

Characterization of C-S-H gels by pair distribution function analysis

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Abstract

Concrete is the most manufactured world commodity and it is made by Portland cement (PC) and several other ingredients. Cement industry is one of the major contributors for greenhouse gas emissions, if cement production is considered as an emitter, it would be the third country just after China and USA. A recent work [1] commissioned by the United Nations Environment Program Sustainable Building and Climate Initiative has identified the use of supplementary cementitious materials (SCMs) as the most favourable approach for lowering CO₂ emissions in the cement industry. In order to develop more sustainable cements, the hydration products must be well understood which is far from straightforward. The hydration reactions of tricalcium silicate, Ca₃SiO₅ (main phase of PC) consist of its dissolution, the formation of the nanocrystalline calcium-silicate-hydrate (C-S-H) gel, jointly with the crystallization of portlandite, Ca(OH)₂ according to equation (1). C-S-H gel seems to be composed by defective nanocrystalline clinotobermorite, amorphous (a few layers thick) Ca(OH)₂ and gel pore water [2].



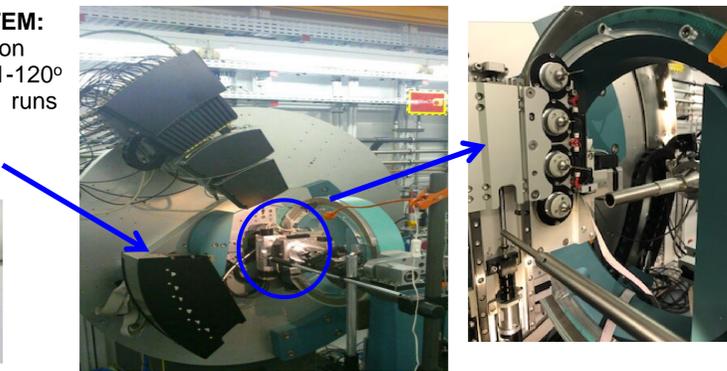
Crystalline- μm Crystalline- μm C-S-H: gel-nanocrystalline-nm // amorphous-nm // amorphous-nm *length scale in chemical reactions with solids is important!*

The main products of reaction (1) are: i) crystalline Ca(OH)₂, ii) nanocrystalline tobermorite, and iii) amorphous Ca(OH)₂. The calcium hydroxide formed in reaction (1) can be employed to yield additional secondary C-(A)-S-H through the pozzolanic reaction with SCMs. The analysis of nanocrystalline/amorphous phases in cement matrices which contain high amounts of crystalline phases is a challenging task. Pair distribution function (PDF) methodology in combination with synchrotron radiation is key to characterize cement pastes. PDF data can give insight about the atomic local structure of the non-crystalline components such as C-(A)-S-H gels. This work focuses on the characterization of amorphous and nanocrystalline phases which are present in cement related pastes by total scattering PDF [2,3].

Data collection

Synchrotron X-Ray Powder Diffraction Station of ALBA, BL04-MSPD

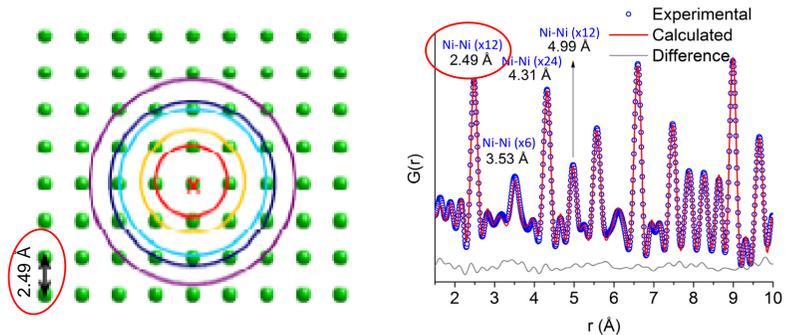
MYTHEN DETECTOR SYSTEM:
Debye-Scherrer configuration (transmission), angular range 1-120° (in 2 θ), 37 minutes per run x 5 runs per sample, $\lambda \sim 0.41 \text{ \AA}$



PDF methodology

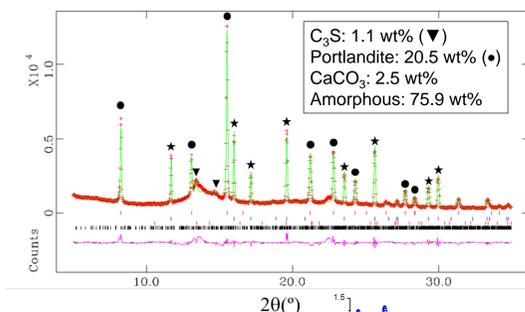
$\rho(r)$ = microscopic atomic pair density
 ρ_0 = average atomic number density
 $S(Q)$ = total scattering structure function

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ$$

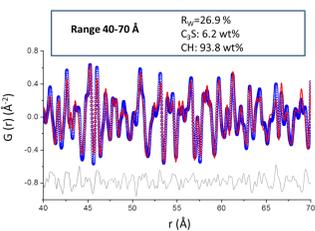


Results & Discussion

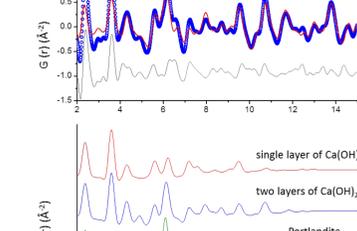
(i) Tricalcium silicate samples [2]



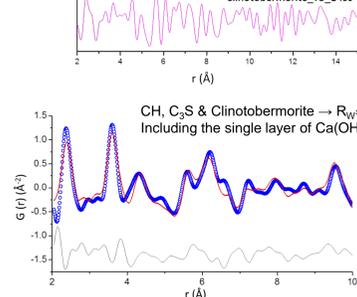
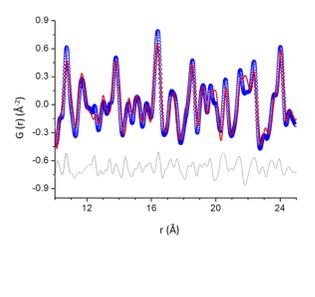
1) High r-range



3) Low r-range



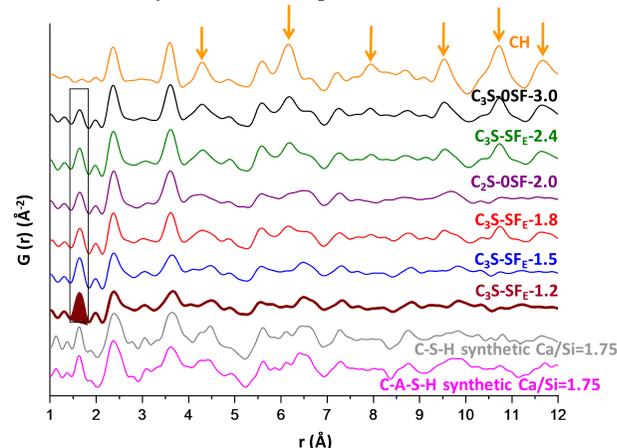
2) medium r-range



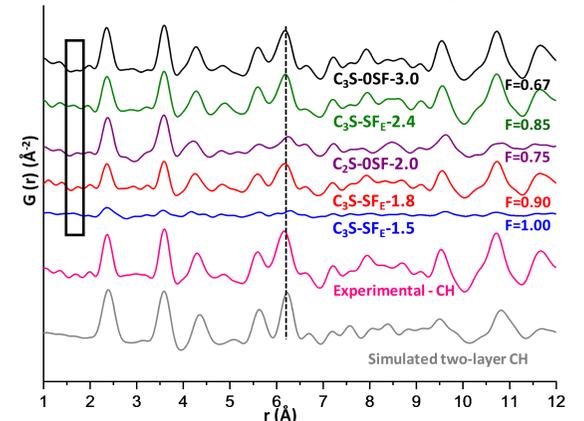
The C-S-H gel formed from the hydration of C₃S is composed by:
- a defective clinotobermorite, Ca₁₁Si₉O₂₈(OH)₂·8.5H₂O
- stretched monolayers (or a few layers) of calcium hydroxide

(ii) Tricalcium silicate samples with silica fume [3] // (iii) C-S-H & C-A-S-H

Raw synchrotron PDF patterns



Differential (subtracted) synchrotron PDF patterns

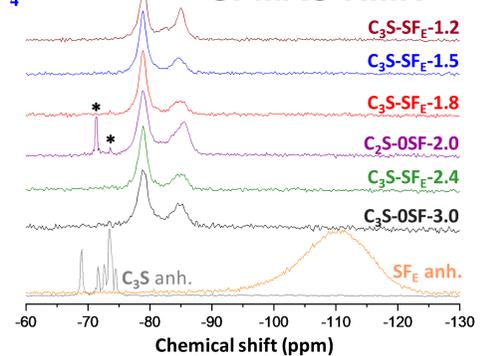


The PDF pattern for C₃S-SF_E-1.2 can be used as a reference for C-S-H gel from alite hydration. Top seven patterns from ALBA. Data for synthetic C-S-H and C-A-S-H taken at Petra synchrotron, unreported. In collaboration with LMC-EPFL (P. Bowen).



Sample	%CH - DTA-TGA	%CH - RQPA	%CH - average	Ca/Si ratio C-S-H gel calculated	Ca/Si ratio C-S-H gel HR-TEM*	Ca/Si ratio max-min HR-TEM	N° points HR-TEM
C ₃ S-SF-3.0	21.6	24.8	23.2	1.70	1.78(21)	2.26-1.45	38
C ₃ S-SF-2.4	16.0	14.4	15.2	1.66	1.82(25)	2.49-1.50	66
C ₂ S-SF-2.0	2.2	2.5	2.4	1.90	1.48(35)	2.30-1.13	94
C ₃ S-SF-1.8	11.7	11.6	11.6	1.25	1.06(8)	1.27-0.88	45
C ₃ S-SF-1.5	2.4	1.3	1.6	1.38			
C ₃ S-SF-1.2	0	0	0	1.20			
C ₃ S-SF-1.2	0	0	0	1.20			

²⁹Si-MAS-NMR



The signal situated at ~-110 ppm (SF), is negligible in all the hydrated pastes which proves that this phase has fully reacted at 4 month of hydration

Conclusions

- PDF approach has allowed studying the local atomic order of the C-S-H gel. The C-S-H gel is composed by a defective clinotobermorite and monolayers of calcium hydroxide.
- In the employed experimental conditions, the secondary C-S-H gel formed by the pozzolanic reaction has the same local structure as the primary C-S-H gel formed by the alite hydration. This conclusion is drawn from the smooth variation of the PDF traces without the appearance of any additional interatomic correlation distance band.
- The excess Ca(OH)₂ formed during alite hydration is highly reactive and fully available for pozzolanic reaction as demonstrated by the Ca/Si=1.20 sample which is well described by a defect-containing tobermorite model.

References

- UN Environment, et al. (2018), Eco-efficient cements: Potential, economically viable solutions for a low-CO₂, cement-based materials industry, *Cem. Concr. Res.* **114**, 2-26.
- Cuesta, A., et al. (2018), Multiscale understanding of tricalcium silicate hydration reactions, *Sci. Rep.* **8**, 8544.
- Cuesta, A., et al. (2021), Local structure and Ca/Si ratio in C-S-H gels from hydration of blends of tricalcium silicate and silica fume, *Cem. Concr. Res.* **143**, 106405.