In-Situ Early Age Hydration Characterization of LC^3 binders

Angeles G. De la Torre

Departamento de Química Inorgánica, Universidad de Málaga, 29071-Málaga, Spain,
mgd@uma.es

Outline

1. Cement Science Group @ UMA presentation #1
2. LC^3 research projects/contracts @ UMA #6
3. Clays studied @ UMA #1
4. Phase and microstructure evolution of LC^3 #2
5. Cement hydration mechanisms #3
6. Understanding pozzolanic reactivity #2
7. Processing and activation of LC^3-50 binders #4
8. Conclusions #1

UNIVERSIDAD DE MÁLAGA

1. Cement Science Group @ UMA presentation

Permanent UMA staff:
Miguel Angel Garcia Aranda, g_aranda@uma.es
María de los Ángeles Gómez de la Torre, mgd@uma.es
María Isabel Santacruz Cruz, isantacruz@uma

Temporary UMA staff:
-

Grant based positions (currently):
Postdoc: 1 [Ana Cuesta, a_cuesta@uma.es]
PhD candidates: 6

Positions under recruitment (currently):
Postdoc: 1, PhD candidate: 1

https://sites.google.com/view/cementscience-uma/home/members

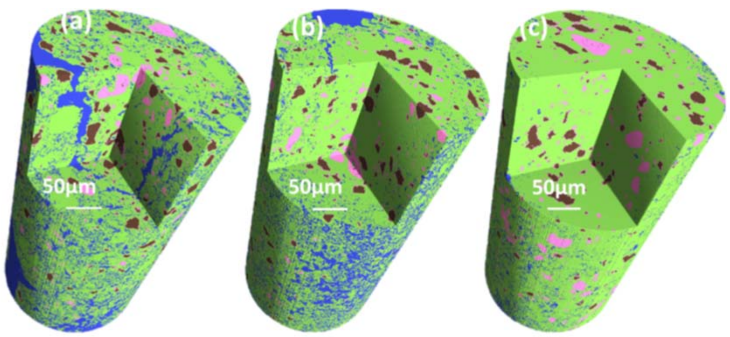
2. LC^3 research @ UMA: public projects

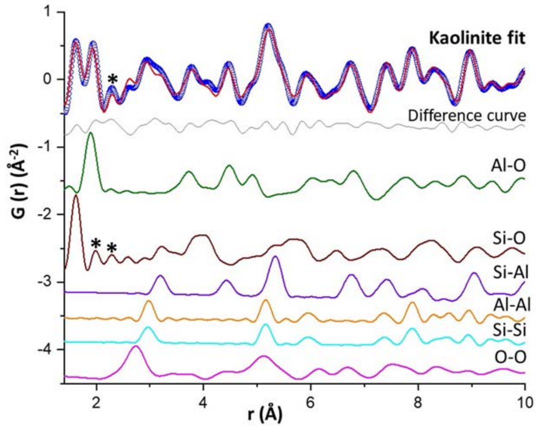
Title: “Microstructure analyses of Limestone Calcined Clay Cements by Advanced Synchrotron Techniques (LC3-micro)”

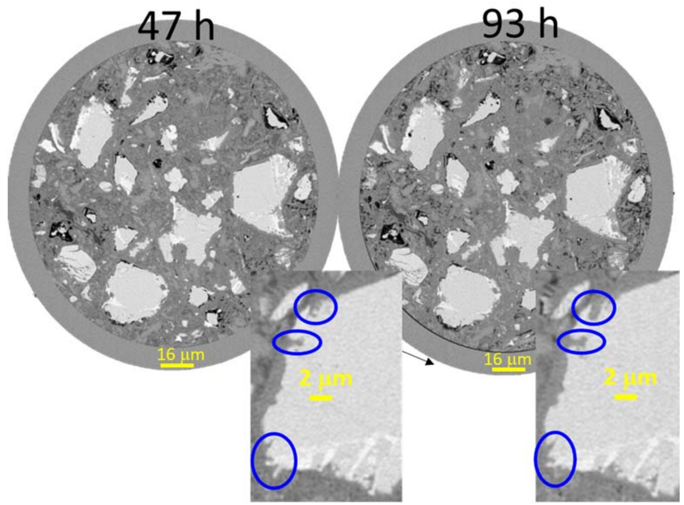
Principal investigator: Ana Cuesta
Funding agency: Ministry of Science, reference: PID2019-104378RJ-I00
From: 2020/10/01 to 2023/09/30

The main objective is to further characterize the microstructures of unaltered limestone calcined clay cement (LC^3-50) binders with Spanish calcined clays mainly through multiscale synchrotron X-ray techniques.

3D synchrotron μ-CT | **Pair distribution function** | **4D synchrotron nano-CT**







2. LC^3 research @ UMA: public projects

Title: "Optimization and Processing of LC^3 Eco-cements with Spanish Clays (ProLC3@Spain)"

Principal investigator: Isabel Santacruz
Funding agency: Ministry of Science, reference: PID2020-114650RB-I00
From: 2021/09/01 to 2025/08/31

The main objective is to improve the performances of LC^3-50 binders produced with Spanish Calcined Kaolinitic Clays by optimizing the use of admixtures to:

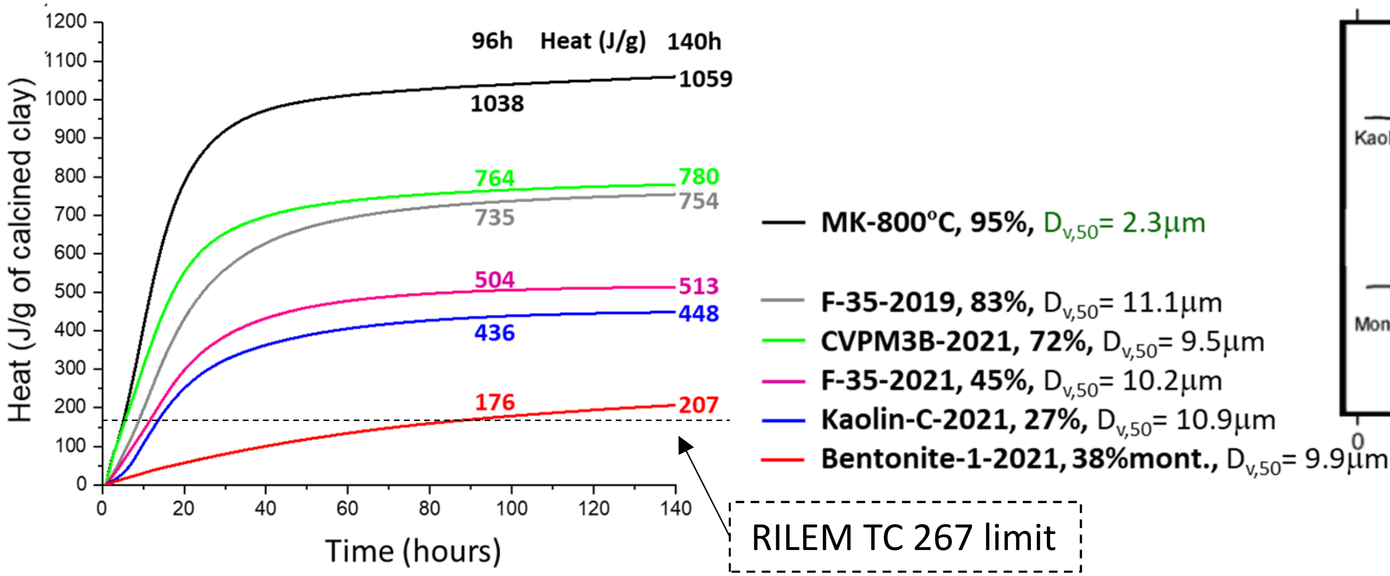
- Improve their rheological behavior at early ages (role of SP & accelerators);
- Accelerate the hydration (mainly the pozzolanic set of reactions) at early ages,
- Increase the mechanical strength features at early and late hydration ages,
- Improve the durability performances.

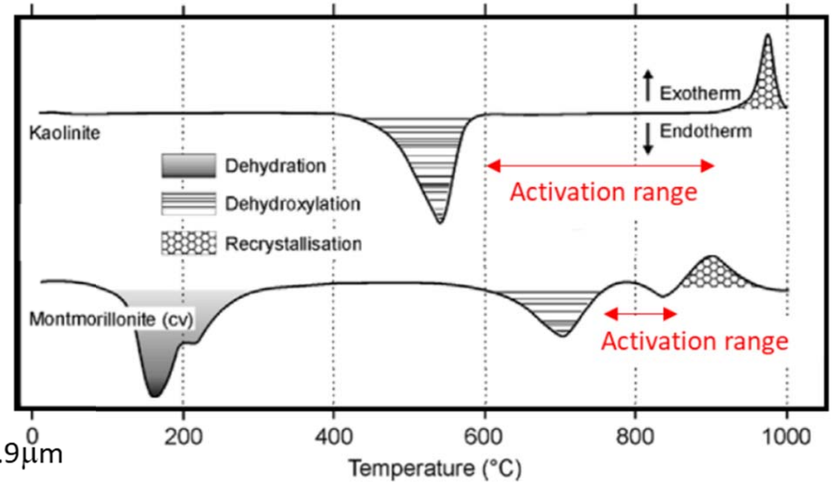
2. LC^3 research @ UMA: public projects

Title: "Low carbon cements based on **smectite clays** (LC^3-smectite)"

Principal investigator: Mª Ángeles Gómez de la Torre
Funding agency: Ministry of Science, reference: TED2021-129170B-I00 (Requested)
From: if awarded, 2023-2024
Convocatoria 2021 - «Proyectos de Transición Ecológica y Transición Digital»

The main objective: Andalucia has not kaolinitic clays but has smectitic clays.
For instance, bentonites from Almeria.
Knowing that the pozzolanic activities of smectites (montmorillonite being the silicate phase) are smaller than those of kaolinites, it is proposed to research on the activation of these clays (both thermally and mechanically). The goal is to produce LC^3 binders (with 50 wt% replacement or lower, but meeting the mechanical strength targets).





2. LC^3 research @ UMA: contracts with companies

Title: "Belite cement admixture activation study" // "Low-CO_2 cement admixture activation study"

Type of contract/agreement: R&D contract, reference OTRI-UMA: 8.06/5.41.5700
Company / Organism: BASF Construction Solutions GmbH // Master Builders Solutions Deutschland GmbH (Germany)
From 2020/12/01 to: 2022/12/31
Principal investigator: Miguel Angel Garcia Aranda

The main objective is to understand and improve the performances of PC-based LC^3-50 binders using the MBSD tailored admixtures: **SPs and accelerators.**

MASTER® BUILDERS SOLUTIONS

2. LC^3 research @ UMA: contracts with companies

Title: "Belite cement hydration studies"

Type of contract/agreement: R&D contract, reference OTRI-UMA: 8.06/5.41.5934
Company / Organism: Buzzi Unicem SpA (Italy)
From 2021/09/01 to: 2022/08/30
Principal investigator: Miguel Angel Garcia Aranda

The main objective is to better understand the hydration features of belite cements and the use of Supplementary Cementitious Materials with activated BCs.

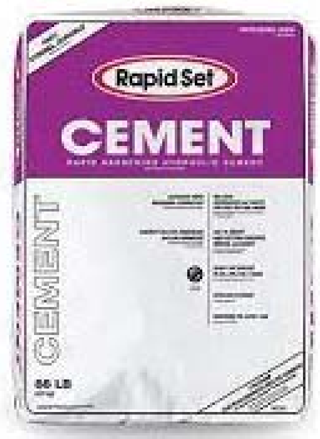
Buzzi Unicem

2. LC^3 research @ UMA: contracts with companies

Title: "Rapid setting-low carbon binders: early hydration study"

Type of contract/agreement: R&D contract, reference OTRI-UMA: 8.06/5.41.6098
Company / Organism: CTS Cement Manufacturing Corporation (USA)
From 2022/01/10 to: 2022/07/09
Principal investigator: Mª Ángeles Gómez de la Torre

The main objective is to study the feasibility of belite calcium sulfoaluminate cements with limestone calcined clays systems.



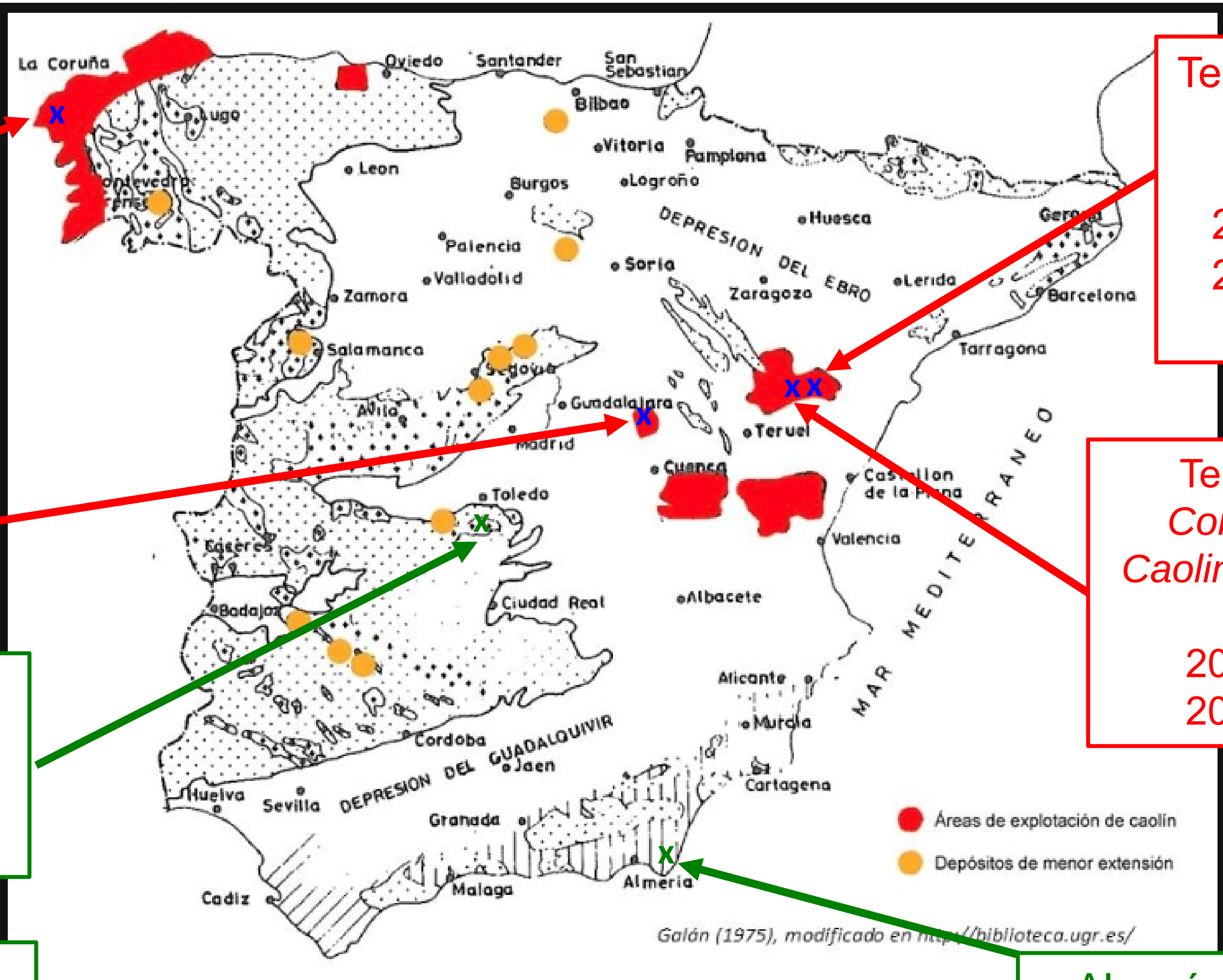
3. Clays studied @ UMA

Coruña (“Vimianzo”)
Caolines Vimianzo
F35
2019 ~ 83 wt% K
2021 ~ 45 wt% K

Guadalajara
(“Poveda de la Sierra”)
Caobar SA
Caolin-C
2021 ~ 27 wt% K
Caolin-CN
2021 ~ 42 wt% K

Toledo
Sepiolsa
Bentonite V-1-2
2021 ~ 80 wt% Sapon.

Morocco
Tolsa, SA
Bentonite 1
2021 ~ 38 wt% Montm.



Teruel (“La Cañada”)
ARCIMUSA
CV-PM3B
2019 ~ 70 wt% K
2021 ~ 72 wt% K
2022 – n.d.

Teruel (“Alcorisa”)
Comercial Sílices y Caolines de Aragón S.L.
SY-1(A)
2019 ~ 74 wt% K
2021 ~ 67 wt% K

Almería (“Los Escullos”)
Sepiolsa
Bentonite Almería
2021 ~ 58 wt% Montm.

Working in LC^3 cements since 2018. Started with the PhD Thesis of Ms. Bernal, to be defended in Autumn 2023

4. Phase and microstructure evolution of LC^3

The challenge: **to measure the hydration of $CaCO_3$**, which is very difficult by powder diffraction because it can have (accidental) carbonation and also there is preferred orientation [104] axis and severe powder diffraction peak overlapping. *To measure it to be able to accelerate limestone reaction.*

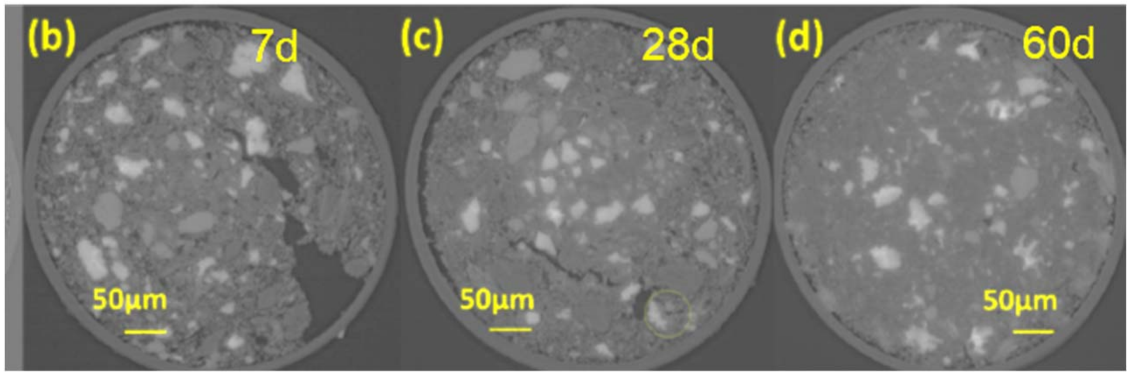
The idea: to use propagation-based synchrotron μ-CT to analyze limestone reactivity. Later lab. μ-CT if possible.

How: by measuring the limestone particles by synchrotron μ-CT and their time evolution

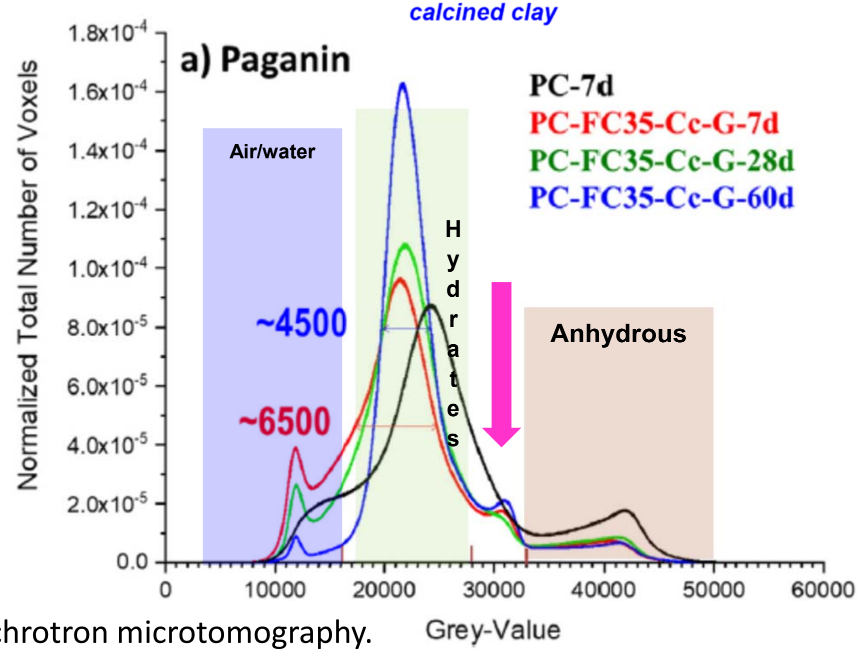
The final goal: *To understand $CaCO_3$ dissolution and carbo-aluminate formation which it seems to improve the mechanical strength development of this low-CO_2 cements.*

A sample to detector propagation distance, 5.5 mm (15 keV beam)

Voxel size: 0.3 μm
Spatial resolution ~1 μm
Capillary diameter = 0.5 mm



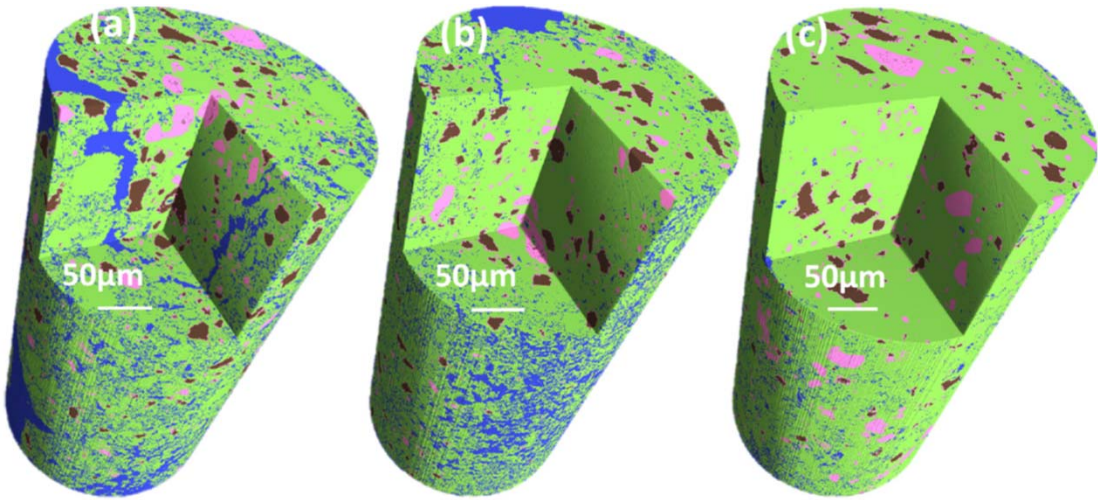
Data taken at TOMCAT SLS, but just one day experiment does NOT allow to follow the SAME particles with time.



Phase and microstructure evolutions in LC3 binders by multi-technique approach including synchrotron microtomography. Bernal et al., *Construction and Building Materials* 300 (**2021**) 124054

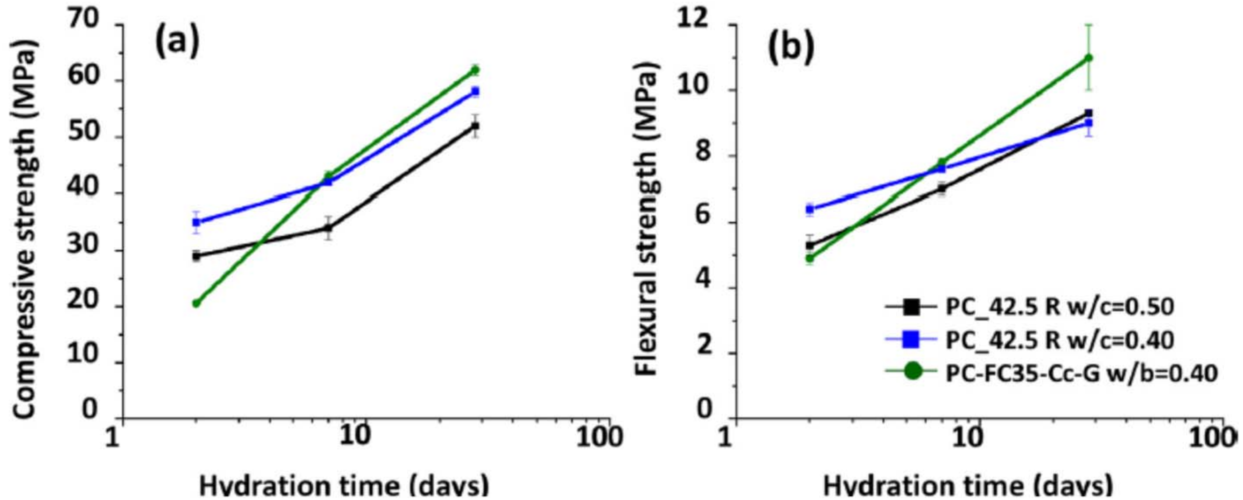
4. Phase and microstructure evolution of LC³

The four components were quantitatively followed with time (BUT in different samples!), which increase the uncertainties



Green: hydrated products
Brown: anhydrous components
blue: water and air porosity
Pink: calcite

- ✓ A reduction of clinker factor of >50%
- ✓ The enhanced mechanical properties are maintained at 28 days
- ✓ Carbonate reactivity is confirmed
- ✓ Decrease of porosity has been measured by synchrotron µ-CT



Phase and microstructure evolutions in LC3 binders by multi-technique approach including synchrotron microtomography.
Bernal et al., *Construction and Building Materials* 300 (**2021**) 124054

5. Cement hydration mechanisms

The challenge: **to measure the hydration of an amorphous component** (i.e. MK, or related meta-clay) in the presence of several other amorphous phases (i.e. C-S-H, C-A-S-H, etc.).

The idea: to *combine powder diffraction and μ-CT* data taken in the **same** hydrating capillary, filled with a paste.

How: by measuring the diffraction signal of the full capillary by LXRPD and always the same volume by μ-CT.

The final goal: *To better understand the hydration of low-CO_2 cements, to be able to accelerate their early-age mechanical strength development.*

LXRPD - MoKα_1 - Capilary

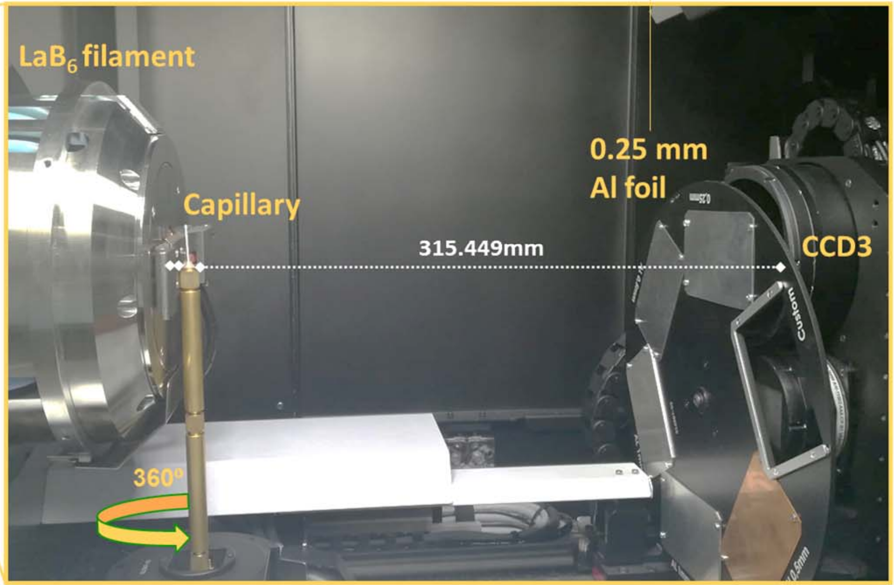
- **Laboratory X-ray Computed Microtomography**

SKYSCAN 2214
(Bruker)
SCAI, Málaga

μ-CT
voxel size ~ 1 μm
spatial resolution 2-4 μm
Capillary diameter = 1.0 mm

55 kV, 130 μA
Voxel size 0.8 μm
4.72h/CT

Beam hardening reduction

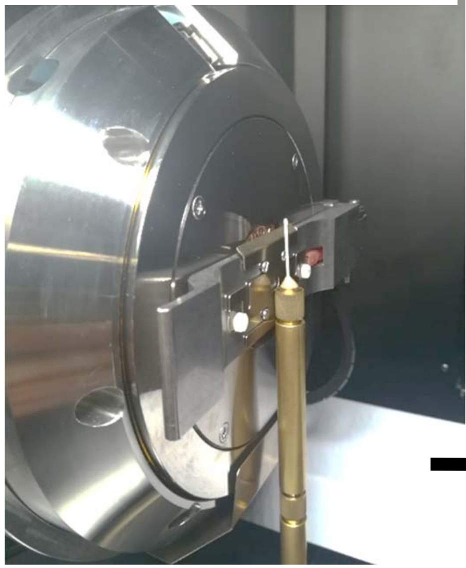


5. Cement hydration mechanisms

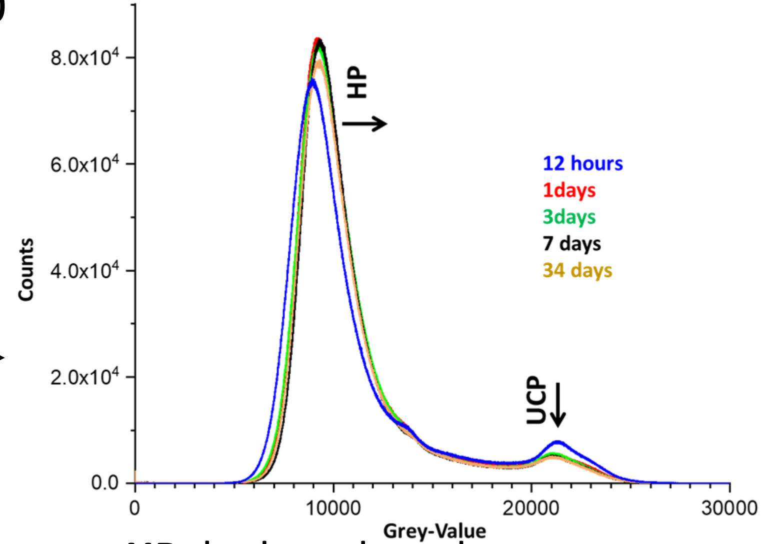
We are at the stage of methodology development

Model paste prepared as: 67 wt% of PC-42.5R, 30 wt% of MK and 3 wt% of GY, w/b=0.50

D8 ADVANCE (Bruker) Mo Kα_1 radiation

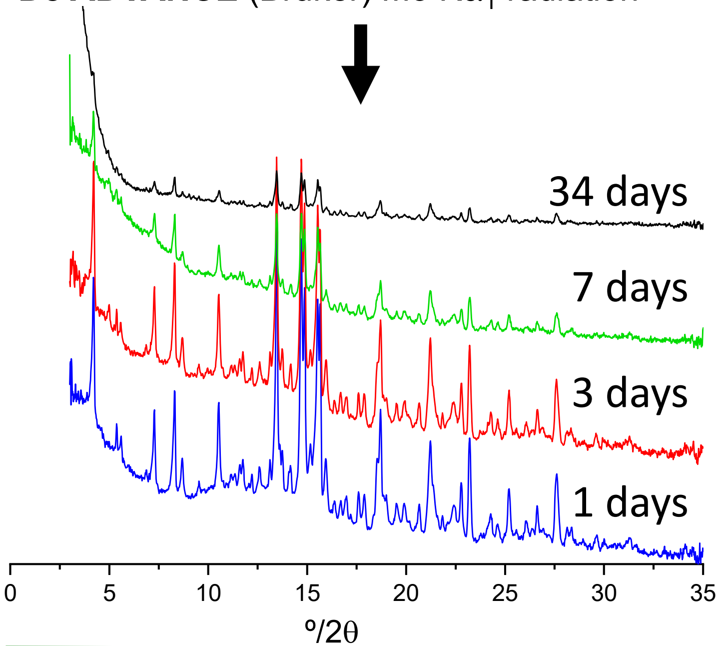


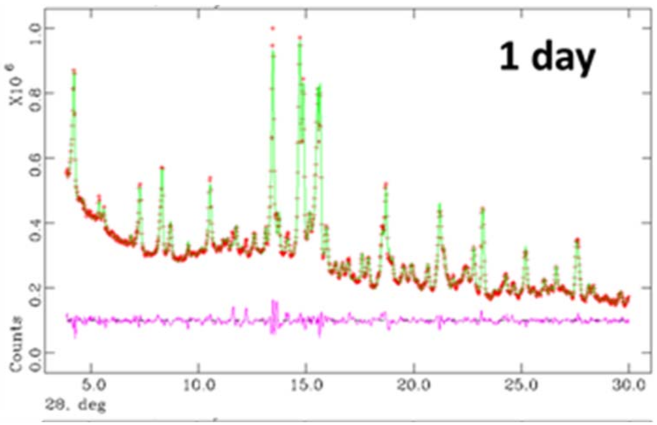
SKYSCAN 2214 (Bruker)

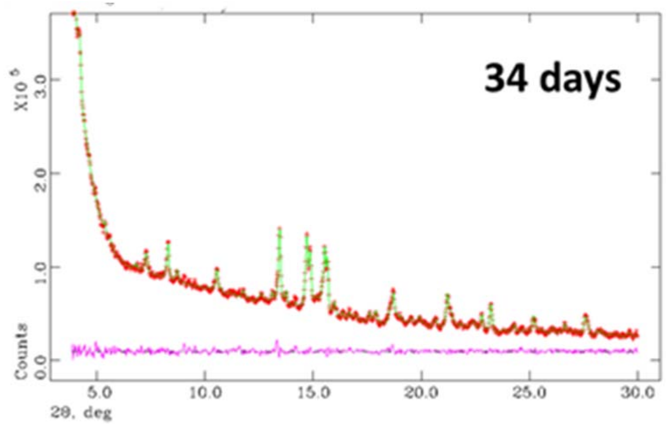


HP: hydrated products

UCP: unhydrated cement products

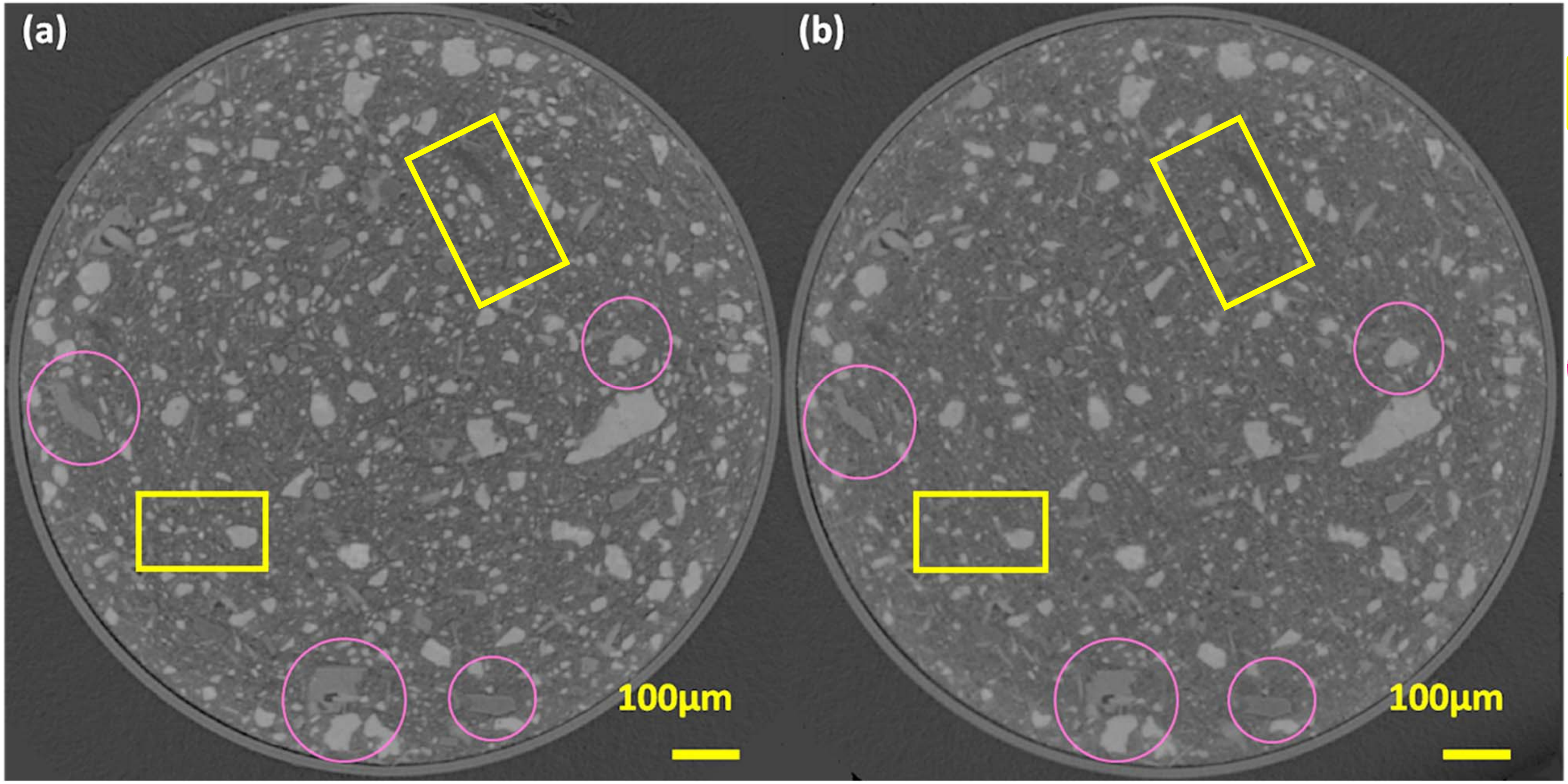






Shirani et al., *Proc. Of the International Conference on Calcined Clays for Sustainable Concrete* (**2022**) submitted

6. Cement hydration mechanisms



Size UCP with t ↓

Size HP with t ↑

Size MK with t ↓

There is additional info in a t-resolved series

Fig. Laboratory µ–CT orthoslices for PC-MK-GY paste, w/b=0.50, hydrated for (a) 12 hours (b) 3 days. Whitish particles: unhydrated cement products, UCP. The dark content is the hydrated products, HP. MK large particles have not reacted at 12 h, and they have greyscale values very similar to HP. The size of the hydration particles increases with hydration time. Capillary diameter: ~1.2 mm.

6. Understanding pozzolanic reactivity

The challenge: to help to 'predict' the pozzolanic reactivity of kaolinitic rocks with different contents of kaolinite.

The idea: to use pair distribution technique to unravel the local disorder of pristine kaolinitic rocks.

How: i) by testing the pozzolanic activity of calcined clays with common tests; ii) by measuring the local structure of kaolinitic rocks by PDF.

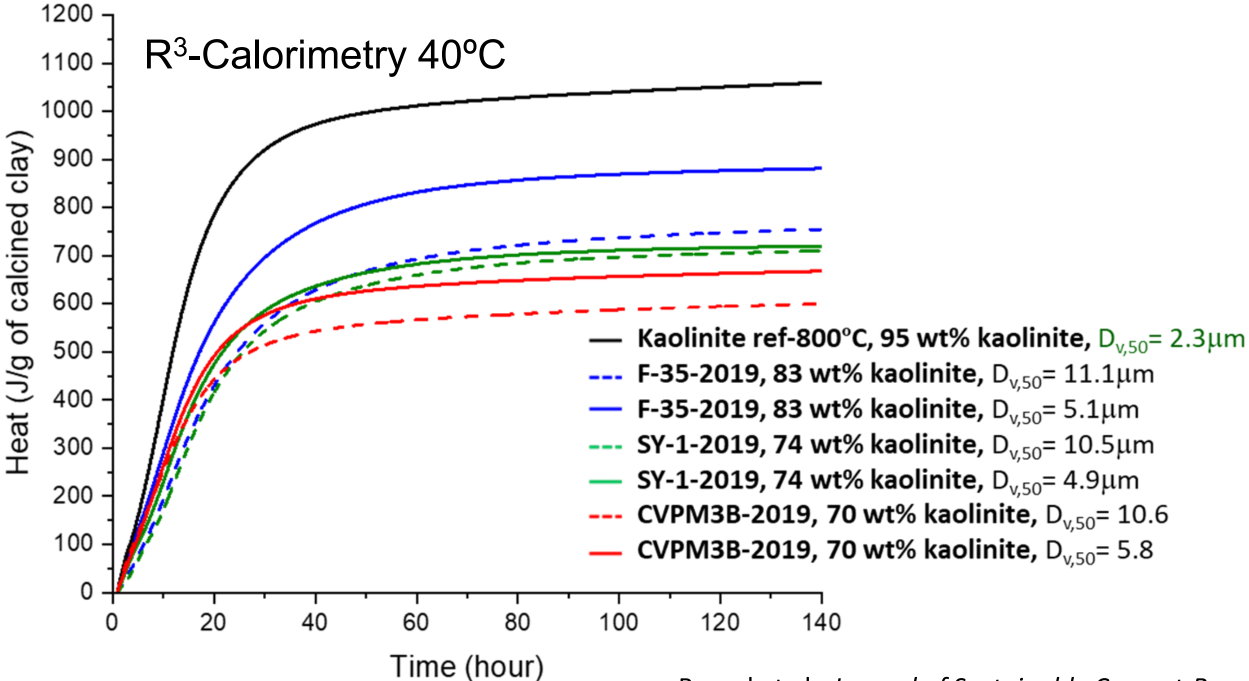
The final goal: *To understand the key parameters that determine the early-age pozzolanic activity of calcined clays.*

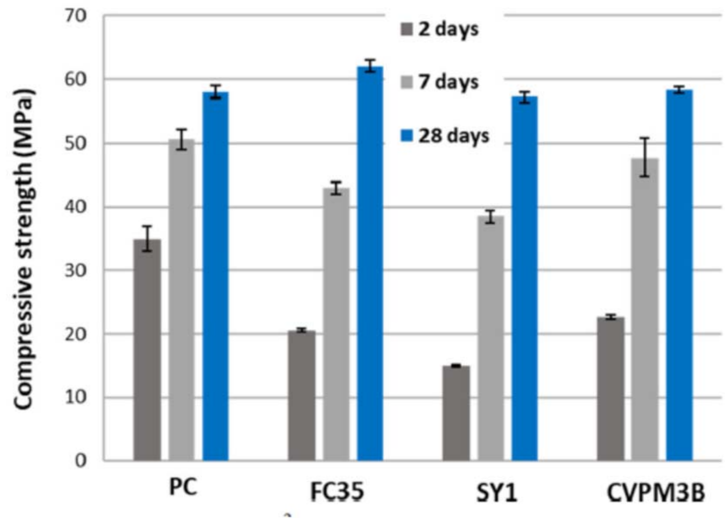
Table 1. Key characterization data for the pristine[a] and calcined[b] clays.

Clays	KGa-1b	FC35	SY1	CVPM3B
Kaolinite content /wt%	95	83	74	70

***K*ey features**

- ✓ **Kaolinite content**
- ✓ **Particle size/surface area**
- ✓ **Local disorder??**





Bernal et al., *Journal of Sustainable Cement-Based Materials* (**2022**) *http://dx.doi.org/10.1080/21650373.2022.2117248*

6. Understanding pozzolanic reactivity

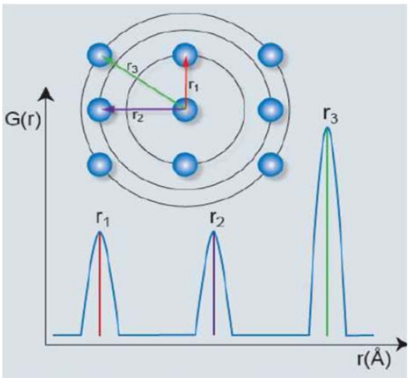
Table 1. Key characterization data for the pristine[a] and calcined[b] clays.

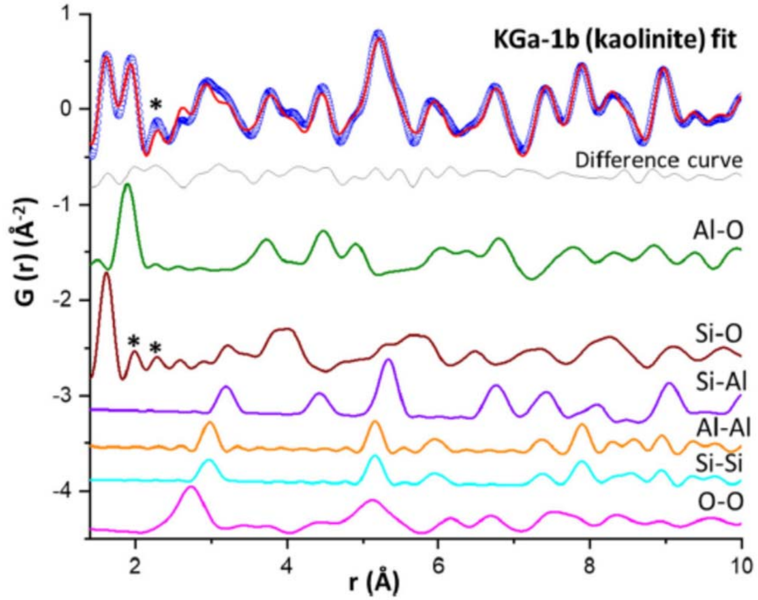
Clays	KGa-1b	FC35	SY1	CVPM3B
Kaolinite content /wt%	95	83	74	70

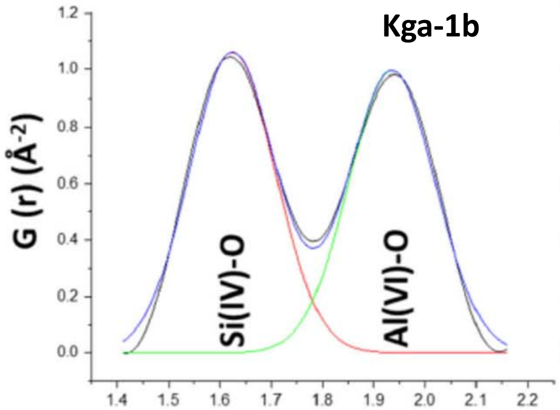
***K*ey features**

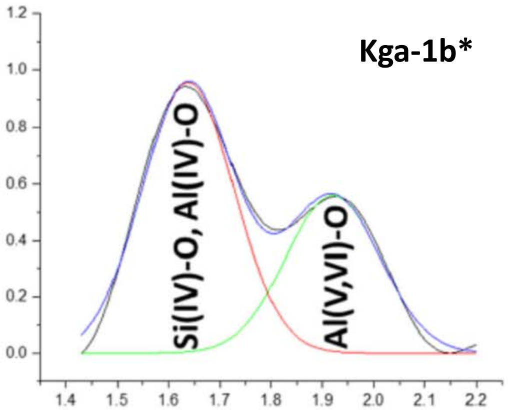
- ✓ **Kaolinite content**
- ✓ **Particle size/surface area**
- ✓ **Disorder of metakaoline**

PDF → probability of finding an atom at a certain distance, r.

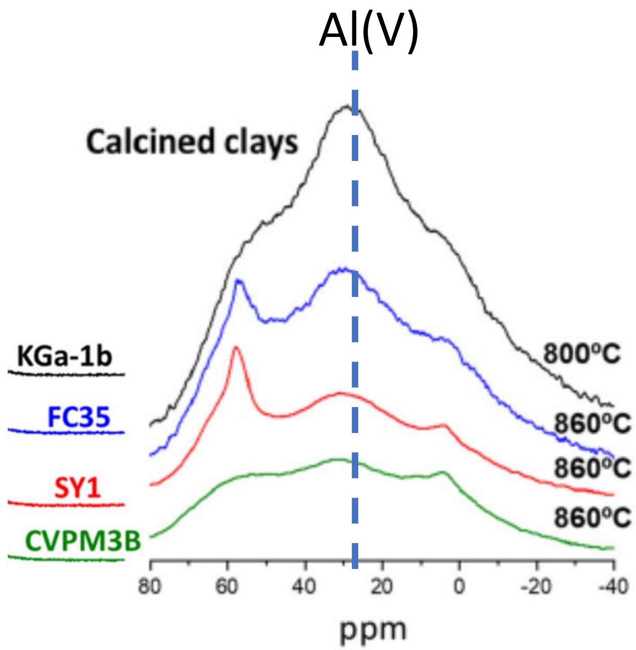








^{27}Al MAS-NMR



Bernal et al., *Journal of Sustainable Cement-Based Materials* (**2022**) *http://dx.doi.org/10.1080/21650373.2022.2117248*

7. Processing and activation of LC³-50 binders:

Slump retention study. Sand/cement ratio 1.78. w/b=0.40, 20ºC. wt% of SP from bottle.
Size of the cone: f_0=100mm, without knocks (free flow).
Slump retention for *SP1, SP2, SP3, SP4, SP5 (all standard SP based) and* ***SP-n*** *(is a new one tailored for LC^3 binders)*

The slump equipment is a truncated metallic cone (bottom diameter of 100 mm, top diameter of 70 mm and height of 60 mm) on top of a polished glass surface

Kaolinite contents of the clays:
CC1 -72 wt%; CC2 -45 wt% *and* ***CC3 -27 wt%***

Accelerators used:
ACC3 *is pure C-S-H seeds*
ACC1 *and* ***ACC2*** *are optimised versions of ACC3 in order to address low-carbon binders*

CoI statement: Results based on a research contract between MBS and UMA

UNIVERSIDAD DE MÁLAGA

7. Processing and activation of LC^3-50 binders:

Cement Science @ UMA

Flow and flow retention of PC and LC^3 binders

Mortars	Slump t_0 (mm)	Slump 30min (mm)	Slump 60min (mm)
PC-52.5R-Ref 0.34wt% SP1	183(1)	156(1)	143(2)
PC-52.5R-CC1 1.00wt% SP1	204(2)	150(3)	109(1)
PC-52.5R-Ref 0.34wt% SP2	207(1)	174(1)	159(3)
PC-52.5R-CC1 0.65wt% SP2	196(2)	106(2)	100(1)
PC-52.5R-Ref 0.50wt% SP3	199(1)	164(1)	142(1)
PC-52.5R-CC1-0.90wt% SP3	204(1)	123(1)	100(1)
PC-52.5R-Ref 0.37wt% SP4	202(1)	148(1)	118(3)
PC-52.5R-CC1 0.75wt% SP4	192(1)	102(1	100(1)
PC-52.5R-Ref 0.72wt% SP5	198(1)	170(1)	170(1)
PC-52.5R-CC1 1.70wt% SP5	206(1)	151(3)	118(2)
PC-52.5R-CC1 1.20wt% SPn.	186(1)	210(1)	196(1)

7. Processing and activation of LC^3-50 binders:

Mechanical Strength

Sand/cement ratio 1.78. w/b=0.40, 20ºC. wt% SP from bottle. Slump without knocks

PC-52.5R-LC^3: 52wt% PC-52.5R-2021 + 30wt% CC + 15wt%Cc (4μm - Omya) + 3wt%CsH_2 (Maruxiña)

Mortars	Strength (MPa)	1d	7d	28d
PC-42.5R-Ref 0.29wt% SP1	Compressive	21.1(4)	52(1)	67(1)
PC-52.5R-Ref 0.34wt% SP1	Compressive	**37.3(6)**	**66.1(8)**	**76(2)**
PC-52.5R-LC3_50-CC1 1.00wt% SP1	Compressive	15.0(2)	52(1)	72(4)
PC-52.5R-LC3_50-CC2 0.62wt% SP1	Compressive	11.7(1)	33(1)	57(2)
PC-52.5R-LC3_50-CC3 0.38wt% SP1	Compressive	8.1(1)	29.0(2)	52(2)

PC-42.5R-Ref 1.00wt% SPn.	Compressive	30(1)	56.8(8)	
PC-52.5R-Ref 1.20wt% SPn.	Compressive	**43.6(5)**	**57(4)**	**74(2)**
PC-52.5R-LC3_50-CC1 1.20wt% SPn.	Compressive	19.9(5)	55(1)	68(2)
PC-52.5R-LC3_50-CC2 1.00wt% SPn.	Compressive	15.1(4)	37.4(7)	
PC-52.5R-LC3_50-CC3 0.50wt% SPn.	Compressive	10.8(2)	35(1)	

All mortars measured with the same initial slump value 200(15) mm

*Kaolinite contents: CC1-**72 wt%**; CC2-**45 wt%** and CC3-**27wt%***

7. Processing and activation of LC³-50 binders:

Mechanical Strength with accelerators

Mortars	Strength (MPa)	1d	7d	28d
PC-52.5R-Ref 1.20wt% SPn.	Compressive	**43.6(5)**	**57(4)**	**74(2)**
PC-52.5R-LC3_50-CC1 1.20wt% SPn.	Compressive	19.9(5)	55(1)	68(2)
PC-52.5R-LC3_50-CC1 1.20wt% SPn. 2.00wt%ACC1	Compressive	**29.0(8)** +46%	67(2) +22%	
PC-52.5R-LC3_50-CC1 1.20wt% SPn. 2.00wt%ACC2	Compressive	**28.4(2)** +43%	68(1) +24%	
PC-52.5R-LC3_50-CC1 1.20wt% SPn. 2.00wt%ACC3	Compressive	**25.5(6)** +28%		

PC-52.5R-Ref 0.34wt% SP1	Compressive	**37.3(6)**	**66.1(8)**	**76(2)**
PC-52.5R-LC3_50-CC3 0.38wt% SP1	Compressive	8.1(1)	29.0(2)	52(2)
PC-52.5R-LC3_50-CC3 0.38wt% SP1 2.00wt%ACC1	Compressive	**23.1(5)** +185%	49(1) +69%	
PC-52.5R-LC3_50-CC3 0.38wt% SP1 2.00wt%ACC2	Compressive	**22.0(4)** +172%	51(1) +76%	
PC-52.5R-LC3_50-CC3 0.38wt% SP1 2.00wt%ACC3	Compressive	**18.6(2)** +129%		

All mortars measured with the same initial slump value 200(15) mm

*Kaolinite contents: CC1-**72 wt%**; CC2-**45 wt%** and CC3-**27wt%***

8. Conclusions

- ✓ The study of the hydration with time of **amorphous components** can be done by synchrotron and Laboratory tomography, avoiding samples alteration.

- ✓ Pair distribution function is an adequate technique to better understand and even 'predict' the pozzolanic reactivity of calcined clays.

- ✓ The use of tailored chemical admixtures (successfully) addresses the technological issues:
  - ➢ Loss of fluidity of LC^3-50 (by a tailored SP)
  - ➢ Low mechanical strengths at early ages of LC^3-50 (by tailored accelerators)
  - ➢ The use of low content kaolinite, i.e. 25 wt%, clays (by tailored SP & accelerators)