Early age cement hydration acceleration followed by *in situ* synchrotron X-ray powder diffraction

Alejandro Morales-Cantero[1], Ana Cuesta[1], Ángeles G. De la Torre[1], Isabel Santacruz[1], Pere Borralleras[2], Miguel A. G. Aranda[1,*]

*g_aranda@uma.es

[1] *Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, Málaga, 29071, Spain*

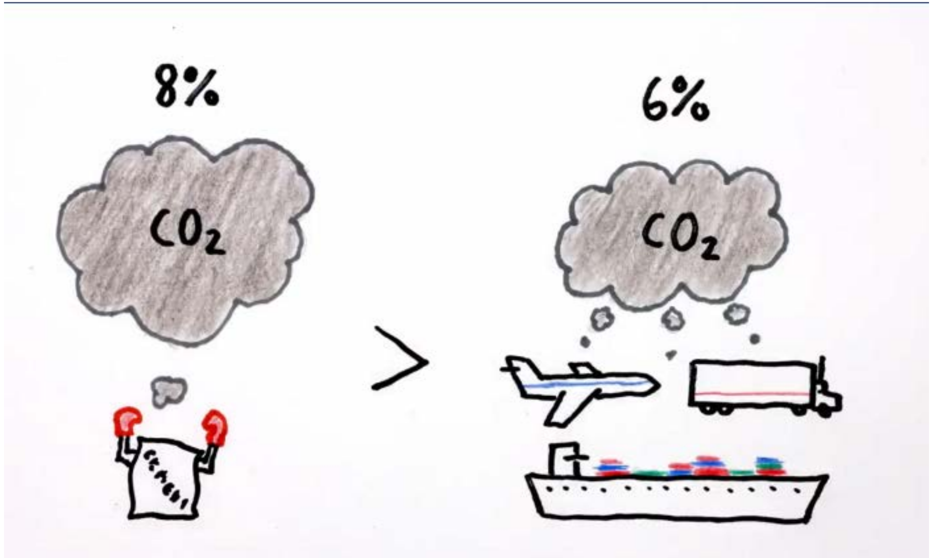
[2] *Master Builders Solutions España S.L.U., Carretera de l'Hospitalet, 147-149, Edificio Viena, 1ª planta, 08940 Cornellà de Llobregat, Spain*

16' + 4'

Outline

1. The relevant societal challenge #3
2. The specific problem #2
3. Case-1: PC and BC hydration acceleration #5
4. Case-2: LC^3 hydration acceleration #4
5. Conclusions

1. Challenge #1
To decrease CO_2 footprint / emissions (direct & indirect)



Portland cement (PC) world production is **~4 Gt/yr, 4.4 Gt in 2020**. ~4000 PC plants in the world.
PC production is expected to range 4-8 Gt/yr by 2100, depending upon the world growth pattern(s).

On average, for every ton of type-I PC, ~0.95 CO_2 t are released, from (i) limestone decomposition, (ii) burning fuel, and (iii) electricity consumption for grinding. This translates into **~8% of the total anthropogenic CO_2** emissions, **3.5 Gt/yr.**

600 Millions house units are needed by 2030. 40 M/units per year. The average house unit size in Hong Kong is 33 m^2 and in the USA/Australia is 230 m^2. The average size of a slum room/unit is ~9 m^2, and there are 1.2-1.5 billion people living in slums. Finally, Africa is predicted to increase from 1.2 billions to 2 billions, in next 30 years. This means many houses (or immigration)…

1. Challenge #2
To decrease Construction and Demolition Wastes (CDW)

The Empire State Building in 1932;

- Today, the concrete use is **~20-25 Gt/yr**.
- The estimated world concrete stock is **315 Gt** which results in 0.3 Gt/yr of CDW.
- The newest model predicts a skyrocket increase of CDW to **~30 Gt/yr by 2100**.

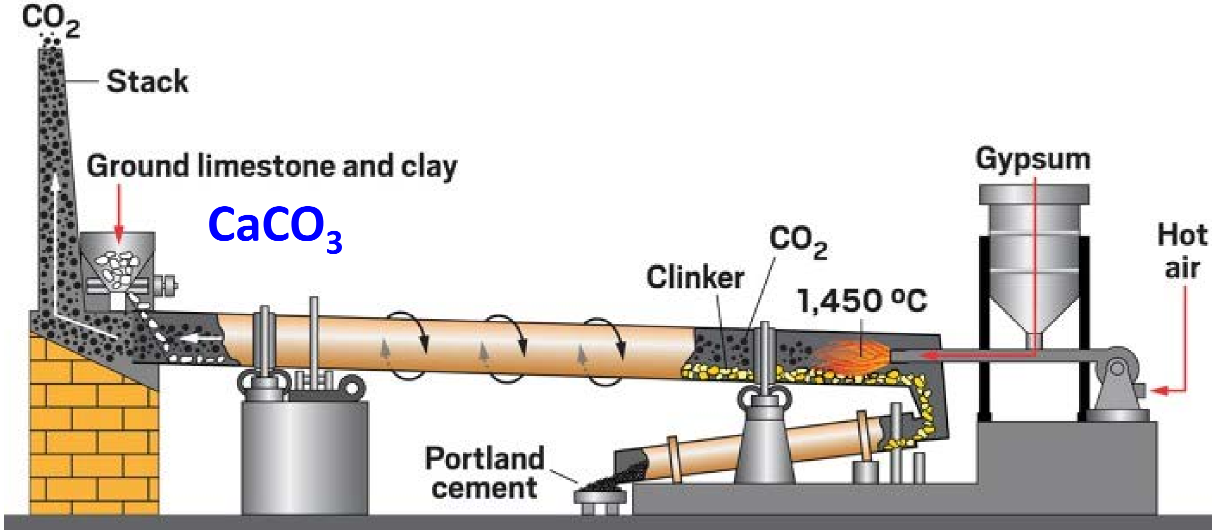
This could not be processed as aggregates, as it will be more than two times the predicted need.

→ **Cements with lower CO_2 footprint and more durable/sustainable.**

Todays expected service live of buildings and infrastructures: <100 years!

1. A solution being widely investigated

To decrease de amount of clinker in the commercialized cement



OPC total CO_2 emissions:

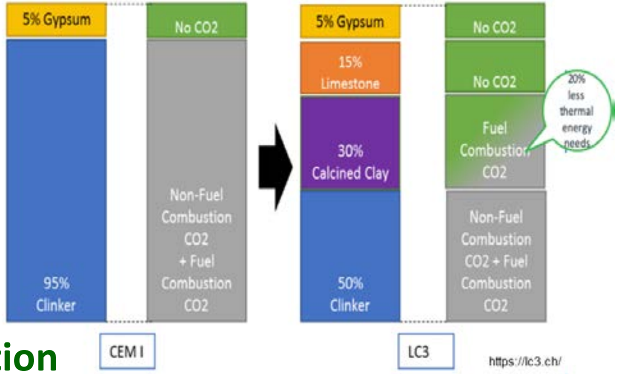
- ✓ ~ 0.54 tons (Limestone)

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

- ✓ ~ 0.34 tons (Fuel)
- ✓ ~ 0.09 tons (Electricity)

LC^3-50 are composed by:

- *50 wt% Portland clinker*
- *30 wt% calcined clay*
- *15 wt% limestone*
- *~ 5 wt% gypsum*



LC^3-50 cement allows ~40 CO_2 footprint reduction

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2. The specific problem. Low mechanical strength performances of low-carbon cements at 3 days or earlier.

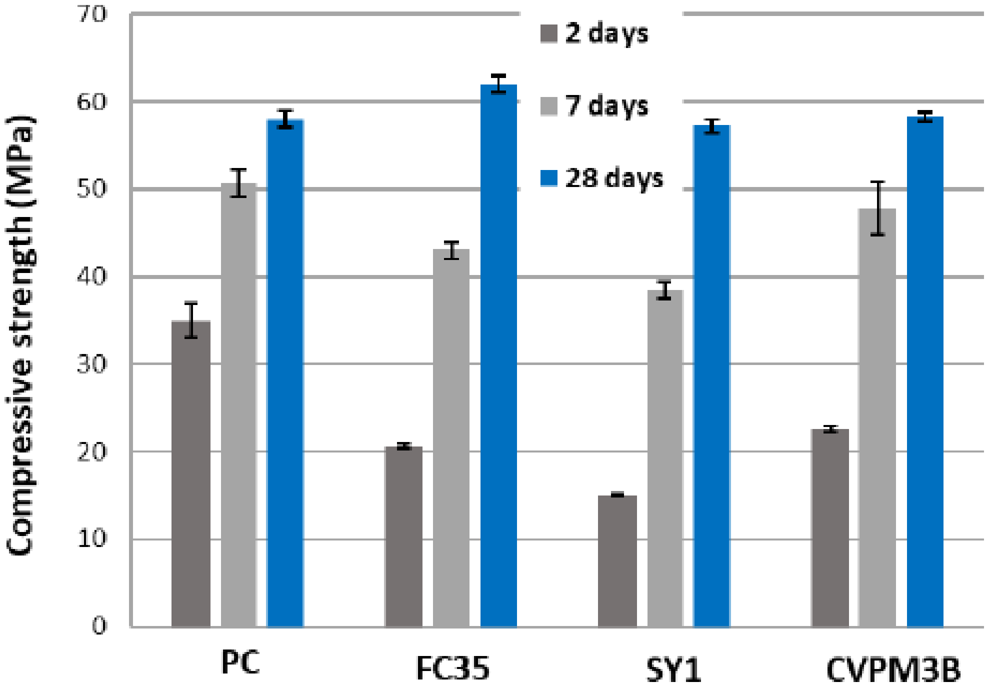

Figure. Mechanical strength data for neat PC-42.5R and LC^3-50 mortars with FC35 (83wt% kaolinite, $D_{v,50}$ ~11 µm), SY1 (74wt% kaolinite, $D_{v,50}$ ~10 µm), CVPM3B (70wt% kaolinite, $D_{v,50}$ ~6 µm) calcined clays (w/b=0.40) at 2, 7 and 28 days of hydration.

There are several activators but some have important drawbacks.

- They may present durability problems (like $CaCl_2$ or relatively large amounts of Na_2SO_4)
- Some could not be sustainable (like sodium thiocyanate)
- Others result in mechanical strength losses at 28 days (like some alkanolamines).

C-S-H seeding accelerates early age cement hydration without degrading mechanical strengths at later ages and without durability issues. *However, the mechanism(s) of the activation was not well known. It was assumed that it just accelerated C-S-H growth (and hence, C_3S dissolution) because its high surface area with low interfacial energy.*

Here we have designed a research by using a commercial PC 42.5 type (reference material) and two Belite cements (one activated by sulphur during clinkering and another typical belite cement), to carry out a mechanistic study.

This approach is being expanded in a second work to LC^3 type cements.

Outline

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Check for updates

C-S-H seeding activation of Portland and Belite cements: An enlightening *in situ* synchrotron powder diffraction study

Alejandro Morales-Cantero [a], Ana Cuesta [a], Angeles G. De la Torre [a], Isabel Santacruz [a], Oliver Mazanec [b], Pere Borralleras [c], Kai Steffen Weldert [b], Daniela Gastaldi [d], Fulvio Canonico [d], Miguel A.G. Aranda [a,*]

[a] *Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, Málaga 29071, Spain*
[b] *Master Builders Solutions Deutschland GmbH, Albert-Frank Str. 32, 83308 Trostberg, Germany*
[c] *Master Builders Solutions España S.L.U., Carretera de l'Hospitalet, 147-149, Edificio Viena, 1ª planta, 08940 Cornellà de Llobregat, Spain*
[d] *Research & Development, Buzzi Unicem, Via Luigi Buzzi 6, 15033 Casale Monferrato, Italy*

Raw data from the following techniques, isothermal calorimetry, rheology, thermogravimetric data, laboratory X-ray powder diffraction patterns, and synchrotron powder diffraction may be openly accessed on Zenodo at: https://doi.org/10.5281/zenodo.5513610

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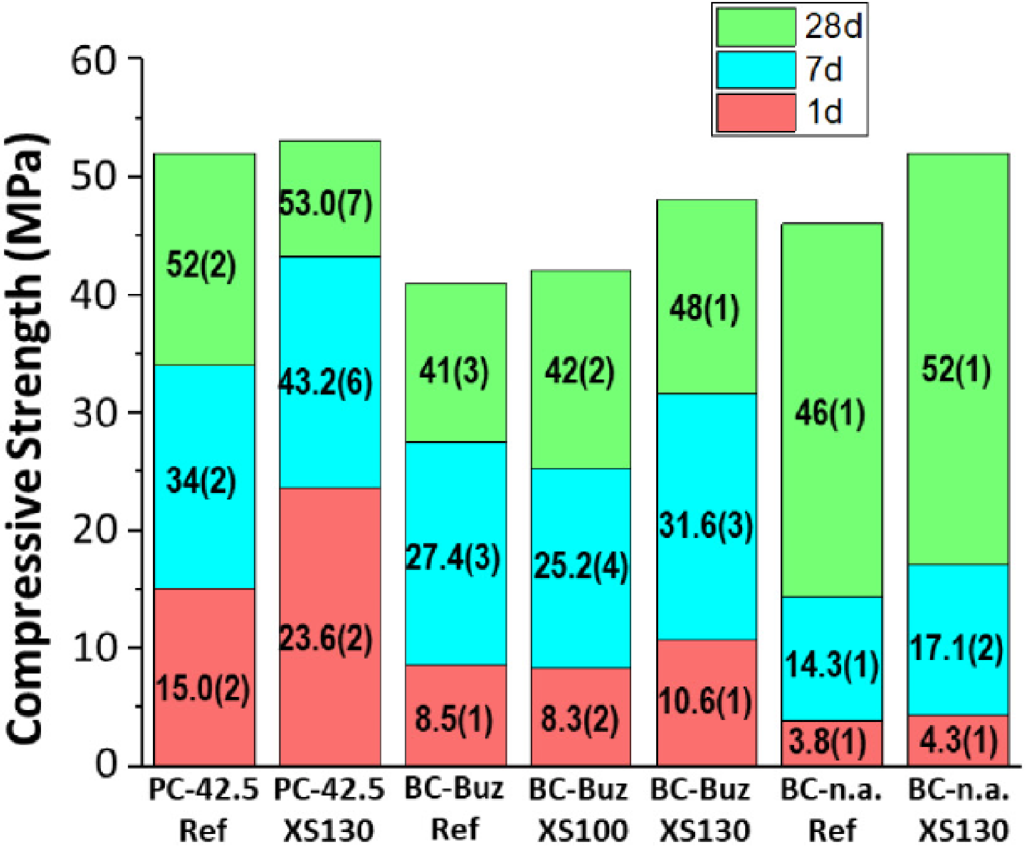
Synchrotron radiation

A B S T R A C T

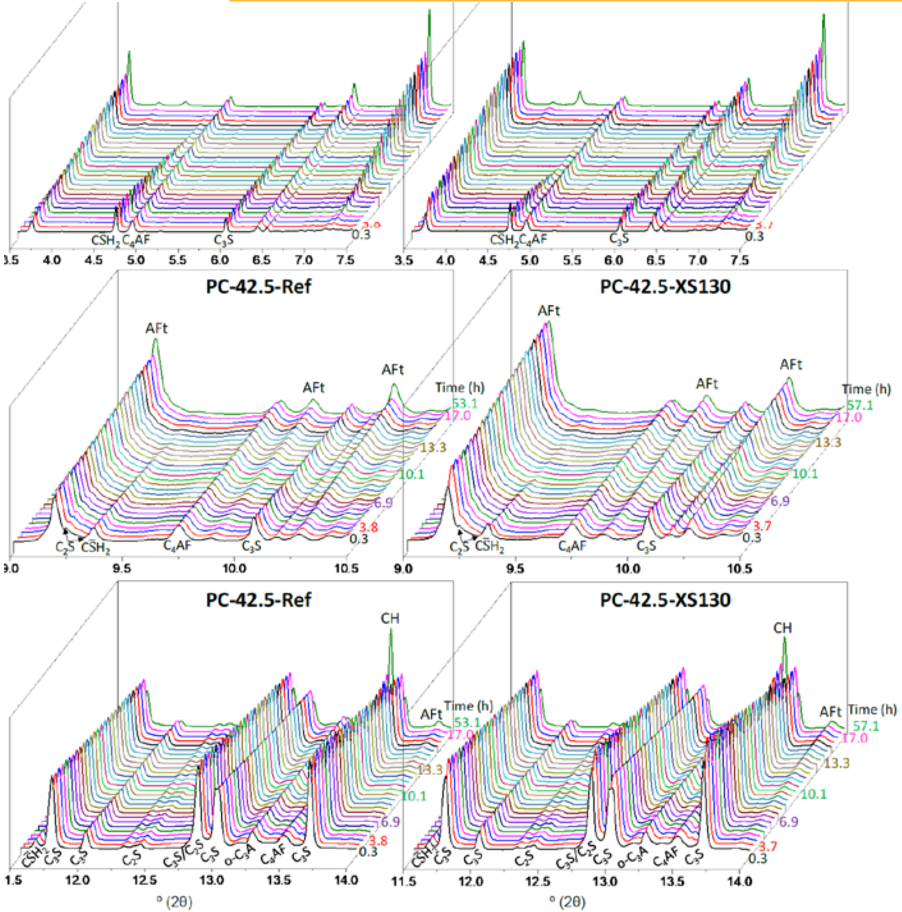
C-S-H seeding in Portland cements is well known from basic scientific works and field applications. Moreover, this activation approach could be beneficial for low-CO_2 cements under development where a general drawback is poor mechanical strengths during the first week of hydration. However, a mechanistic understanding of the different processes taking place when seeding is still not developed. Here, we contribute to this knowledge gap by studying one commercial Portland cement and two industrial trial belite cements. Three different admixtures are employed, *viz.* two types of commercial C-S-H seeding and triisopropanolamine as a typical alkanolamine. A multitechnique approach is employed including calorimetry, ultrasonic pulse velocity, thermal analysis and Rietveld analysis of laboratory X-ray powder diffraction data. Chiefly, an *in situ* X-ray synchrotron diffraction study has allowed mapping out the evolution of every crystalline phase. Furthermore, the use of an internal standard permitted to measure the changes in the overall amorphous content. In a nutshell, alite and belite (phases) hydrations are not significantly accelerated by C-S-H seeding for the three studied cements. Conversely, sulphate and aluminate phase dissolutions are enhanced. Faster ettringite crystallisation contributes to the observed improved mechanical properties at early ages. Moreover, a synergistic effect between C-S-H seeding and alkanolamine addition is proved. The importance of these findings for the possible acceleration of low-CO_2 cement hydration is discussed.

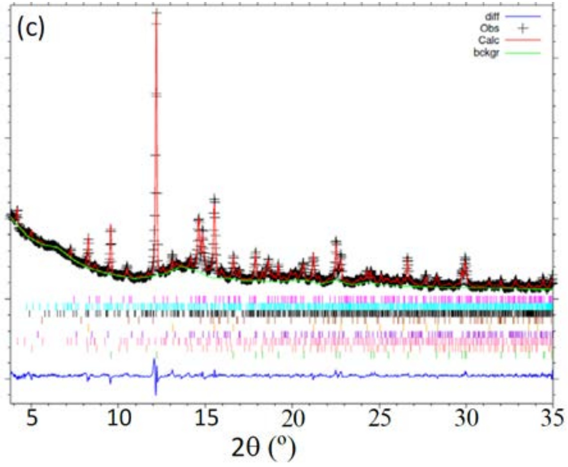
https://doi.org/10.1016/j.cemconres.2022.106946

3. Case-1: PC and BC mechanical strength evolution



3. Case-1: PC and BC raw SXRPD data (MSPD@ALBA, Mythen)





The t-dependent raw SXRPD data were analyzed by the Rietveld method to derive the quantitatively phase contents as function of time and the addition of the chemical admixtures. **RQPA results**

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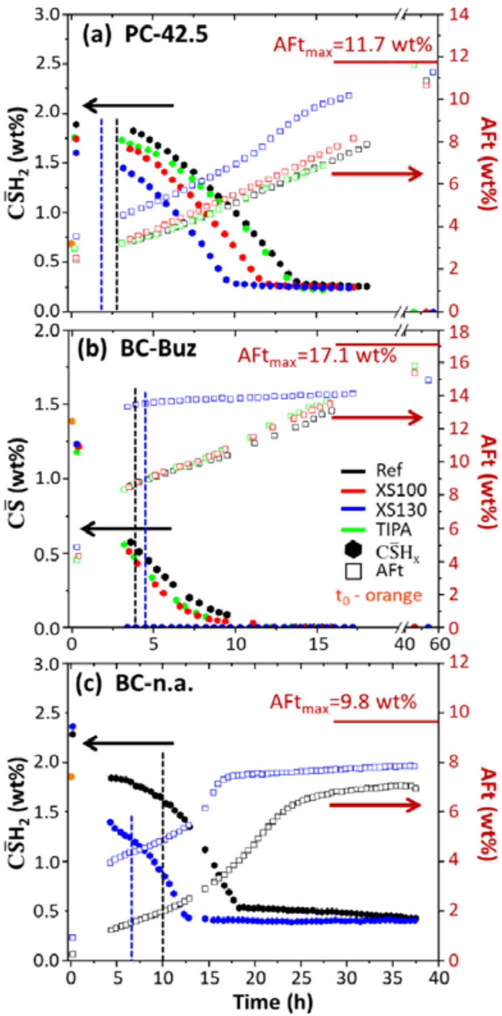
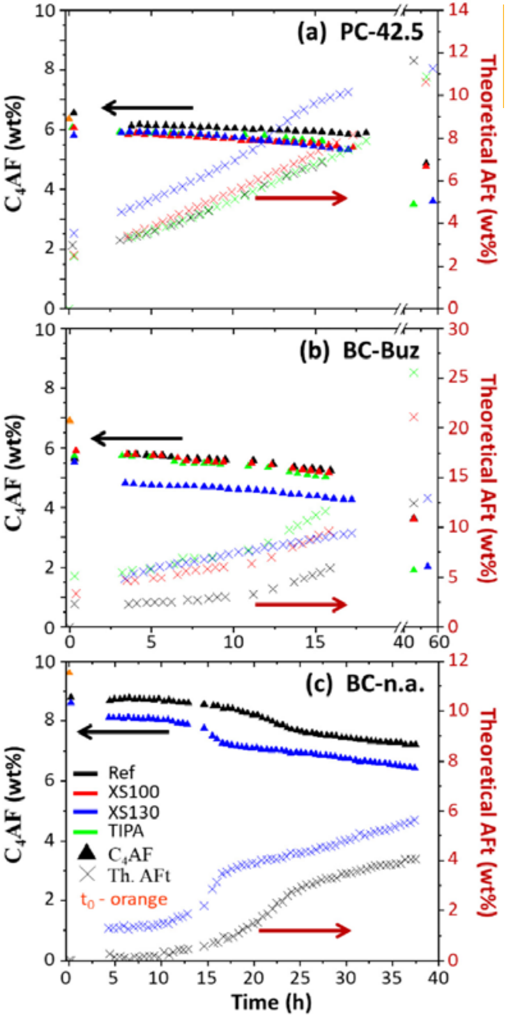
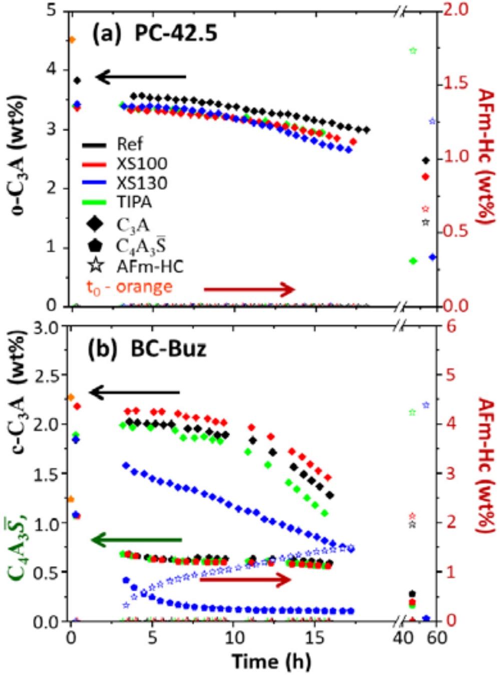




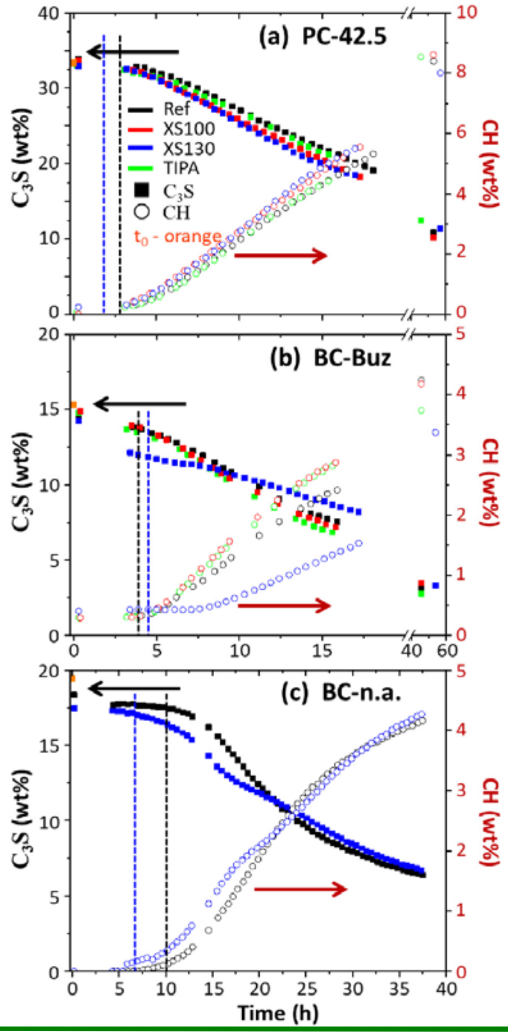


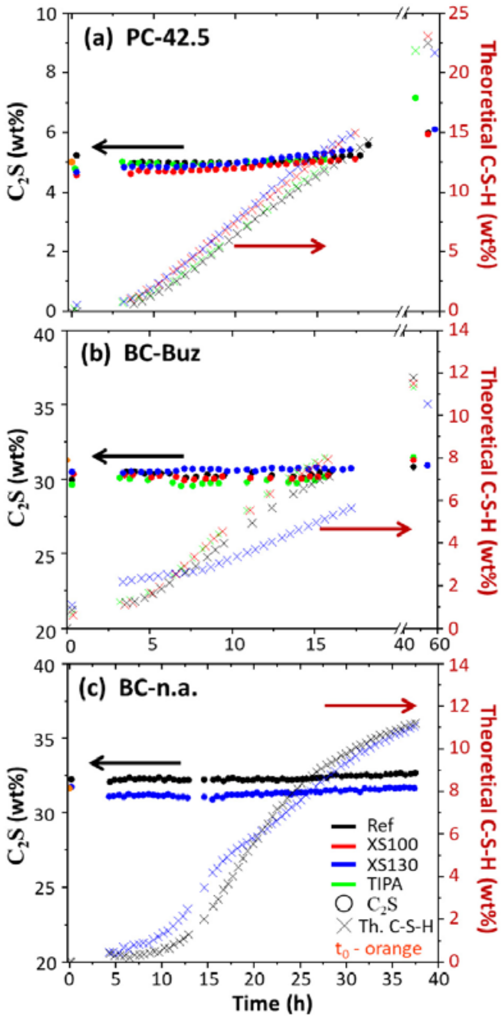
RQPA results for

(left) calcium sulfates

(intermediate) alumino-ferrite

(right) tricalcium aluminate


(a) PC-42.5
Ref
XS100
XS130
TIPA
C_3S
CH
t_0 - orange
C_3S (wt%)
CH (wt%)
(b) BC-Buz
(c) BC-n.a.
Time (h)


(a) PC-42.5
(b) BC-Buz
(c) BC-n.a.
C_2S (wt%)
Theoretical C-S-H (wt%)
Ref
XS100
XS130
TIPA
C_2S
Th. C-S-H
t_0 - orange
Time (h)

Case-2: LC^3 hydration acceleration

Alejandro Morales-Cantero[a], Ana Cuesta[a], Angeles G. De la Torre[a], Isabel Santacruz[a], Oliver Mazanec[b], Pere Borralleras[c], Kai Steffen Weldert[b], Miguel A.G. Aranda[a]

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[c] *Master Builders Solutions España S.L.U., Carretera de l'Hospitalet, 147-149, Edificio Viena, 08940 Cornella de Llobregat, Spain*

UNPUBLISHED

SXRPD data taken in situ during hydration at MSPD with Mythen, experiment **2021095288**. 2022-March

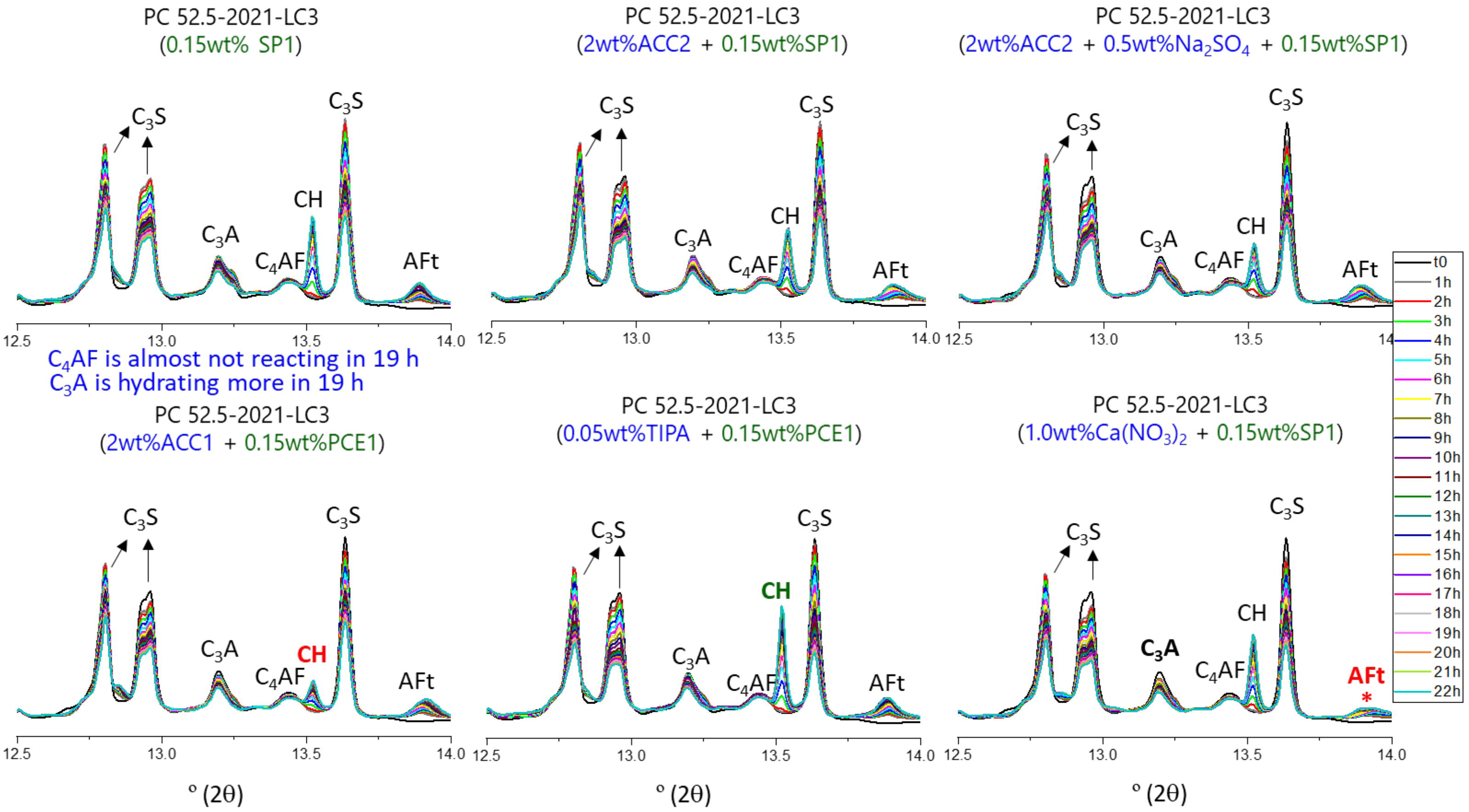
Data under analysis by the Rietveld approach

Case-2: LC^3 hydration acceleration

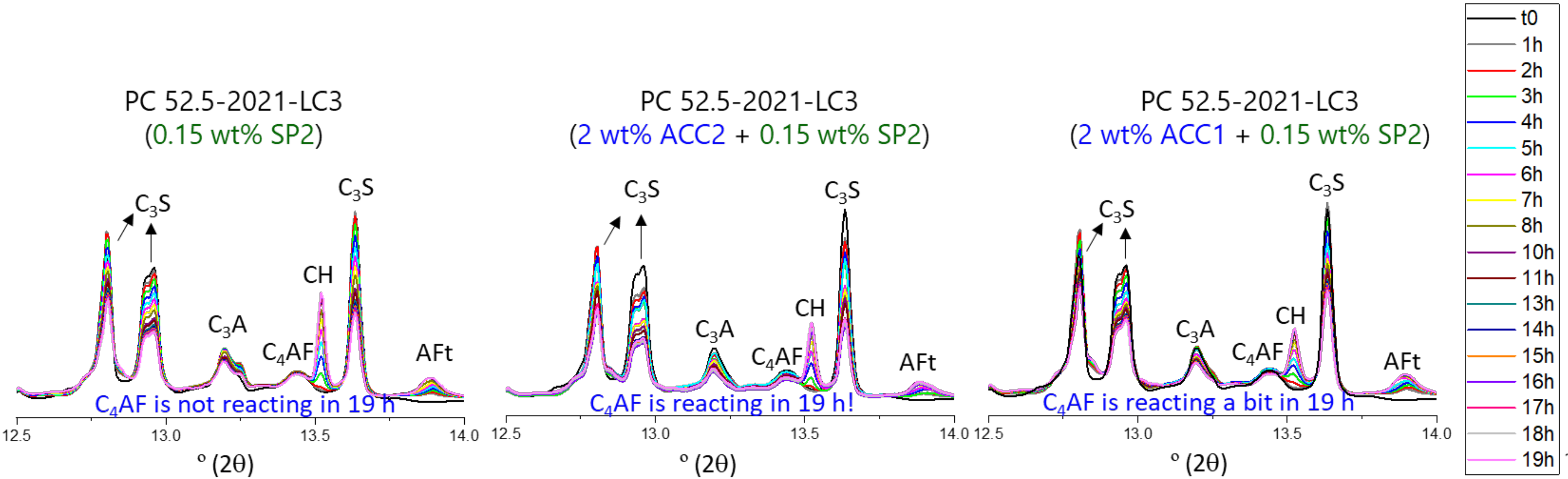
Mortars	Strength (MPa)	1d	7d	28d
PC-52.5R-2021-Ref 0.34wt%SP1	Compressive	**37.3(6)**	66(1)	76(2)
PC-52.5R-LC3-CC1-1.00wt%SP1	Compressive	15.0(2)	52(1)	72(4)
PC-52.5R-LC3-CC2-0.62wt%SP1	Compressive	11.7(1)	33(1)	57(2)
PC-52.5R-LC3-CC3-0.38wt%SP1	Compressive	8.1(1)	29(1)	52(2)
PC-52.5R-LC3-CC3-0.38wt%SP1-2.00wt%ACC1	Compressive	**23(1)**	2022/09/08	2022/09/30
PC-52.5R-LC3-CC3-0.38wt%SP1-2.00wt%ACC2	Compressive	**22(1)**	2022/09/08	2022/09/30

Mortars	Strength (MPa)	1d	7d	28d
PC-52.5R-2021-Ref 1.20wt%SP2	Compressive	**43.6(5)**	57(4)	74(2)
PC-52.5R-LC3-CC1-1.20wt%SP2	Compressive	19.9(5)	55(1)	63(3)
PC-52.5R-LC3-CC2-1.00wt%SP2	Compressive	15.1(4)	37(1)	2022/09/30
PC-52.5R-LC3-CC3-0.50wt%SP2	Compressive	10.8(2)	35(1)	2022/09/30
PC-52.5R-LC3-CC1-1.20wt%SP2-2.00wt%ACC1	Compressive	**29(1)**	2022/09/08	2022/09/30
PC-52.5R-LC3-CC1-1.20wt%SP2-2.00wt%ACC2	Compressive	**28(1)**	2022/09/08	2022/09/30

Case-2: LC^3 hydration acceleration



Case-2: LC^3 hydration acceleration



Conclusions

Two main conclusions can be drawn from this work, so far:

Firstly, synergy between C-S-H seeding and alkanolamines is proved as the dissolutions of calcium sulphate and aluminate phases are further enhanced when compared to single admixture dosage.

Secondly, C-S-H seeding accelerates the Portland and Belite cement hydration at early ages mainly by boosting calcium sulphate(s) and calcium aluminate(s) availabilities. In the studied experimental conditions, and at early hydration ages, alite and belite phase reactivities are not significantly enhanced.

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We thank MSPD-ALBA for the beamtime and support during data collection

I thank all collaborators from UMA, ALBA, Master Builder Solutions and Buzzi.
This is a large team effort.

***2-yr postdoc position** open for X-ray imaging (ML) & powder diffraction (RQPA) in LC³. Drop email to:* **g_aranda@uma.es**