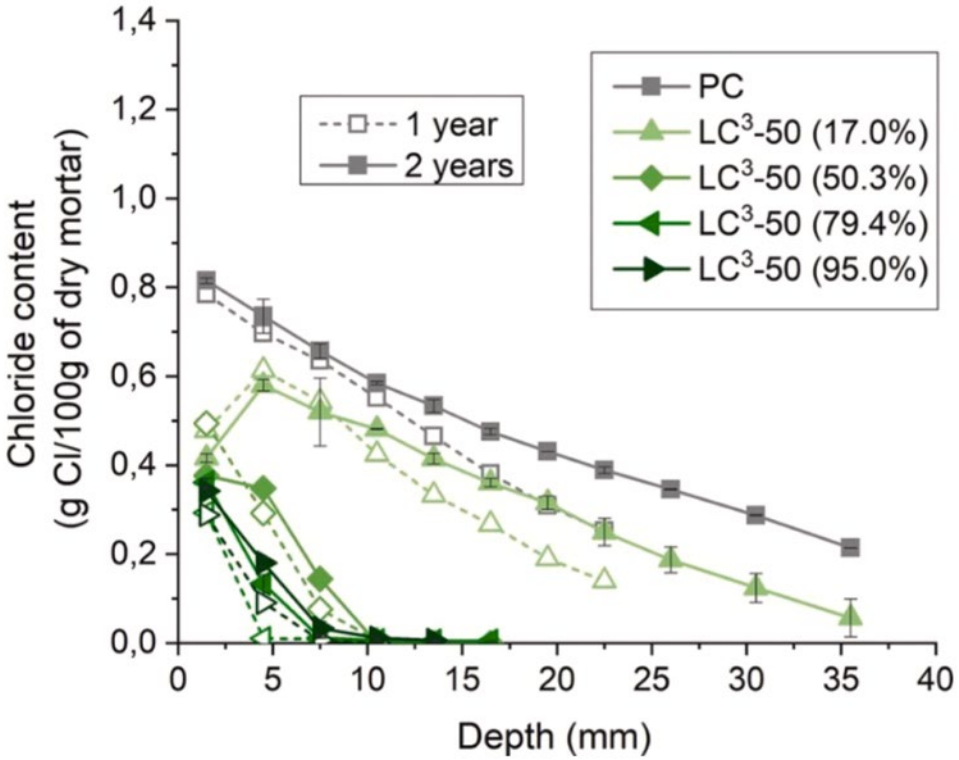
Permeable Porosity Vs Pore diameter of OPC, FA30 and LC^3 at 28 days

Alkali Silicate Reaction

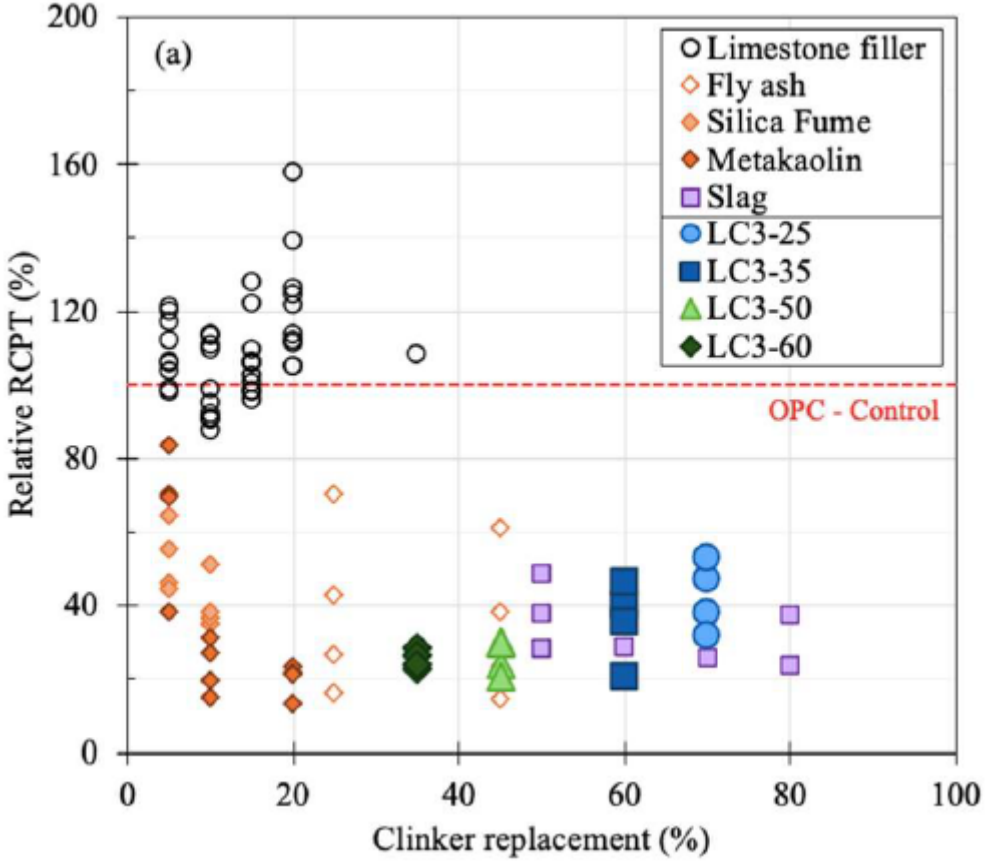
- Avoid reactive aggregates
- Add SCMs like calcined clay



Chloride Ingress



RCPT of different blended cements



Journey of LC^3

Journey of LC^3

Standardisation, market preparation and first applications

2013

- First industrial production of LC3 in Cuba.
- House in Santa Clara, Cuba, completely built with LC3

2014

- ASTM approves C595 standard with new formulation for blended cements
- House in Jhansi, India, using first production of LC3 for walls, roofing tiles and floors

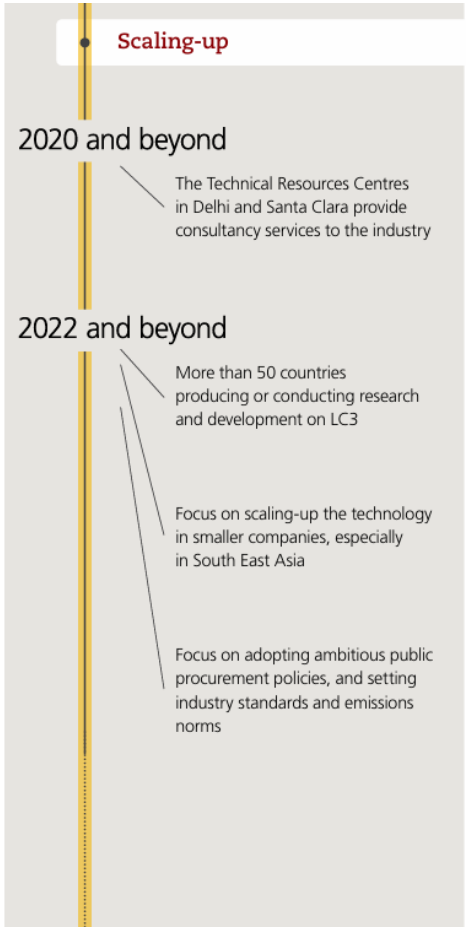
2015

- New office for the SDC at the Swiss embassy in New Delhi, India, using LC3 blocks

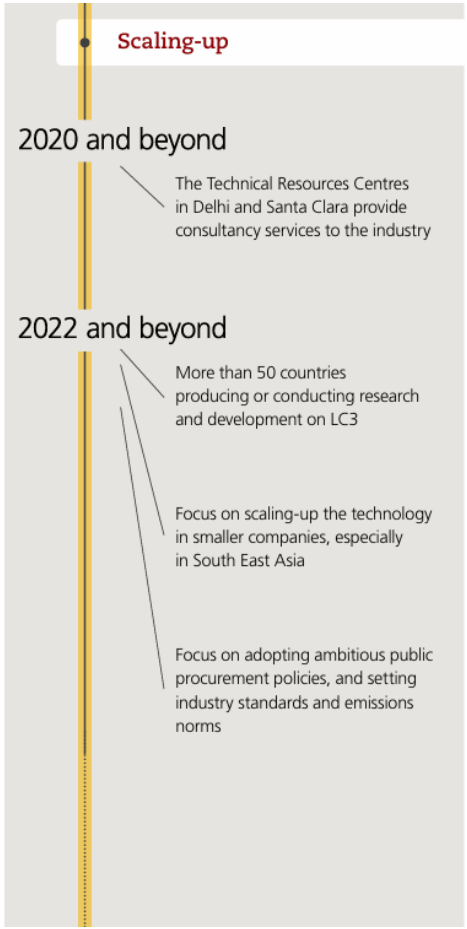
2017

- Verification of the economic advantages of the material

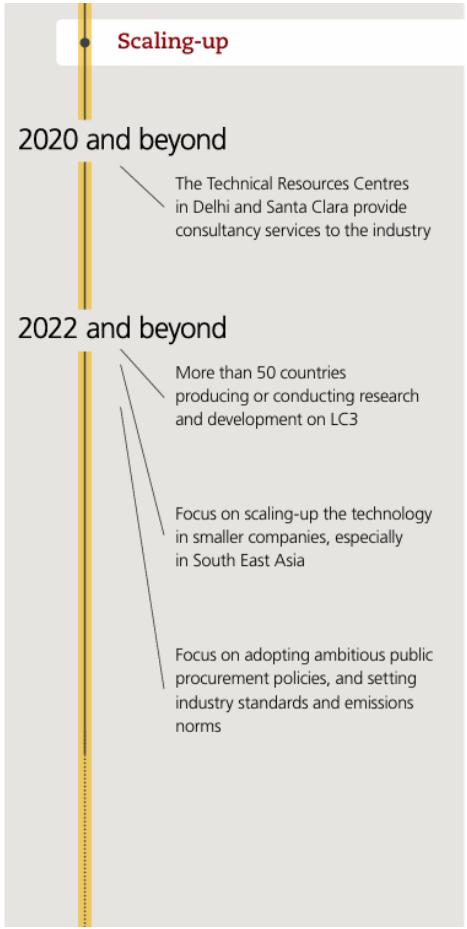
Journey of LC^3



Journey of LC^3



Journey of LC^3



Benefits of LC^3

Reduced carbon

LC3 **reduces the energy-intensive clinker**[1] content to **50 per cent**, thus **reducing the CO_2 emissions** by up to **40 per cent** compared to Ordinary Portland Cement (OPC).

Scalability

The **abundance of suitable materials** means **LC3 can be produced in 75 per cent of cement plants worldwide.**

Resource efficiency

For LC3, both **limestone**, which is not suitable for clinker production, and **non-ceramic clays**, **which are often waste, can be used**.

Cost effectiveness

Because **calcining clay is often cheaper than clinker**, LC3 **saves up to 25 per cent of the production costs.**

High performance

LC3 performs as well or better than OPC with the advantage of **greater resistance** to the penetration of chloride ions – the main cause of **reinforcement corrosion**.

Partnerships for the goals
Fostering partnerships between academia, politics and industry

No poverty: Promoting affordable housing materials

Climate action
Reducing greenhouse gas emissions

Industry, innovation and infrastructure
Promoting low-carbon materials for infrastructure and housing

Responsible consumption and production
Promoting the utilisation of waste materials and the efficient use of natural resources

Sustainable cities and communities
Promoting resource efficient cities and the use of local materials