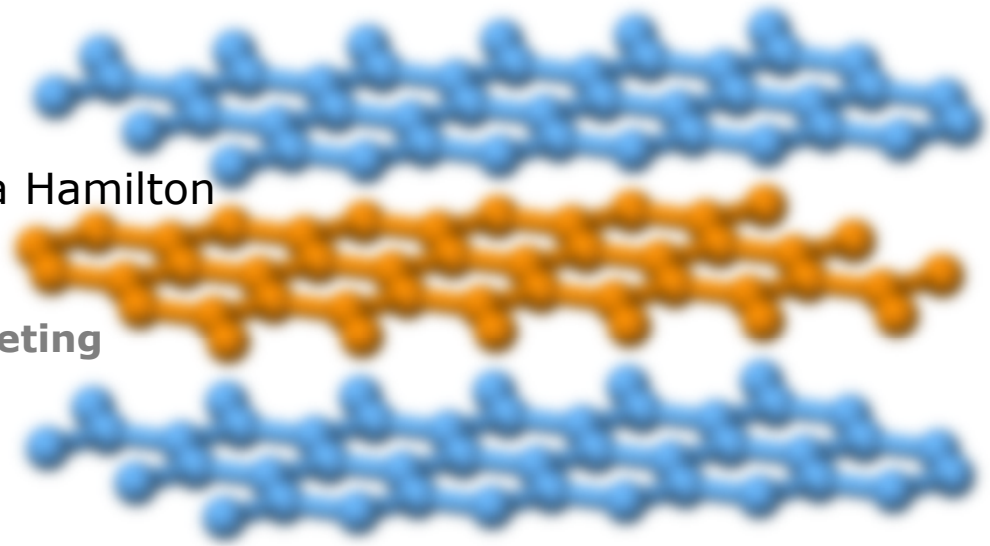
Novel Nanoparticle Cement

for crack sealing and water transport:

from structural study to lab-scale application



Riccardo Maddalena, Dr Andrea Hamilton
University of Strathclyde, UK

Theme 4 – Structural Integrity Meeting
23rd November 2015
Glasgow UK

University of Strathclyde Engineering

INTRODUCTION

NANOPARTICLE CEMENT

C-S-H STRUCTURAL STUDY

RADIONUCLIDE IMMOBILIZATION

LOW PRESSURE NANOSILICA INJECTION

FUTURE WORK

DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority

Introduction

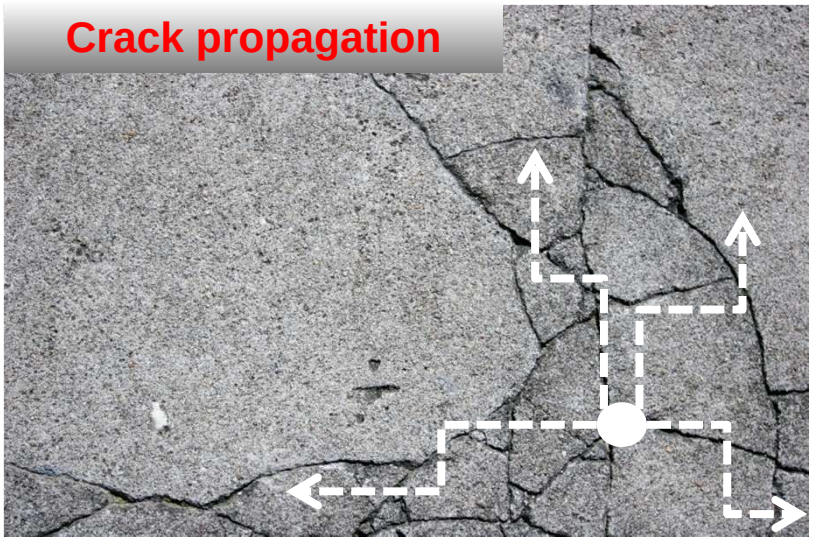
Deterioration of concrete and its durability has been the main concern in the last decades

[J. Collins 2010 - www.bridgehunter.com]

[Engineering and Technical Consultants, 2010]

Introduction

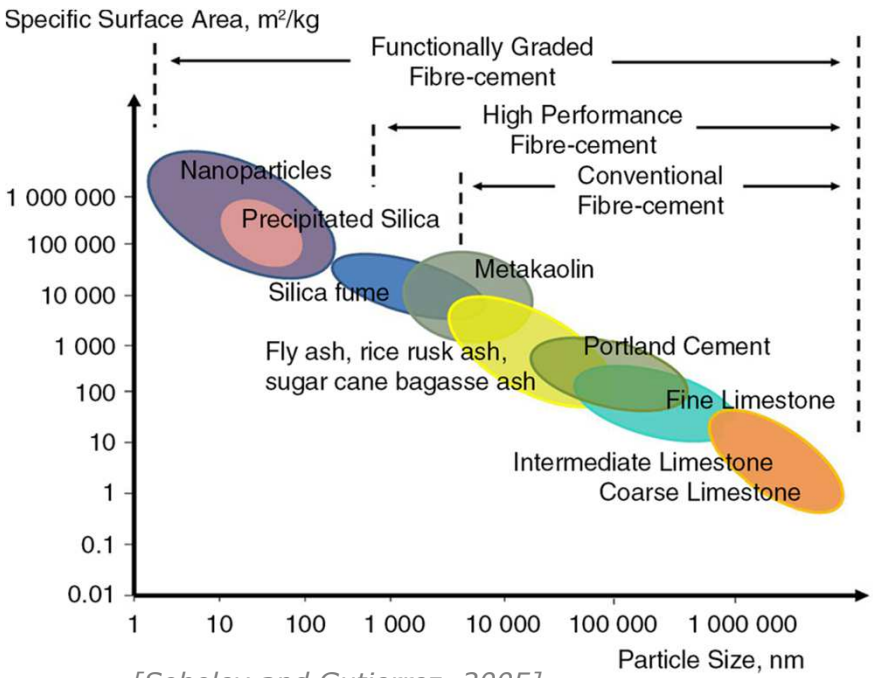
- Chemical attack due to chlorides or other corrosive compounds
- Freeze and thaw cycles exposition
- Erosion due to saline environment
- High moisture transport through concrete elements



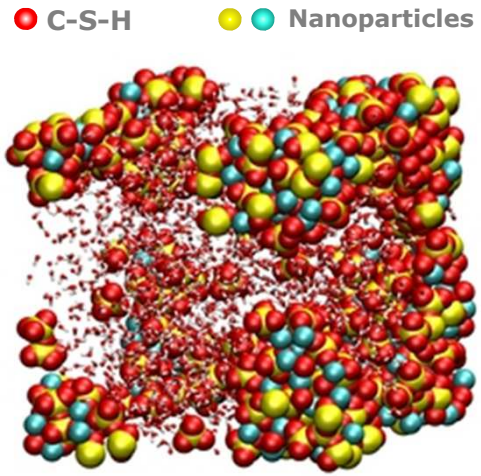
The main effect is the formation of nano-micro-macro-**dangerous** cracks. Those can in turn involve several reactions, increasing the moisture content, air entrainment, contamination flux and compromise the safety, standard conformity and workability of the concrete structures.

Nanoparticle cement

Nanoparticle materials have been studied in concrete science: they act as a *filler*, reducing the water penetration content (or other potential contaminants), improving compressive strength, and enhancing the long term durability of concrete.

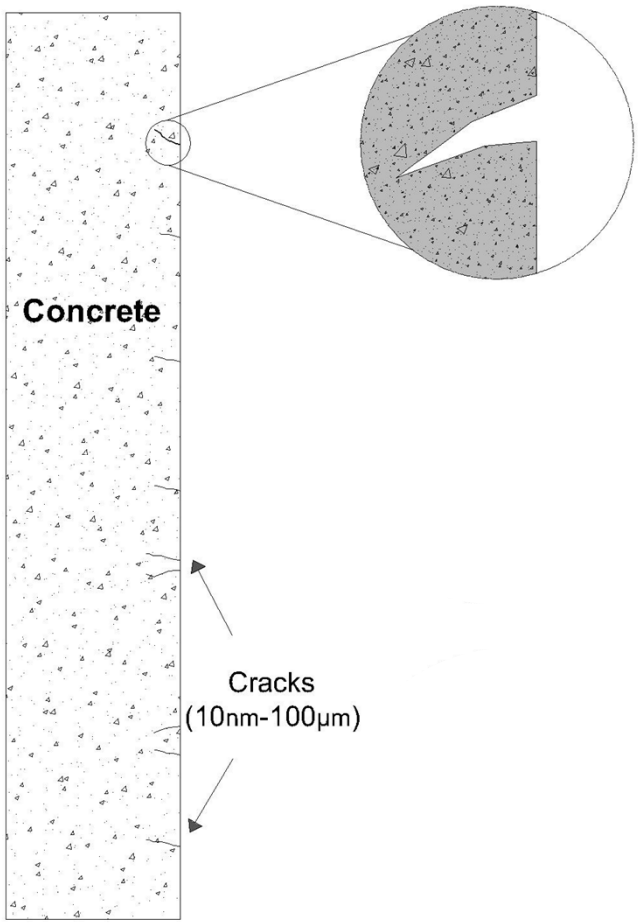


[Sobolev and Gutierrez, 2005]

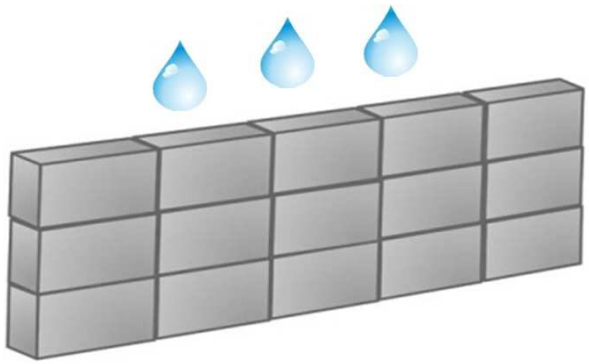


[Griebel, Bonn University, 2010]

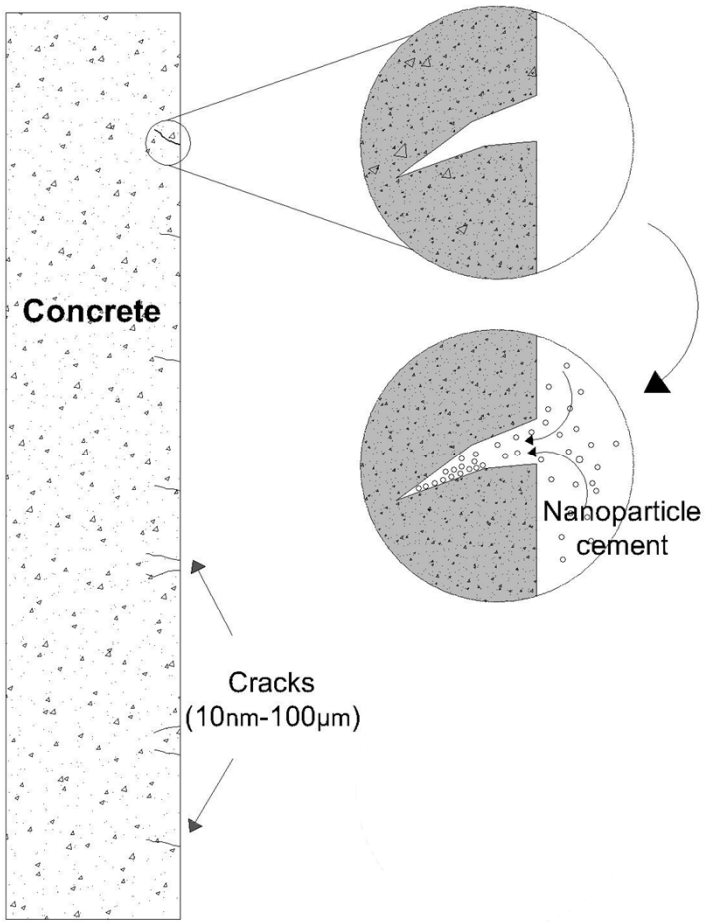
Nanoparticle cement



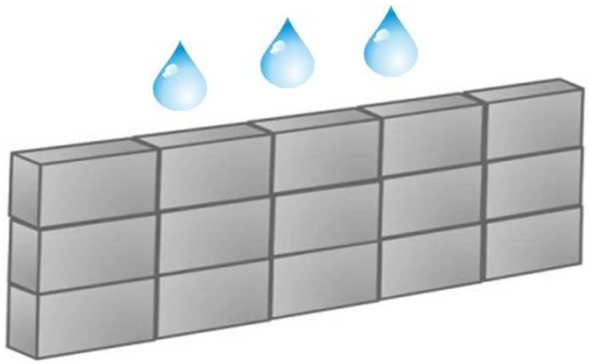
Aim of the project is to investigate new cement mixtures able to seal nano-cracks, preventing deterioration and giving and adequate (controlled) impermeability to existing concrete structures.



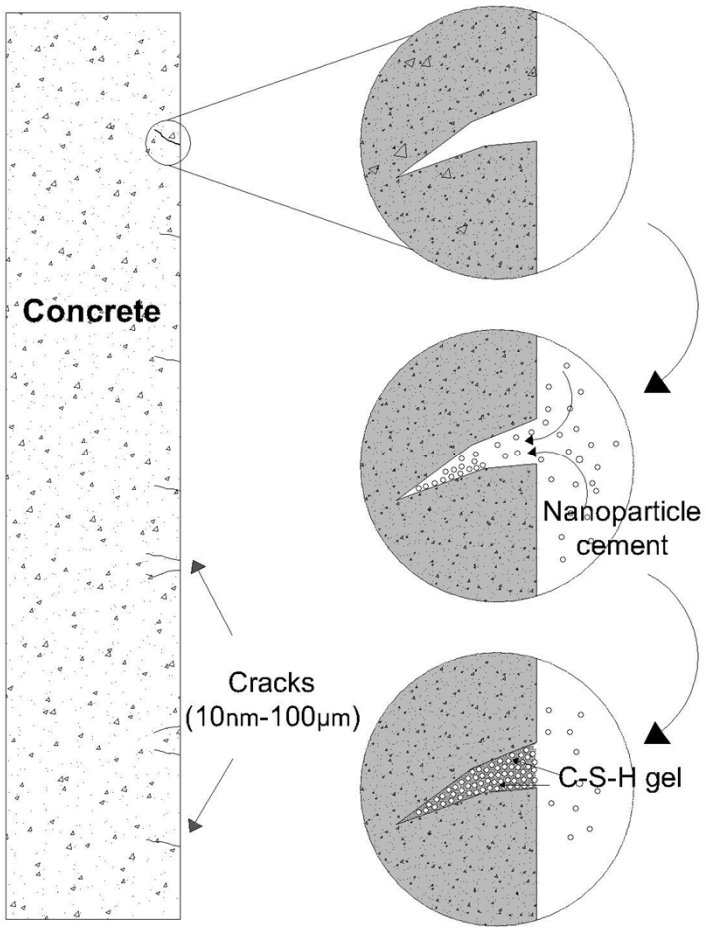
Nanoparticle cement



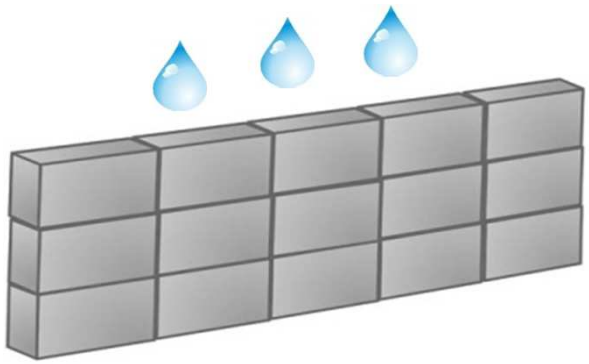
Aim of the project is to investigate new cement mixtures able to seal nano-cracks, preventing deterioration and giving and adequate (controlled) impermeability to existing concrete structures.



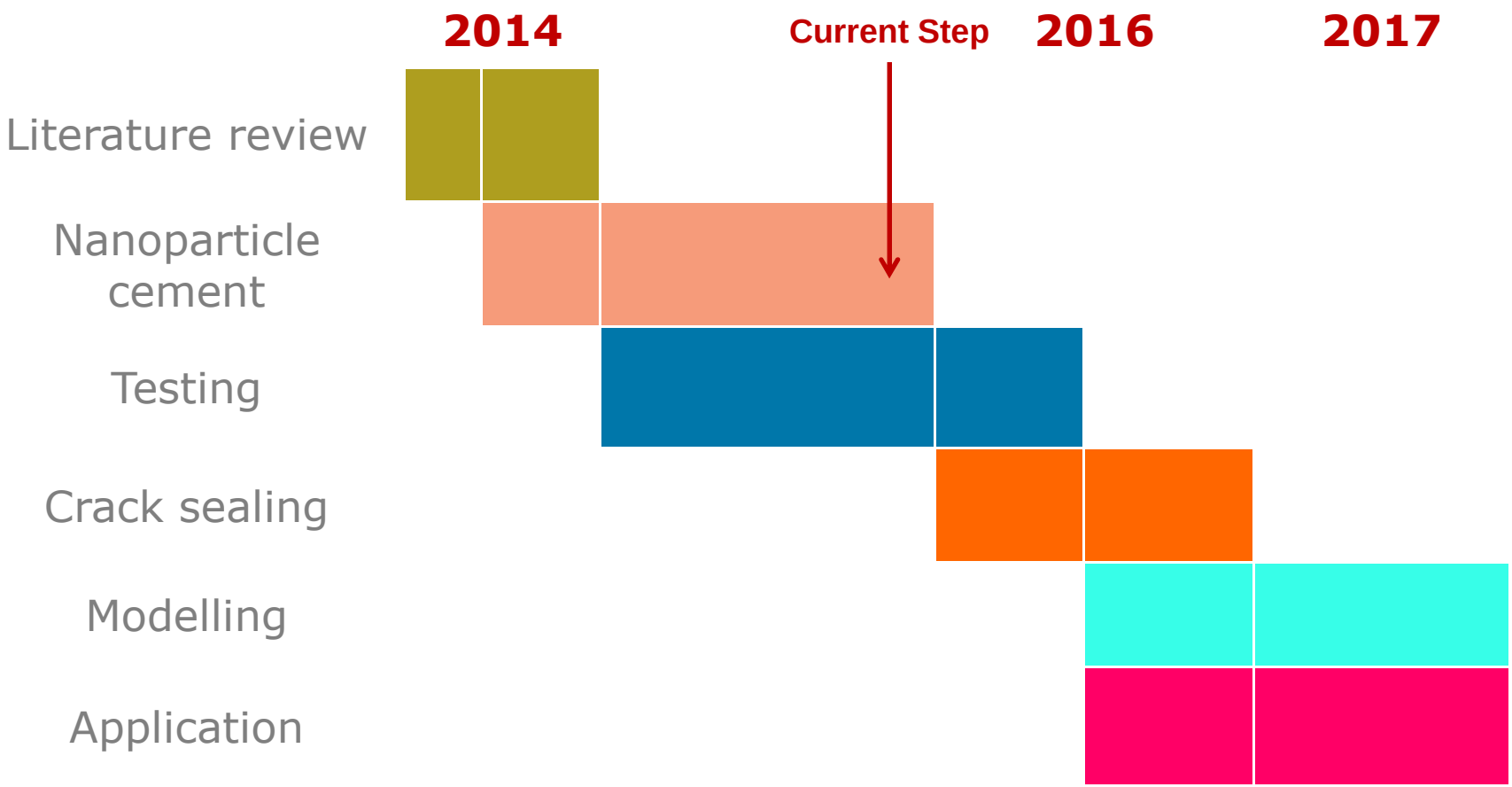
Nanoparticle cement



Aim of the project is to investigate new cement mixtures able to seal nano-cracks, preventing deterioration and giving and adequate (controlled) impermeability to existing concrete structures.

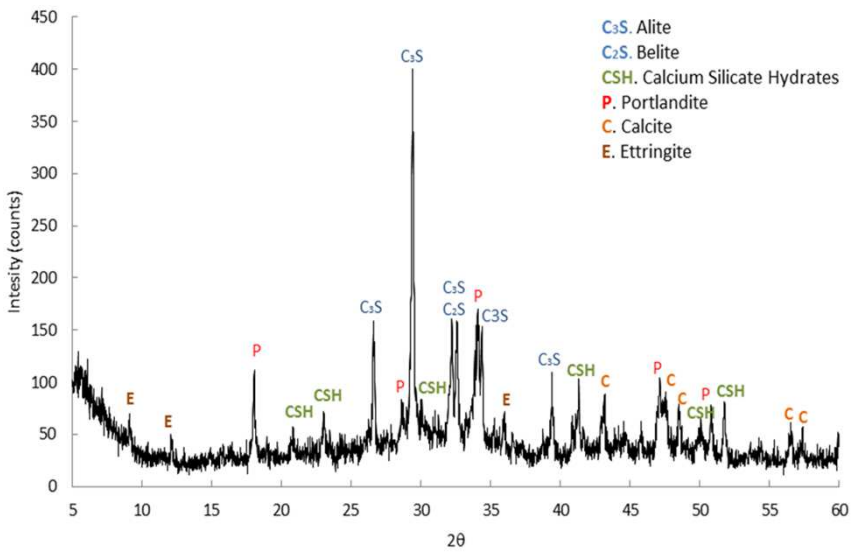


GANTT Chart


2014
Current Step
2016
2017
Literature review
Nanoparticle cement
Testing
Crack sealing
Modelling
Application

Calcium Silicate Hydrate

Calcium-silicate-hydrate (C-S-H) is one of the main results of Portland clinker hydration. It forms by chemical reaction between water and tri- or di-calcium silicate (alite C_3S and belite C_2S respectively), typical clinker minerals.



X-Ray diffraction pattern of 13 days aged Ordinary Portland cement.

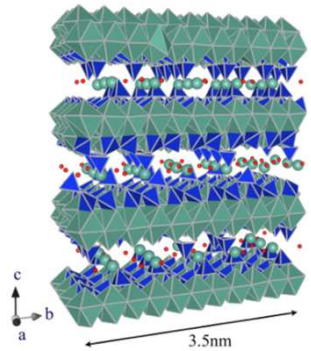
C-S-H is a gel-like mineral phase, which makes up approximately 2/3 of hydrated Portland cement paste.

It is responsible for ***strength and hardening*** in cement paste and concrete.

Calcium Silicate Hydrate

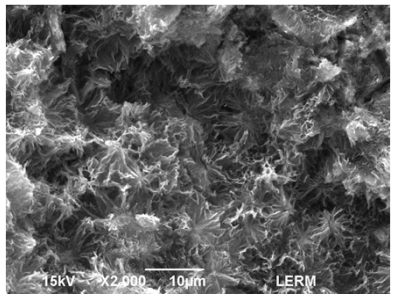
In literature there are 2 main models representing C-S-H structure: tobermorite-like model, C-S-H(I) and jennite-like, C-S-H(II). They have a layered structure based on a calcium sheet flanked on each side by linear silicate tetrahedra chains.

The structure of C-S-H is strongly influenced by the C/S molar ratio and when it varies it may lead to different crystallographic structural models.



Model of 11Å tobermorite-like C-S-H. [Skinner et al., 2010]

Crystalline or amorphous?



C-S-H gel in Portland cement. [Lerm, 2014]

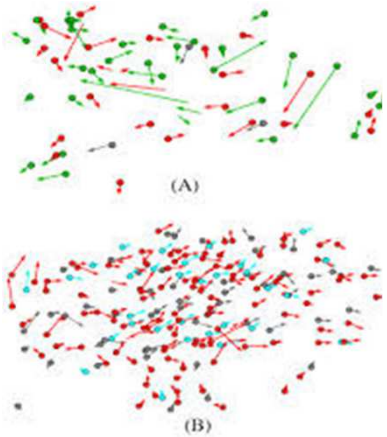
C-S-H may be considered gel-like but it is not amorphous: it has a proper pattern, showing rather broad peaks. More accurately it is a semi-crystalline phase.

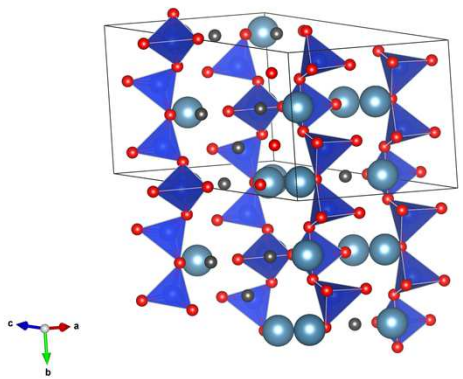
Defining its morphologic and crystallographic "identity" has been object of research in the last 50 years.

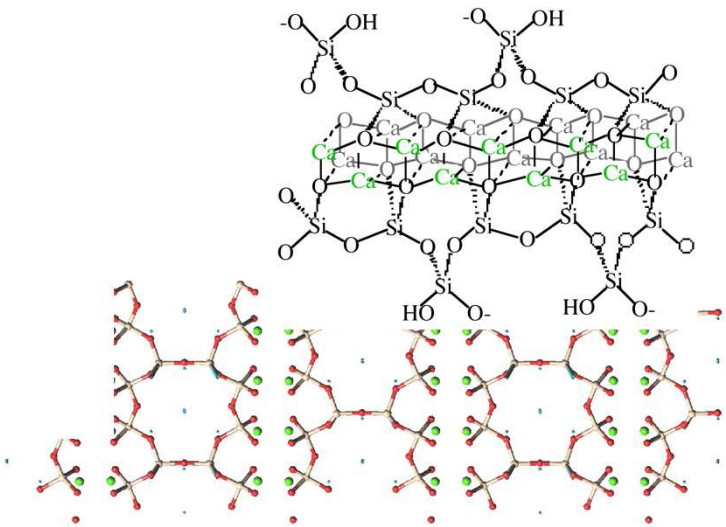
Key Points

University of Strathclyde Engineering

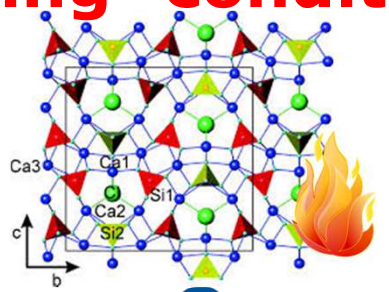
→**C-S-H gel: what is the best structural fit when C/S varies?**







→**C-S-H gel: does drying conditions affect the crystallinity?**



DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority

C-S-H synthesis

Synthetic C-S-H was made using two different calcium sources: calcium hydroxide **CH**, reagent grade and calcium oxide **C**, obtained by calcination of calcium carbonate, reagent grade. Two different silica particle sizes were used: silica fume **SF** (0.15 - 0.30 μm) and nanosilica **NS** (5 – 35 nm). Decarbonated water was used in the mixes.

C-S-H paste was manually mixed and cast in cubic moulds. After 24 hours specimens were demoulded and placed in a sealed environment to prevent **carbonation**.

Sample mix	CH	SF	NS	Target ratio
	wt %	wt %	wt %	
CH System				C/S
3CH-SF	75	25	-	>1
1CH-SF	50	50	-	0.81
3CH-NS	75	-	25	>1
1CH-NS	50	-	50	0.81
CO System				C/S
1CO-SF	50	50	-	1.07
1CO-NS	50	-	50	1.07

N_2-drying

After 28 days of curing at 21 °C and RH 100%, specimens were placed in an acetone bath for 24 hours and then dried under a constant nitrogen flow for additional 24 hours. Samples so prepared were identified as N_2.

Oven-drying

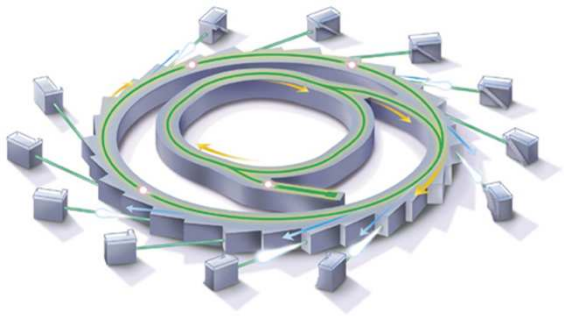
In order to study the effect of low temperature oven-drying, N_2 samples were further dried in oven at 60 °C until a stable weight was reached.

C-S-H Characterization

University of Strathclyde Engineering

Synchrotron X-Ray Diffraction

Monochromatic 2D diffraction, λ = 0.15508 Å

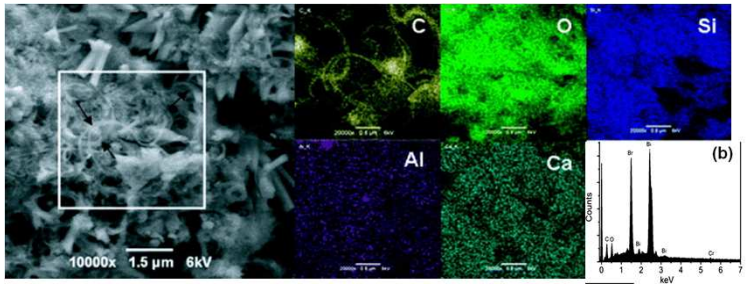


Raman Spectroscopy

100 - 4000 cm^{-1}, 785 nm laser, map size 100 μm grid

Scanning Electron Microscopy

FE-SEM, 20.0 kV and EDX mapping



DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

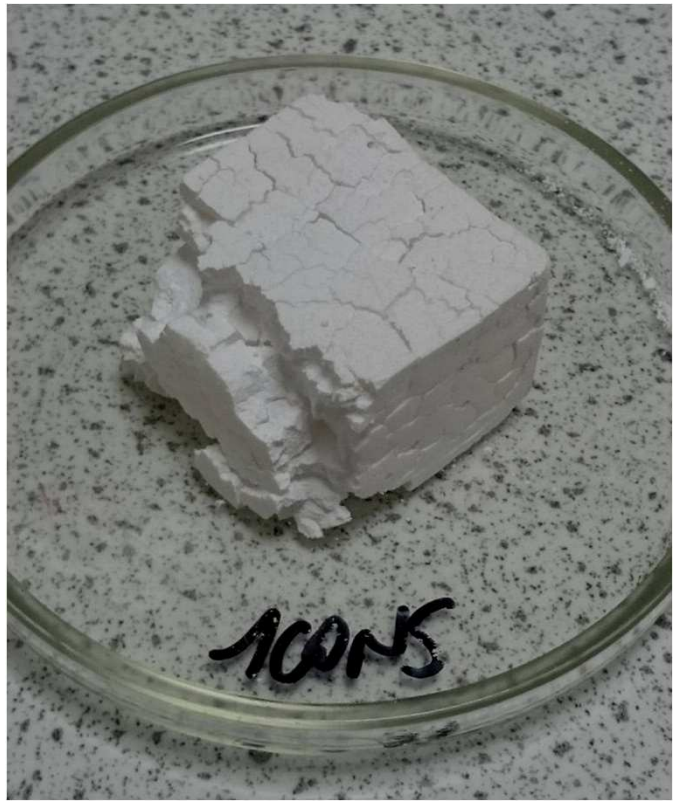
Sellafield Ltd

NDA Nuclear Decommissioning Authority

Calcium Silicate Hydrate

N_2-dried samples show some compressive strength (~ 7 MPa), while oven-dried samples are fragile, brittle and fully cracked.

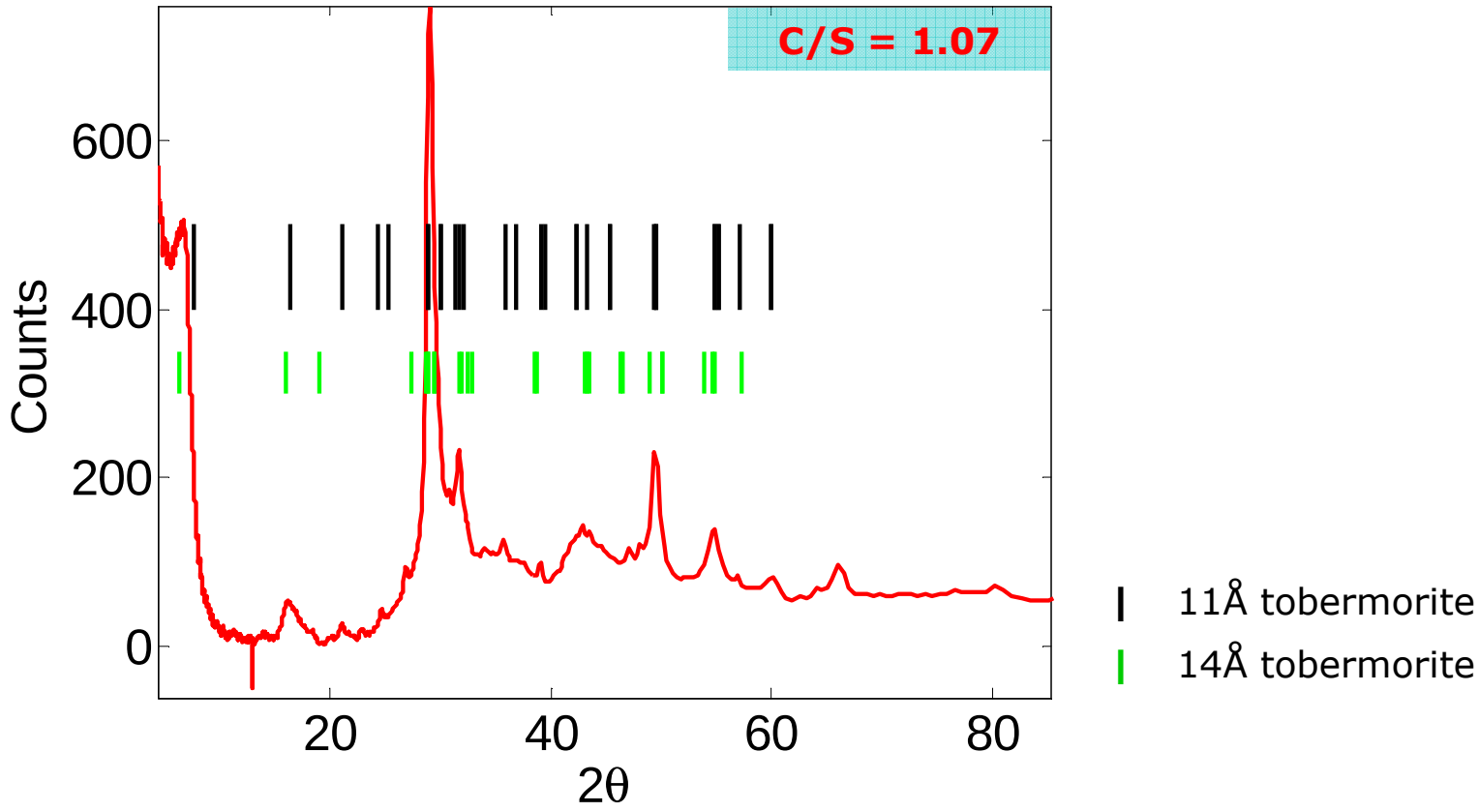
after
oven-drying
60°C
24 hours



1CO-NS sample oven-dried at 60 °C.

Results

Synchrotron X-ray diffraction

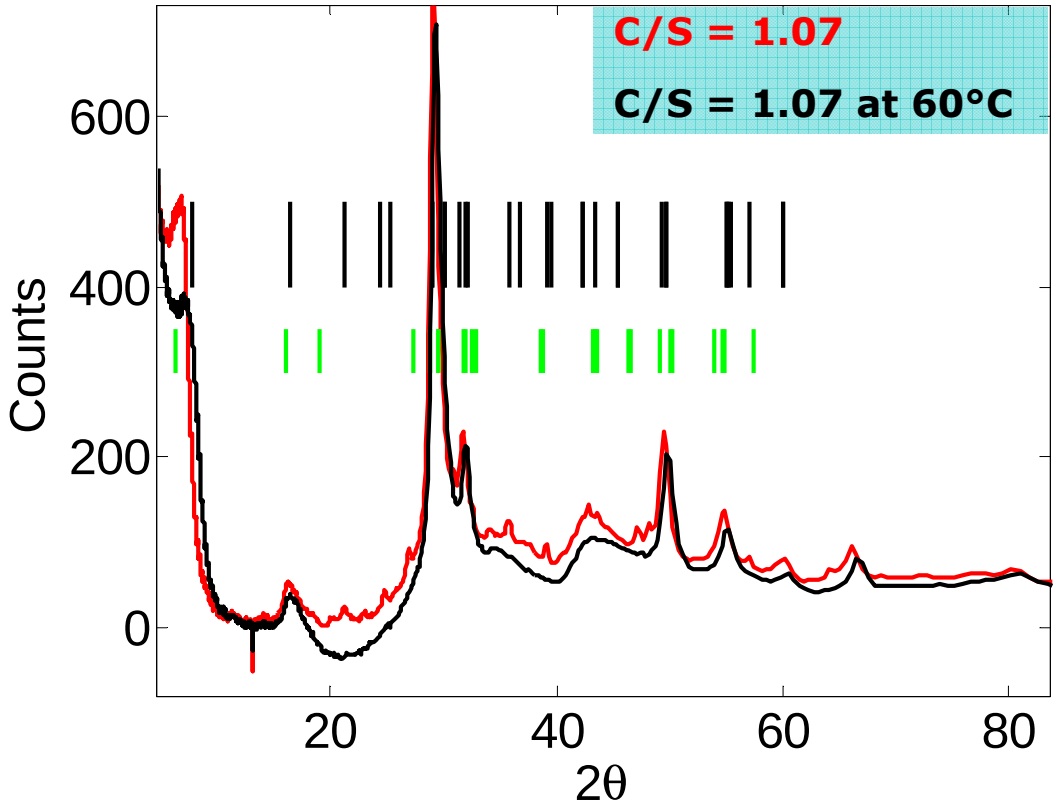


Pattern shows broad peaks associated with **nanocrystallinity** and turbostratic stacking disorder.

Structure includes elements of both 11A and 14A tobermorite.

Results

Synchrotron X-ray diffraction



Heating gently to 60 °C for 24 hours (black) produces loss of crystallinity

| 11Å tobermorite

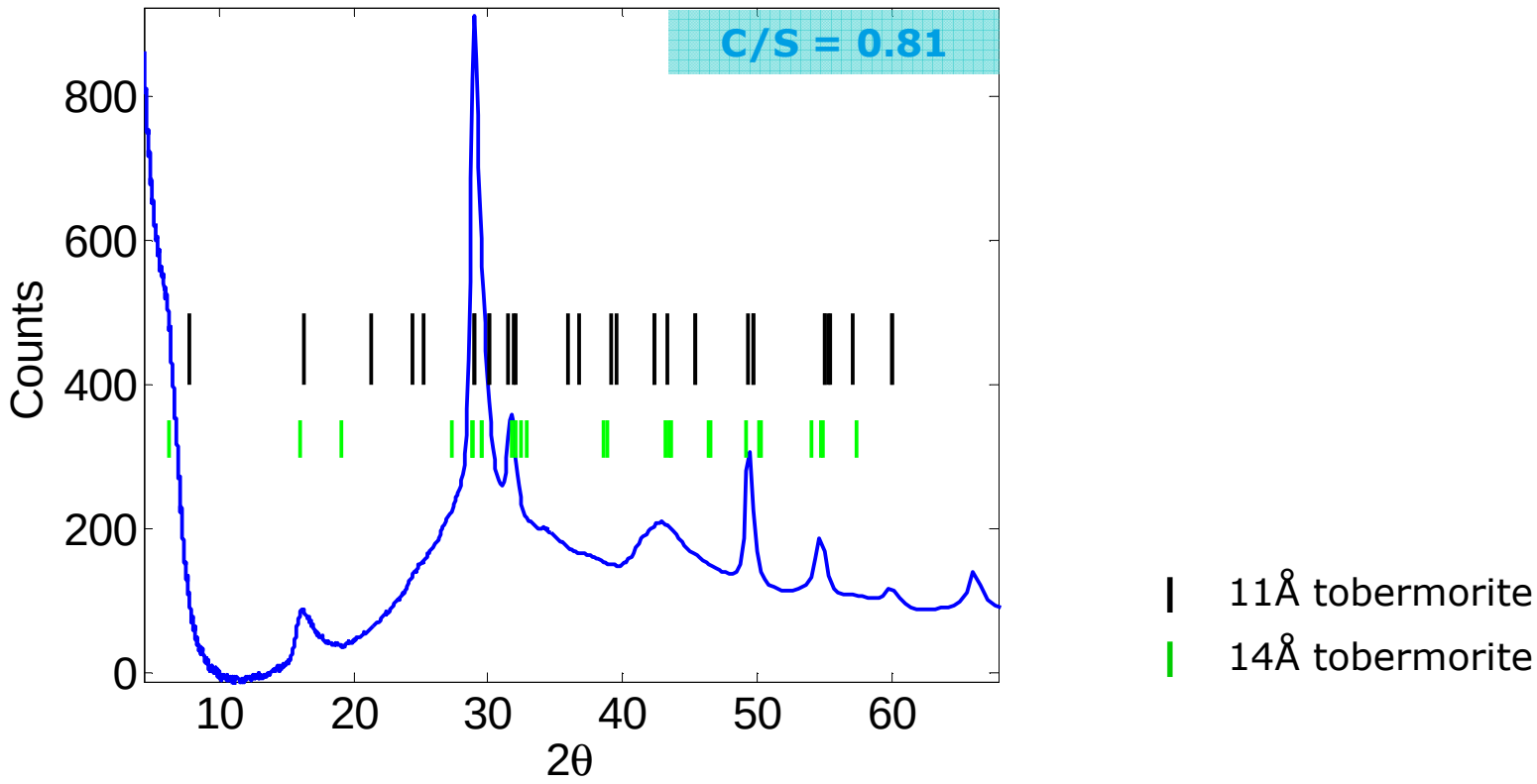
| 14Å tobermorite

Tobermorite [0, 0, 2] moves from 13Å to 11.9Å from dehydroxylation of interlayer spacing.

Strongest reflection [0, 2, 0]/[2, -2, 0] shrinks by 1.6%.

Results

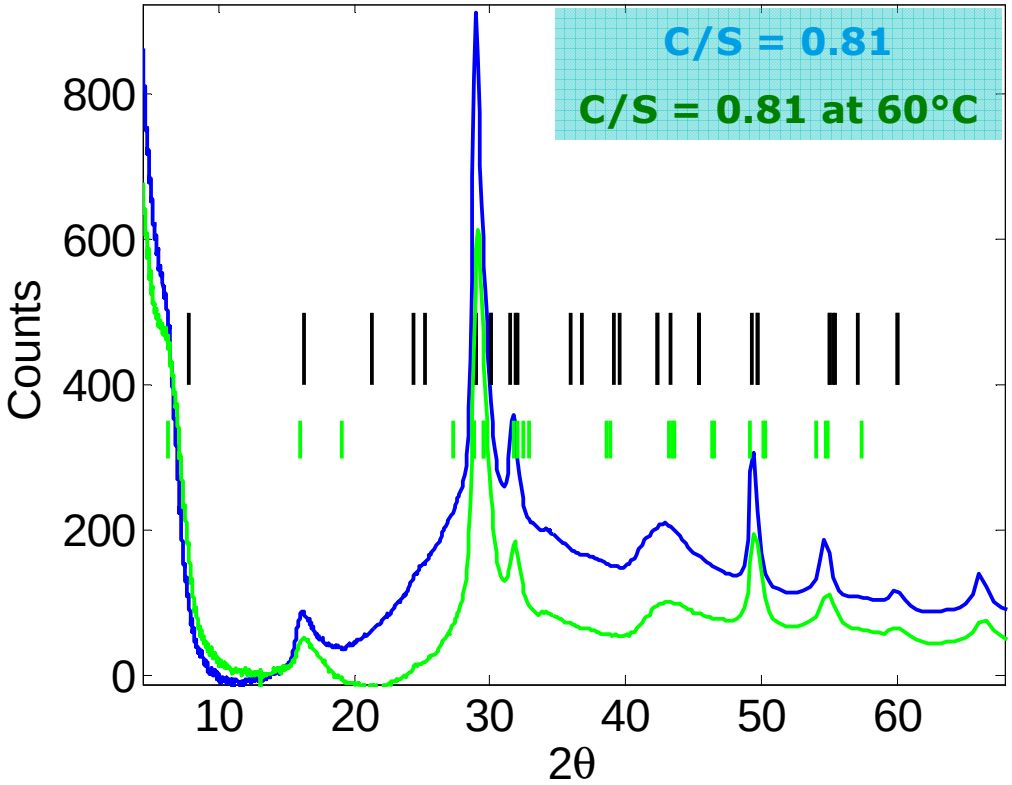
Synchrotron X-ray diffraction



Pattern shows better fit to 14Å tobermorite than the C/S = 1.07 and significantly <u>less crystallinity</u>.

Results

Synchrotron X-ray diffraction



| 11Å tobermorite

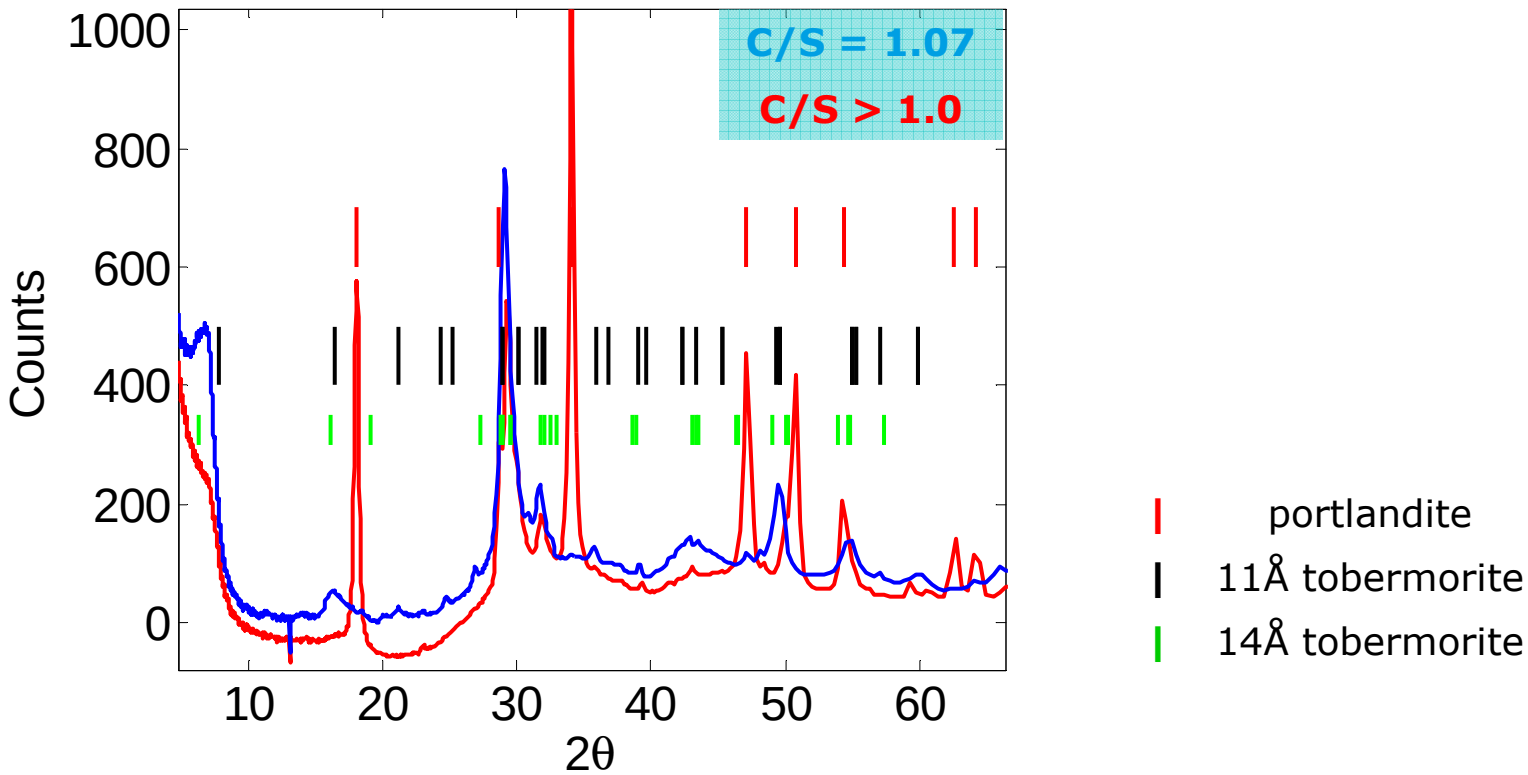
| 14Å tobermorite

→ Heating shows a basal spacing [0, 0, 2] collapse of 14Å to 13.3Å from dehydroxylation.

→ Markedly less than collapse of C/S = 1.07 but basal spacing is much broader and less defined.

Results

Synchrotron X-ray diffraction



A clear shift of the main peak (at around 29 °2Θ) is observed. It is attributed to shrinkage in the crystallographic ***b***-direction from omission of bridging tetrahedra.

According to Garbev et al., the shift is correlated to the C/S ratio.

Results

Synchrotron X-ray diffraction

SAMPLE	Peak [°θ]	d-spacing [Å]	C/S ratio
3CH-NS	29.30	**3.046**	> 1.0
1CO-NS	29.11	**3.065**	1.07
1CH-NS	28.98	**3.079**	0.81
3CH-NS (60°C)	29.35	**3.041**	-
1CO-NS (60°C)	29.28	**3.047**	-
1CH-NS (60°C)	29.09	**3.067**	-

Garbev et al. (*) found that d-spacing values decrease when C/S increases. Here d-spacing values are also inversely proportional to the C/S ratio.

** Garbev et al., - J. Am. Ceram. Soc., 91 [9] 3005–3014 (2008).*

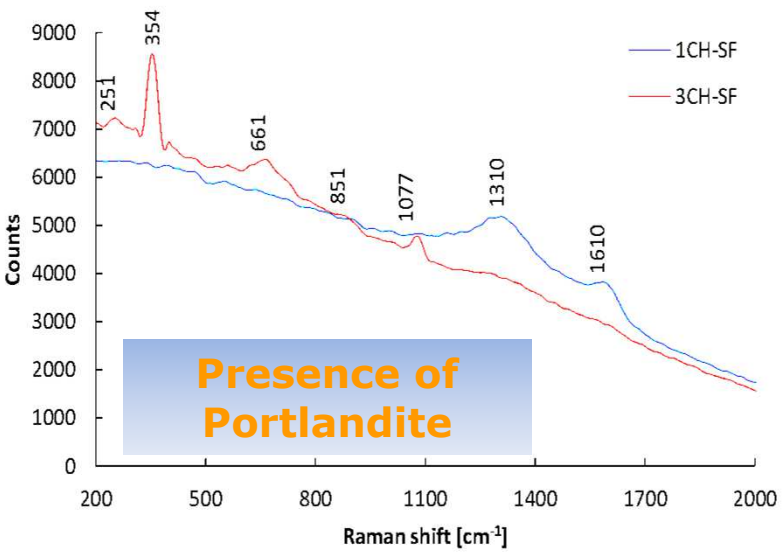
Basal spacing [0 0 2] increases in 2Θ angle on heating (decrease in d-spacing) showing dehydroxylation of interlayer OH^- and resulting shrinkage. Basal spacing very weak for 3CH-NS and *hard to see*.

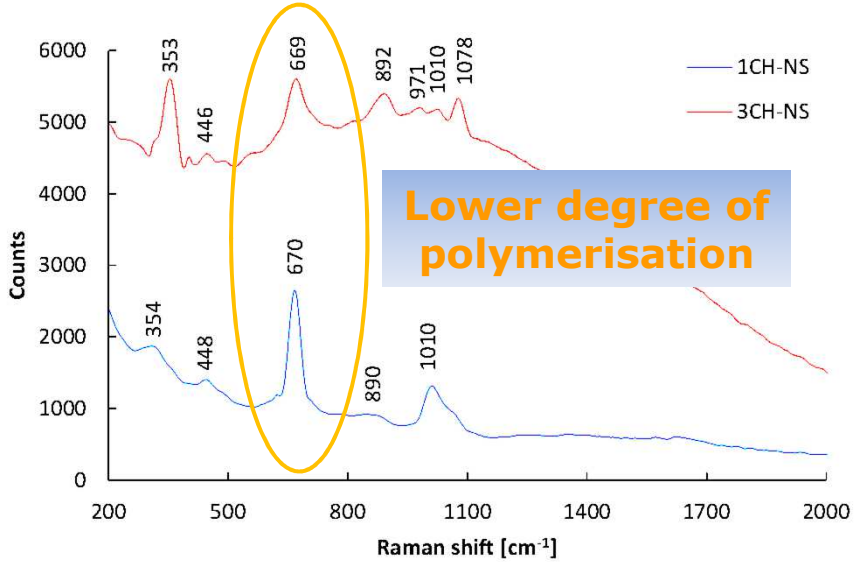
SAMPLE	d-spacing shift on heating
1CO-NS	**13 Å ⟶ 11.9 Å**
1CH-NS	**14 Å ⟶ 13.3 Å**

Results

Raman Spectroscopy

Influence of C/S ratio and silica particle size



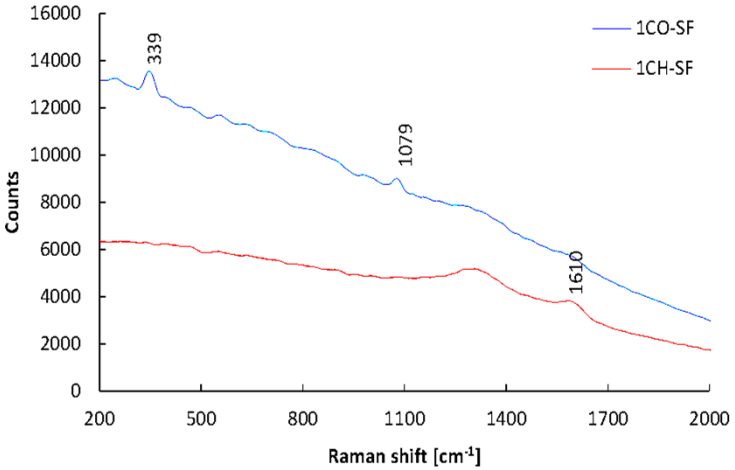


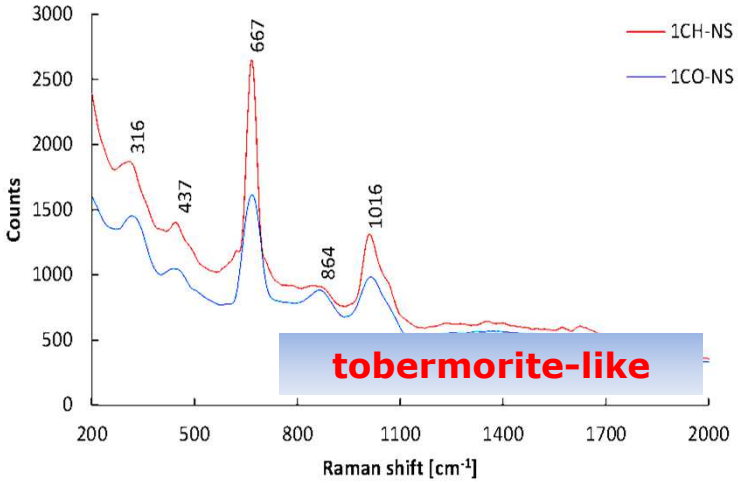
BAND [cm^{-1}]	DESCRIPTION	BAND [cm^{-1}]	DESCRIPTION
200 - 325	Ca-O lattice vibration	850 - 1015	Si-O-Si symmetric stretching
325 - 380	Ca-O lattice vibration in C-S-H	1070 - 1090	CO_3^- symmetric stretching
440 - 480	Internal deformation of SiO_4^- tetrahedra	~ 1600	O-H bending of H_2O
660 - 670	Si-O-Si symmetric bending	~ 3300	O-H stretching of H_2O

Results

Raman Spectroscopy

Comparison between **calcium hydroxide** and **calcium oxide** system



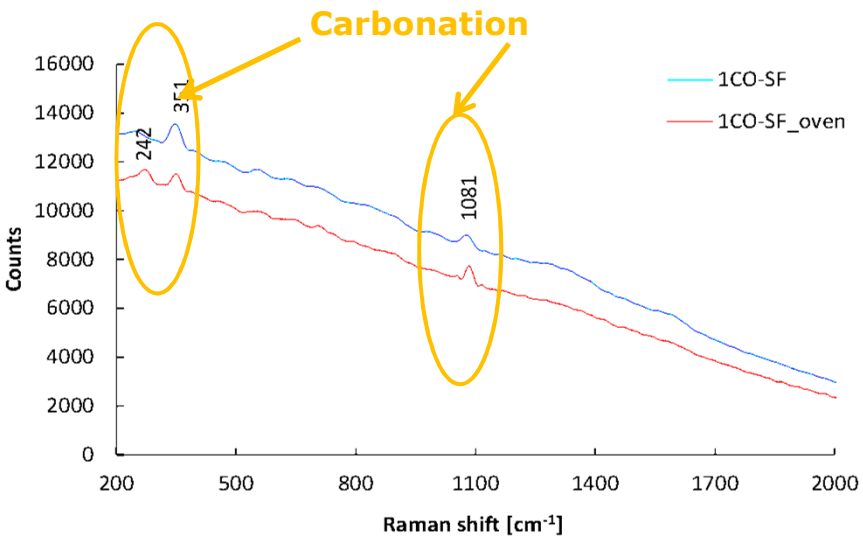


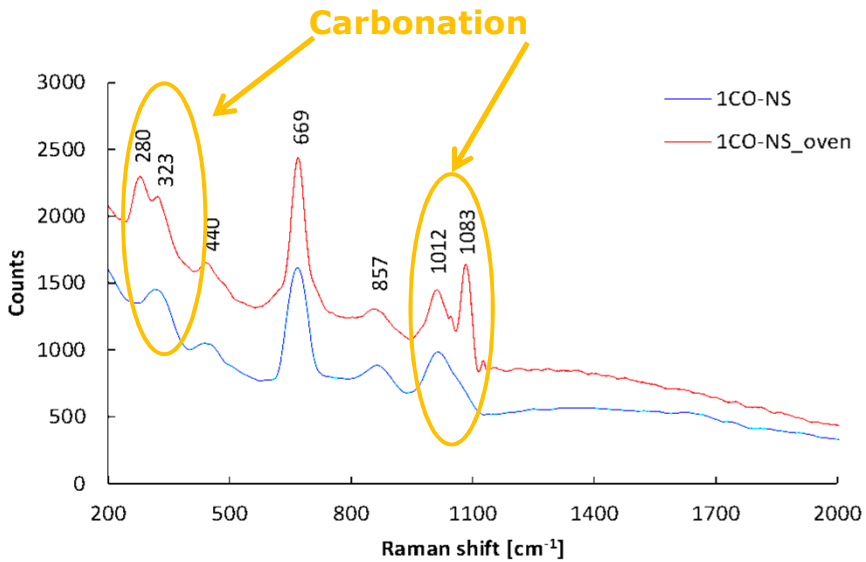
BAND [cm^{-1}]	DESCRIPTION	BAND [cm^{-1}]	DESCRIPTION
200 - 325	Ca-O lattice vibration	850 - 1015	Si-O-Si symmetric stretching
325 - 380	Ca-O lattice vibration in C-S-H	1070 - 1090	CO_3^- symmetric stretching
440 - 480	Internal deformation of SiO_4^- tetrahedra	~ 1600	O-H bending of H_2O
660 - 670	Si-O-Si symmetric bending	~ 3300	O-H stretching of H_2O

Results

Raman Spectroscopy

Comparison between **N_2**-dried and **oven**-dried samples



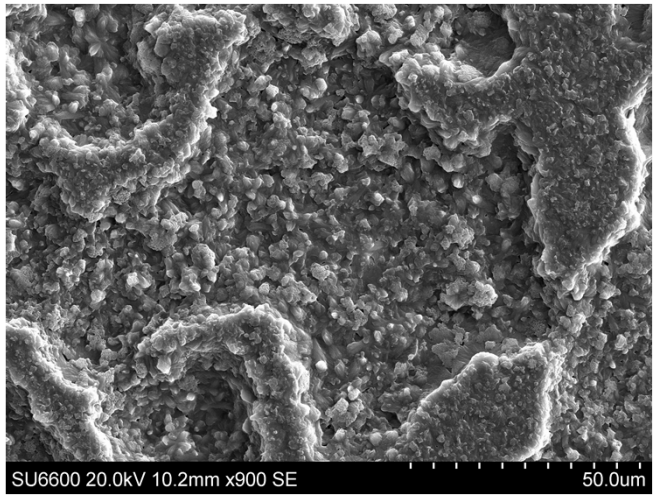


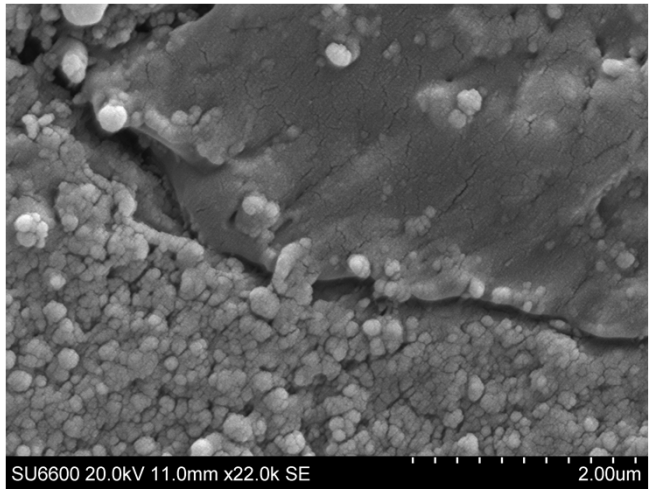
BAND [cm^{-1}]	DESCRIPTION	BAND [cm^{-1}]	DESCRIPTION
200 - 325	Ca-O lattice vibration	850 - 1015	Si-O-Si symmetric stretching
325 - 380	Ca-O lattice vibration in C-S-H	1070 - 1090	CO_3^- symmetric stretching
440 - 480	Internal deformation of SiO_4^- tetrahedra	~ 1600	O-H bending of H_2O
660 - 670	Si-O-Si symmetric bending	~ 3300	O-H stretching of H_2O

Results

FE-SEM imaging and mapping

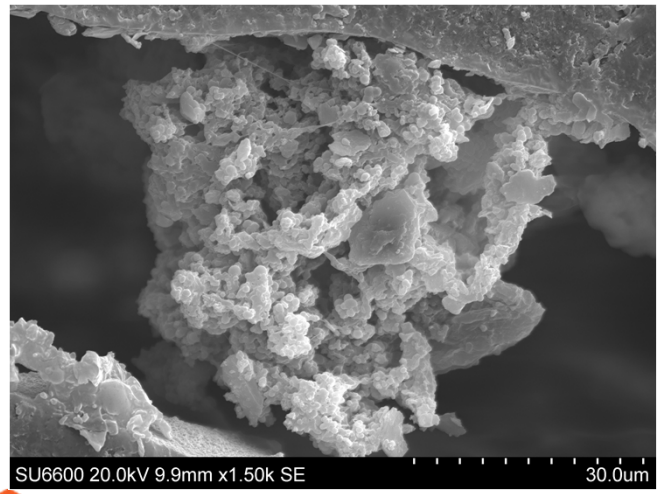
C-S-H synthesized by mixing calcium hydroxide and silica fume or nanosilica

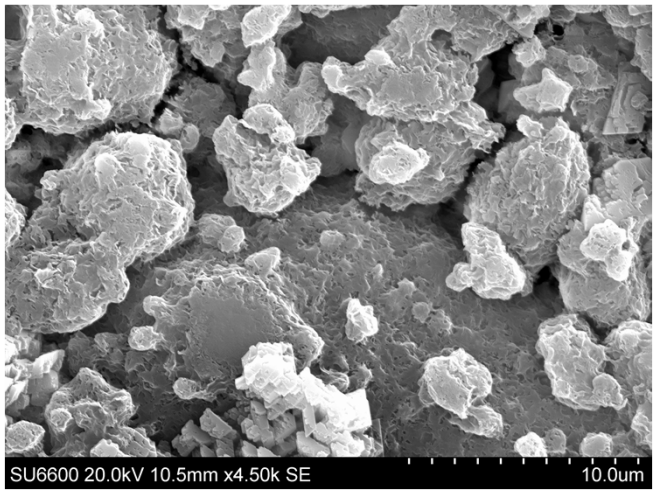




1CH-SF

Gel-like structure





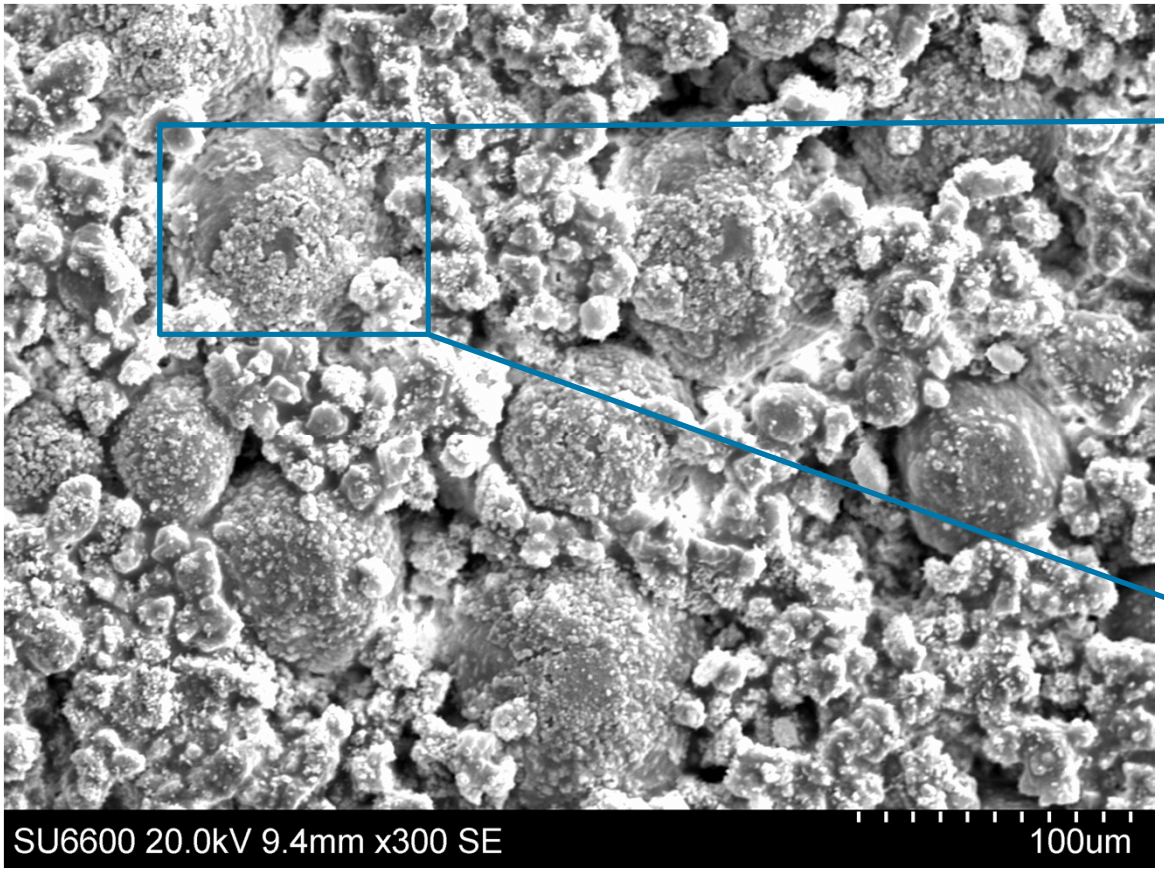
1CH-NS

plate-like structure

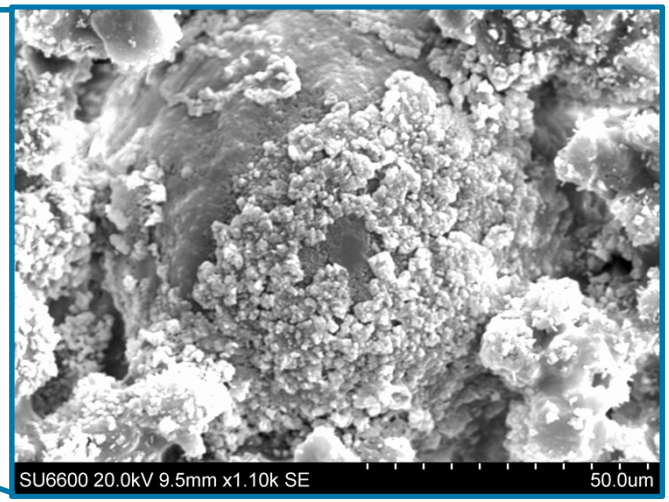
Results

FE-SEM imaging and mapping

C-S-H synthesized by mixing calcium oxide with silica fume



1CO-SF

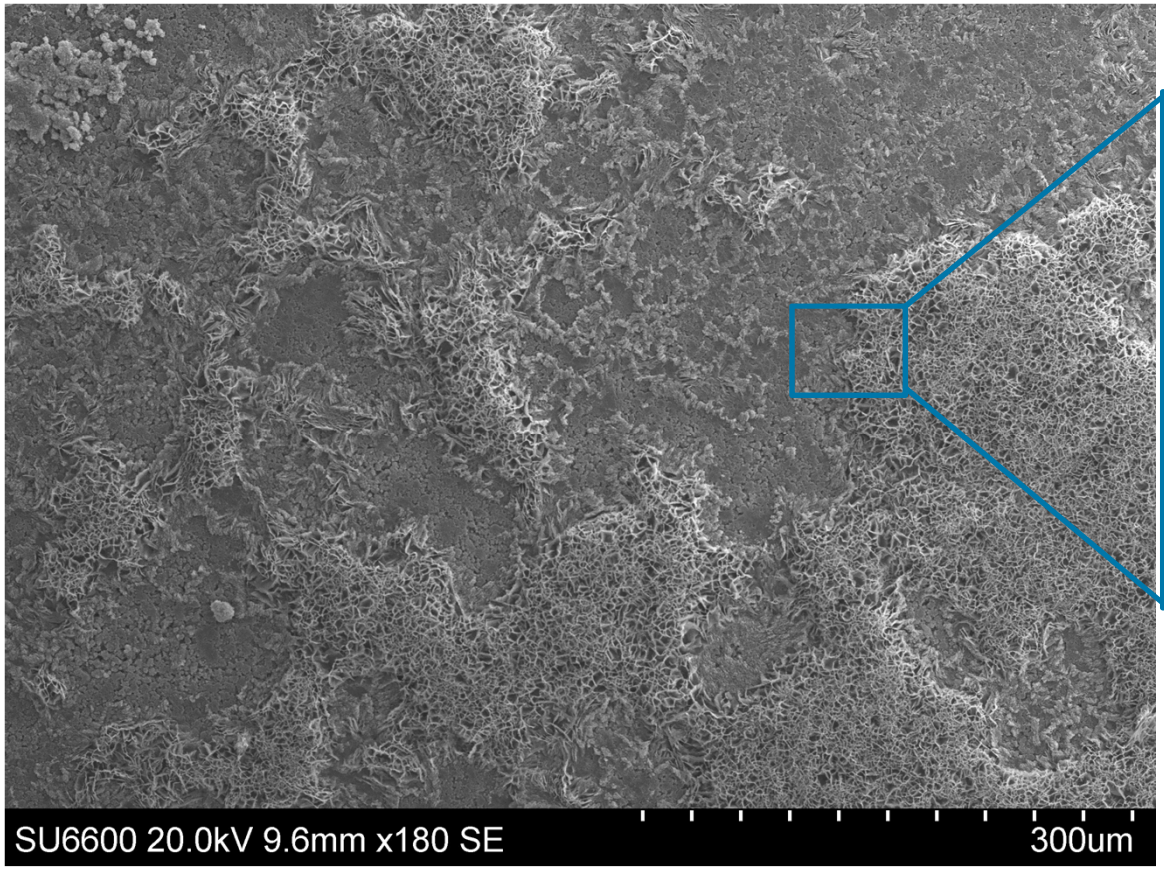


C-S-H formed as agglomerates around the surface of silica particles

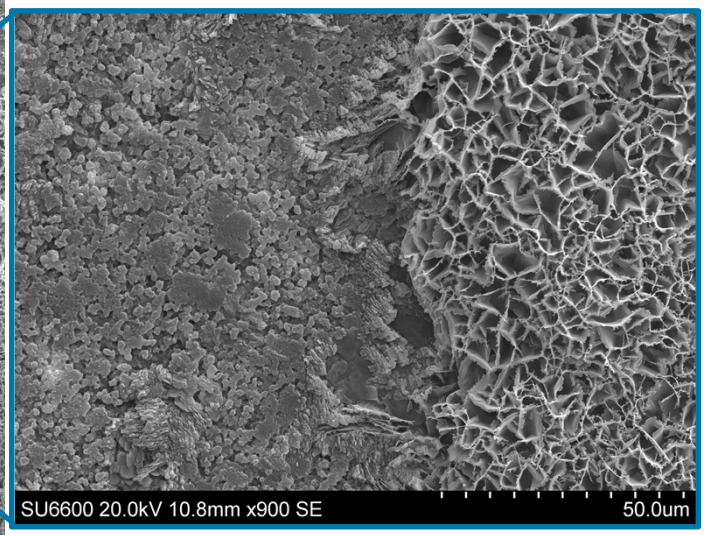
Results

FE-SEM imaging and mapping

C-S-H synthesized by mixing calcium oxide with nanosilica



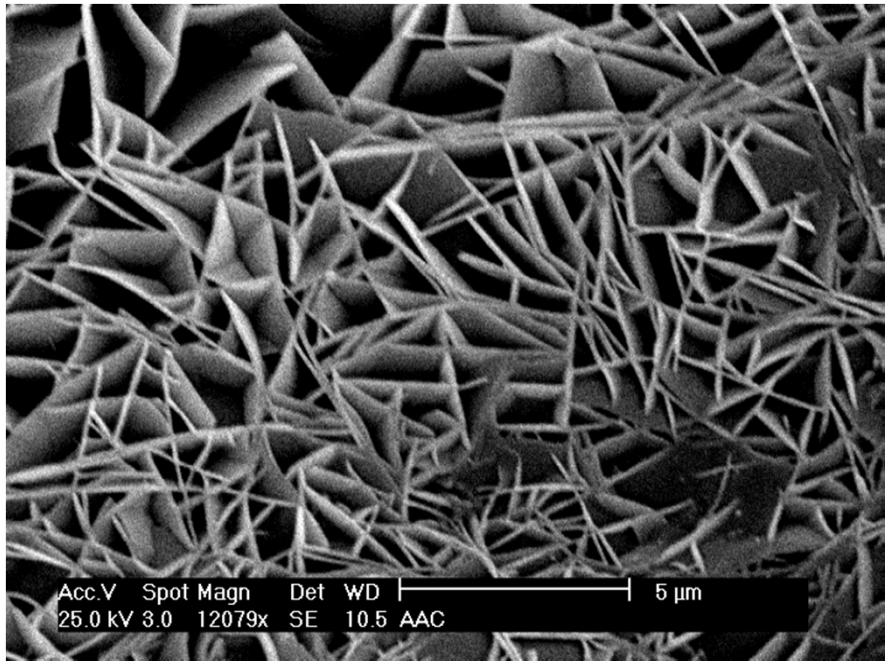
1CO-NS



C-S-H formed with a disordered plate-like structure

Results

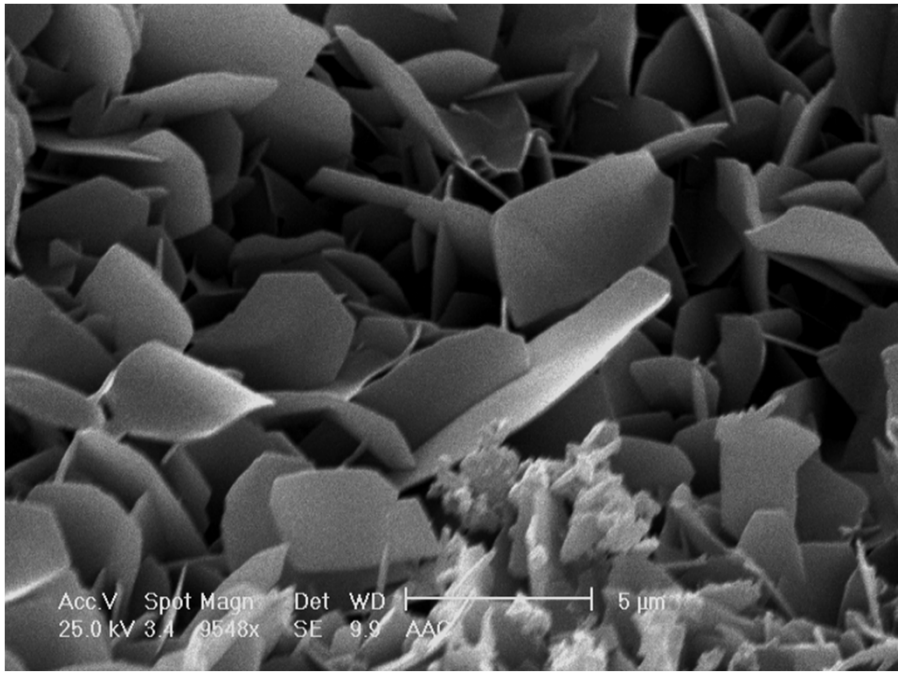
FE-SEM imaging and mapping



Plate/lamellar-like structure

EDX-SEM of pure Tobermorite

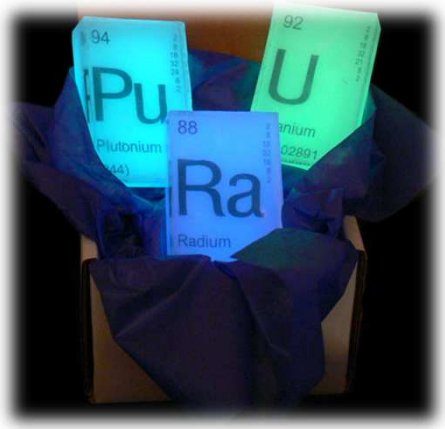
(A. Hamilton 2004)



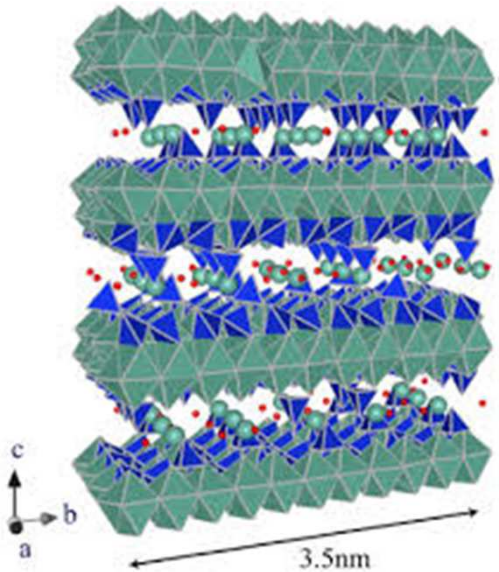
Radionuclide immobilization

University of Strathclyde Engineering

From previous morphological investigation, C-S-H crystal structural can be altered varying its C/S ratio or synthesis conditions, in order to "**house**" other atoms in its interlayer spacing.



Radionuclides



C-S-H

DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority

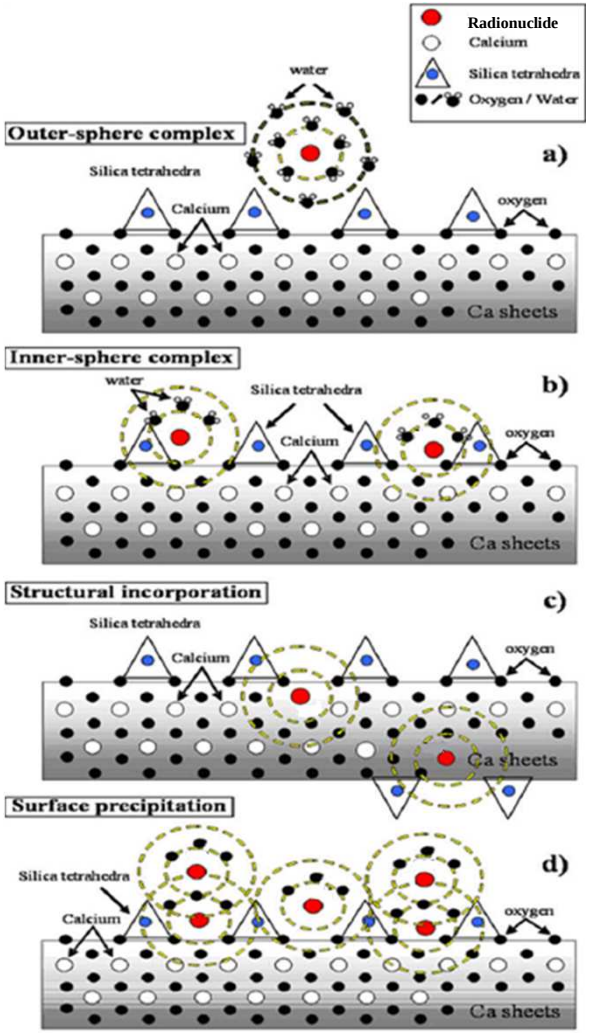
Radionuclide immobilization

University of Strathclyde Engineering

Interaction mechanism of radionuclides with C-S-H phases

There are three main possible reactions that lead to the immobilisation of radionuclides into the C-S-H structure:

1. complex formation reactions:
   a) outer sphere or b) inner sphere;
2. sorption, ion exchange mechanisms:
   c) structural incorporation;
3. surface precipitation:
   d) co-precipitation.



[Mandaliev et al., 2010]

DISTINCTIVE

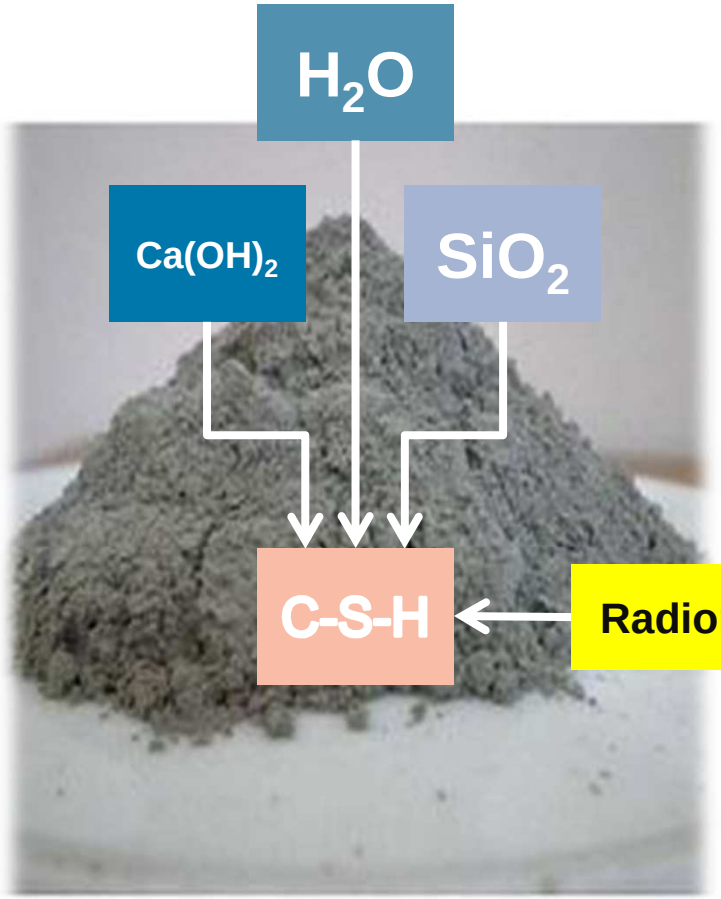
NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority

Radionuclide immobilization

University of Strathclyde Engineering

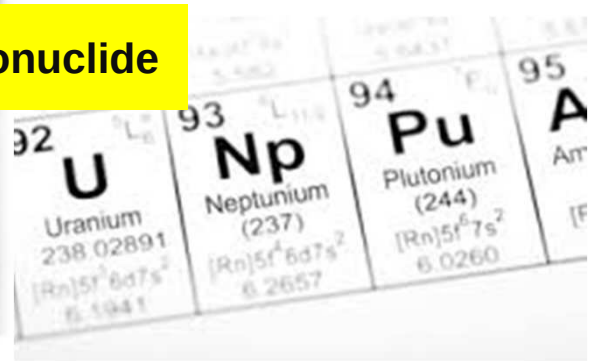


Different radionuclides are investigated:

^{3}H ^{90}Sr ^{99}Tc ^{137}Cs ^{239}Pu ^{232}Th

1. Synthesis and formation of C-S-H phase in presence of radionuclides.

2. Sorption of radionuclides into C-S-H phases with time.



DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

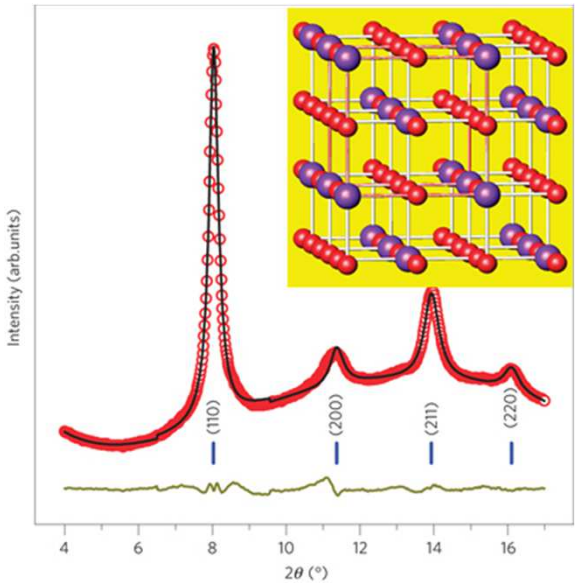
Sellafield Ltd

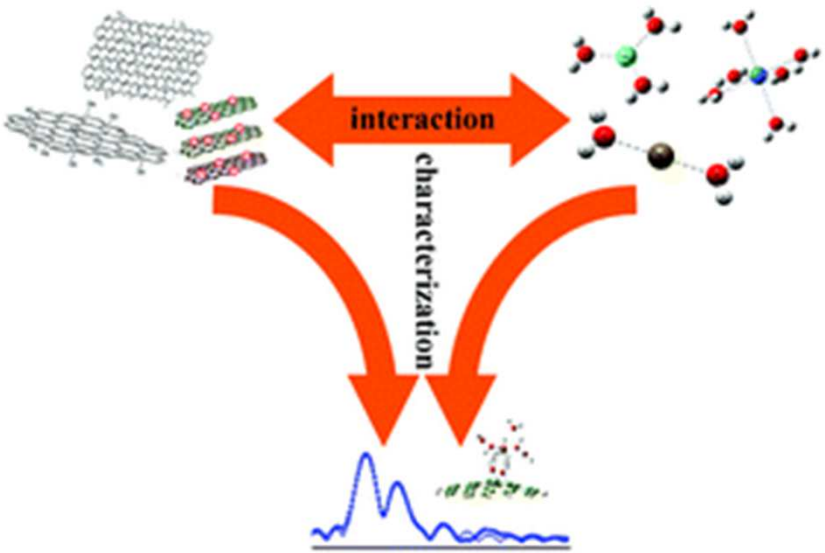
NDA Nuclear Decommissioning Authority

Radionuclide immobilization

Characterisation of C-S-H paste is the key to fully understand the interaction mechanism of radionuclides with C-S-H phases.

Synchrotron X-Ray Diffraction provides structural information and morphology of C-S-H phases formed in presence of radionuclides.

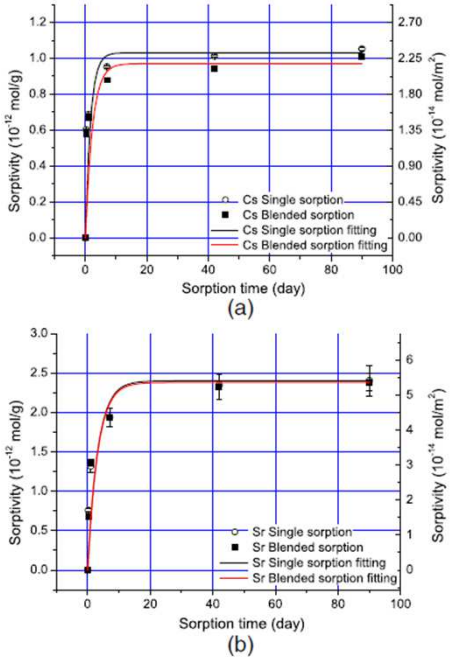




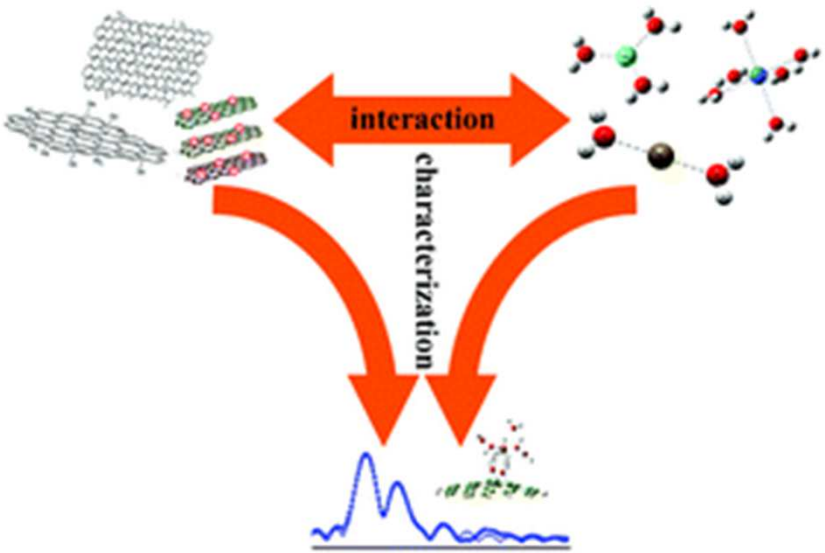
Radionuclide immobilization

Characterisation of C-S-H paste is the key to fully understand the interaction mechanism of radionuclides with C-S-H phases.

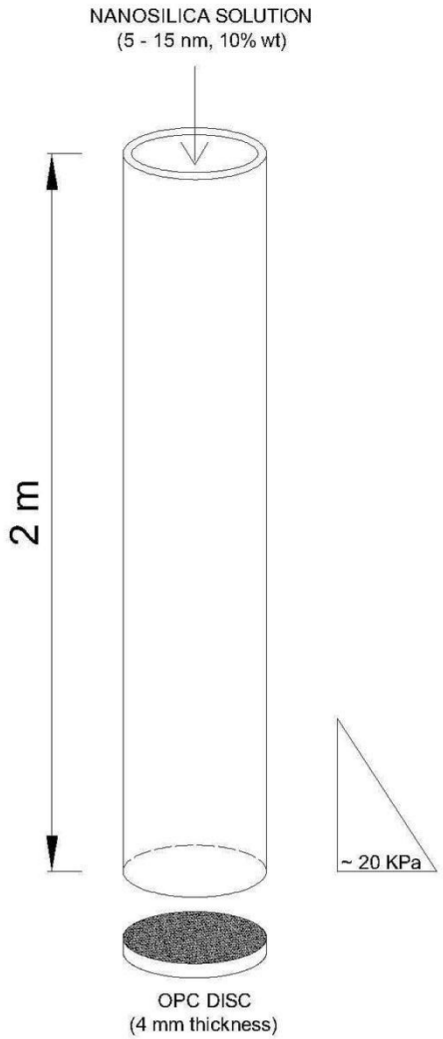
Sorption test gives quantitative analysis about the immobilisation capability of radionuclides into C-S-H phases



[K. Li, X. Pang, Cement and Concrete Research, 2014]

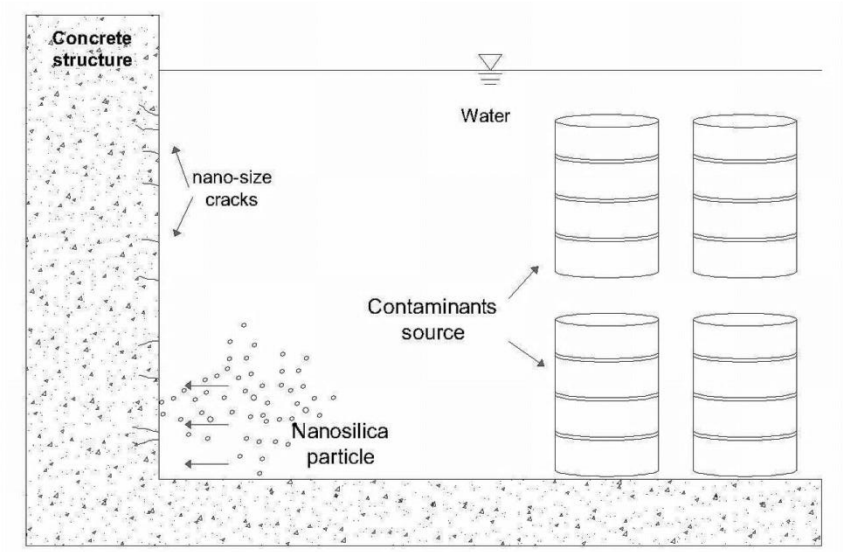


Nanoparticle injection



Low-pressure nanosilica injection will be investigated at lab-scale.

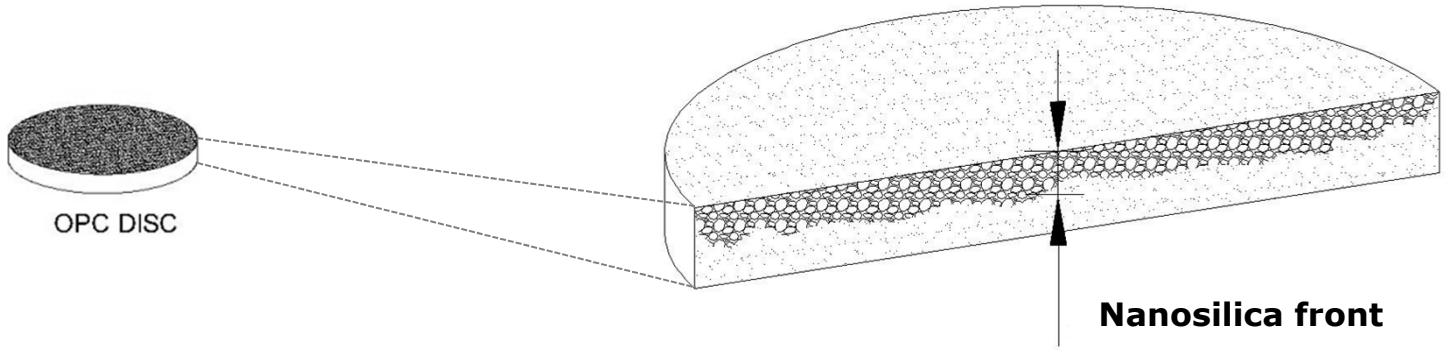
A solution of **nanosilica** (particle size range of 5 – 15 nm) will be injected through a *28 days cured OPC* disc (thickness 4 mm) at a ~ **20 kPa** of hydrostatic pressure.



Application of low-pressure injection in legacy ponds concrete structures

Nanoparticle injection

Nanosilica particles will be forced to penetrate into *cement pores* in which an elevated **portlandite** content (naturally present in hydrated OPC as a result of hydration process) can be found. The particles will react with the **calcium hydroxide** to form additional **C-S-H** and precipitate in the pores.



EXPERIMENTAL PARAMETERS

Pressure of injection

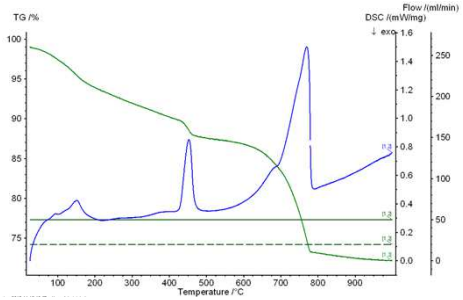
Concentration of nanosilica

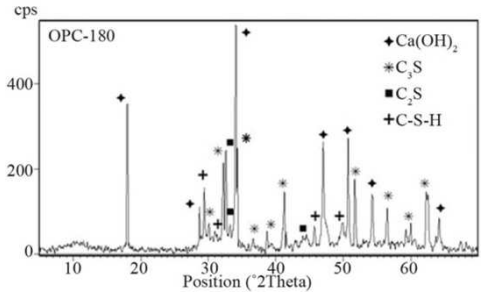
Time of injection

Nanoparticle injection

After injection time the OPC disc will be analysed:

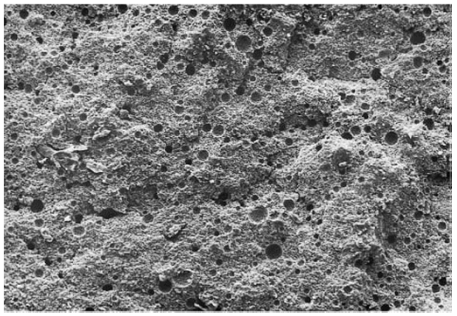
- TGA/DTA/DSC analysis;
- Powder X-Ray diffraction;
- FE-SEM imaging and chemical mapping;
- AFM surface study;
- Mercury Intrusion Porosimetry.





Expected results:

- Decrease of porosity;
- Decrease of Portlandite content;
- Increase of C-S-H;
- Decrease of permeability;



Conclusions

1. **Nanoparticles in cement show a higher reactivity compared to traditional OPC.**
2. **C-S-H synthesis** methods and different calcium sources affect the formation of C-S-H and structural changes have been observed.
3. C-S-H structure can be altered and tailored in order to ***house*** other atoms.
4. **Immobilisation** of radionuclides into C-S-H phase can occur through different mechanism: from structural incorporation to surface interaction.
5. Injection of nanosilica promotes *decrease of porosity* and formation of **additional C-S-H**. Controlling the C/S ratio and other parameters, this additional C-S-H could be tailored in order to immobilise radionuclides and precipitate into nano-cracks.

WORK IN PROGRESS

Future works include experiments to study the mechanism of interaction of radionuclides with C-S-H phases, silica injections and analytical characterisations.

Workflow chart

University of Strathclyde Engineering

C-S-H Structural studies

Radionuclide

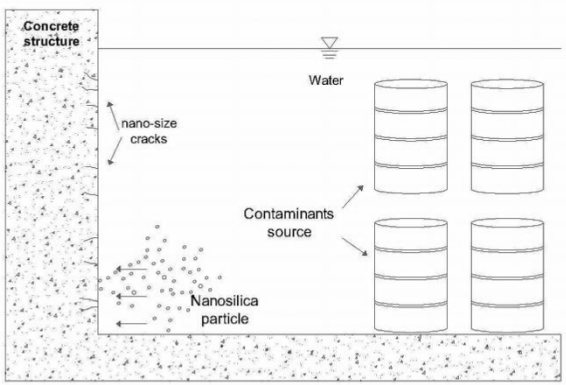
Nanosilica injection

Tailoring C-S-H

C-S-H and radionuclide interaction

Additional C-S-H formation

Crack healing and radionuclide immobilisation into cracks



DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority

University of Strathclyde Engineering

Riccardo Maddalena , Dr. Andrea Hamilton*

University of Strathclyde, Glasgow - UK

DISTINCTIVE

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA Nuclear Decommissioning Authority