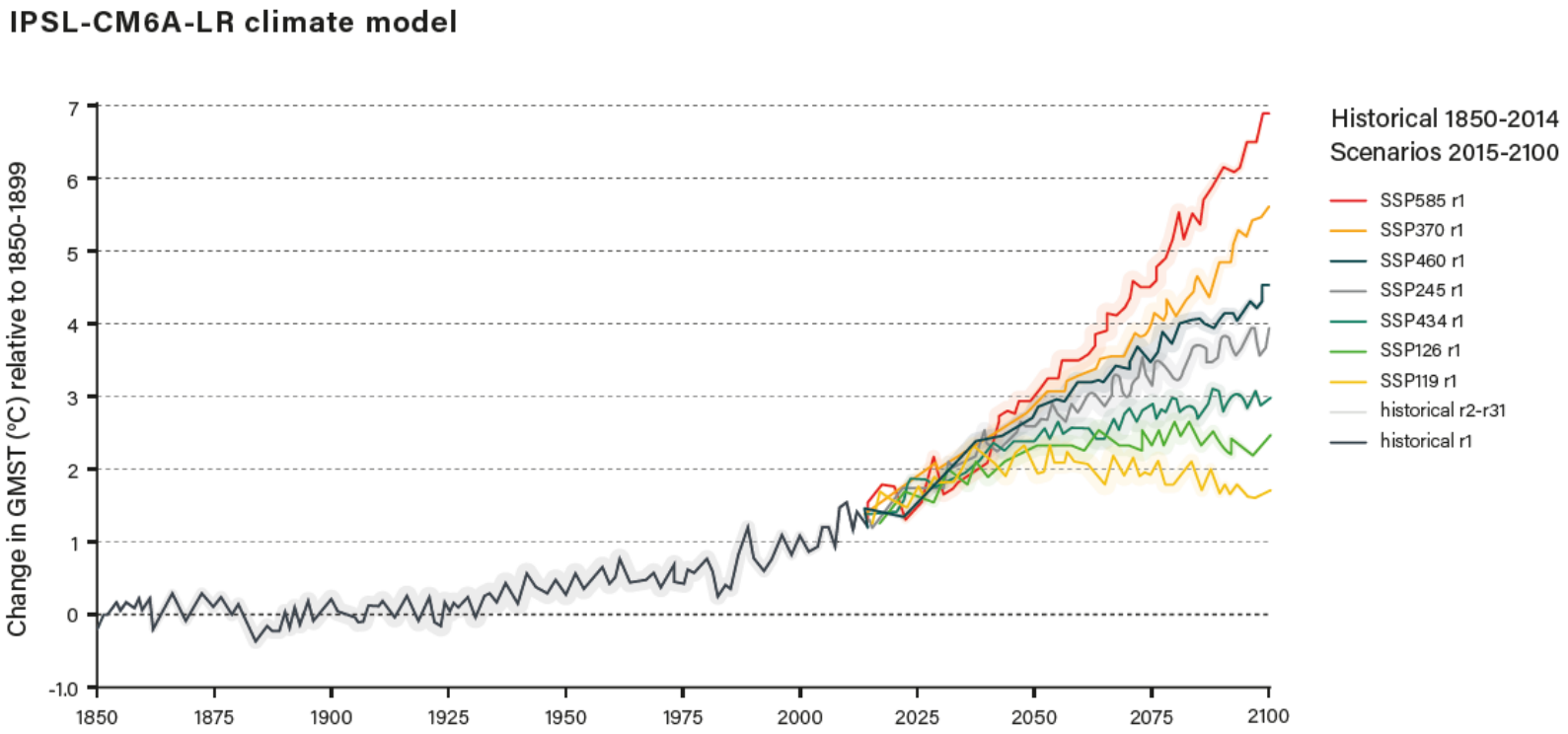
Realistic options to reduce CO2 emissions from Cement and Concrete:

Role of clinker and hydration

Karen Scrivener, FREng
EPFL
Switzerland

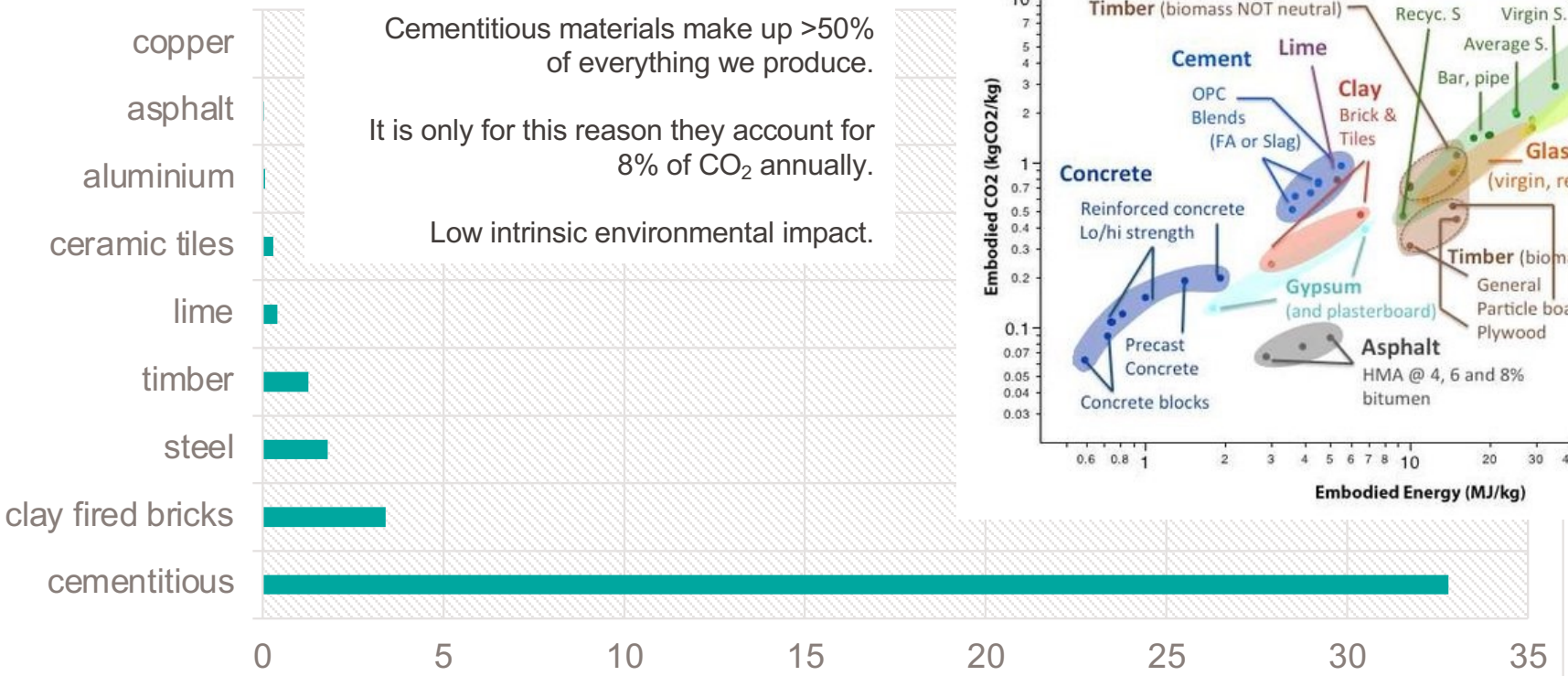
École polytechnique fédérale de Lausanne

We need to act fast

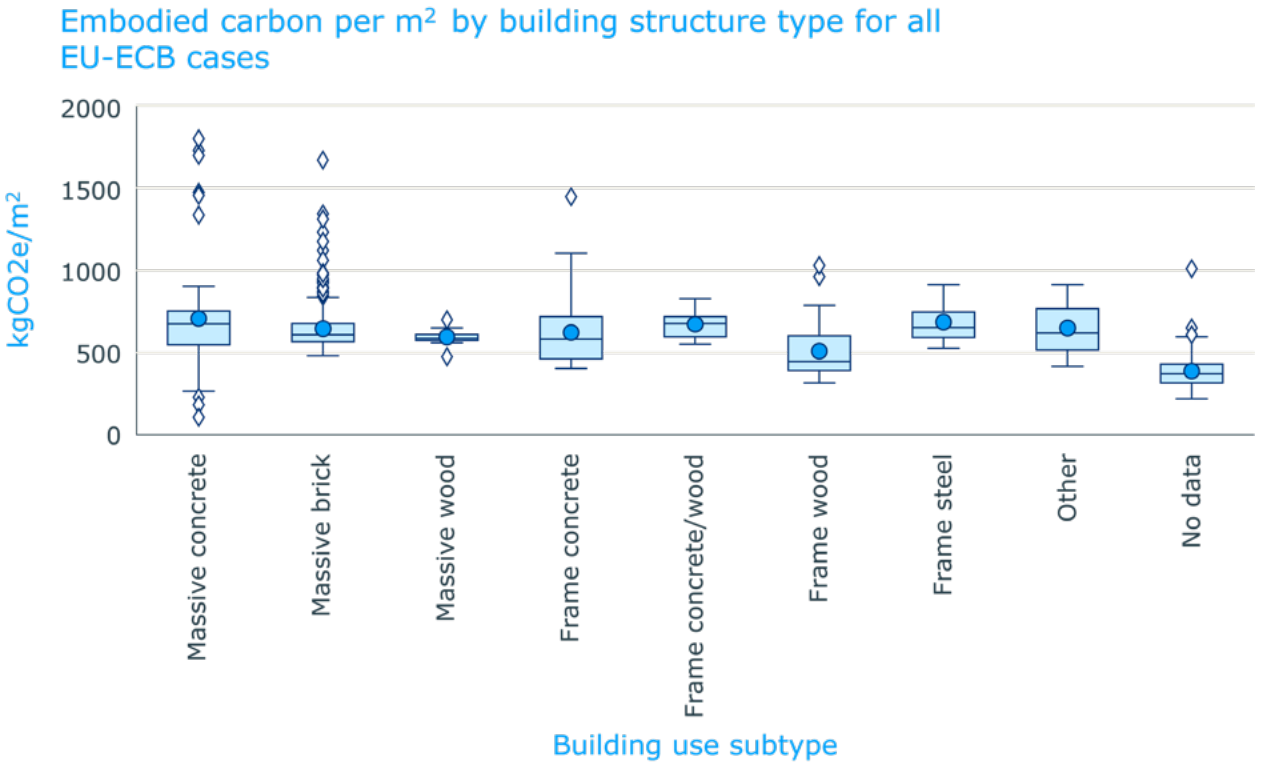


Source: Jean-Marc JANCOVICI, jancovici.com

Concrete + Mortar are irreplaceable

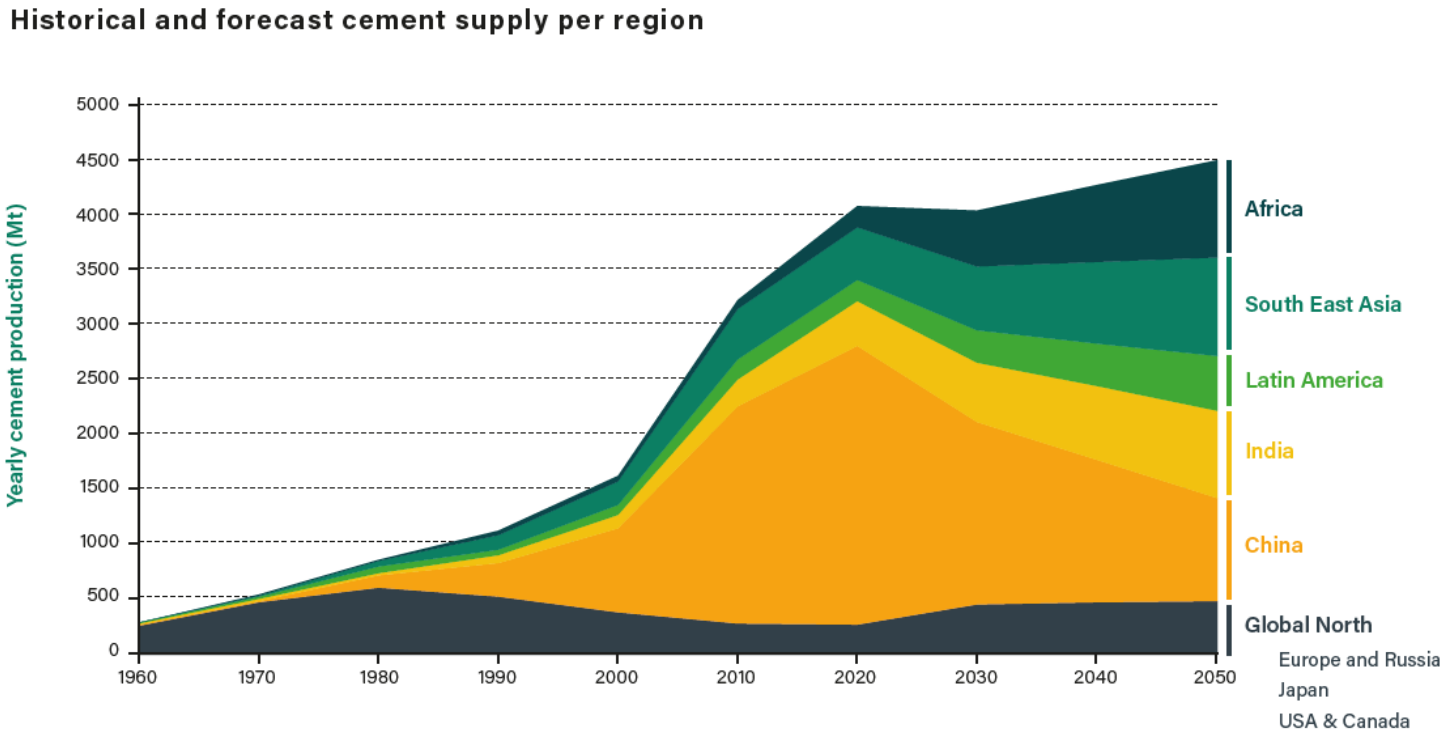


Would it help to replace concrete by other materials?



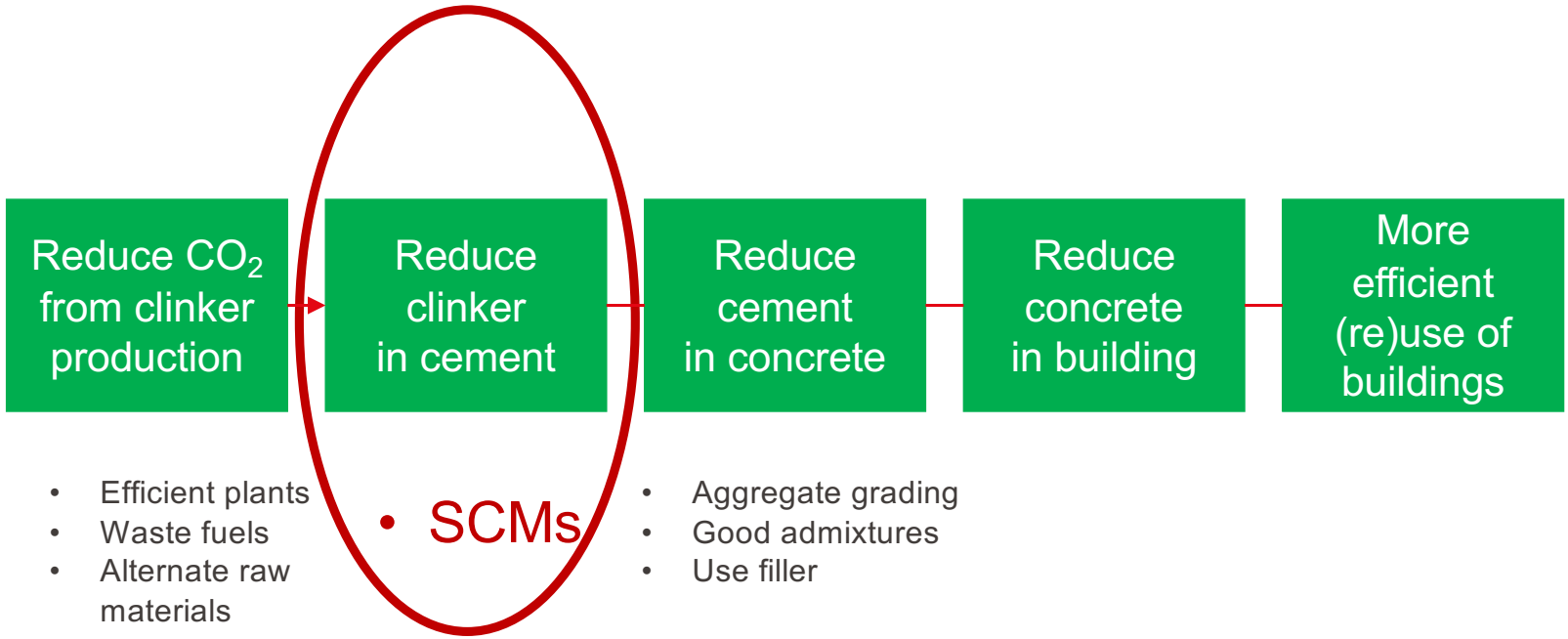
- Röck M, Sørensen A, Tozan B, Steinmann J, Le Den X, Horup L H, Birgisdottir H
  Towards EU embodied carbon benchmarks for buildings – Setting the baseline: A bottom-up approach, 2022, https://doi.org/10.5281/zenodo.5895051.

Demand for cement in the Global South



We need solutions for people in developing countries

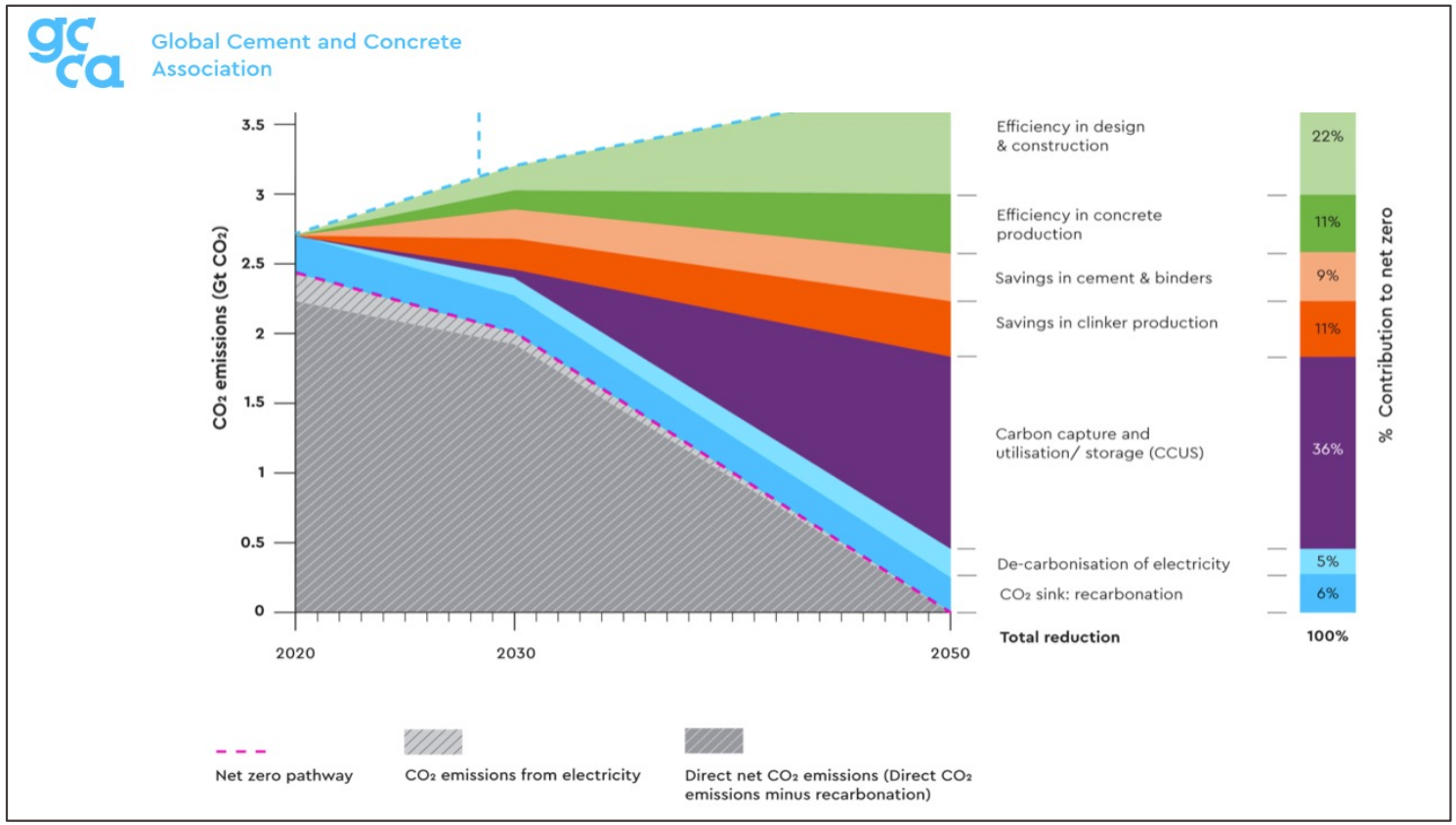
Report for European Climate Foundation 2017



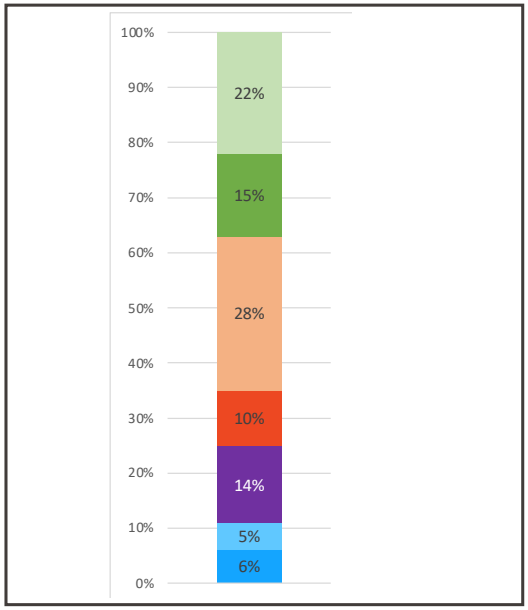
Substantial reductions in emissions > 80% can be achieved by working through the whole value chain

During this course we will look at several of these steps and considered them in an LCA analysis, here I will look a bit more at the role of clinker and hydration

Drivers for CO_2 reductions: multiple approaches necessary



Expectation by LC3-project



Slag and fly ash will disappear even in India, but calcined clay allows high levels of substitution.

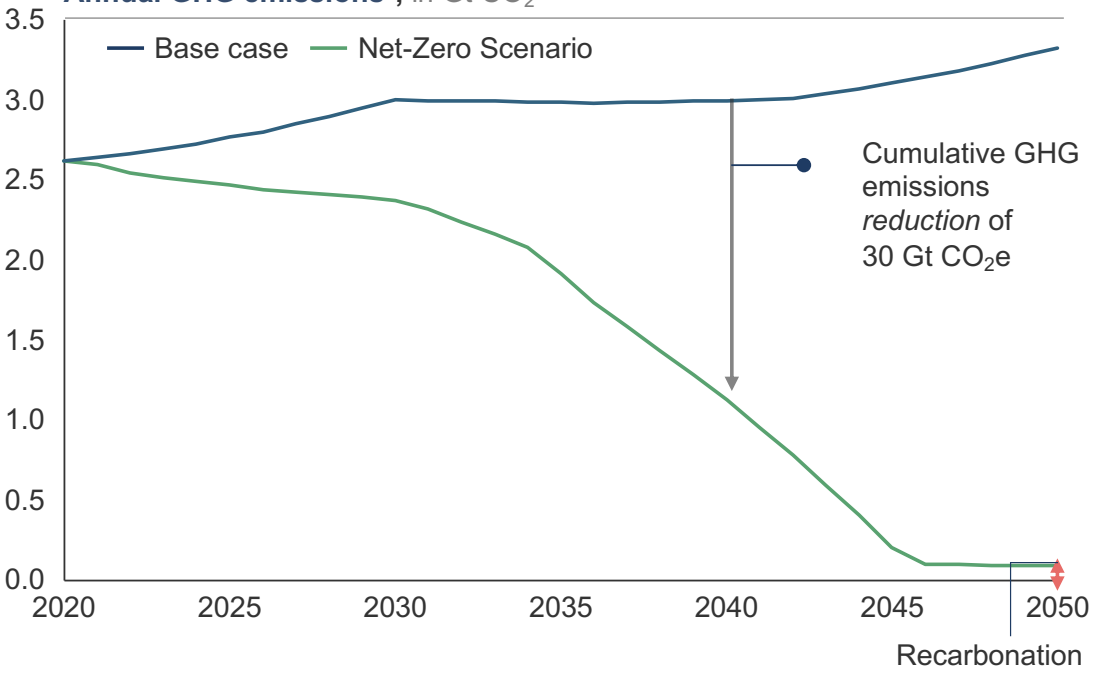
Small reduction potential of clinker factor from GCCA due to the (doubtful) Chinese clinker factor of 55%

Mission Possible Partnership

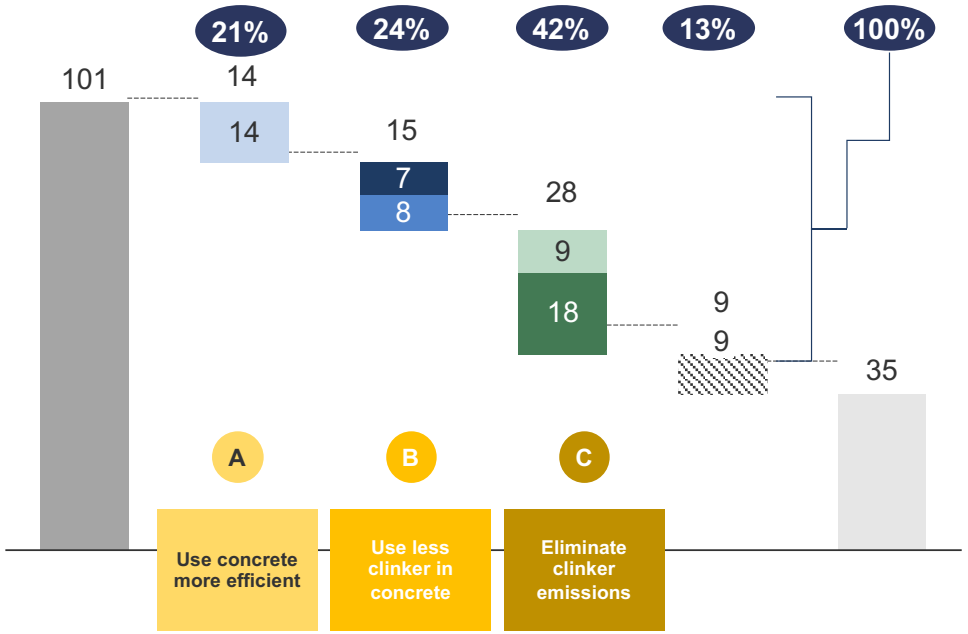
Net-Zero Scenario

Efficiency in design and construction
Efficiency in concrete production
Savings Cement & binders[2]
Switching to alternative fuels and energy efficiency
CCUS
Recarbonation
Unabated

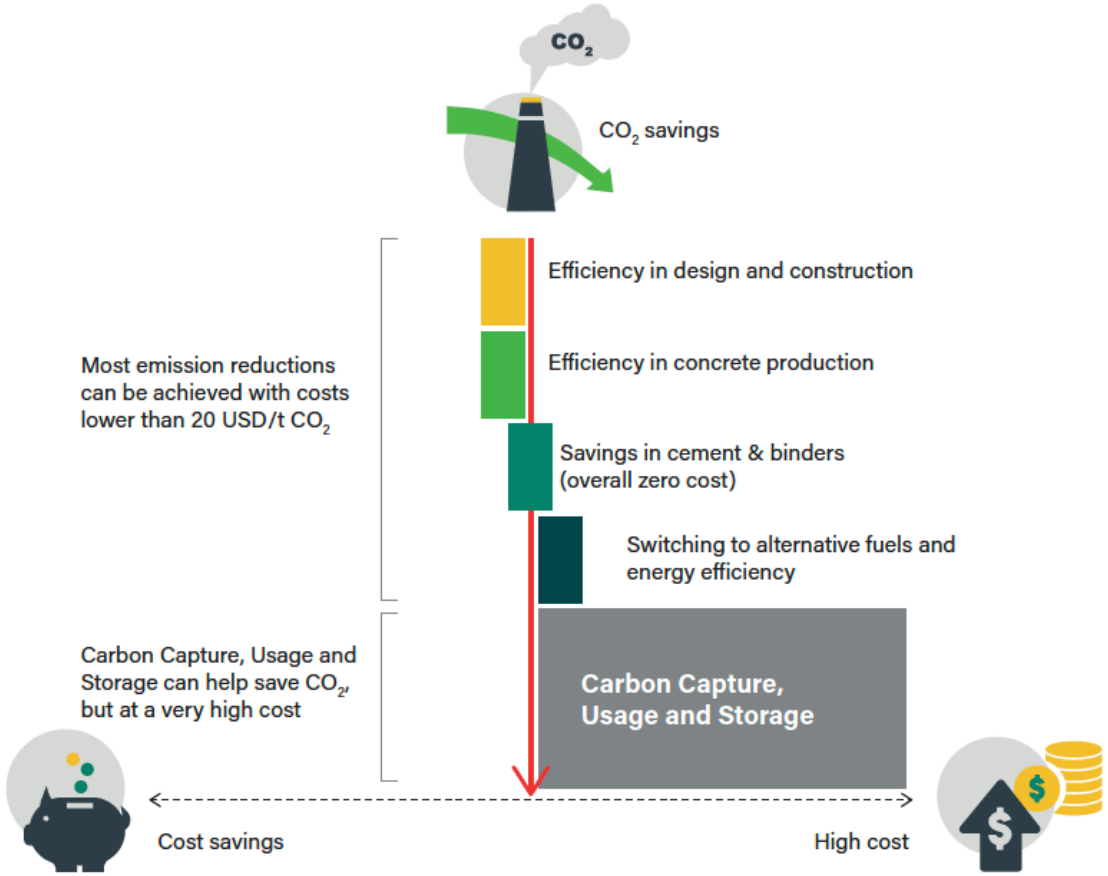
Annual GHG emissions[1], in Gt CO_2



Cumulative GHG emissions[1] between 2022 and 2050, in Gt CO2



Much of the path to net zero is low cost



EPFL

nature communications

Article

https://doi.org/10.1038/s41467-023-40302-0

Near-term pathways for decarbonizing global concrete production

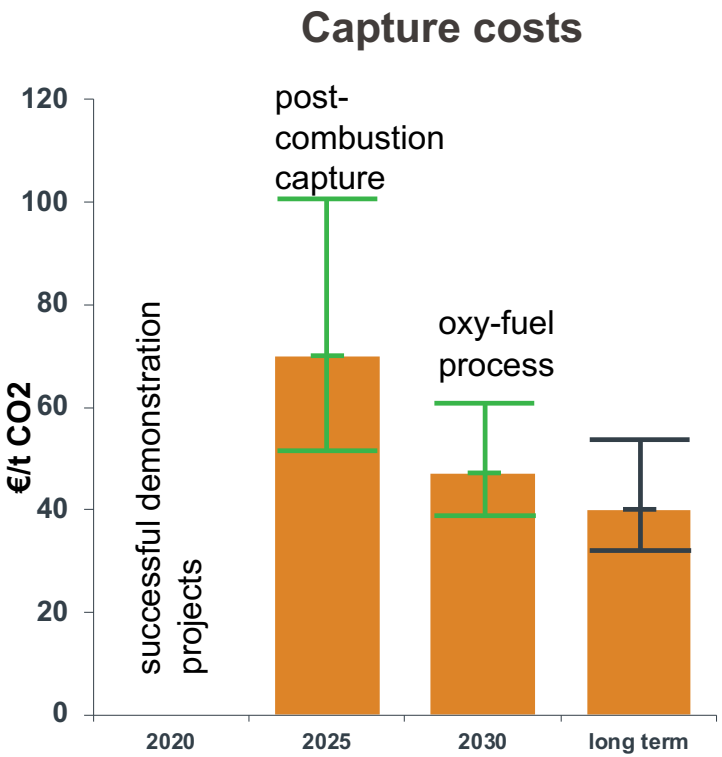
Received: 27 January 2023

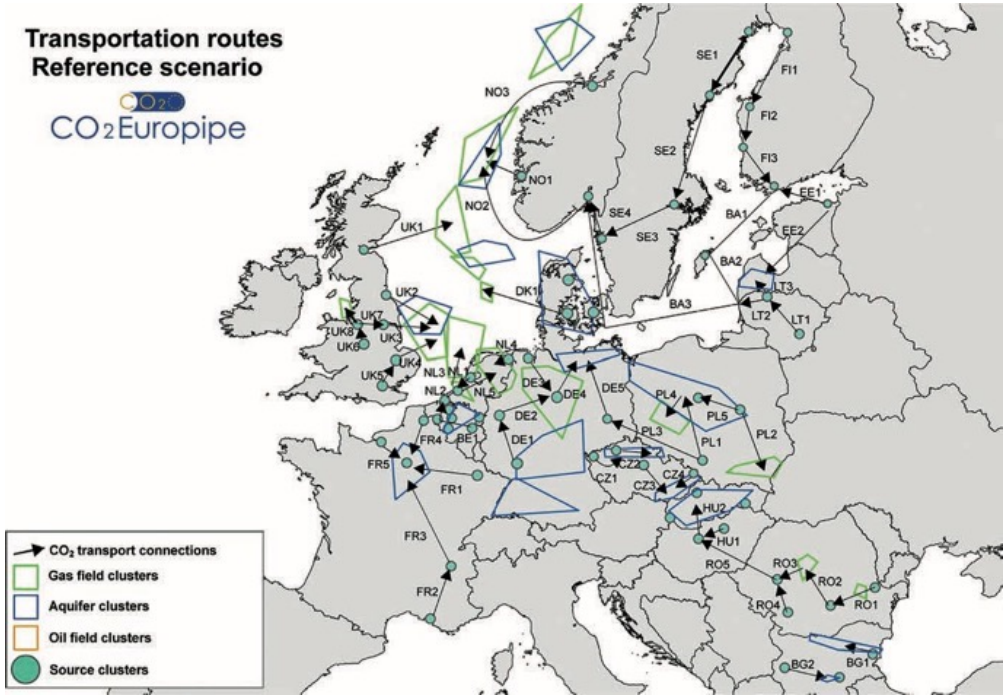
Accepted: 21 July 2023

Josefine A. Olsson [1], Sabbie A. Miller [1] ✉ & Mark G. Alexander [2]

Calculated 76% with these strategies

Carbon Capture and Storage





At the very least it will be expensive
Reducing now will be a very sound investment

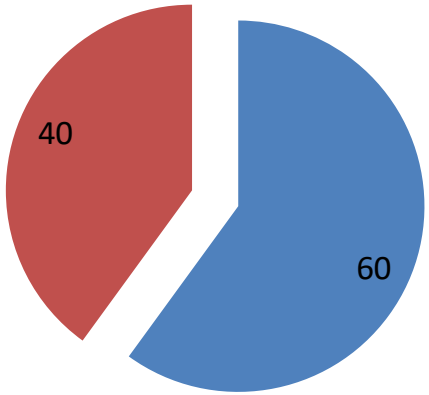
Scale of production >>> any “use” scenario
Need to build network to transport to storage sites

Origins of CO_2 emissions in clinker production: CO_2 from the clinker remains around 90% through to the Concrete

The production process is highly optimised up to around 80% of thermodynamic limit.

It is estimated that **< 2%** further savings can be made here

Use of waste fuels, which can be **> 80%** reduces the demand for fossil fuels



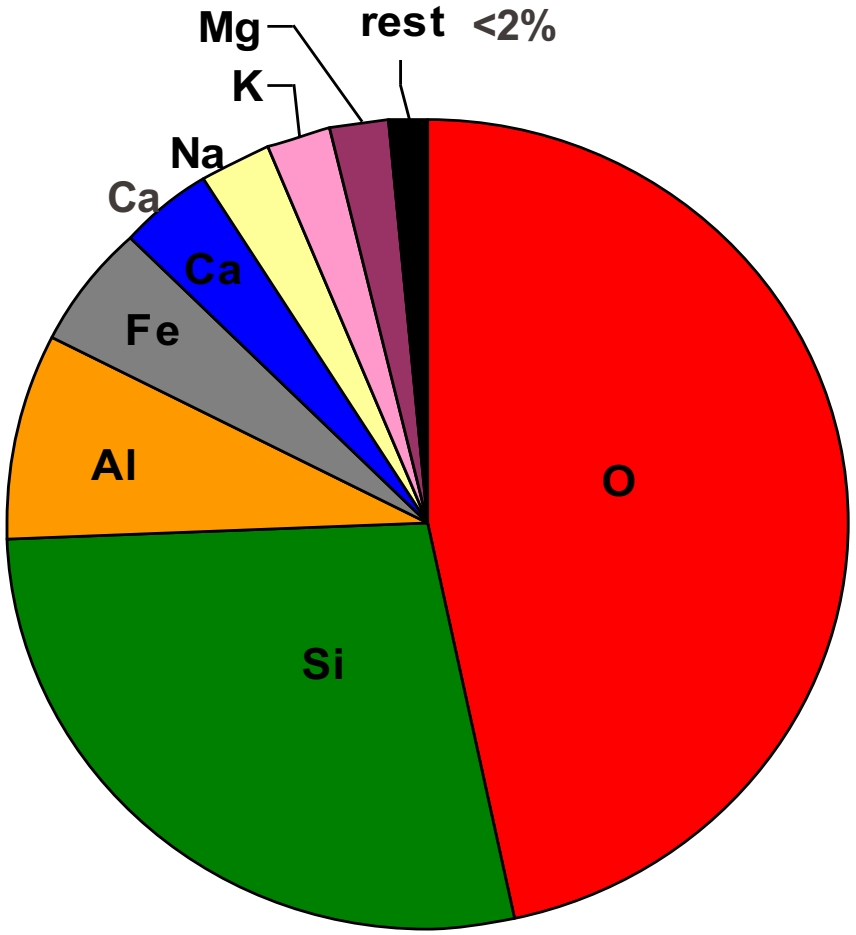
1 tonne of clinker leads to the emission of 750 – 900 kg CO_2
Average 850kg/t

$CaCO_3 \rightarrow CaO + CO_2$

Limestone 80% of raw material

Can we make cement with a different chemistry?

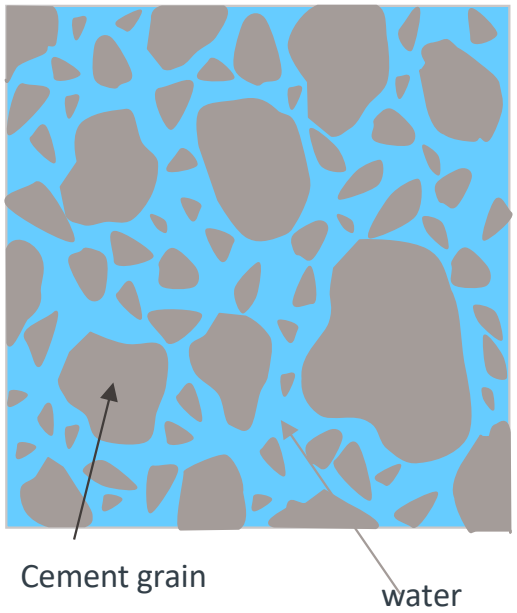
What is available on earth?



8 elements make up more than **98%** of the earth's crust

How does cement work?

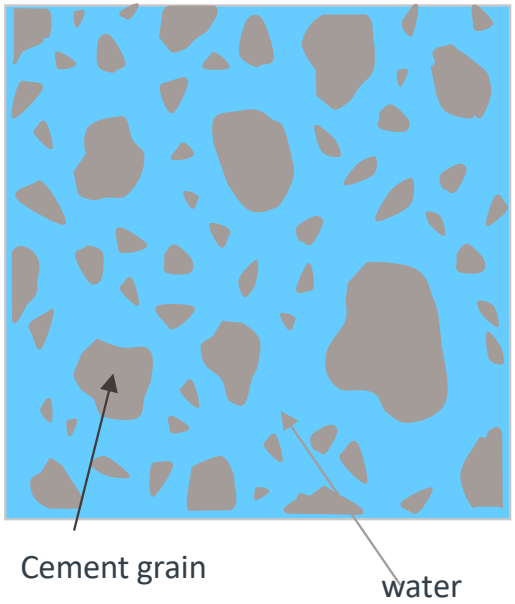
How cement works:



We mix the grey cement powder with water.

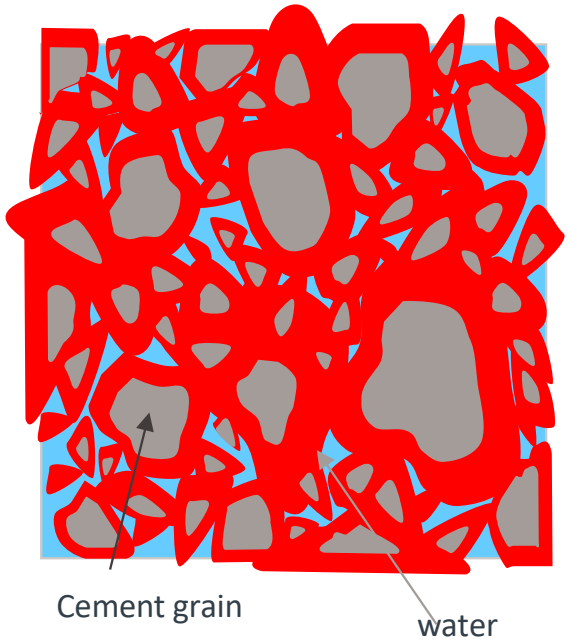
To start with the grains are just floating about in the water and we can cast the concrete into moulds

How cement works:



The cement grains dissolve in the water

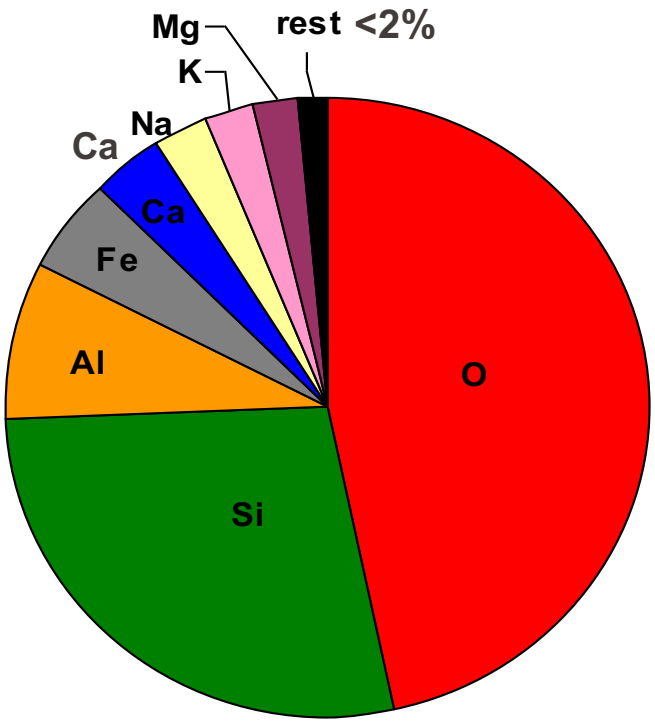
How cement works:



The cement grains dissolve in the water

And then precipitate *Hydrates* – new solids which have higher volume and hold the grains together: creating a rigid solid

What is available on earth?

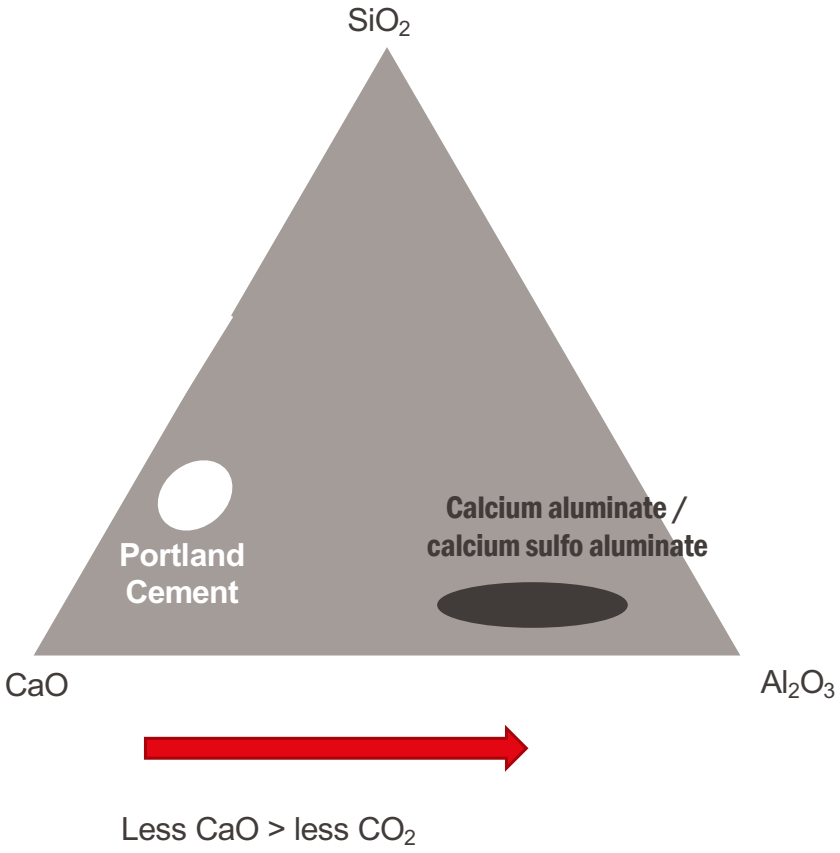


Na_2O
K_2O
} Too soluble

Fe_2O_3
MgO
} Too insoluble in alkaline solutions

CaO
SiO_2
Al_2O_3
} The most useful

Hydraulic minerals in system CaO-SiO_2-Al_2O_3



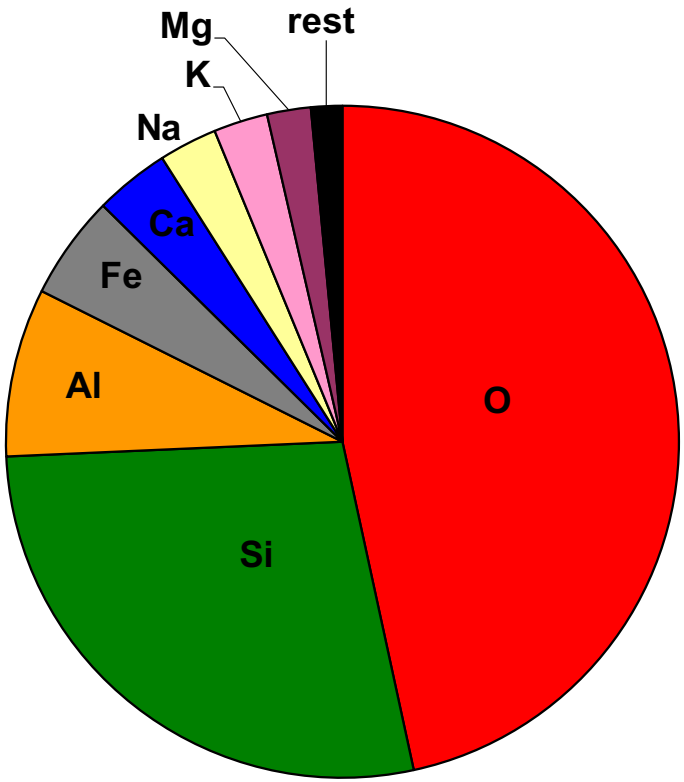
BUT, what sources of minerals are there which contain Al_2O_3 >> SiO_2 ?

Bauxite – localised, under increasing demand for Aluminium production, EXPENSIVE

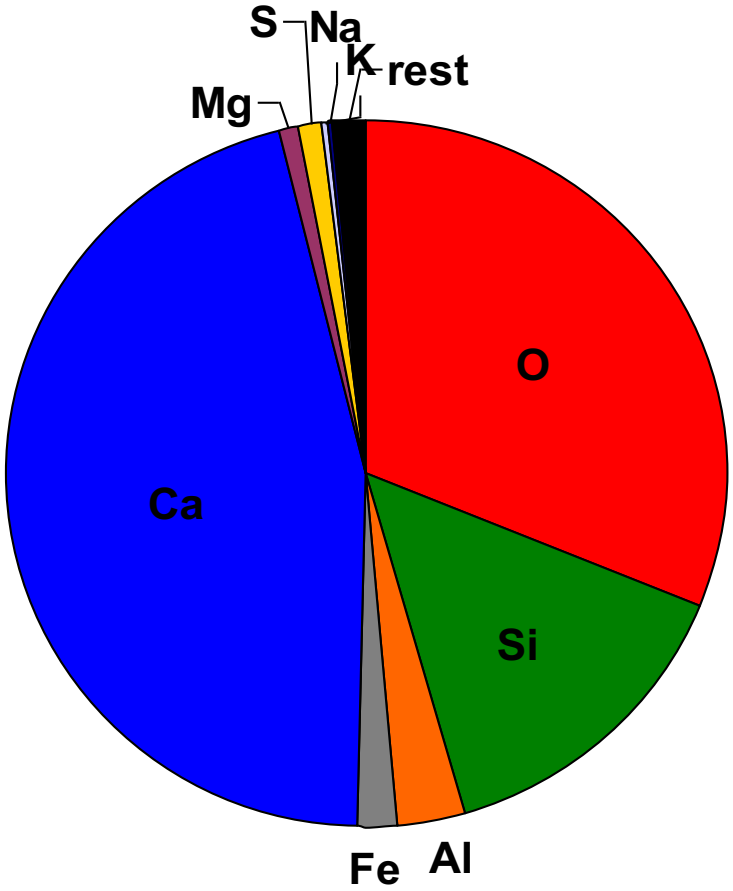
Even if all current bauxite production diverted would still only replace 10-15% of current demand.

Even after nearly 50 years CSA production in China is <0.1% of OPC
and falling

Composition of earth's crust



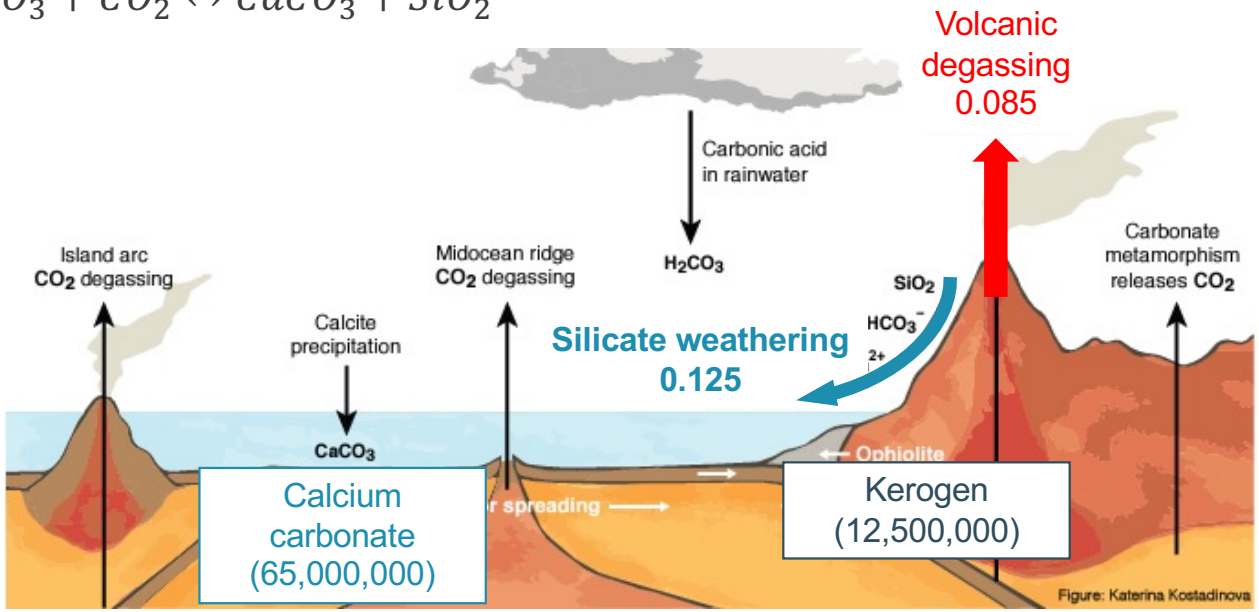
Composition of ciment



80% limestone
20% clay

The advantages of limestone

- A concentrated source of calcium due to geological slow carbonate silicate cycle
- Long time scales
  - Lithosphere: Small fluxes, large reservoirs
  - $CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2$



[numbers in Gt C per year, number in parentheses in Gt C; source: Kasting, 2019; Hilton & West, 2020]

Slide from Ruben Snellings

KULeuven

Basalt

Name of oxide	Content, % by weight
SiO_2	46.5 – 51.5
Al_2O_3	15.0 – 19.0
MgO	4.0 – 10.5
CaO	7.5 – 11.5
$FeO+Fe_2O_3$	8.0 – 12.0
K_2O+Na_2O	3.0 – 6.0
TiO_2	0.3 – 2.5
Cr_2O_3	0.02 – 0.05
MnO	< 0.1
Other	Up to 100

Source research gate

Dissolve in acid

Precipitate oxide separately

Common technology
in mining industry

Make clinker with uncarbonated calcium oxide

Estimated cost ~ $800 / ton
>80% reject materials

Accelerated weathering: ground basalt

https://un-do.com/enhanced-rock-weathering/

Ca from Seawater?

400ppm, simply due to the enormous volumes to process

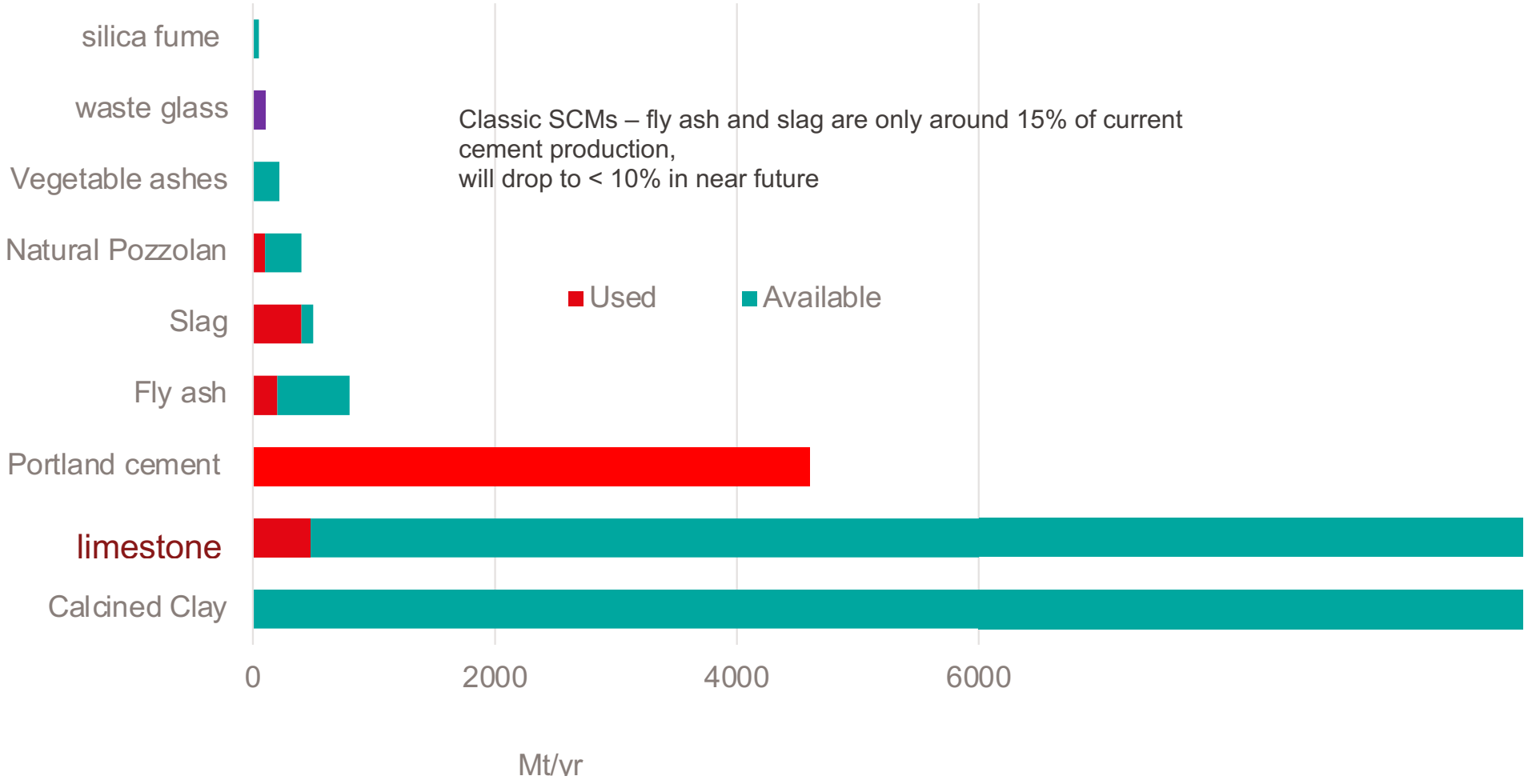
Cost >100x, present process

“Portland” cement is an inevitable consequence of the chemistry and geology of the earth

No alternative can be produced in quantities needed:

But a large fraction can be substituted with less reactive materials (SCMs)

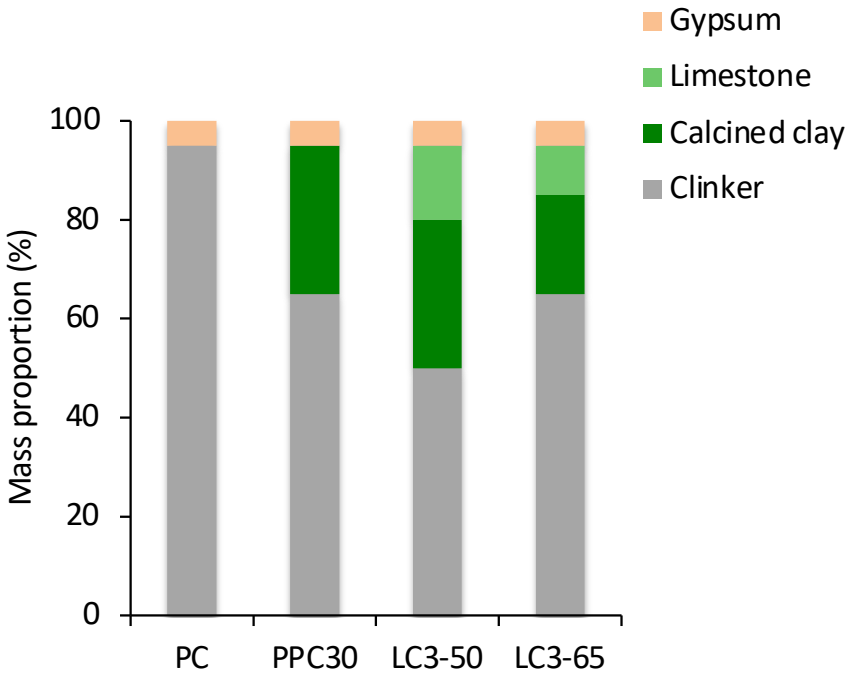
Availability of SCMs



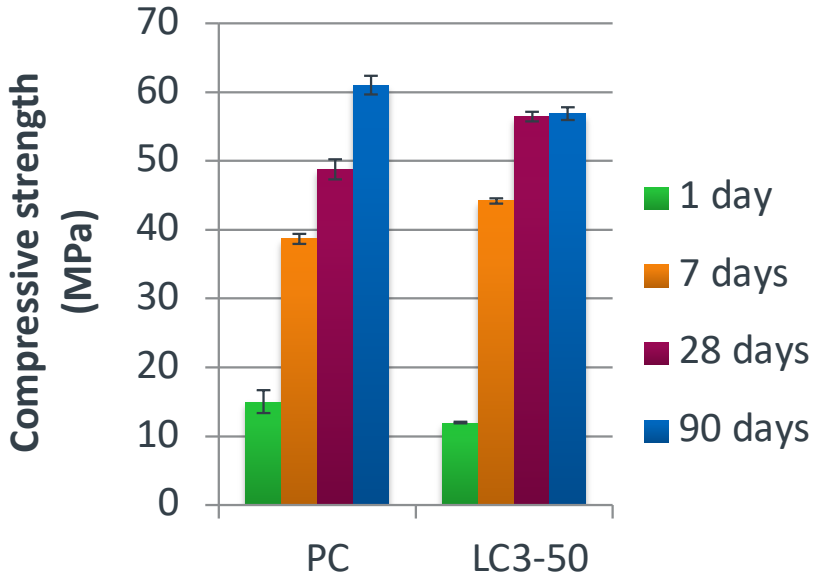
There is no magic solution

- **Blended with SCMs will be best solution for sustainable cements for foreseeable future**
- **Only material really potentially available in viable quantities is calcined clay.**
- **Synergetic reaction of calcined clay and limestone allows high levels of substitution:**
  EPFL led LC^3 project supported by SDC. Started 2013

What is LC^3

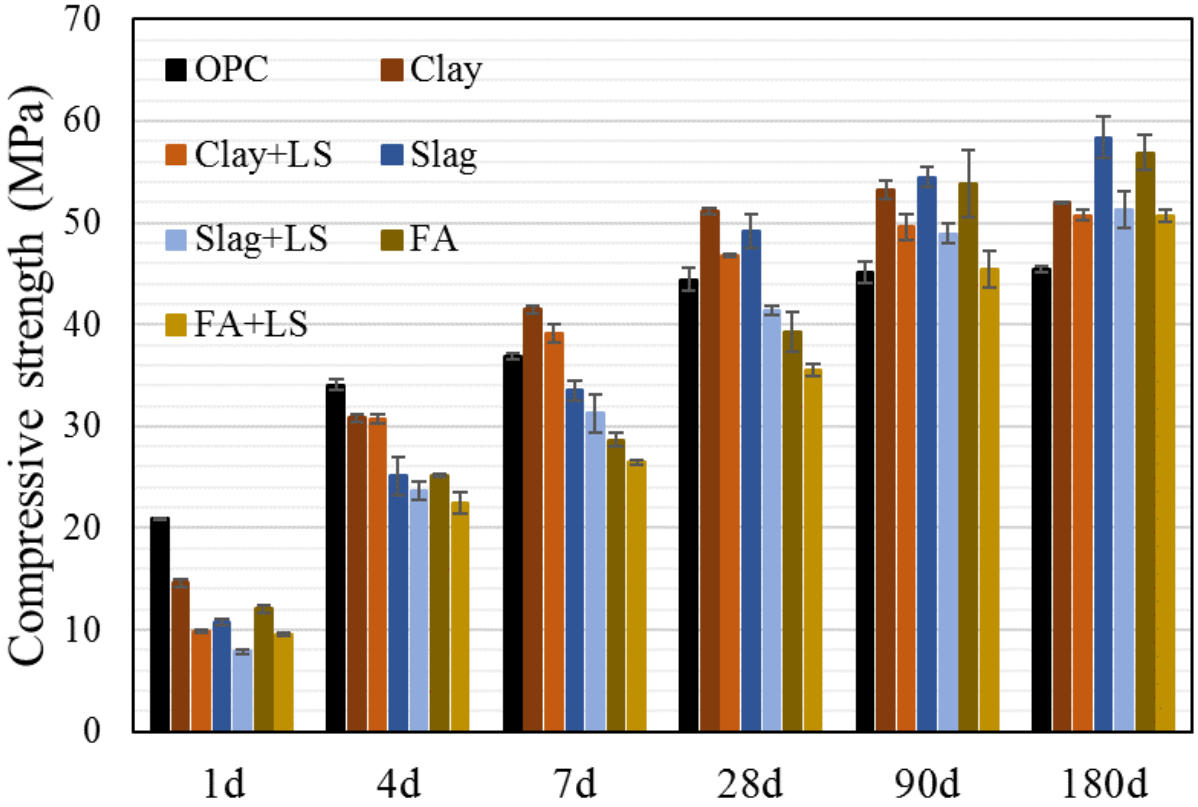


LC^3 is a family of cements, the figure refers to the **clinker** content



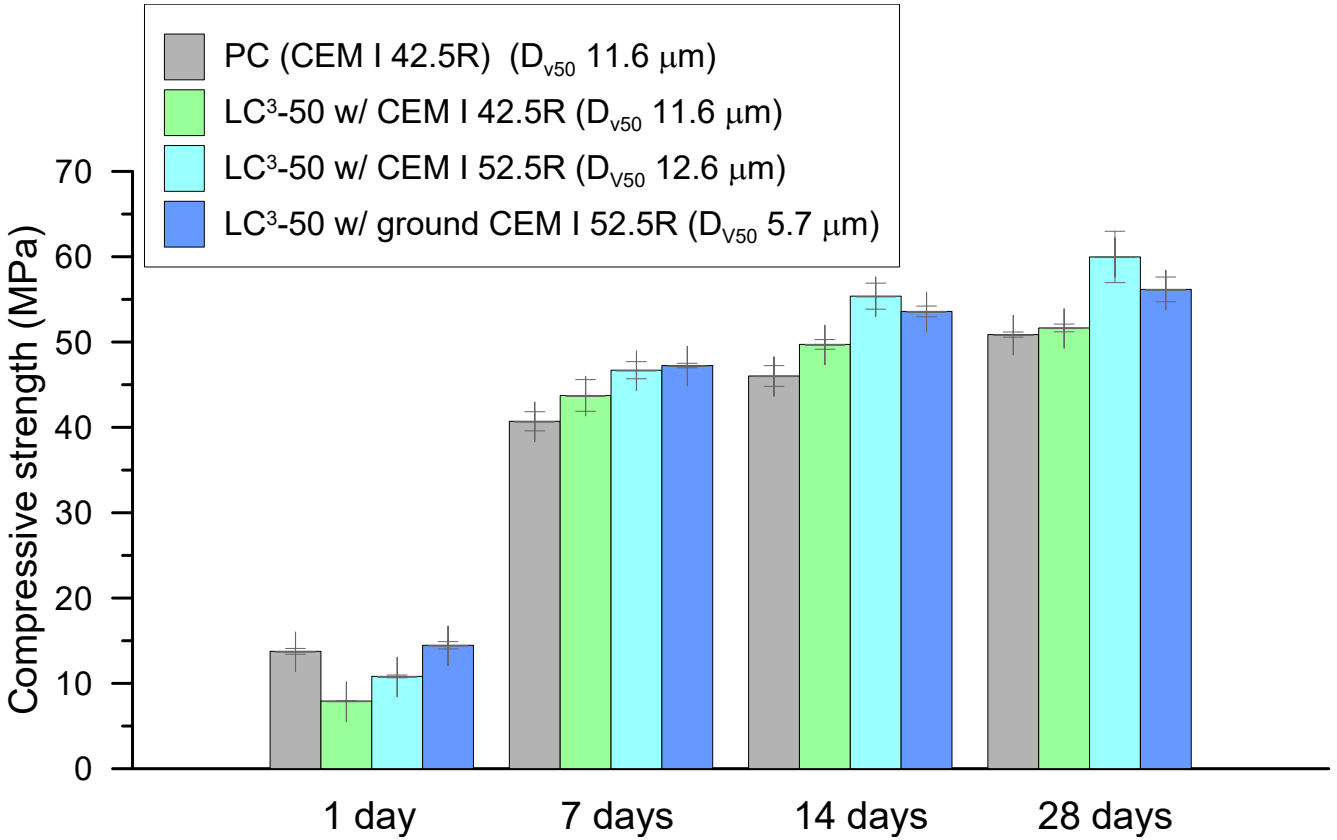
- 50% less clinker
- 40% less CO_2
- Similar strength
- Better chloride resistance
- Resistant to alkali silica reaction

Comparison of calcined kaolinitic clay, slag and fly ash

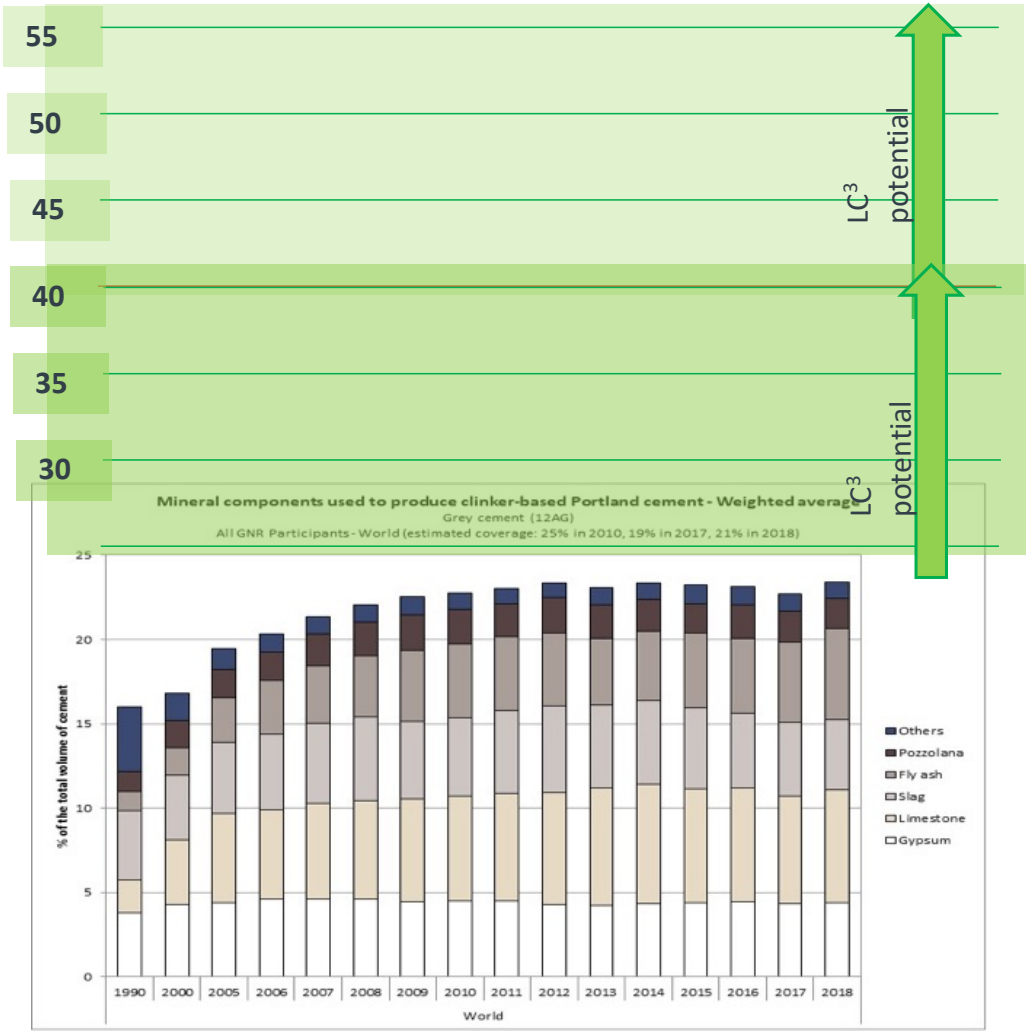


Binary systems 70% clinker, 30% SCM
Ternary systems, with limestone 50% clinker, 30% SCM, 15% limestone

Possible to get early strength by grinding clinker finer



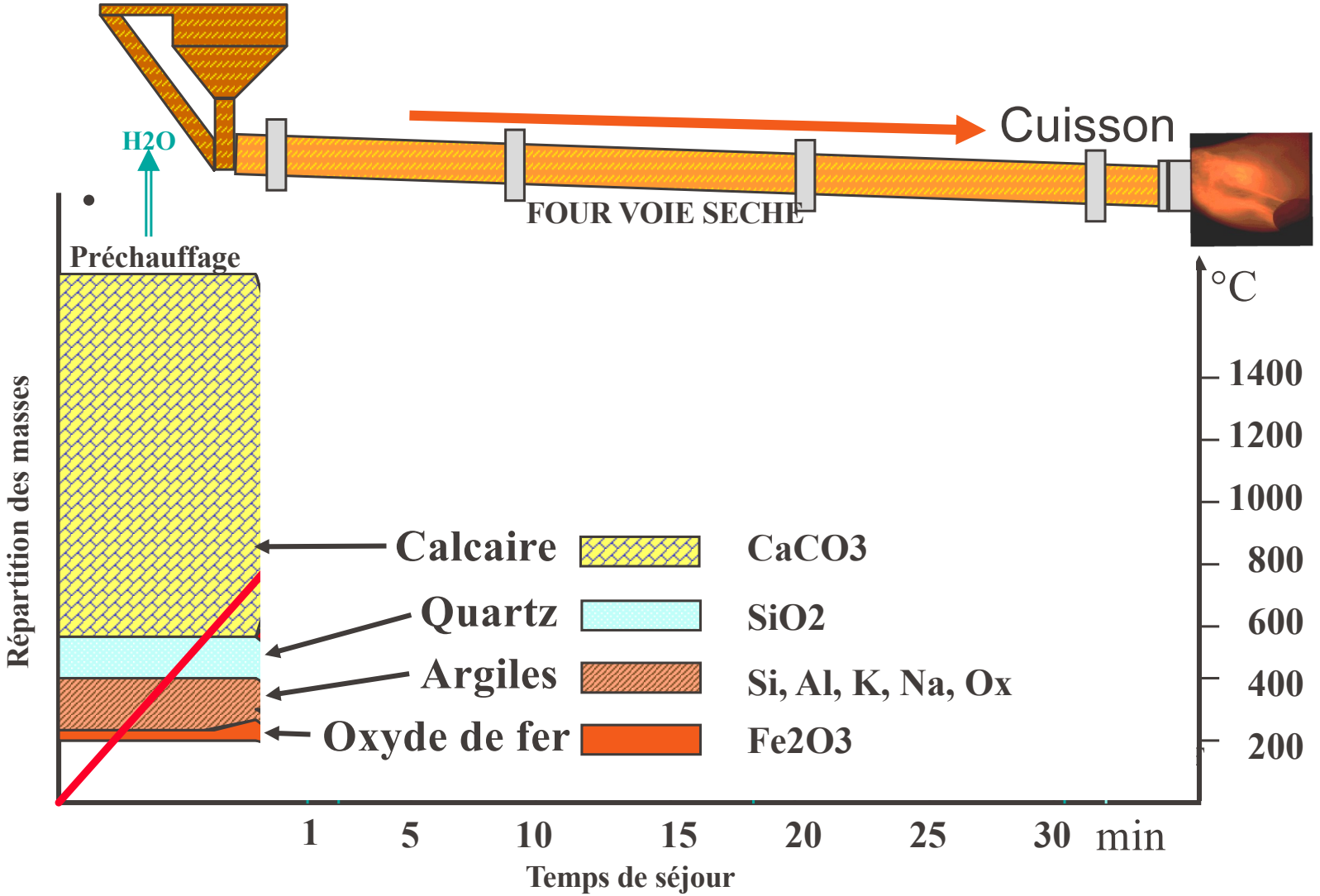
Calcined Clay only SCM which can expand substitution



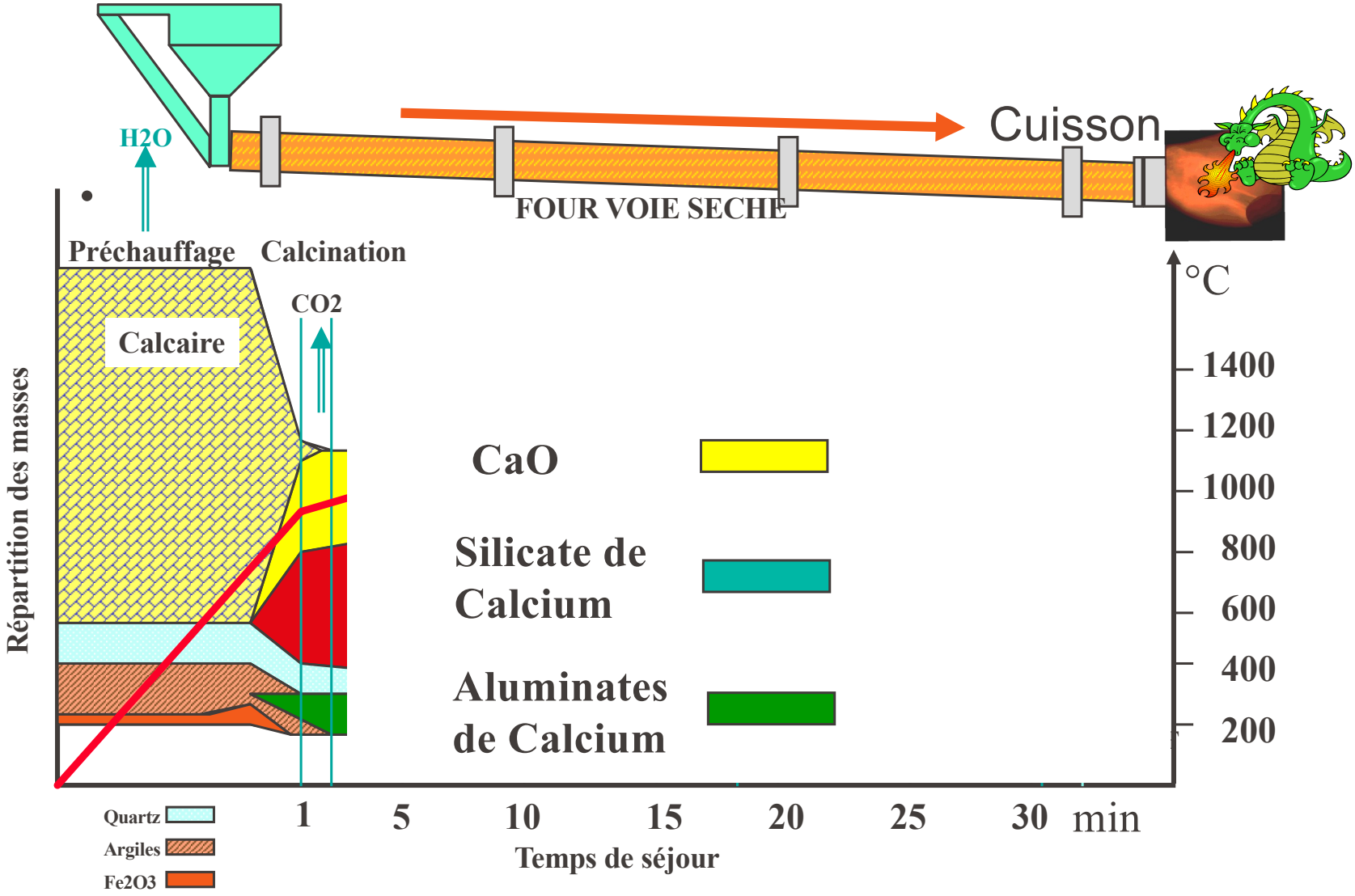
> 800 million Tonnes CO2/yr

> 400 million Tonnes CO2/yr

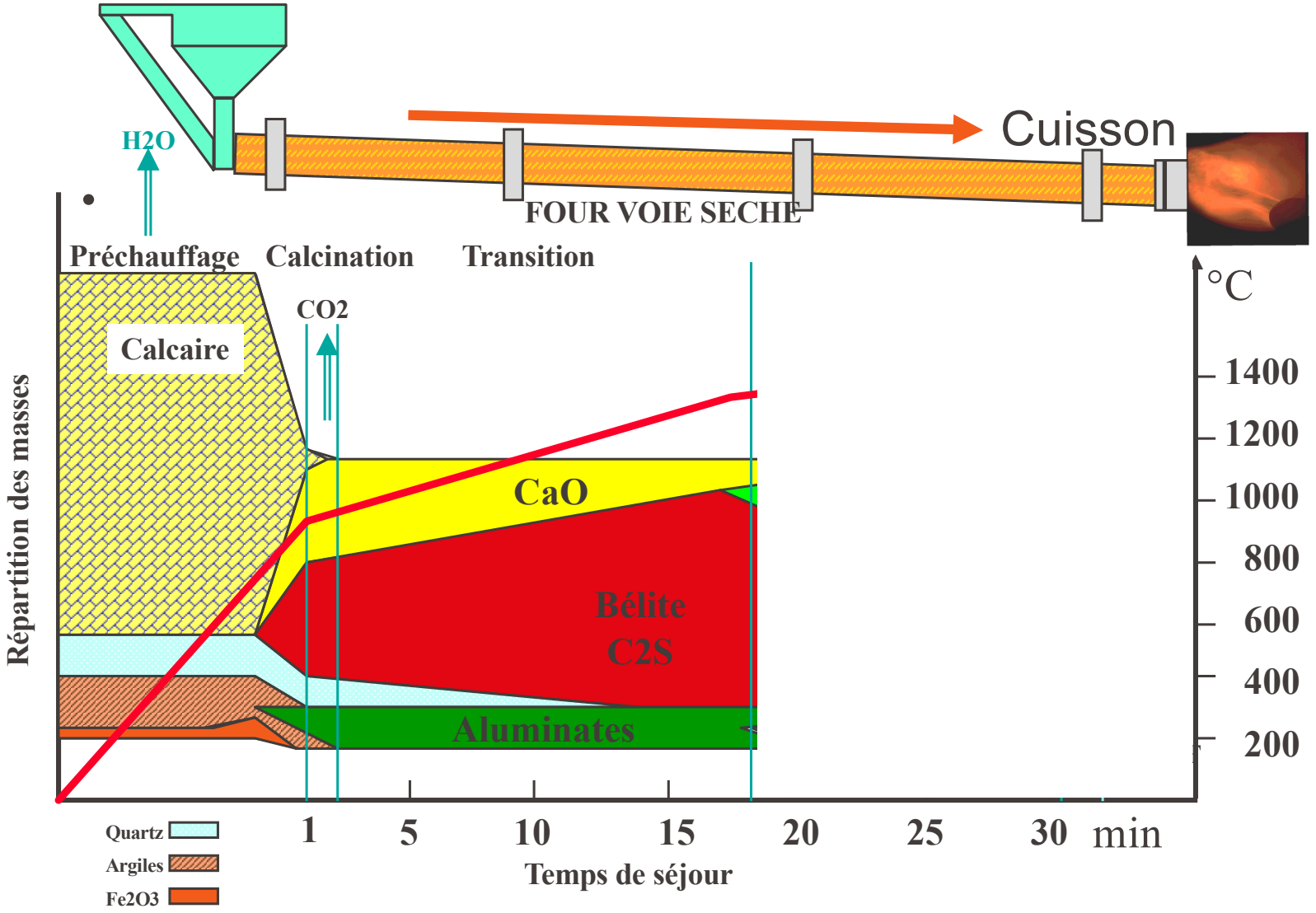
Looking again at clinker



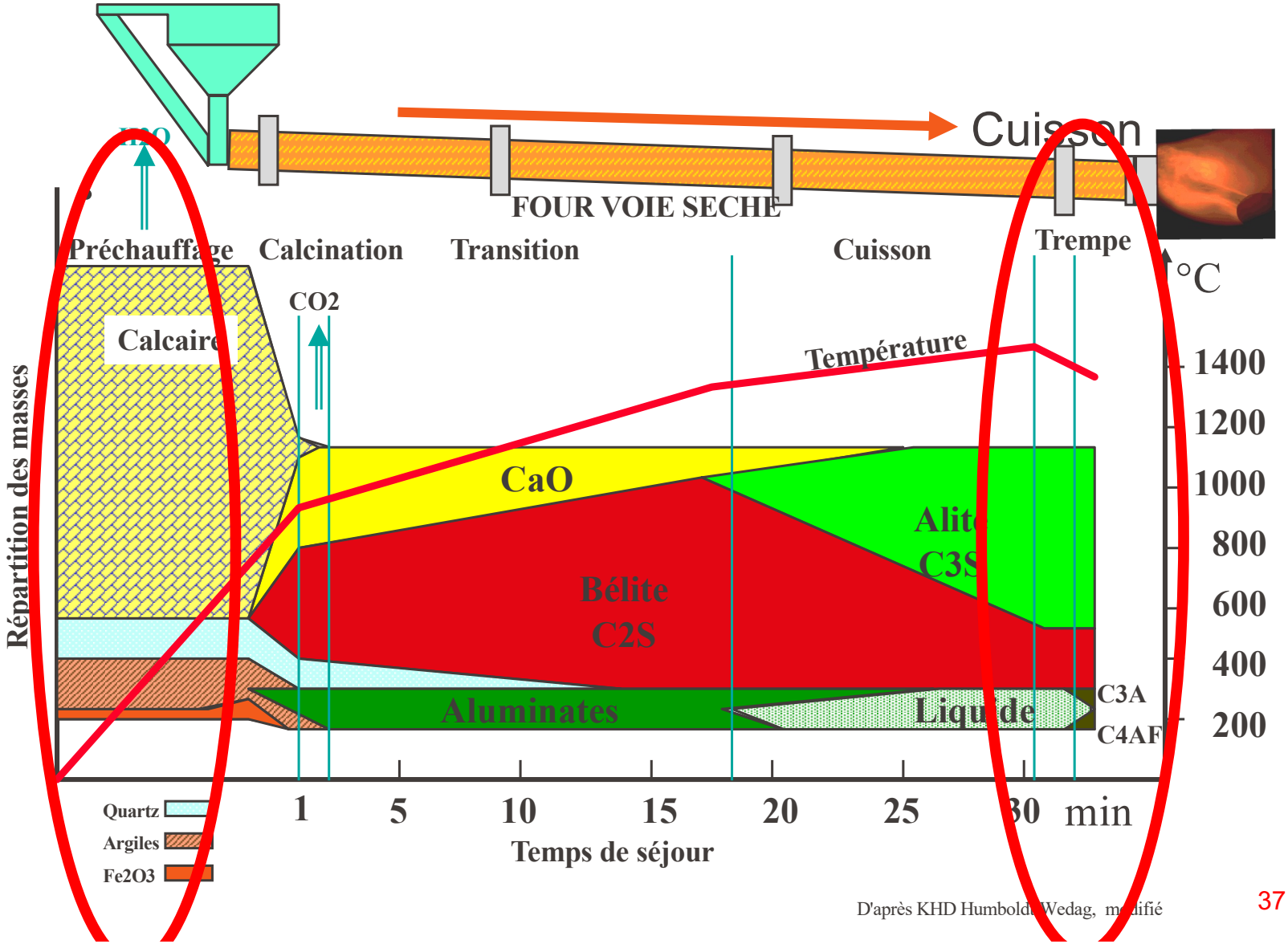
D'après KHD Humboldt Wedag, modifié



D'après KHD Humboldt Wedag, modifié

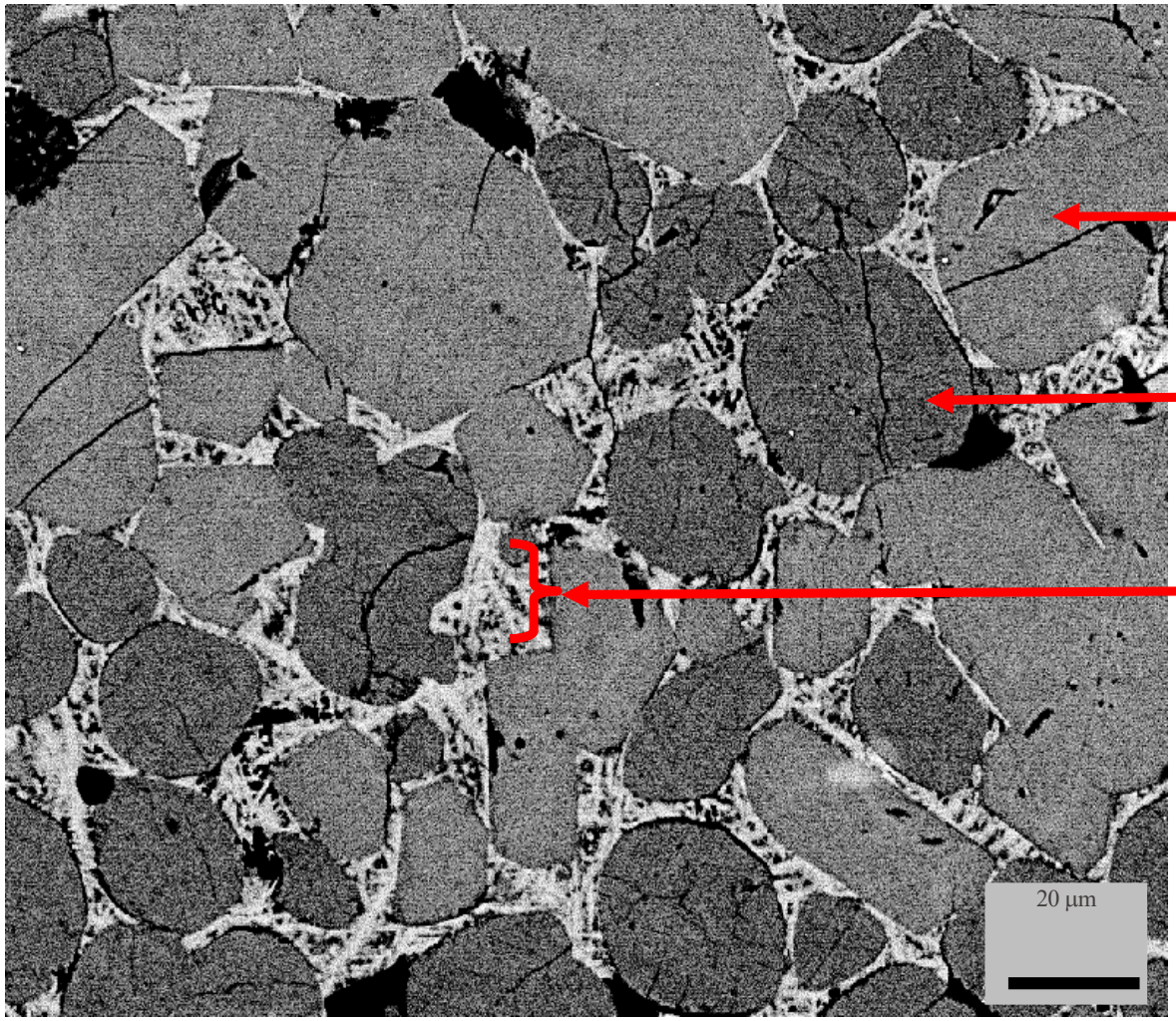


D'après KHD Humboldt Wedag, modifié



D'après KHD Humboldt Wedag, modifié

Microstructure « idéale » du clinker

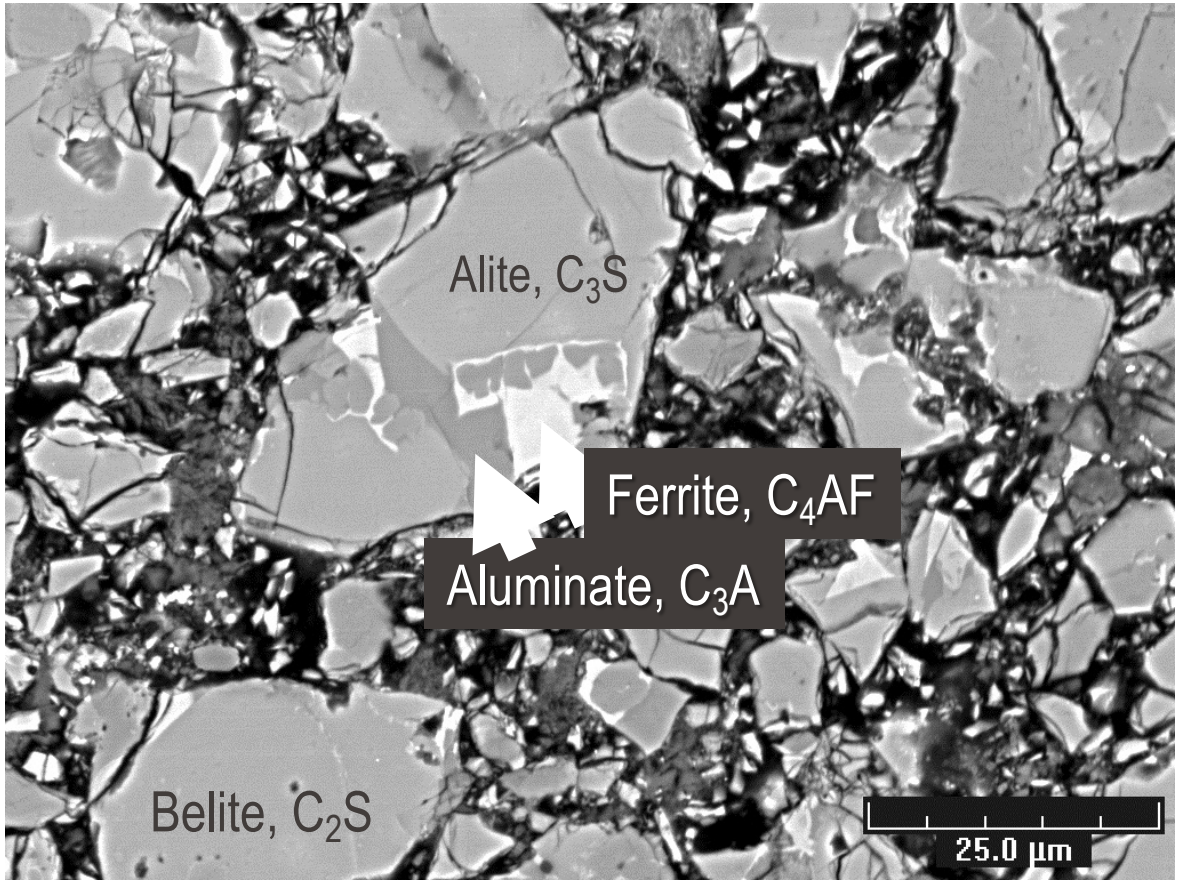


« alite »
C_3S, impure

« belite »
C_2S, impure

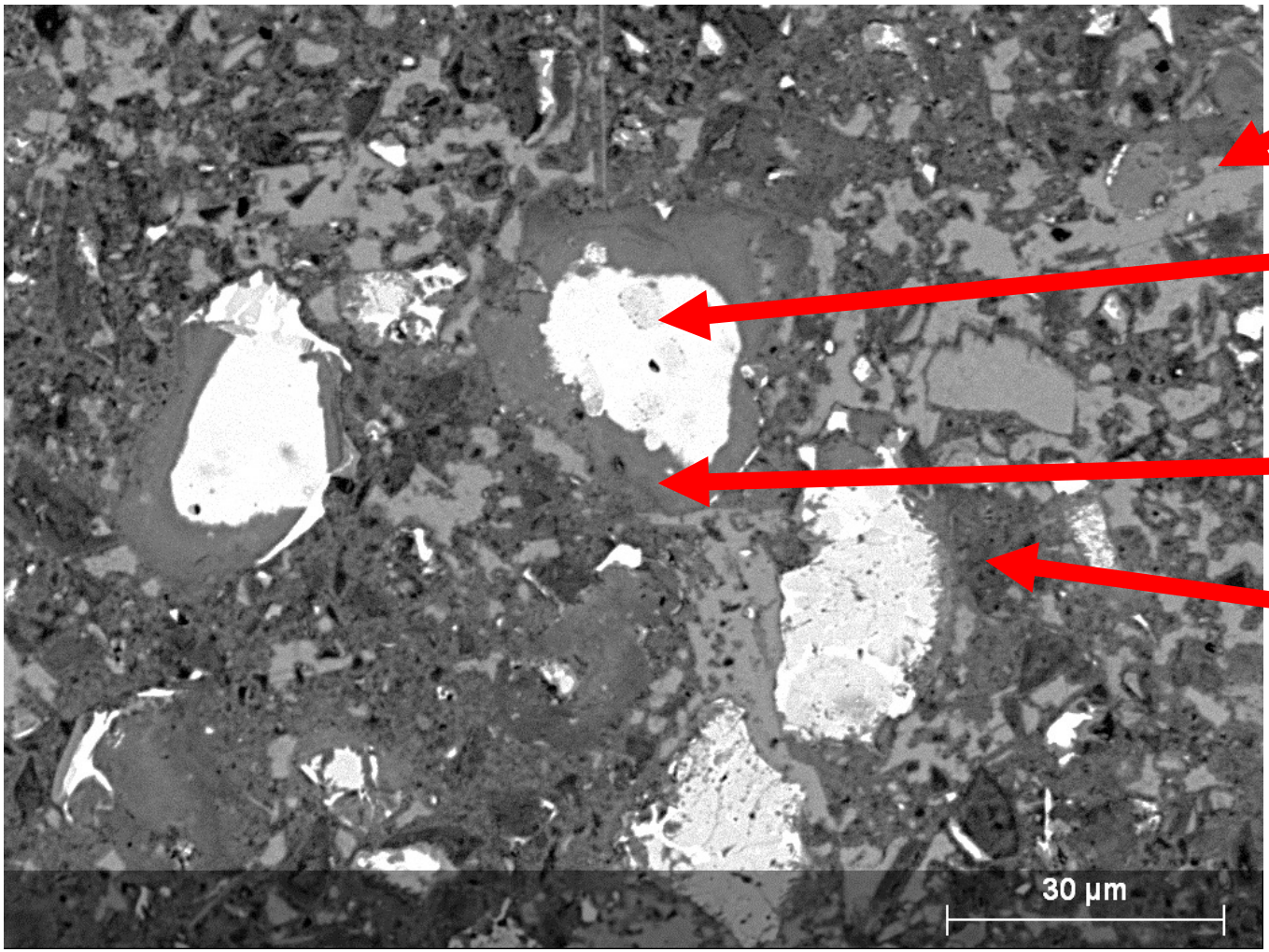
phases «interstitielles»
« celite »
C_3A, impure
+ solution solide de ferrite
« C_4AF »,
liquide pendant la cuisson

Real cement



4 main phases, multi phase grains, rough, angular grains

Hydrated cement paste



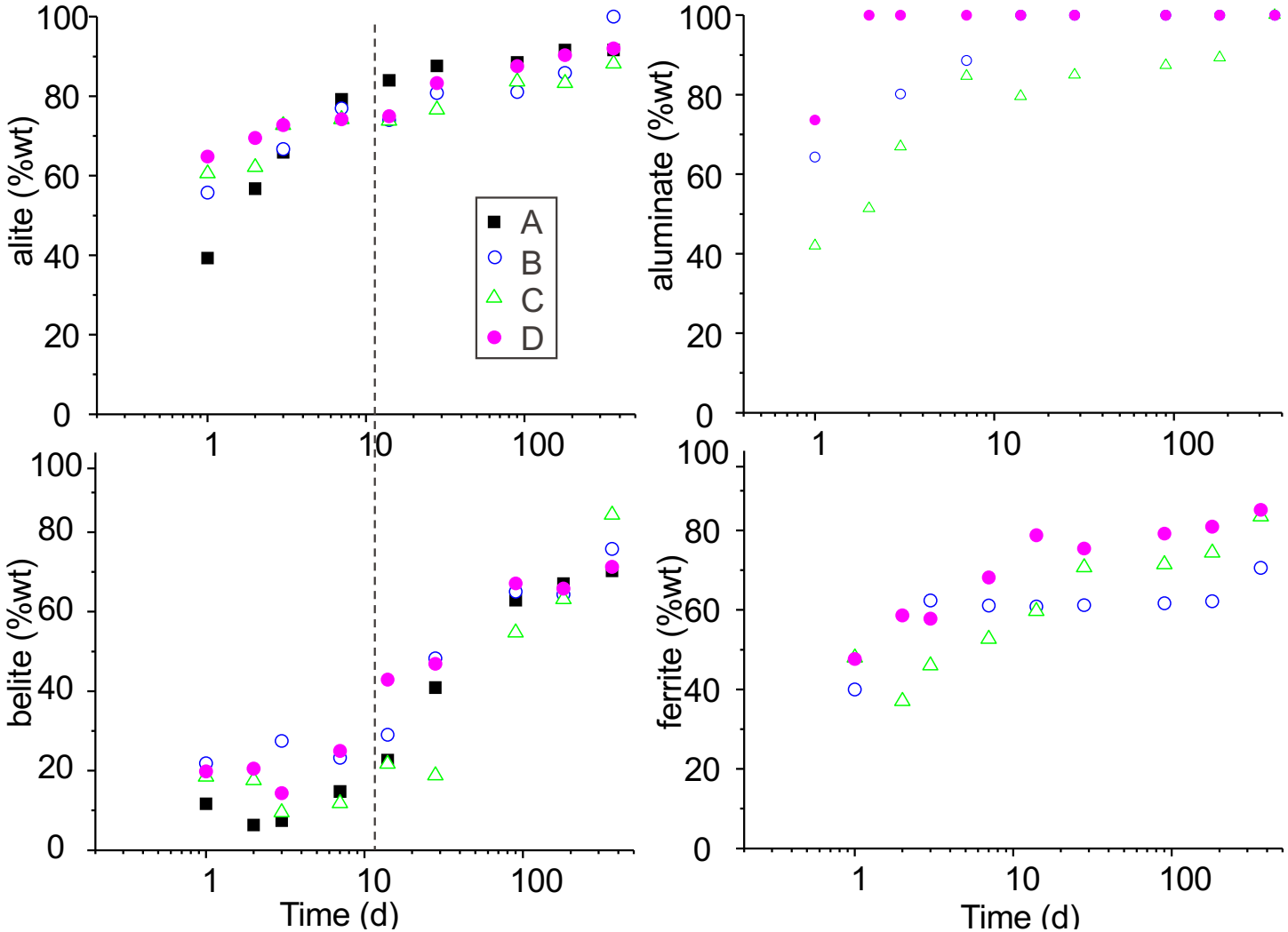
Calcium hydroxide

Unreacted cement
Anhydrous

Inner C-S-H

Outer hydrates
C-S-H
AFm
AFt

PhD Kocaba 2010



EPFL

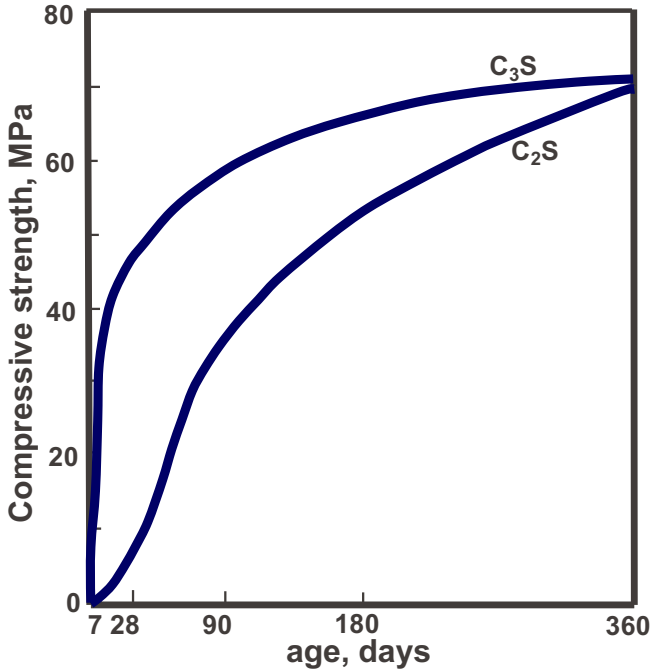
Belite is a “waste of lime”

>60% of CO_2 emissions from limestone decarbonisation

$$CaCO_3 \rightarrow CaO + CO_2$$

Clinker compound:	Chemical CO_2 emissions, kg/tonne
Alite (C_3S)	579
Belite (C_2S)	512

Belite rich clinkers ~10% reduction more than offset by slower kinetics



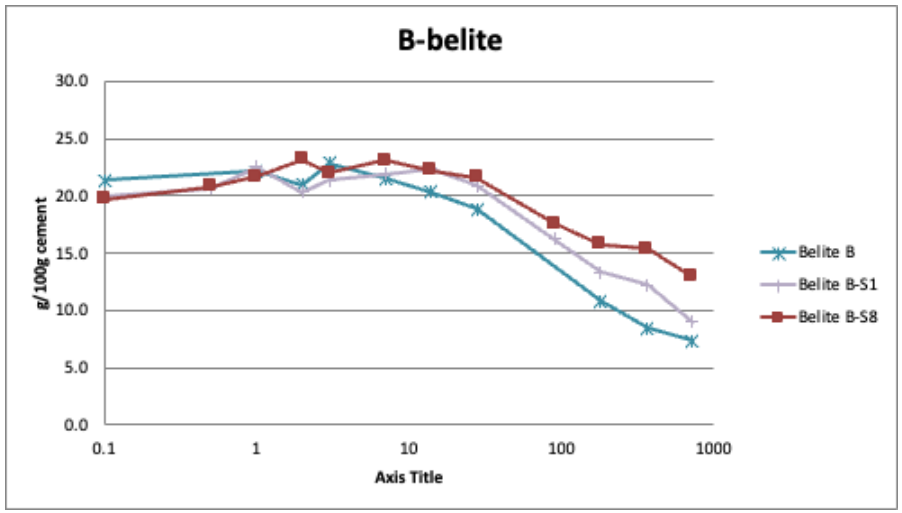
Belite is a "waste of lime"

$$C_3S + 5.3H \Rightarrow C_{1.7}SH_4 + 1.3CH$$

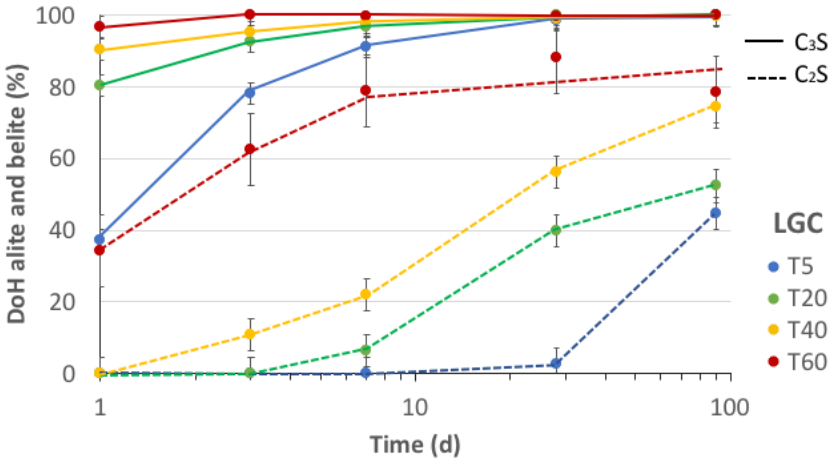
$$C_2S + 4.3H \Rightarrow C_{1.7}SH_4 + 0.3CH$$

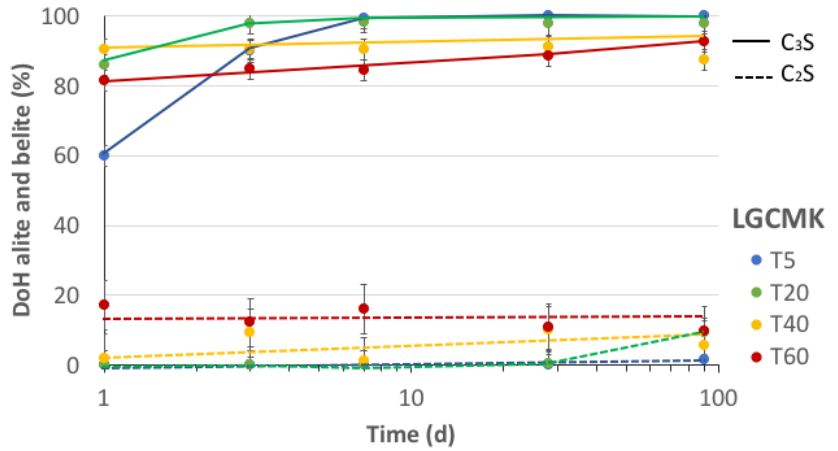
Less than ¼ of CH!

Highly reactive SCMs inhibit belite reaction



Kocaba thesis 2010





Chitvoranund thesis 2021

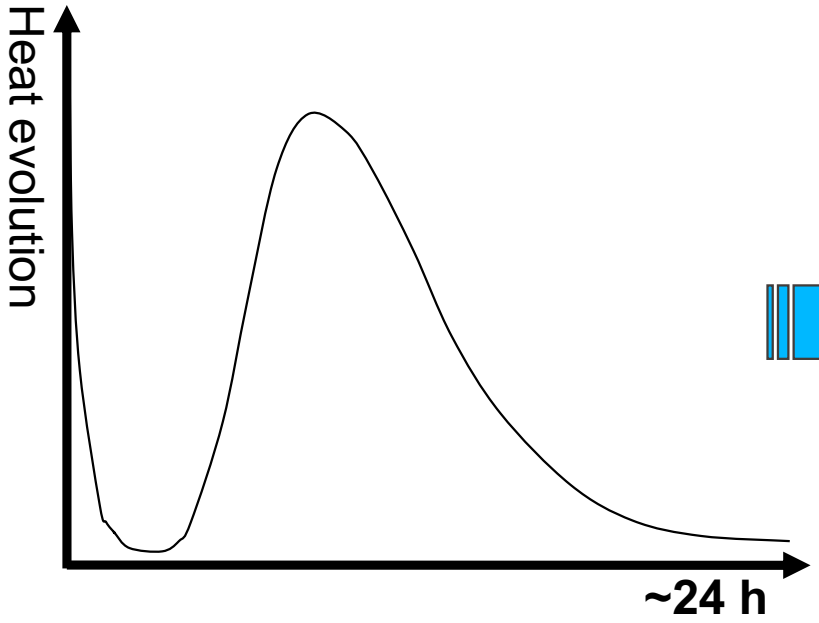
Typical clinker composition

SiO_2	20,5	(19 – 21)
Al_2O_3	6	(4-7)
Fe_2O_3	2,5	(2-3)
CaO	64	(62-65)
MgO	1,2	(1-4)
SO_3	2,8	(2,5-3,2)
K_2O	0,5	(0,3-1)
Na_2O	0,2	(0,2-0.5)
PaF(LOI)	1	(1-2)
CaO libre	1	(0,5-1,5)
resid insol	0,3	(0,2-0,4)

C_3S	67
C_2S	15
C_3A	5
« C_4AF »	6

~10% of Ca tied up in non reacting belite

Hydration process: limitation

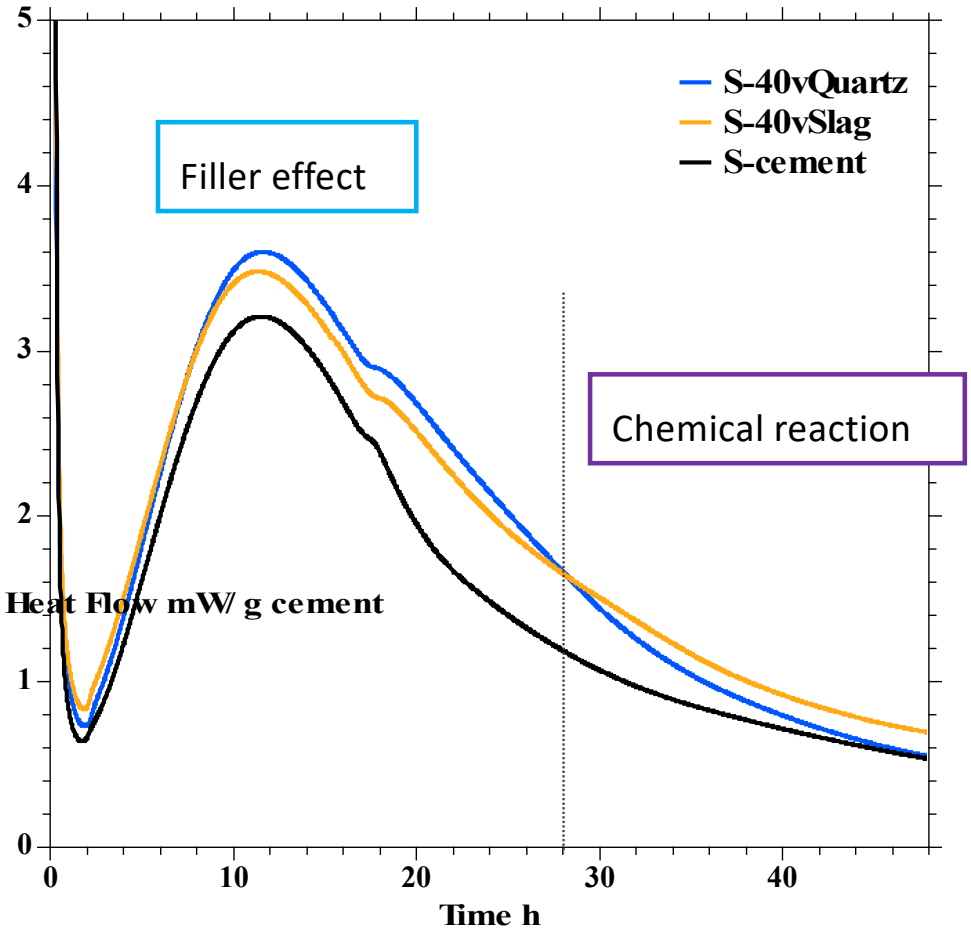


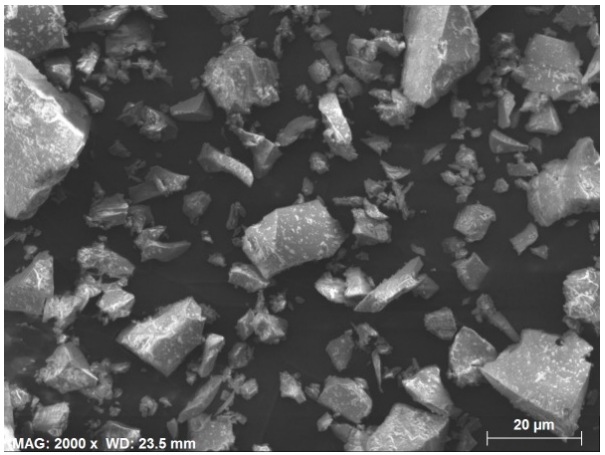
28 days

~ 50% reaction
~ 25% strength

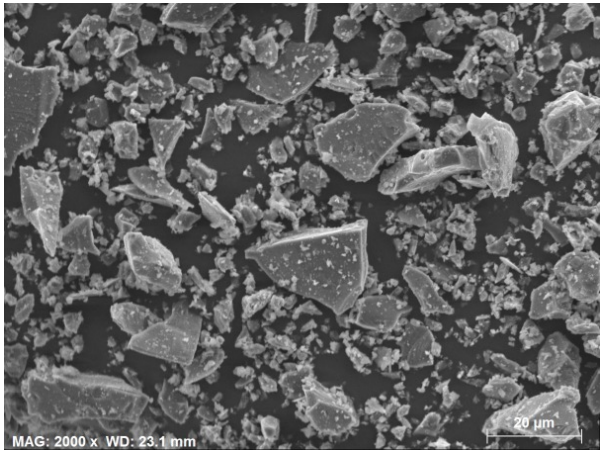
~ 80% (+30) reaction
~ 80% (+65) strength

The first 24 hours is all about the clinker phases





Slag

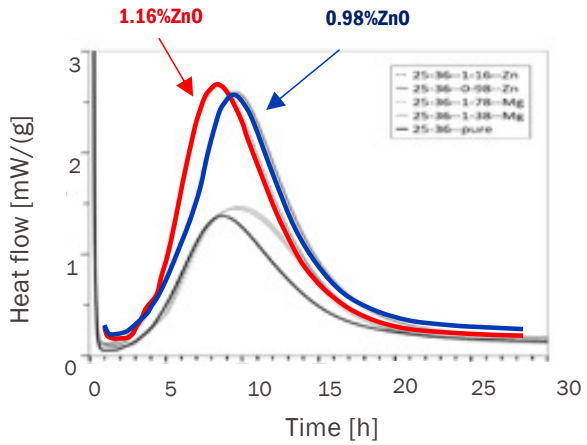


Quartz

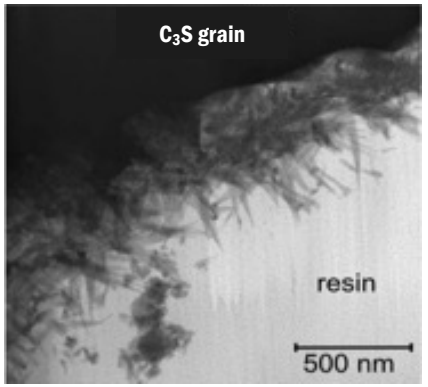
Can we change the reaction rate of clinker?

Zn in alite?

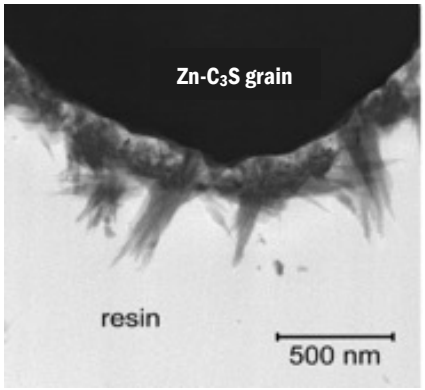
Isothermal Calorimetry



- Minor amounts of Zn in C_3S increases by double the heat released
- Longer needles with Zn doping - Incorporation of Zn in C-S-H



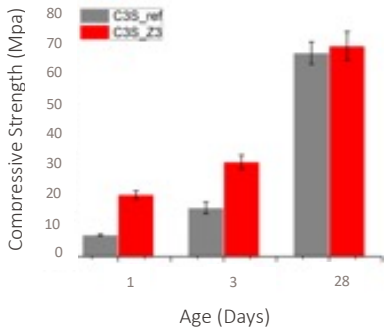
C_3S



Alite 1.16% zinc

Mechanical Properties

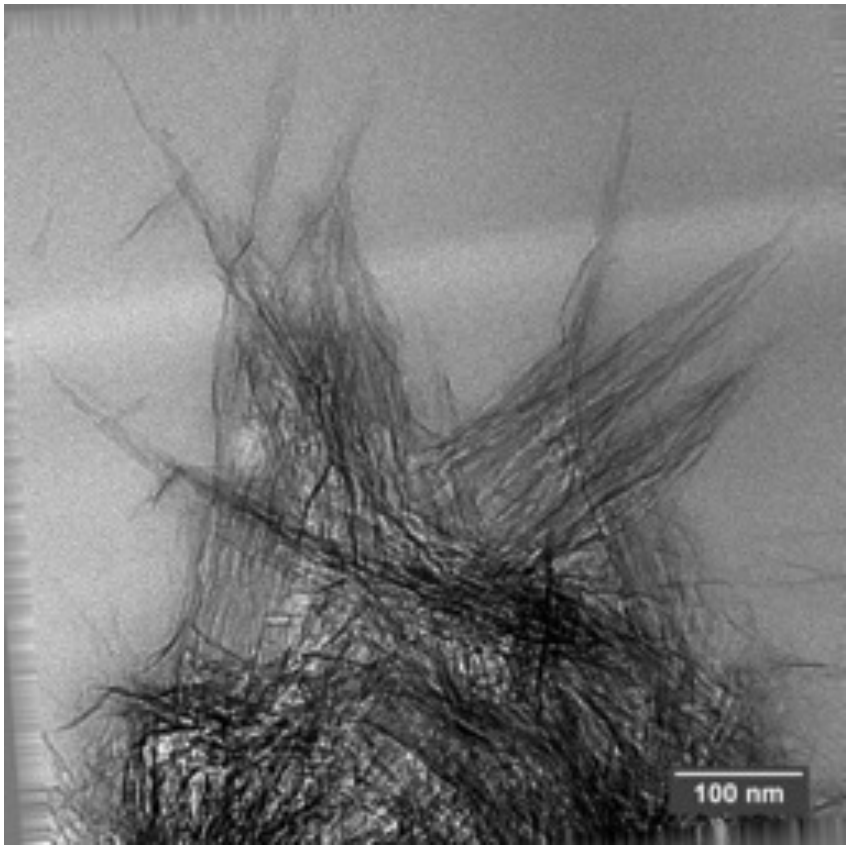
Compressive strength enhanced until 3 days

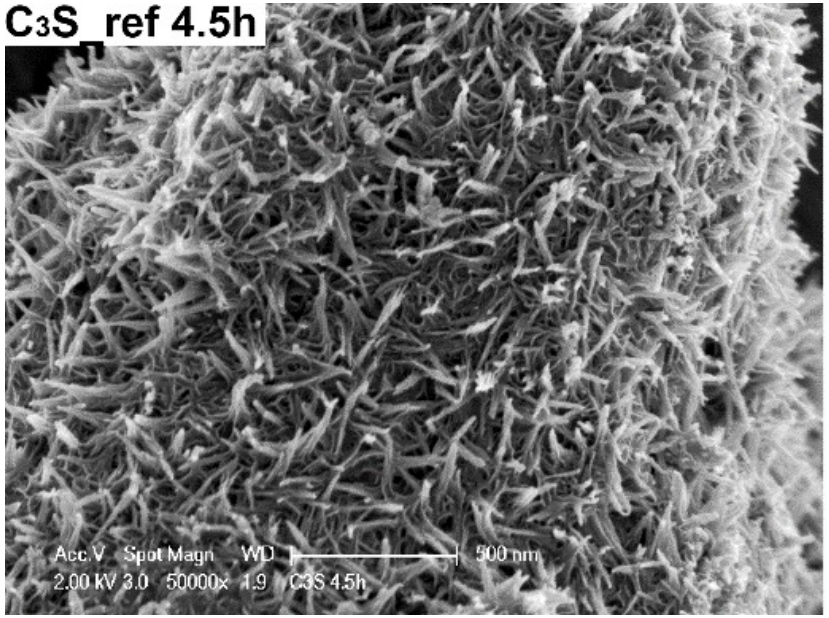


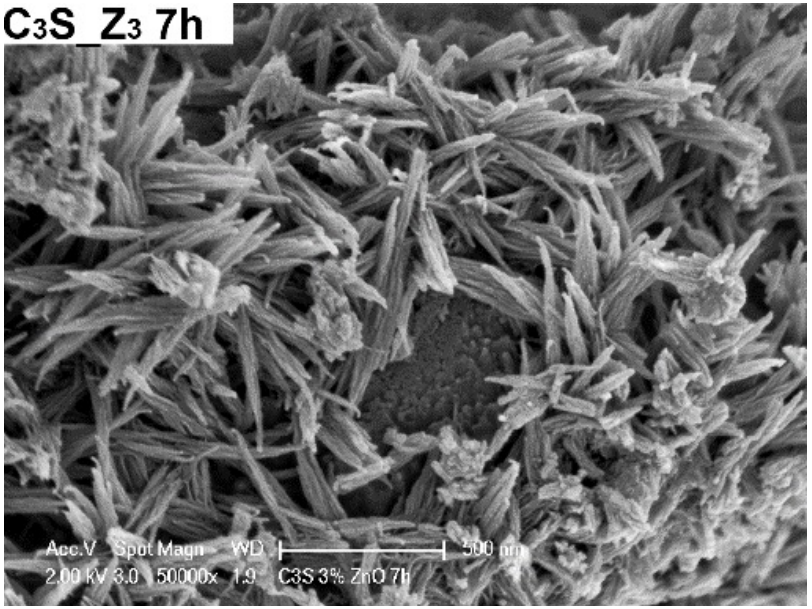
Reactivity enhancement in the main cement phase (C_3S) + Compressive strength enhanced until 3 days

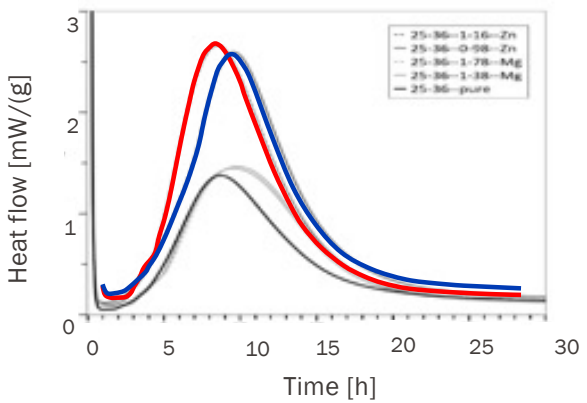
"Zn in C_3S increases the reactivity, therefore it has potential to increase cement reactivity as well"

[Bazzoni , 2014] [Li, unpublished work]


100 nm


C3S_ref 4.5h
Acc.V Spot Magn WD 500 nm
2.00 kV 3.0 50000x 1.9 C3S 4.5h


C3S_Z3 7h
Acc.V Spot Magn WD 500 nm
2.00 kV 3.0 50000x 1.9 C3S 3% ZnO 7h



1. Can the effects seen on C_3S be translated into more realistic systems?

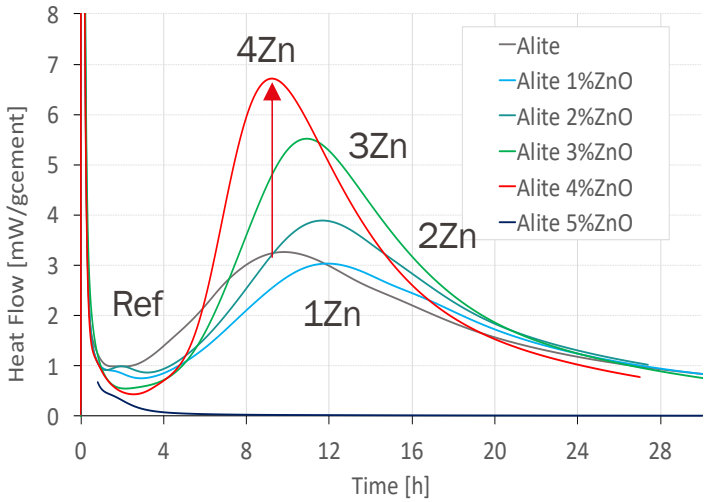
Zn enhances alite hydration but not in real systems

- Understand the differences
- Is there is a way to make it work? ⟶ **Challenge**

Thesis Andrea Teixeira

Different Behavior

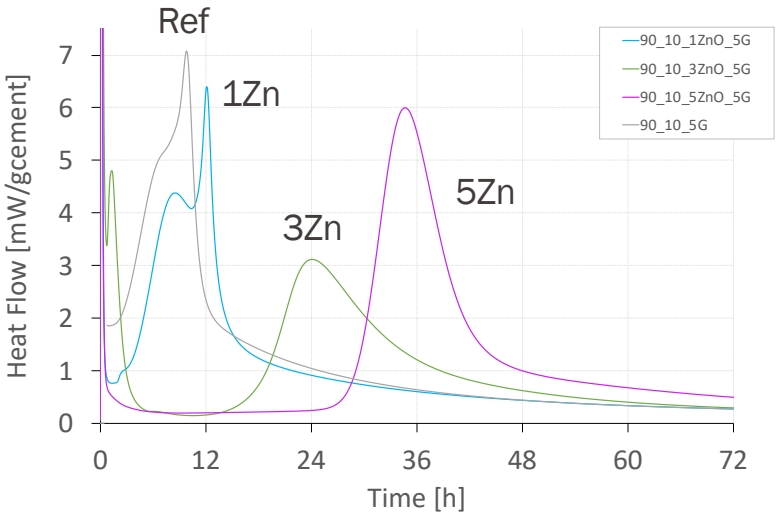
Alite System



- Heat released enhanced with ZnO
- Linear effect up to 4%ZnO

Polyclinker + 5% Gypsum

Intended 90% Alite – 10% C_3A



- Longer induction period

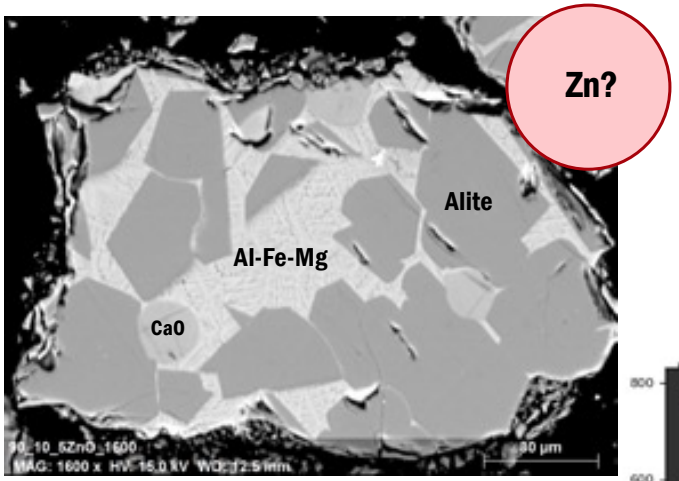
ZnO retards alite hydration in polyclinker

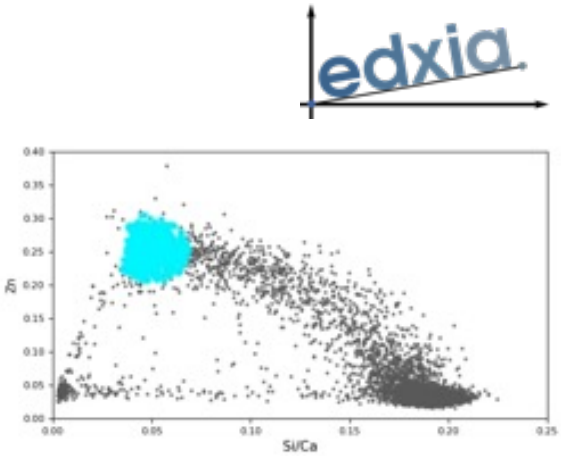
➡ Why?

What is The Main Problem?

Where is the Zn going?

Polyclinker 5%ZnO

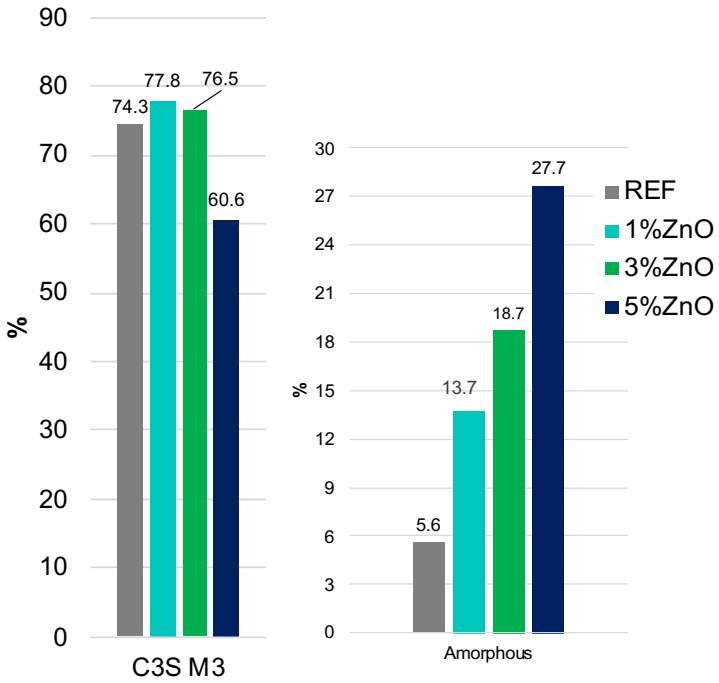




Zn is mainly concentrated in the interstitial phase.

XRD Quantification Polyclinker System

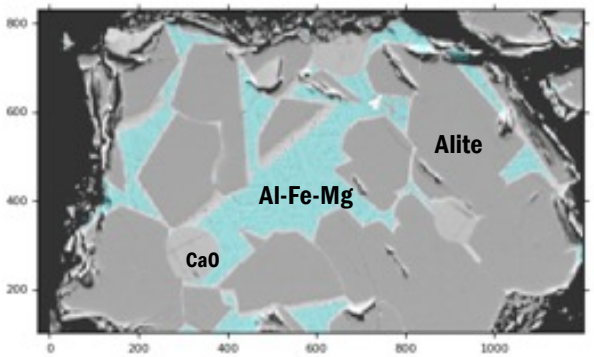
Linear increase in amorphous content, 5%ZnO has 27% of this phase.



Sulfation Correction

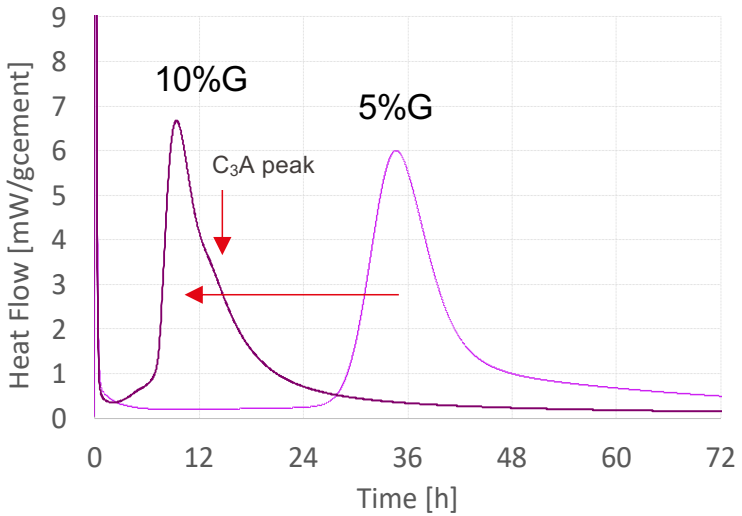
Hypothesis

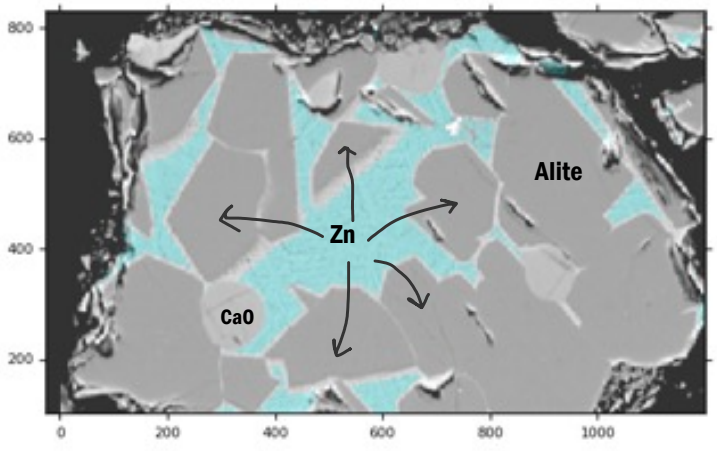
Zinc is mainly concentrated in the "amorphous" phase. As its dissolution is fast, there is a fast release of Zn ions to solution retarding alite reaction.



More gypsum can be added to control the reaction of the amorphous phase and therefore, avoiding Zn release.

Polyclinker 5%ZnO

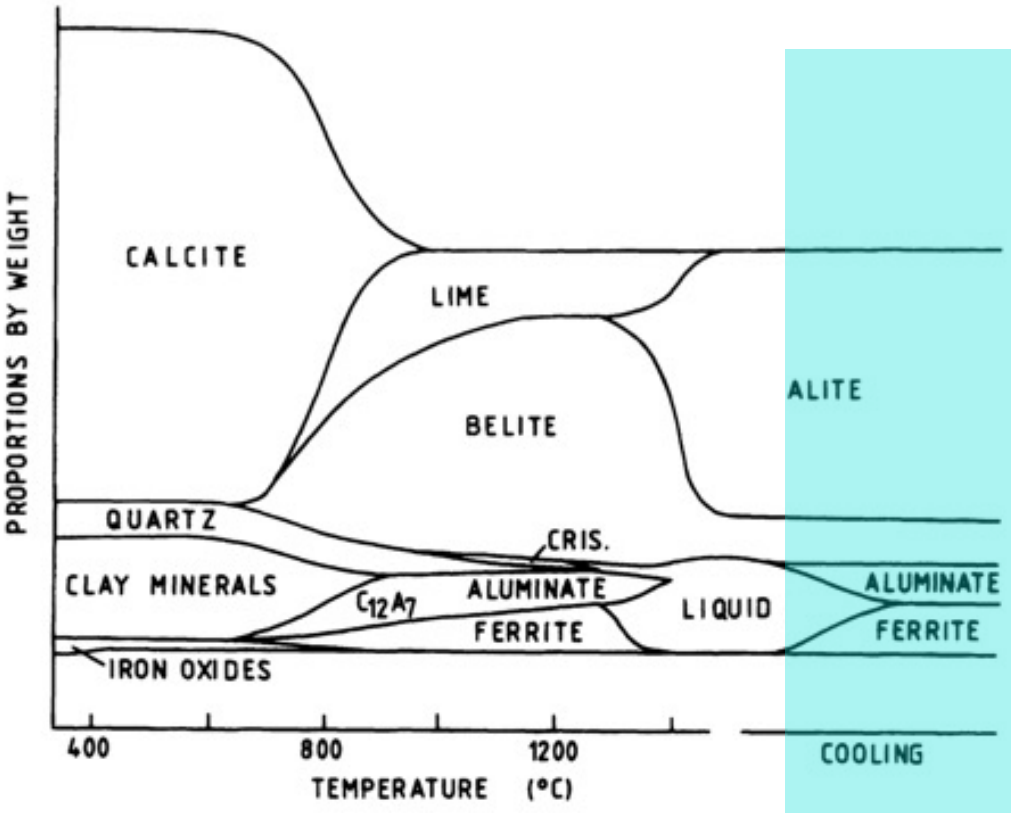




2. Are there ways to retain Zn in alite?

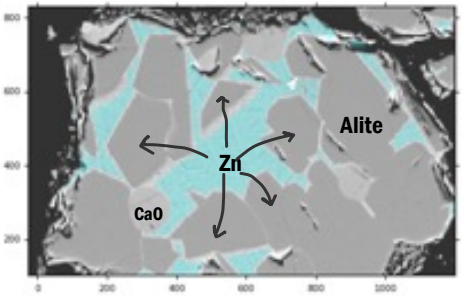
- Cooling rate
- Interstitial phase composition (C_4AF polyclinker)
- Lower amount of interstitial phase

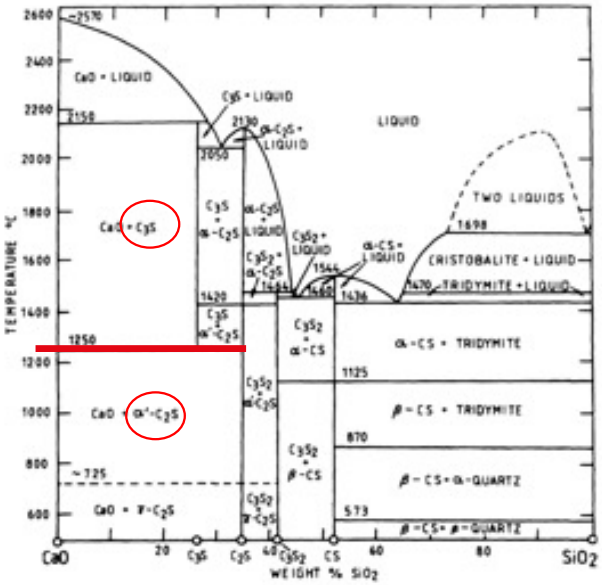
How to make it work?



Crystallization

- High dependence on cooling rate





- Slow cooling until 1250 °C

- [P. Stutzman, 2004] [Discussion with A. Pisch]

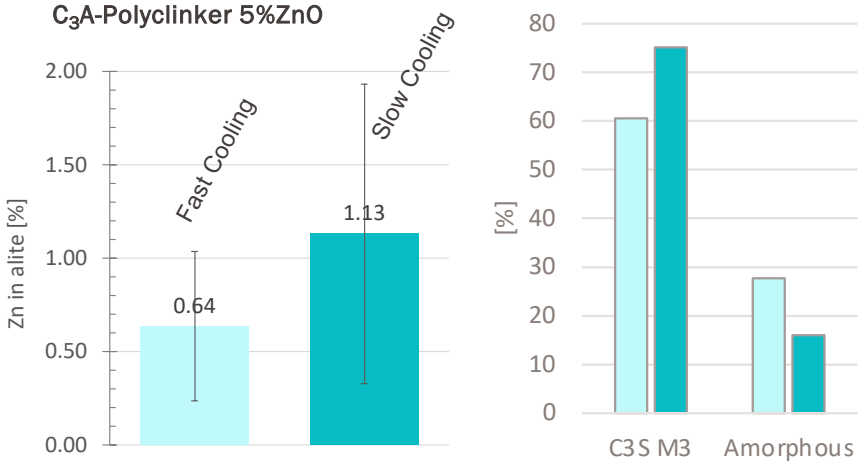
Slow cooling = more Zn in alite

Hypothesis

Zinc is mainly concentrated in the "amorphous" phase. As its dissolution is fast, there is a fast release of Zn ions to solution retarding alite reaction.

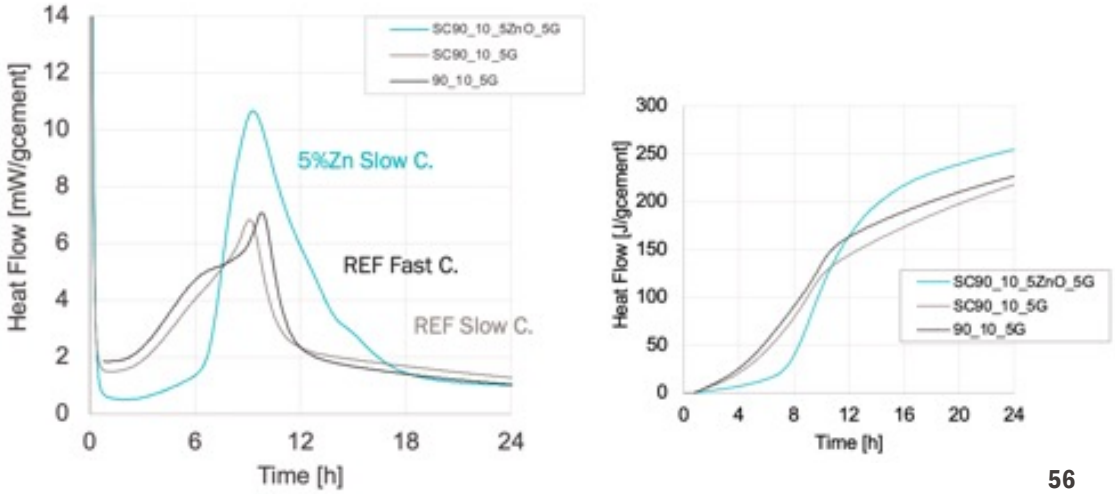
Change in cooling rate from quenching to slow cooling (1250 °C)

↳ More Zn in alite

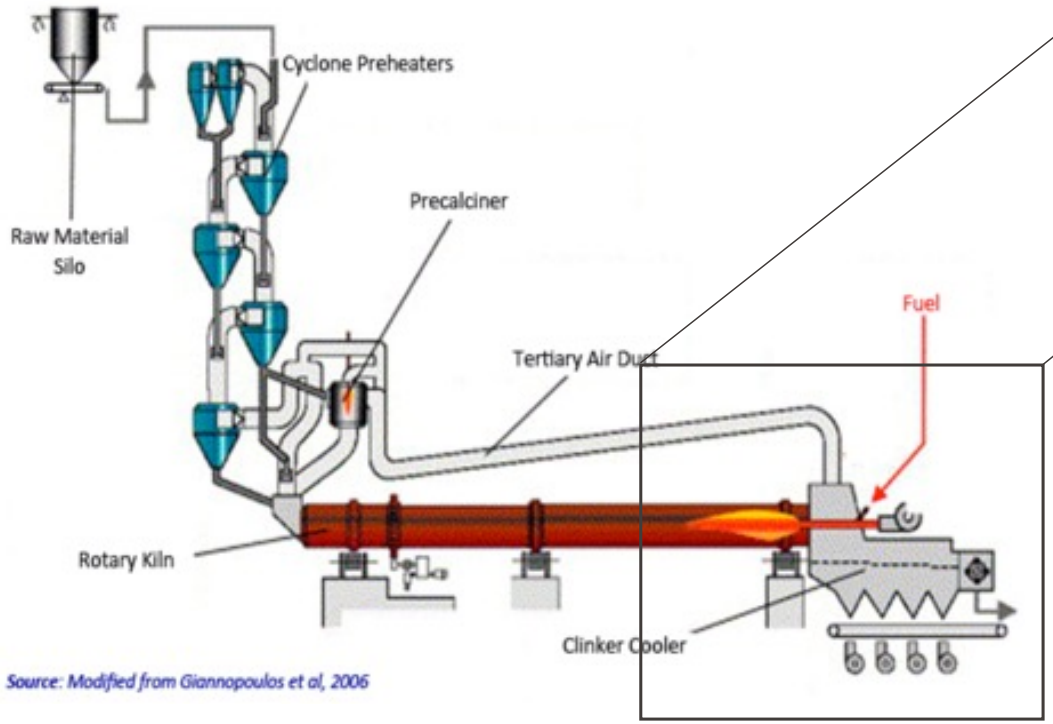


Alite hydration is enhanced with slower cooling rate

↳ More zinc is in alite and less in interstitial phase



It Could Be Implemented in the Industry!



The flame can be placed to the front a little so that the thermal shock is not that big, giving time to ions to a better distribution

- [http://www.iipinetwork.org/wp-content/letd/content/clinker-making.html]

where now?

Thank You

Karen Scrivener

École
polytechnique
fédérale
de Lausanne