MICROSTRUCTURAL CHARACTERISATION OF PASTES PRODUCED WITH RECYCLED CEMENT

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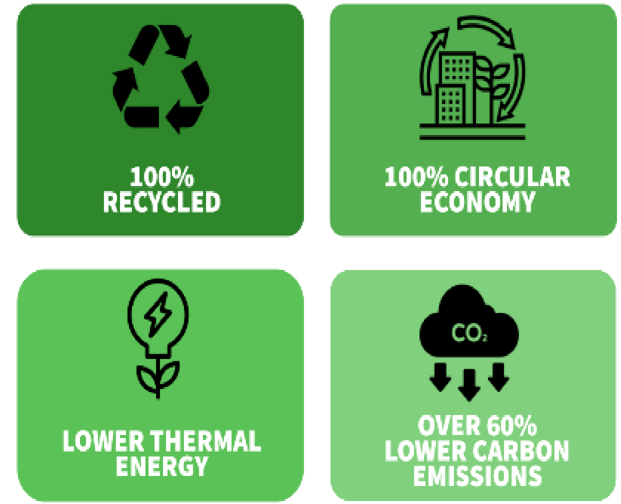
Recycled cement (RC)



Target (GCCA)

- CDW reuse
- Save natural resources
- ↓ 25% CO_2 (2030)
- Net zero concrete (2050)

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Recent domain

- Production and characterization of RC
- Preliminary mechanical characterization of RC pastes/mortars
- <u>Our research group:</u>
  - Comparable to CEM 32.5
  - Retrievement of cement waste from concrete

≅ 85-90 v% purity

Further research

Hydration behaviour and microstructure of RC

Objectives:

- **Microstructural characterization of recycled cement pastes**
- Comparison with reference Portland Cement pastes
- Porous structure and **phase development since early age** (8 hours to 28 days)

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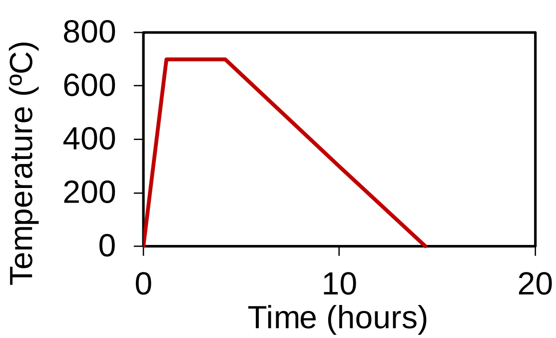
Experimental Program

Materials:

- <u>Origin Cement Paste:</u>
  - w/b=0.55; CEM I 42,5R; (>90 days)
  - $f_{cm,28d}$ = 41 MPa
- <u>Recycled Cement:</u>
  - Grinding and milling (d<250 μm)
  - Thermoactivated (700 ºC)



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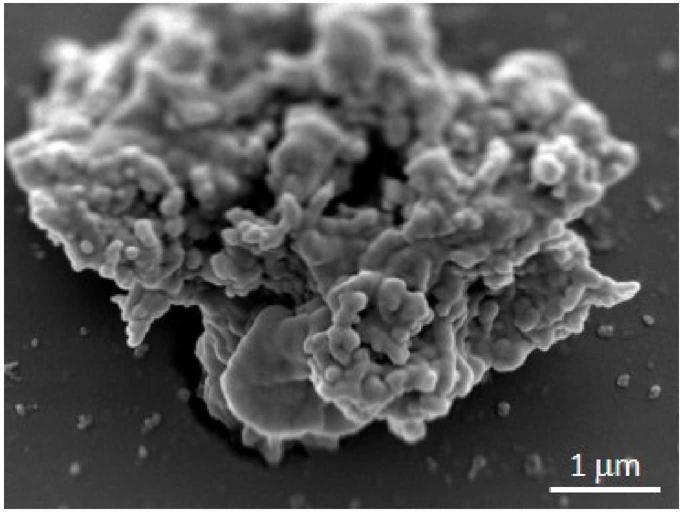
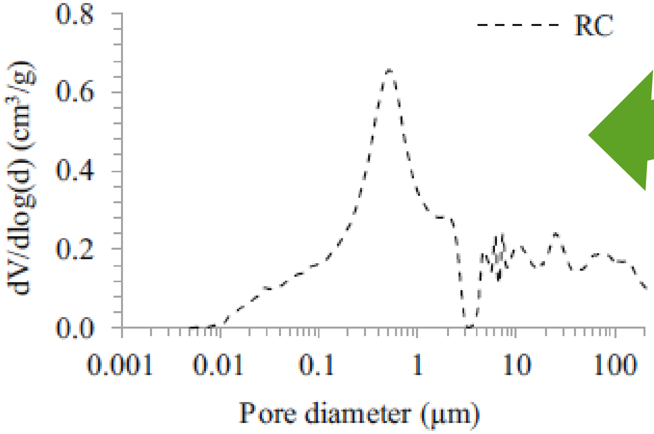
Recycled Cement:

- Porous nature - 48% accessible porosity (MIP)
- BET SA ≅150 000 cm^2/g (≅ 8-9x OPC)
- Free lime ≅ 14%
- RC particle size – 1 order magn. higher

High water demand





Paste compositions:

- **RC** paste (w/b=0.72) (normal consistency)
- Reference **OPC** pastes:
  - **CEM_0.72** - Equal w/b (0.72)
  - **CEM_0.31** - Similar workability (w/b=0.31)

Mix	w/c	Composition	
		binder mass kg/m^3	water mass kg/m^3
CEM_0.72	0.72	909	655
CEM_0.31	0.31	1497	464
RC	0.72	871	627

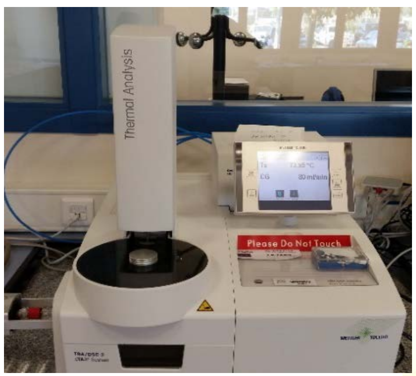
100% RC

Six 160x40x40 mm specimens – wet cured – 8 hours to 28 days

Test Methods:

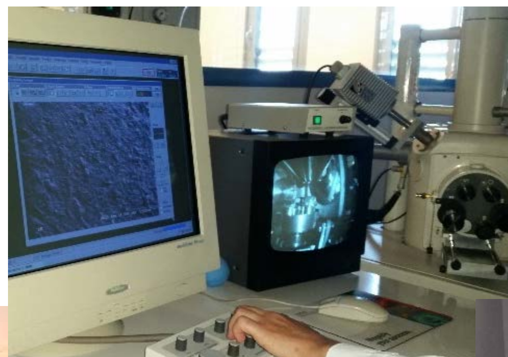
- Mechanical strength
- Microstructural analysis

Flexural and compressive strength (1,3,7,28 days)



Thermogravimetry (TG)

Isothermal calorimetry (IC)



SEM analysis (SE-SEM and BSE)

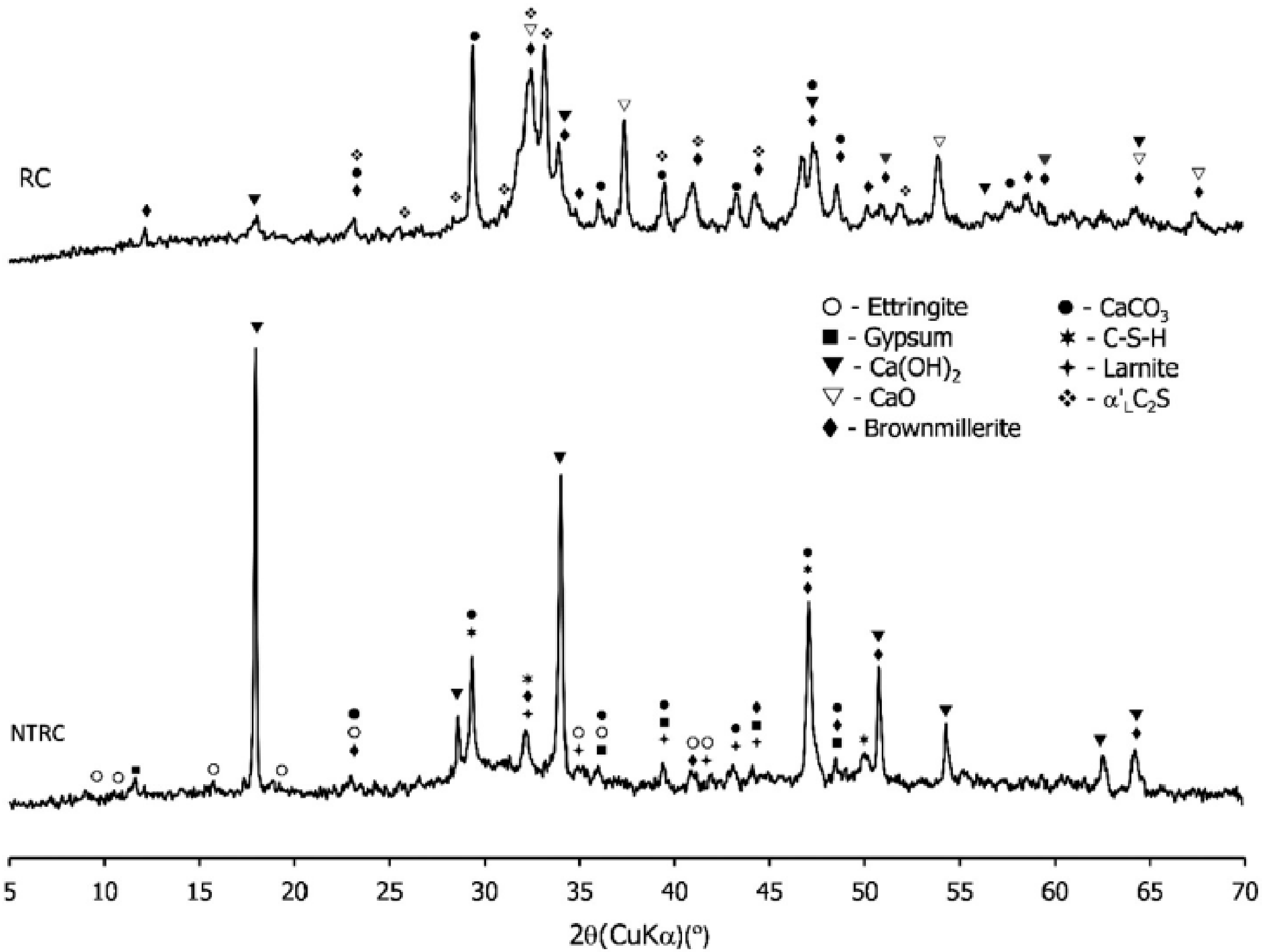
Mercury intrusion porosimetry (MIP)

Nitrogen Adsorption (NA)

Results and discussion

XRD analysis – Non-treated RC (NTRC) vs Treatead RC

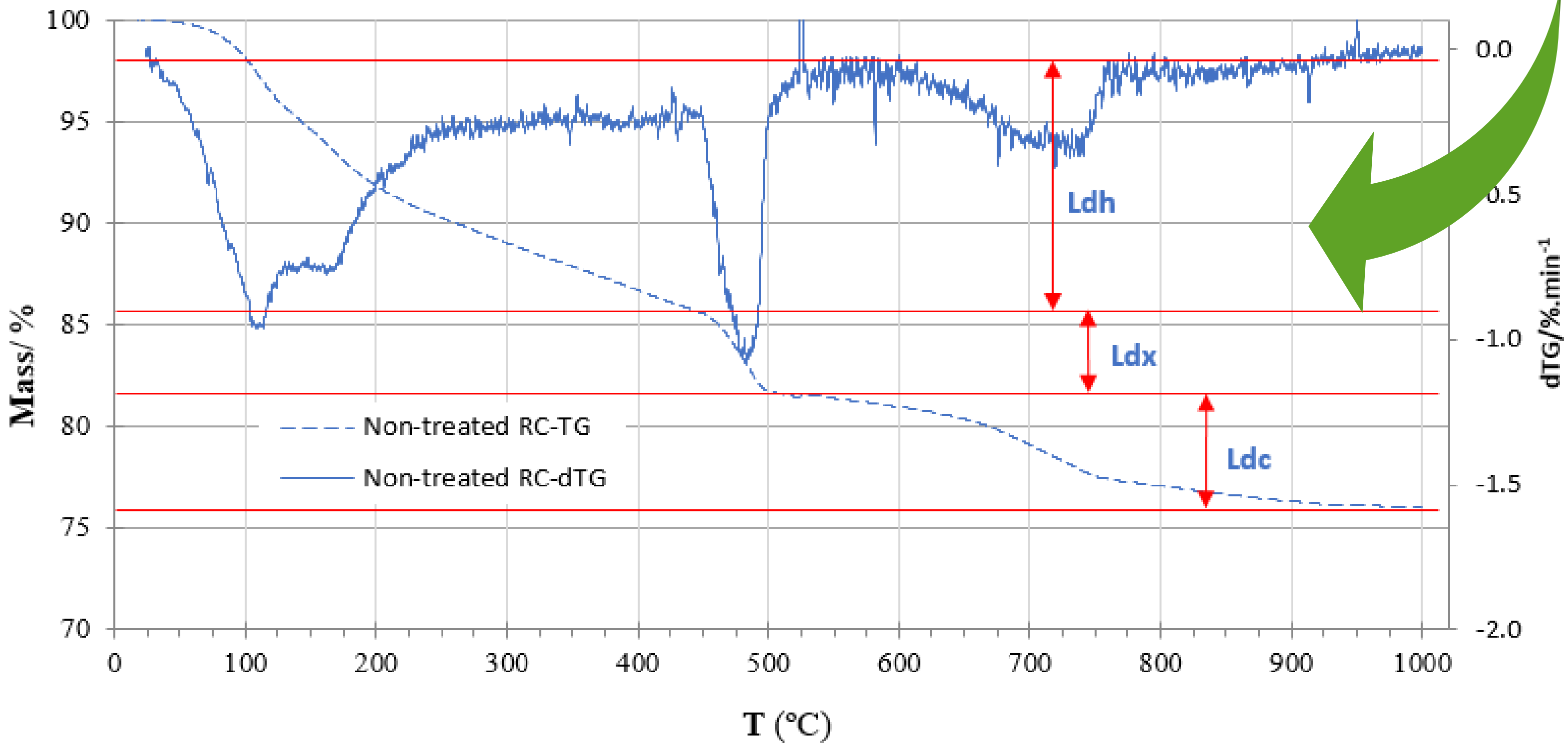
- **α’$_H$C$_2$S**; CaO; CaCO$_3$



Thermogravimetry (TG/DTG) – Non-treated RC

- Increase of carbonation products – 6.2% (vs OPC)
- **Well-hydrated cement waste** (78% α_H, W_B=18%)

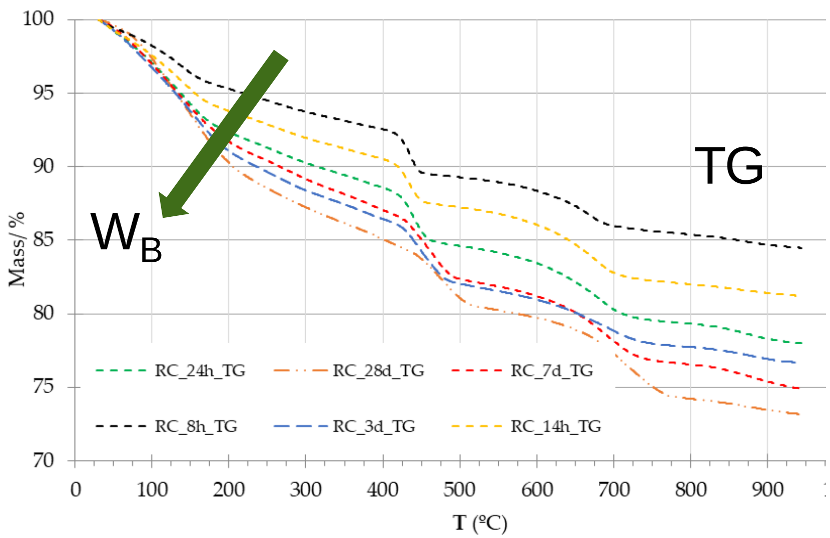
$$W_B = W_{B\,CSH-CH} + \frac{M_{H_2O}}{M_{CO_2}}(L_{dc} - L_{dca})\,(\%)$$

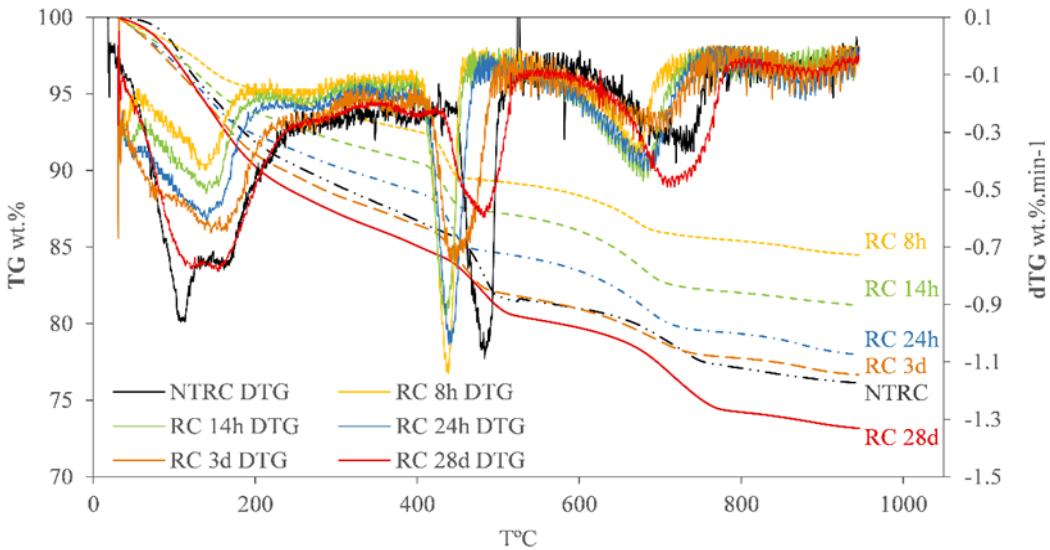


Thermogravimetry (TG/DTG) – Hydrated RC – 8h to 28d

- ↑ W_B and $W_{B,C\text{-}SH}$ with age ⇒ **High rehydration capacity**
- ↑ W_B and α_H in RC (up to 3 days) ⇒ **higher initial reactivity** (surface area, solubility)

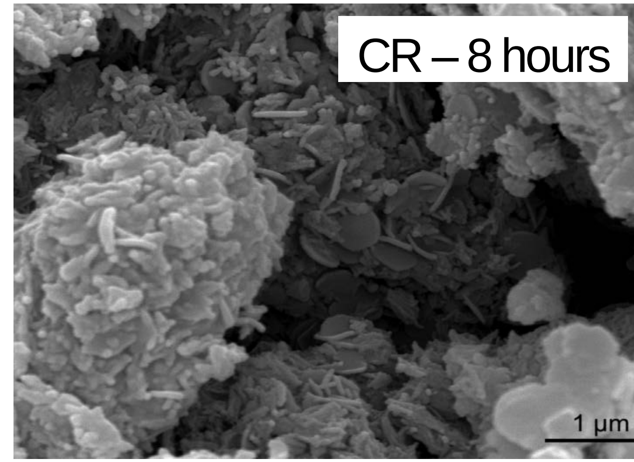
Pastes	8 hours			14 hours			1 day			3 days			28 days		
	$W_{B,CSH}$	W_B	α_H	$W_{B,CSH}$	W_B	α_H	$W_{B,CSH}$	W_B	α_H	$W_{B,CSH}$	W_B	α_H	$W_{B,CSH}$	W_B	α_H
RC 0.72	5.8	**8.7**	**38**	7.2	**10.6**	**46**	8.6	**13**	**56**	10.6	**14.8**	**65**	13	**17.8**	**78**
CEM 0.72	3.8	**5.6**	**25**	5.3	**8.7**	**38**	8.7	**13.6**	**59**	8.2	**13.1**	**57**	13.1	**18.1**	**79**
CEM 0.31	5.2	**7**	**31**	7.3	**10.3**	**45**	7.9	**11**	**48**	8.2	**11.4**	**50**	12.2	**16.2**	**71**



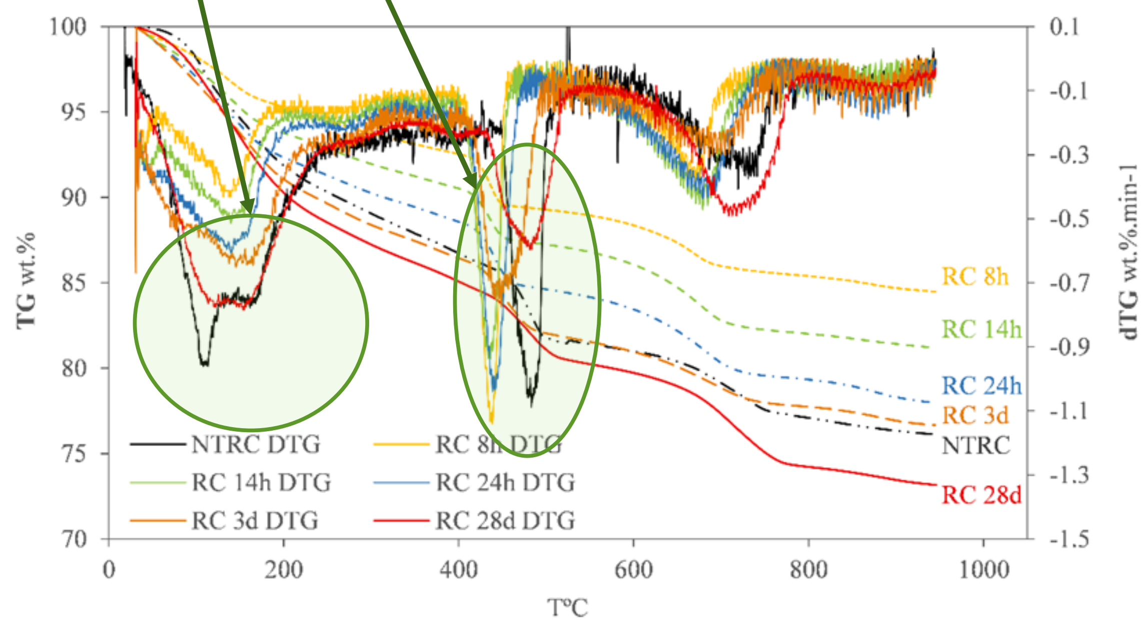


Thermogravimetry (TG/DTG) – Hydrated RC – 8h to 28d

- Lower amount of AFt phases
- **AFm phases since early age (8 h)**
- Less CH of lower binding energy (part carbonated)



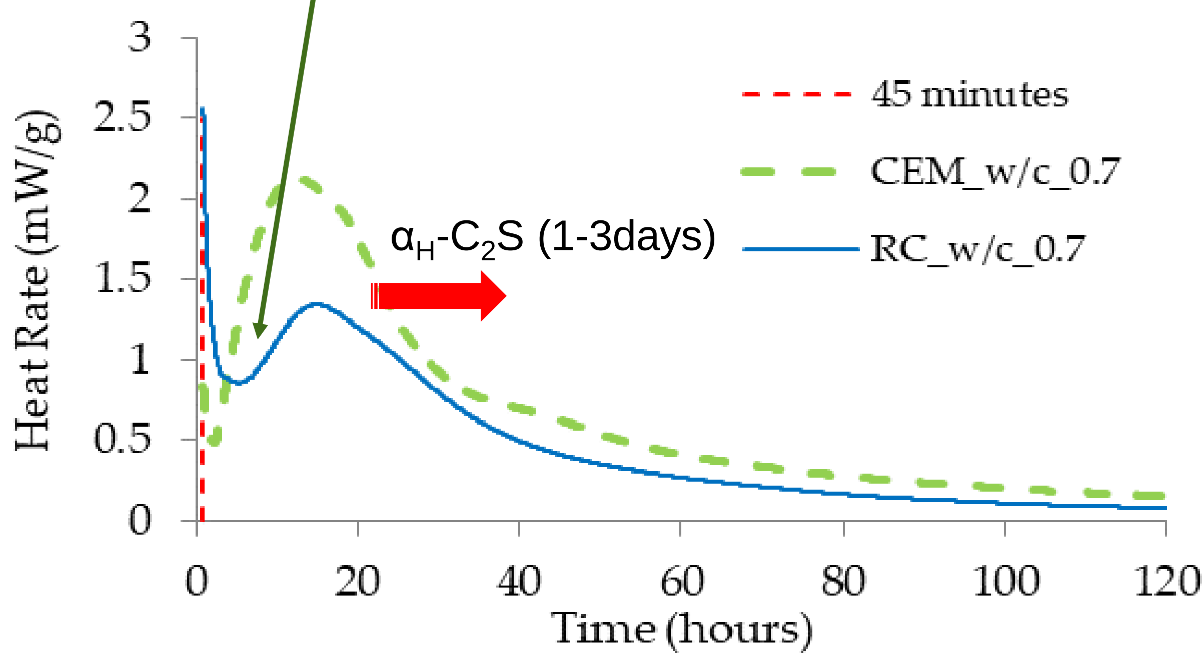
Pastes	CH content (%)				
	8h	**14h**	**24h**	**3d**	**28d**
RC 0.72	12.0	13.9	17.8	17.5	19.7
CEM 0.72	7.5	13.9	20.1	20.1	20.9
CEM 0.31	7.6	12.6	12.5	13.4	16.3



Isothermal calorimetry (IC) – Hydrated RC – 8h to 28d

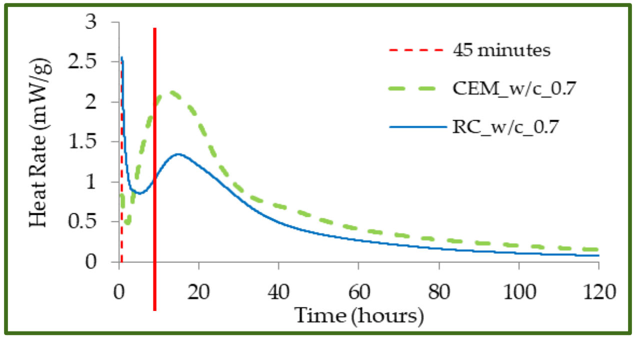
- Heat release up to 3h ⇒ ≅ 3 x OPC
- **Rehydration of free lime and AFm phases** (no shoulder from AFm)
- **Slower formation of external CSH** (delayed induction period)

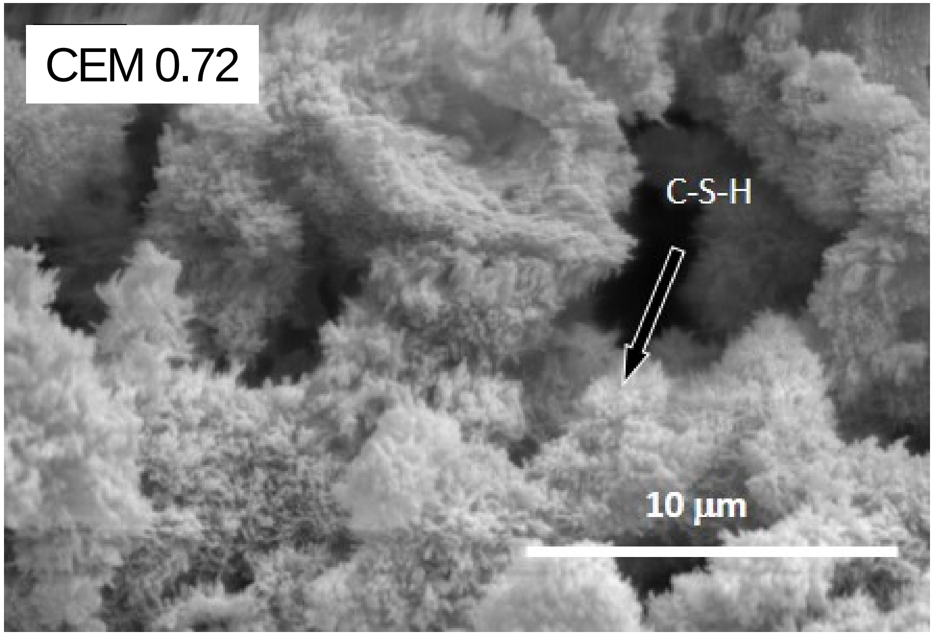
Pastes	Setting time Start	Setting time End
RC	280	417
CEM I 42.5	170	315

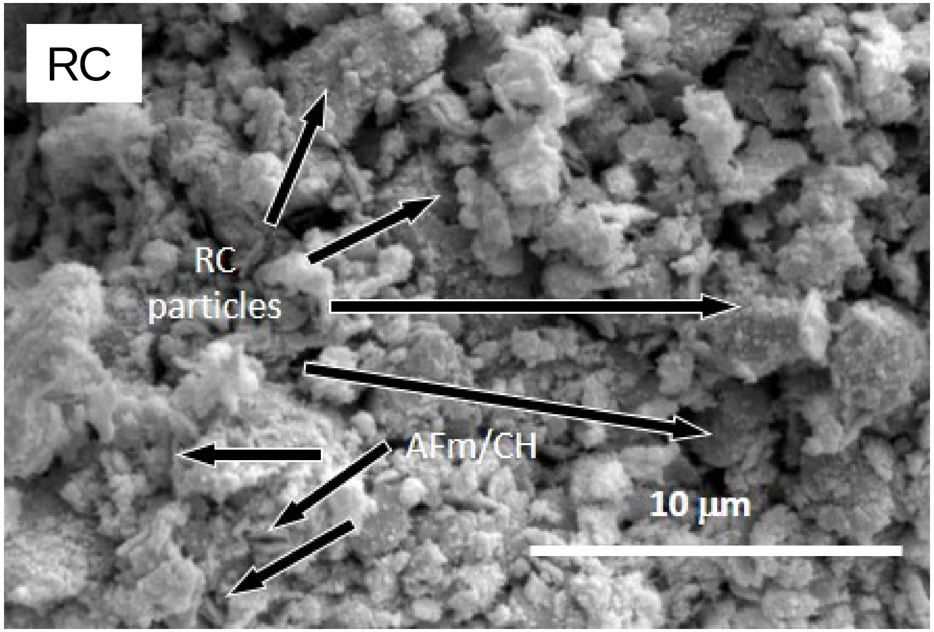


SEM analysis

Equal w/b - 8 hours







First CSH in a loose porous structure, poorly consolidated
No AFt phases

Agglomeration of high surface area RC
Platted-like products (AFm/CH)
No significant formation of CSH

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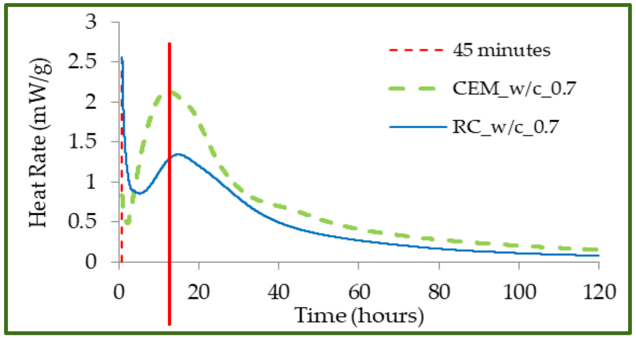
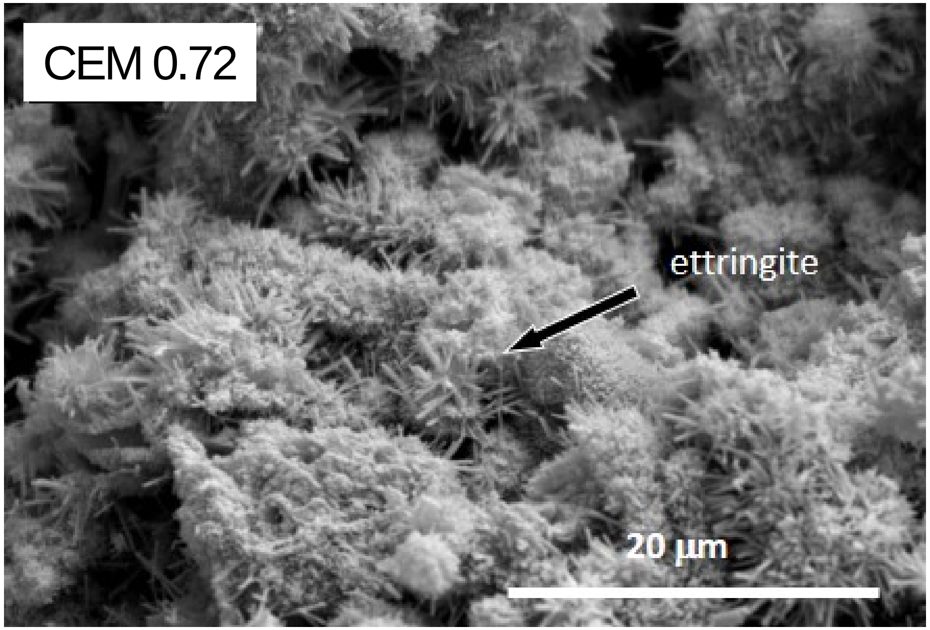
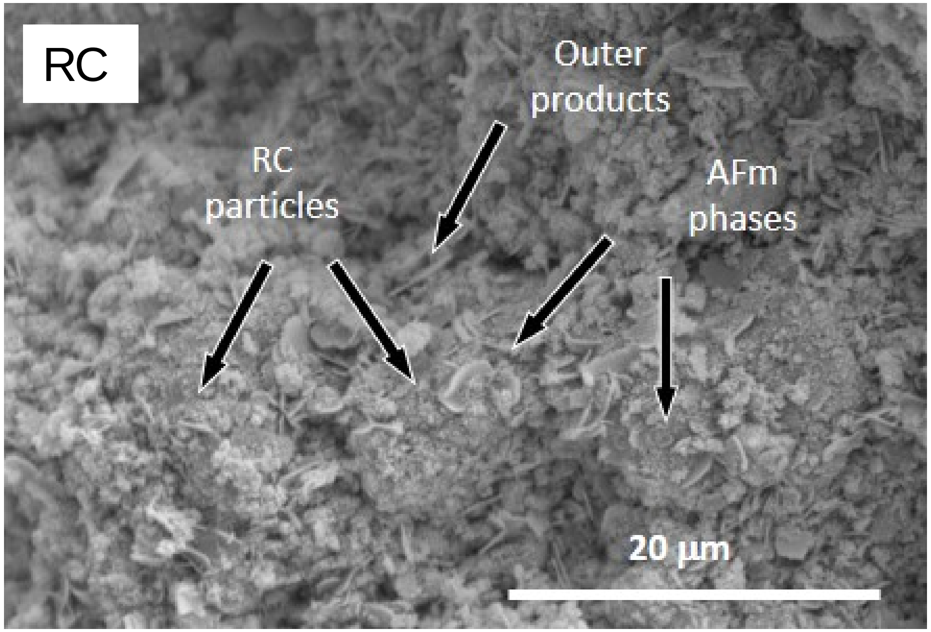
SEM analysis

Equal w/b - 14 hours





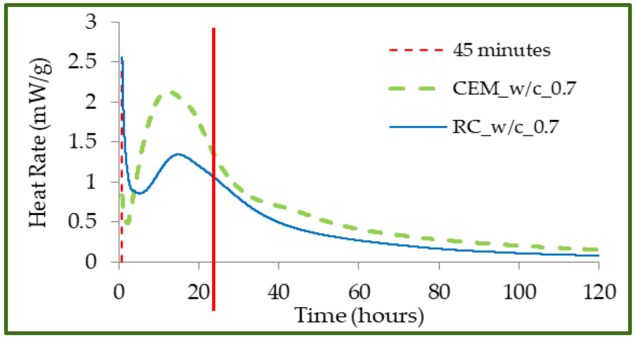


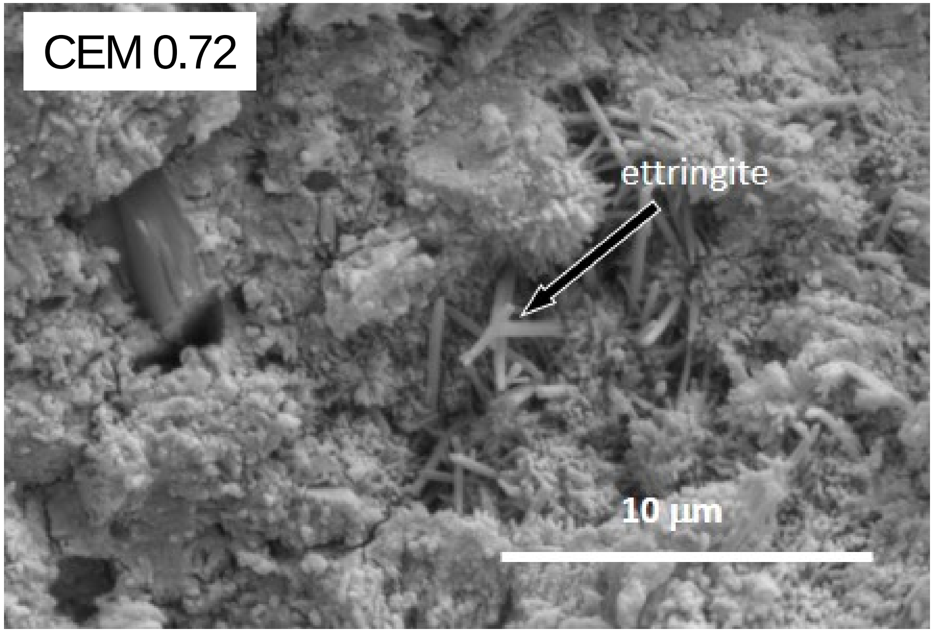
Significant increase of hydration products (AFt, CH, CSH)
Poorly bonded particles

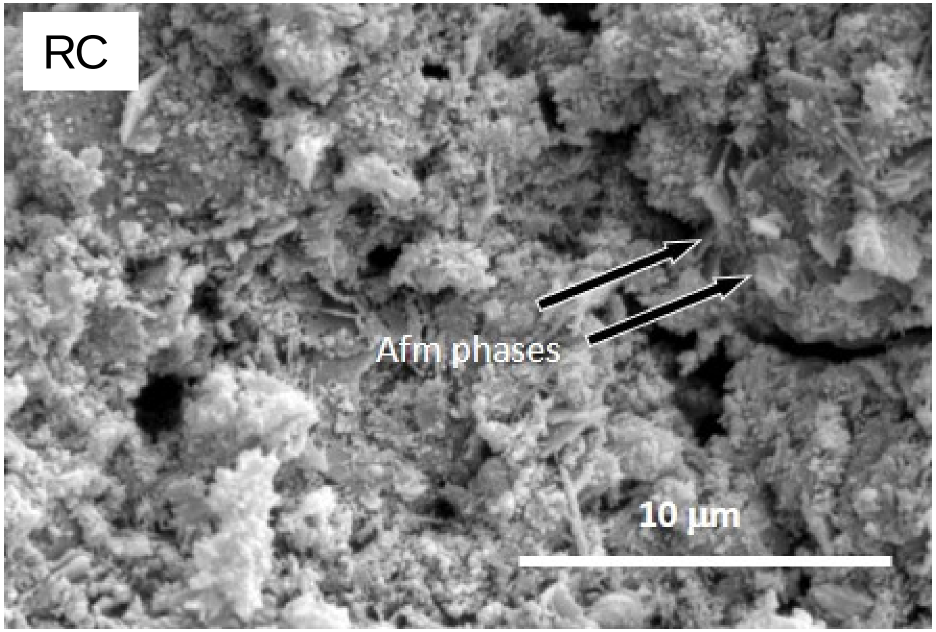
Still low amount of CSH
Essentially AFm and CH
Ascending acceleration stage

SEM analysis

Equal w/b - 24 hours





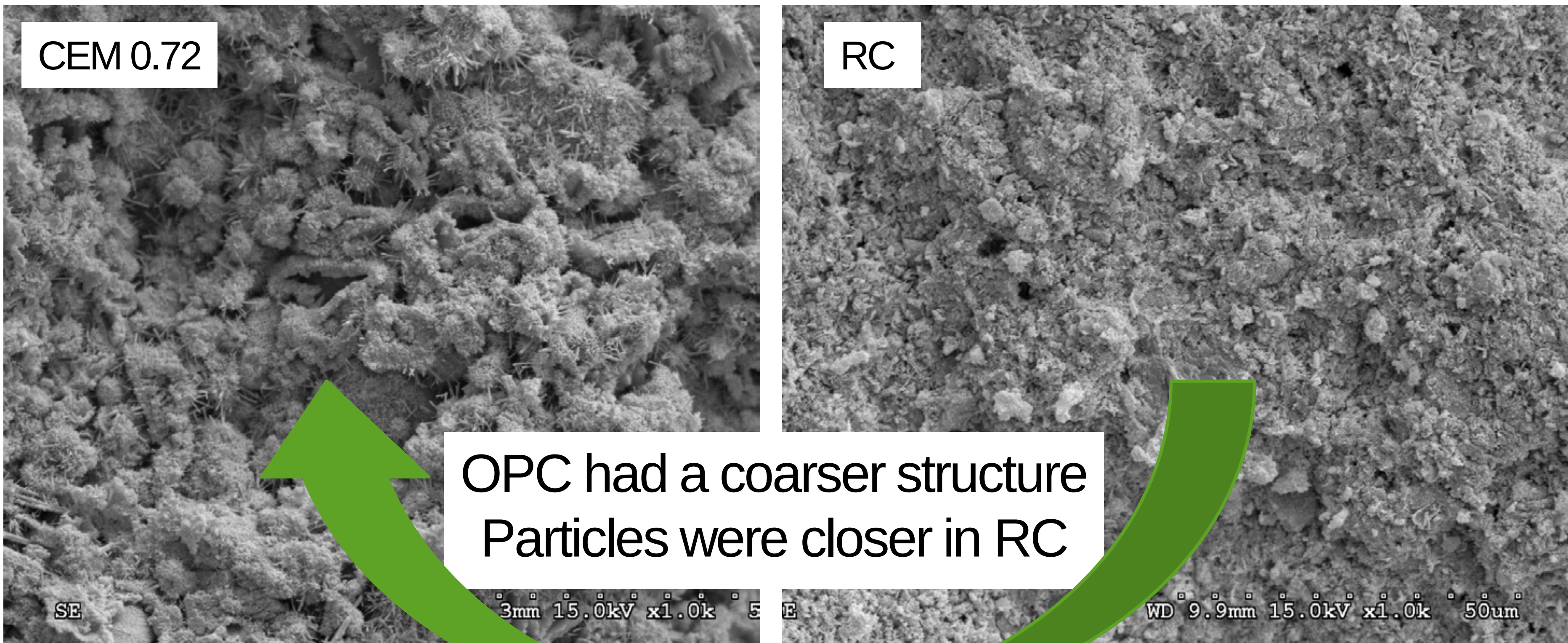


Still highly porous structure, with coarse AFt and CH – similar to 14 hours

Formation of CSH was significant microstructure was slightly denser in RC than in OPC

SEM analysis

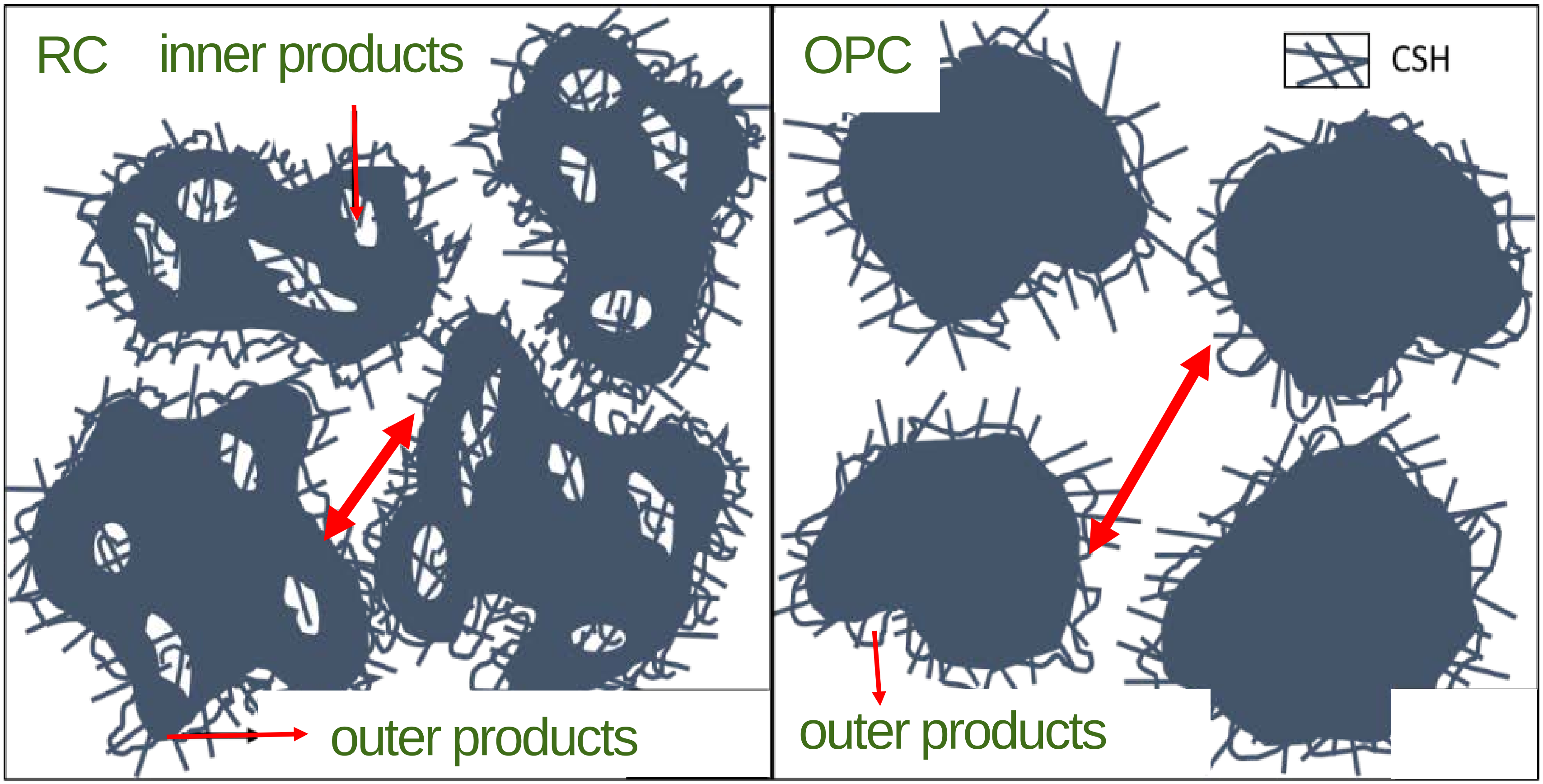
Equal w/b - 24 hours



OPC had a coarser structure
Particles were closer in RC

Structural model

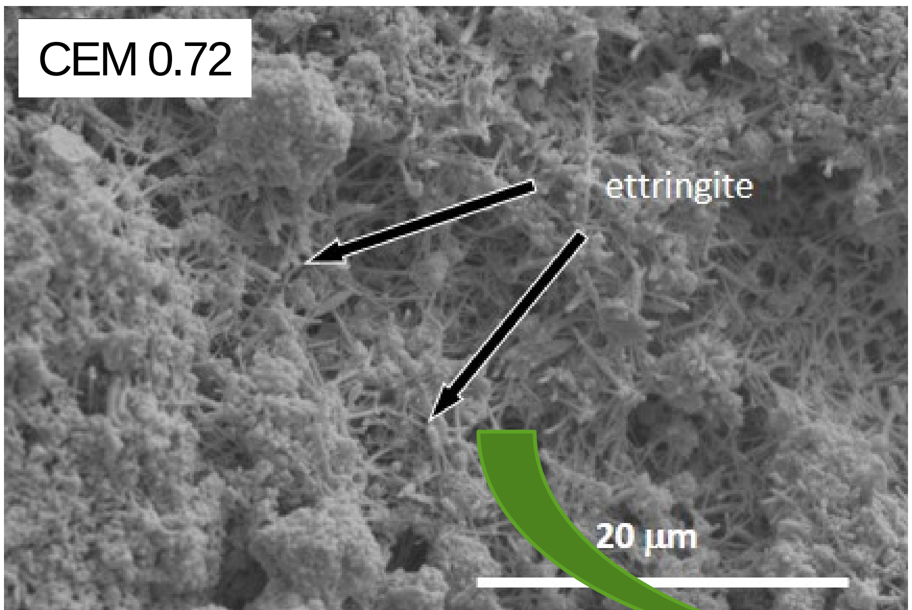
RC – Two-phase microstructure

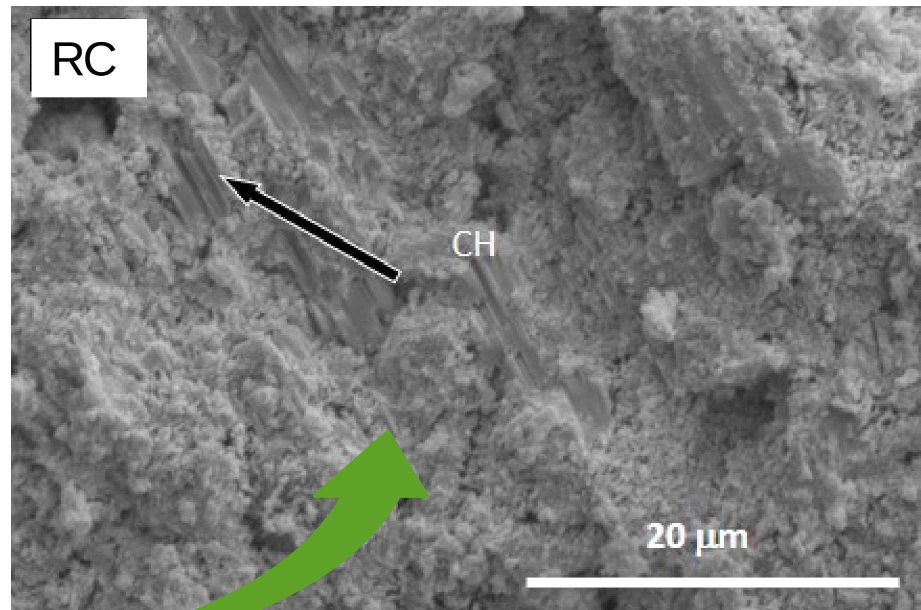


Lower w/b ⇒ refining the microstructure

SEM analysis

Equal w/b - 3 days



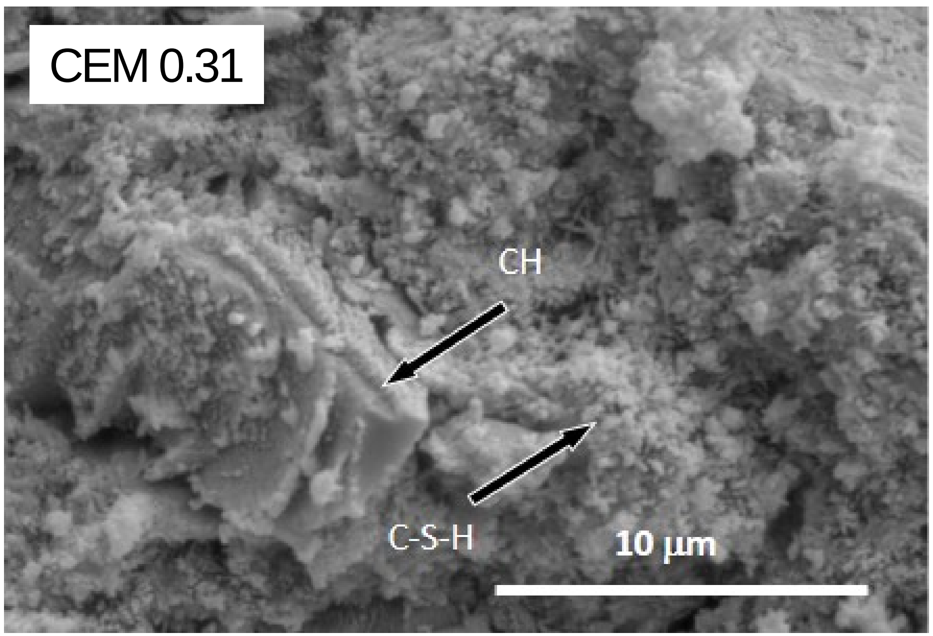


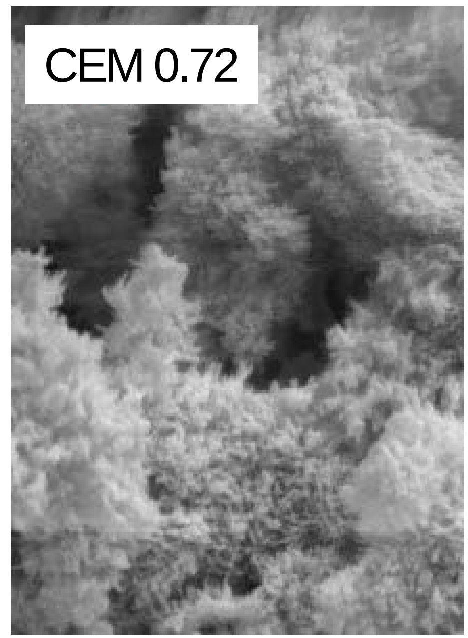
Porous structure
Lose microstructure
Massive amount of AFt

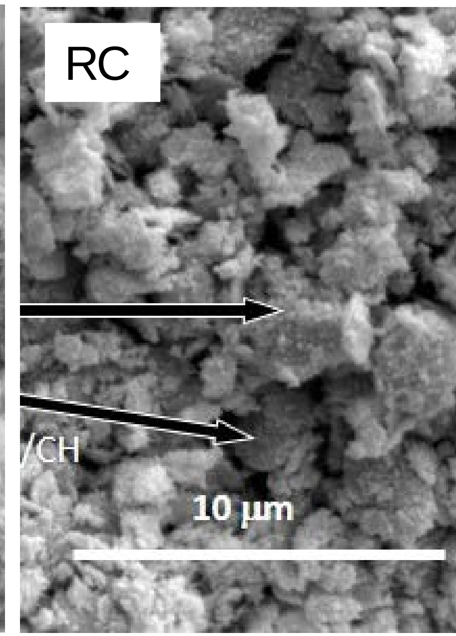
Greater hydration progress
Denser structure of RC
AFm intermixed with CSH and CH

SEM analysis

Pastes of equal workability and lower w/b – 8/24 hours





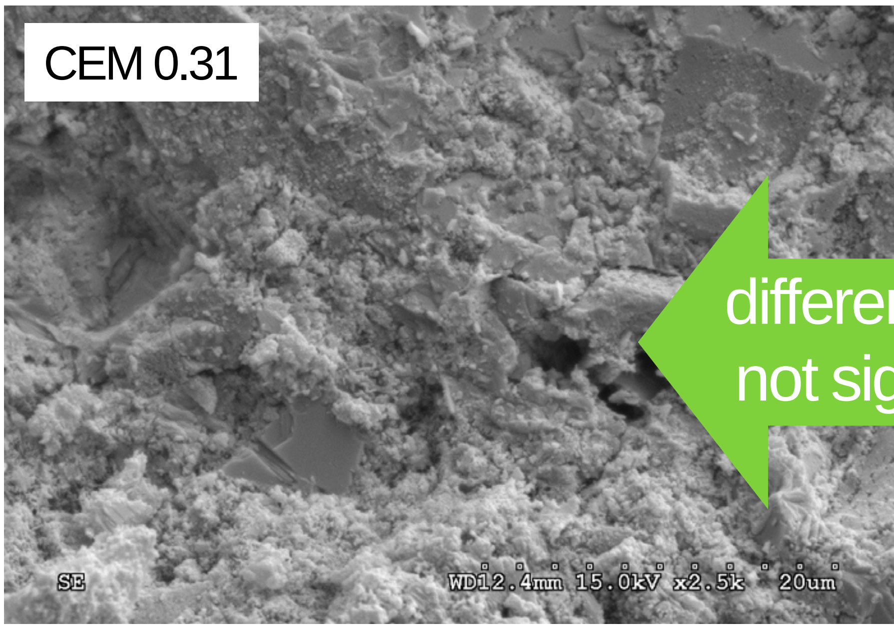


Denser microstructure
Fast hydration (CSH / CH)

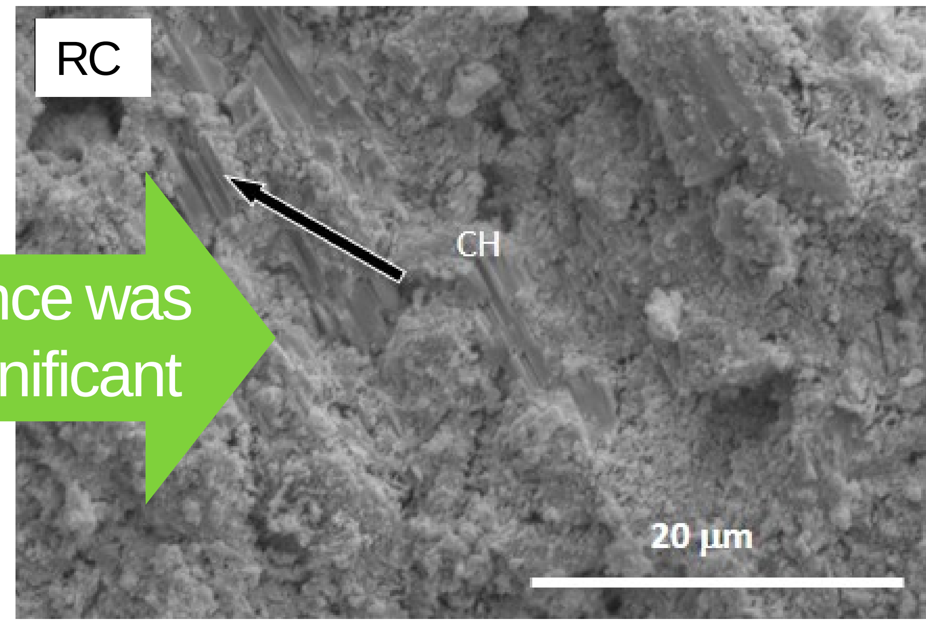
Much higher porosity

SEM analysis

Equal workability – 3 days



difference was not significant

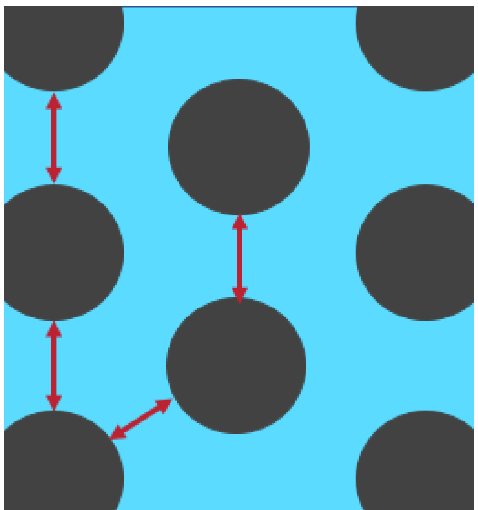


Dense microstructure
Low w/b

Dense outer microstructure
outer w/b is also low

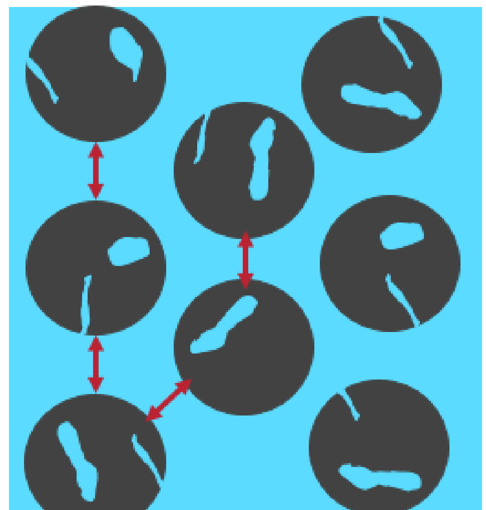
Structural model

Lower outer w/b in RC and CEM_0.31 paste



CEM 0.72

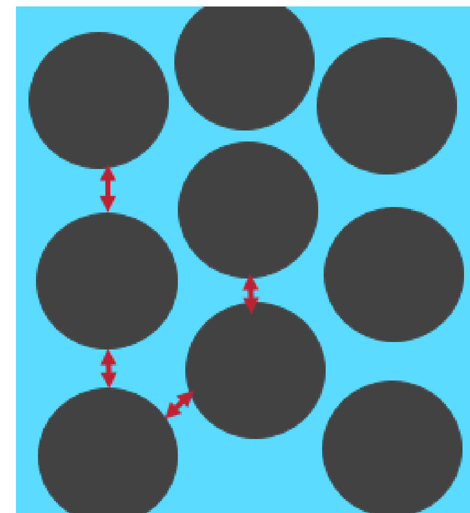
w/b = 0.72



CEM 0.72

w/b = 0.37

≅



CEM 0.31

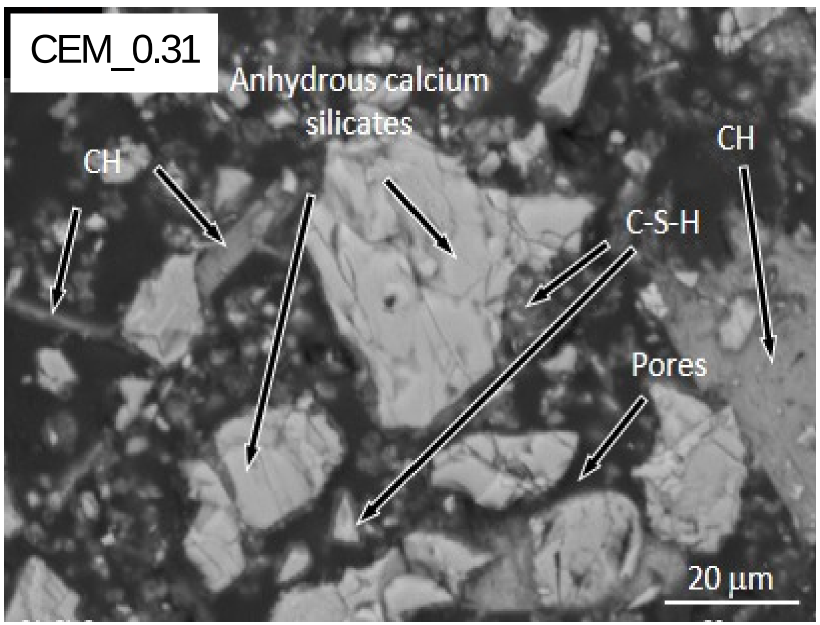
w/b = 0.31

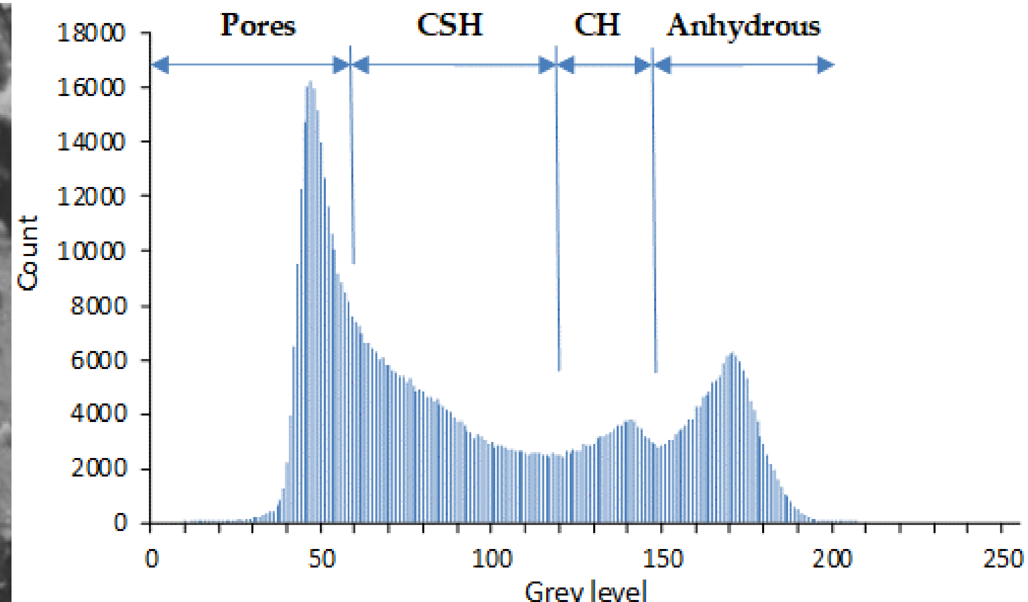
Simple estimate ⇒ **30% water absorption** and **15% free lime** in RC
⇒ the external w/b would be about **0.37**, close to 0.31

Backscattered (BSC) quantitative analysis

- Distinguish of different **hydration products** and **porosity**

$\Rightarrow$ **Evolution of CH, CSH, porosity, anhydrous grains overtime**

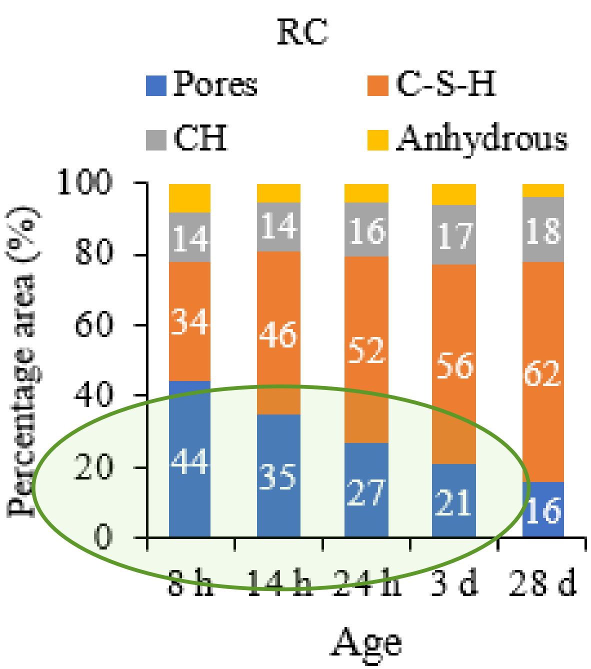


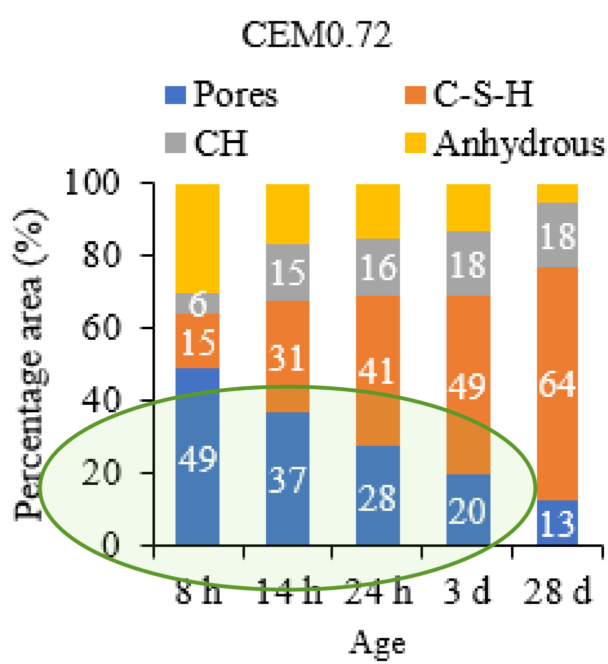


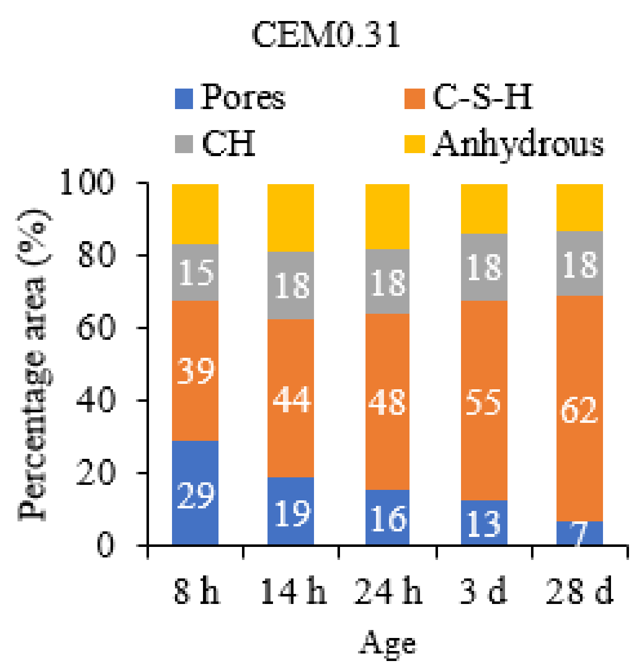
Distinguished by different grey level

BSC quantitative analysis (low accuracy for < 1-10 μm)

- **Progressive hydration of RC** over time
- **Lower coarse porosity** in RC than in OPC **up to 3 days**
- Volume of hydration products higher in OPC at 28 days

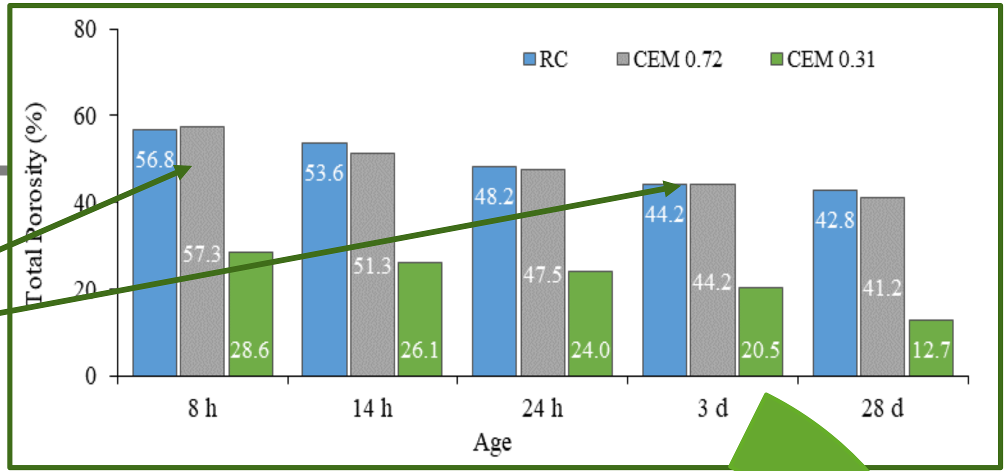


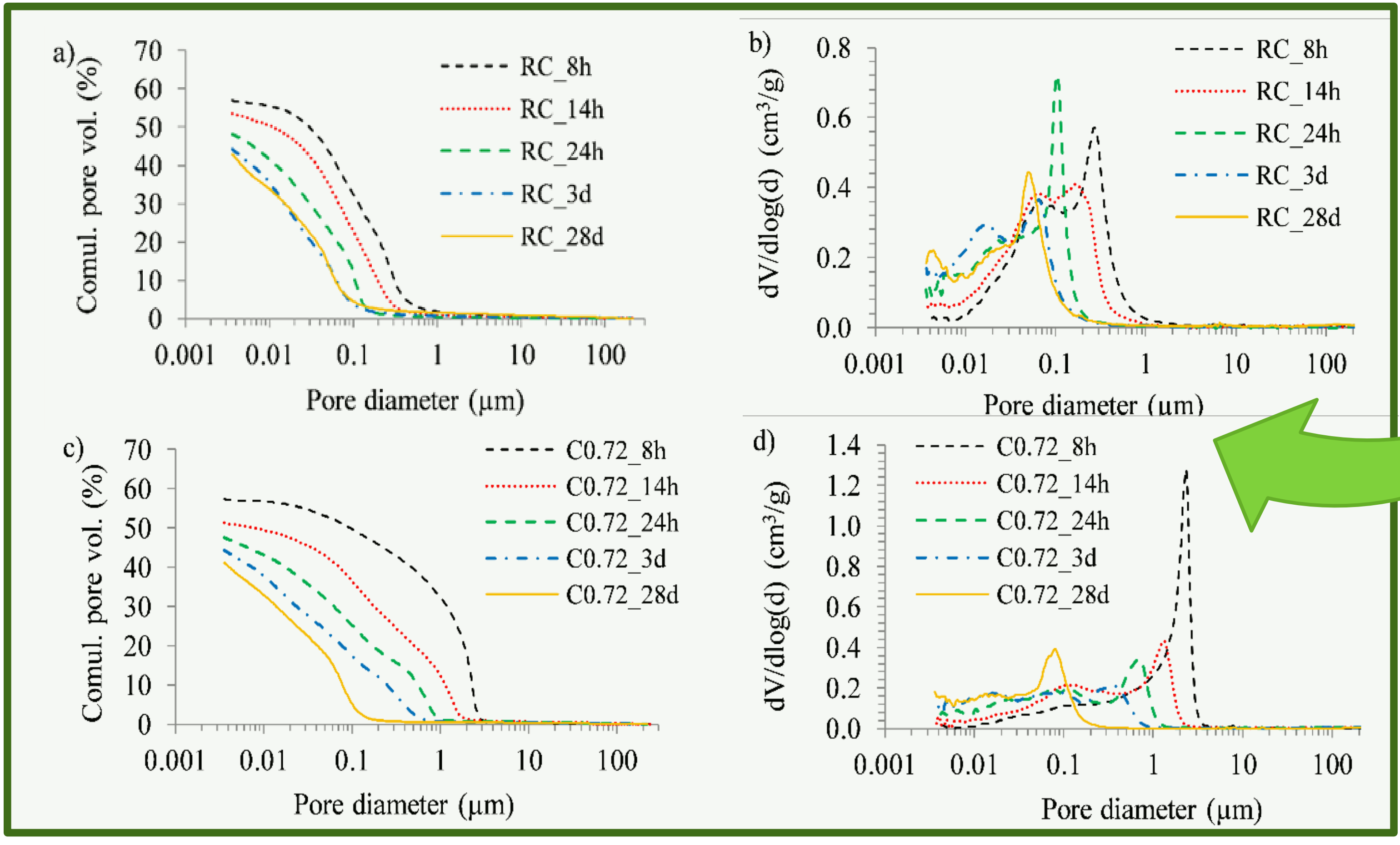




MIP analysis

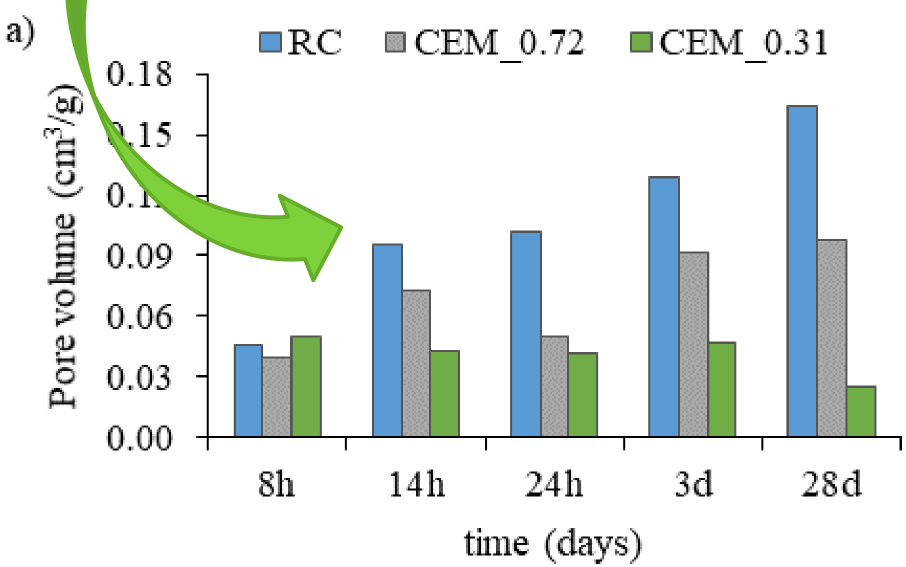
- Similar total porosity
- More refined porosity in RC

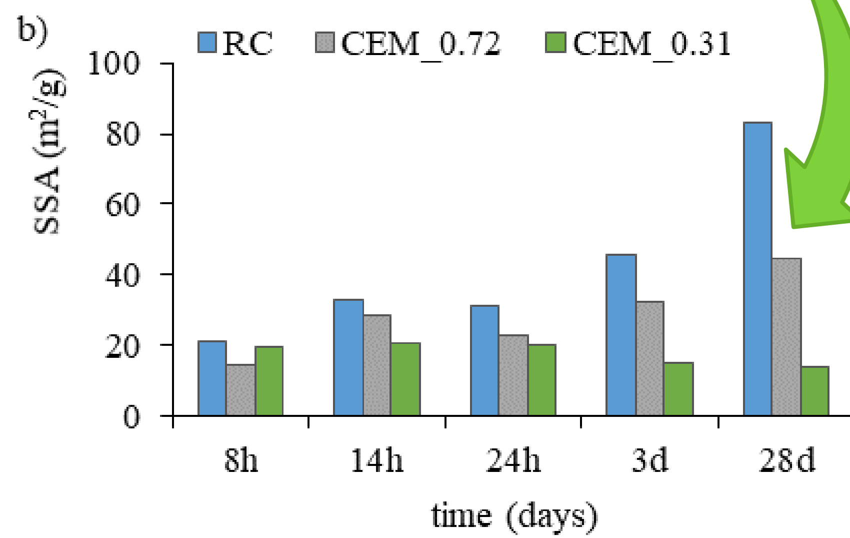




N_2 adsorption tests

- Higher volume of small pores in RC (<50 nm)
- Higher surface area in RC



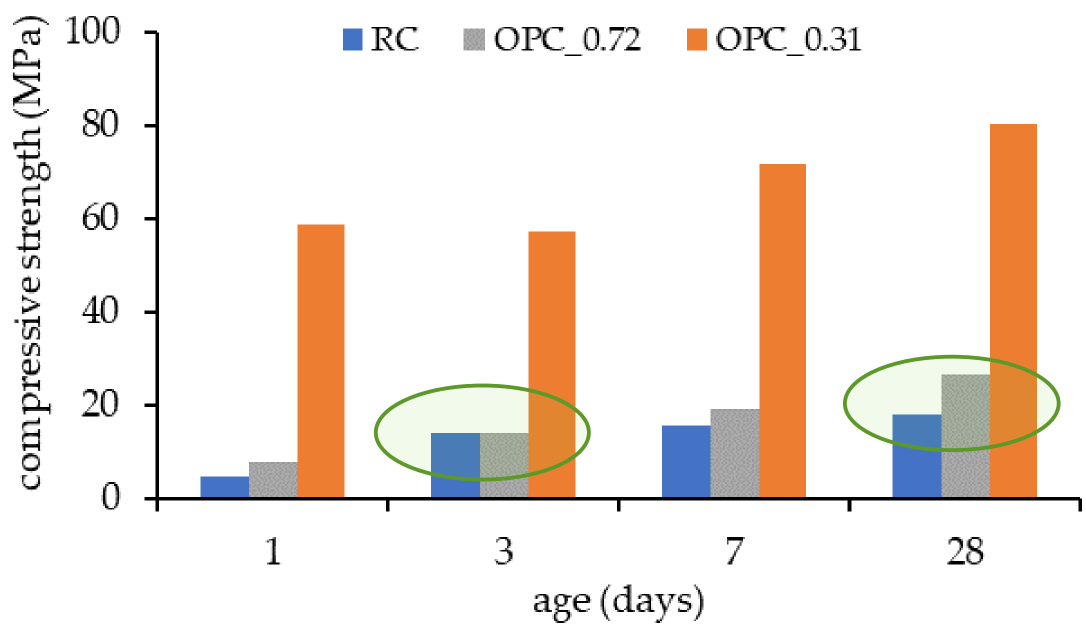


Porous nature of RC $\Rightarrow$ More refined porosity

Mechanical strength

- **For equal w/b**
  - ⇒ **similar strength at 3 days** (reactivity of α_H-C_2S; particle proximity)
  - ⇒ 43% **lower at 1 day** (less CSH; particle size and agglomeration)
  - ⇒ 32% **lower at 28 days**

  (↓ volume of outer hydration products; weaker particles of RC)



Conclusions

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Conclusions:

RC showed **high rehydration capacity,** with the same types of hydration products, but AFm phases since early age (8 hours)

The **reactivity of RC** was **higher between 1 and 3 days**

RC paste is characterized by a dual structure, where porous RC is surrounded by an outer hydrated matrix

Showing **lower outer w/b and a more refined microstructure**

RC 28 days strength was about 70% of that of OPC paste

RC has a high potential to be used as an alternative hydraulic binder or supplementary cementitious material

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Thank you for your attention

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