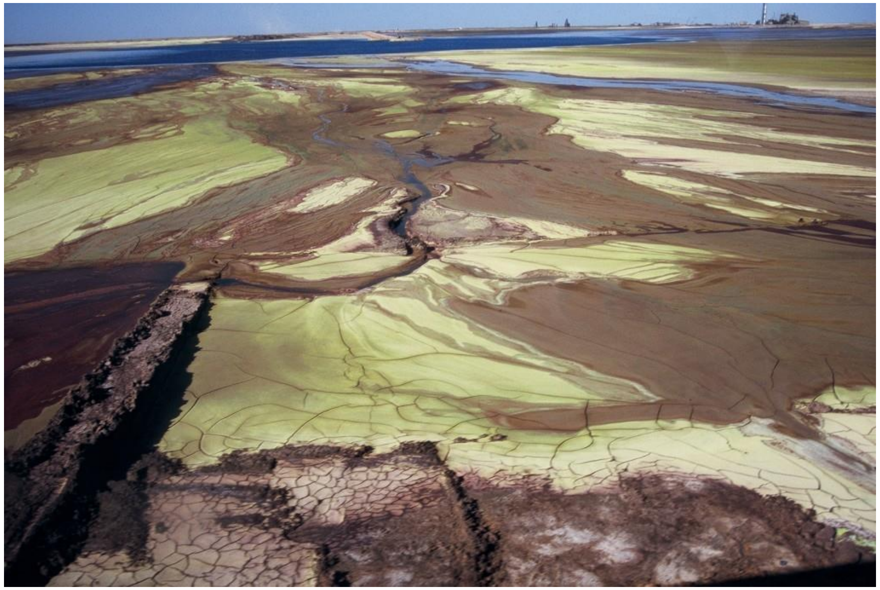
Production of mycogenic phosphate biominerals for the remediation of radioactive contamination

Thomas Mullan
University of Strathclyde

Theme 4 Meeting
16/10/17
Penrith, Cumbria



Mine Tailings at Olympic Dam, Australia
australianmap.net/olympic-dam-uranium-mine/

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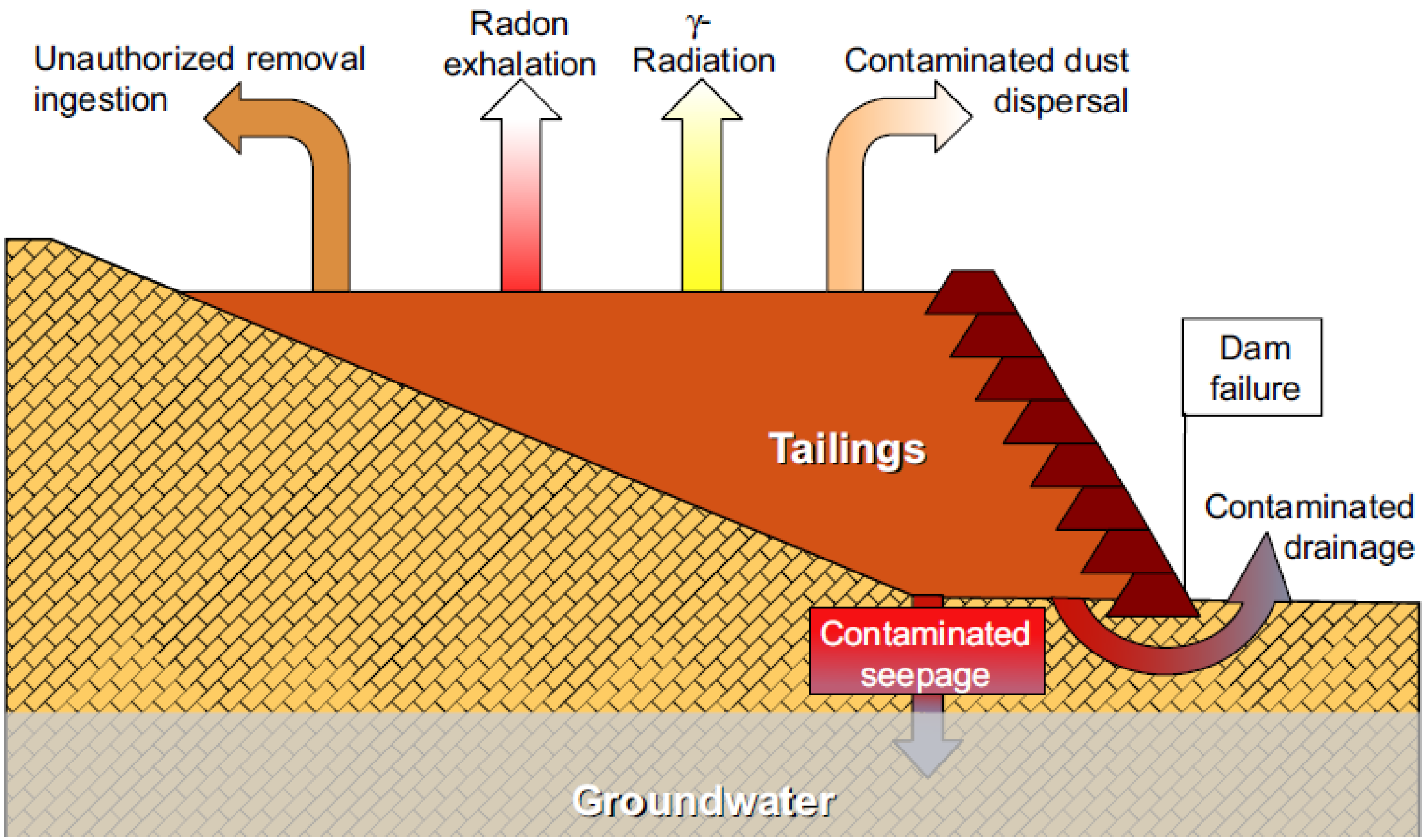
Context: Uranium mining



Sketch of a tailings impoundment

Falck (2015) in Environmental Remediation and Restoration of Contaminated Nuclear and Norm Sites

Phosphate based remediation strategies

Fluorapatite ($Ca_{10}(PO_4)_6(F)_2$)
dakotamatrix.com/mineralpedia/5891/fluorapatite

Monazite
geology.com/minerals/monazite.shtml

Pyromorphite
($Pb_{10}(PO_4)_6(Cl)_2$)
Hughes & Rakovan (2015) *Elements*, **11**, 165–170.

Hydroxyapatite
($Ca_{10}(PO_4)_6(OH)_2$)
www.surgiwear.co.in/neurosurgery/implants-1/bone-grafting-products/synthetic-hydroxyapatite.html

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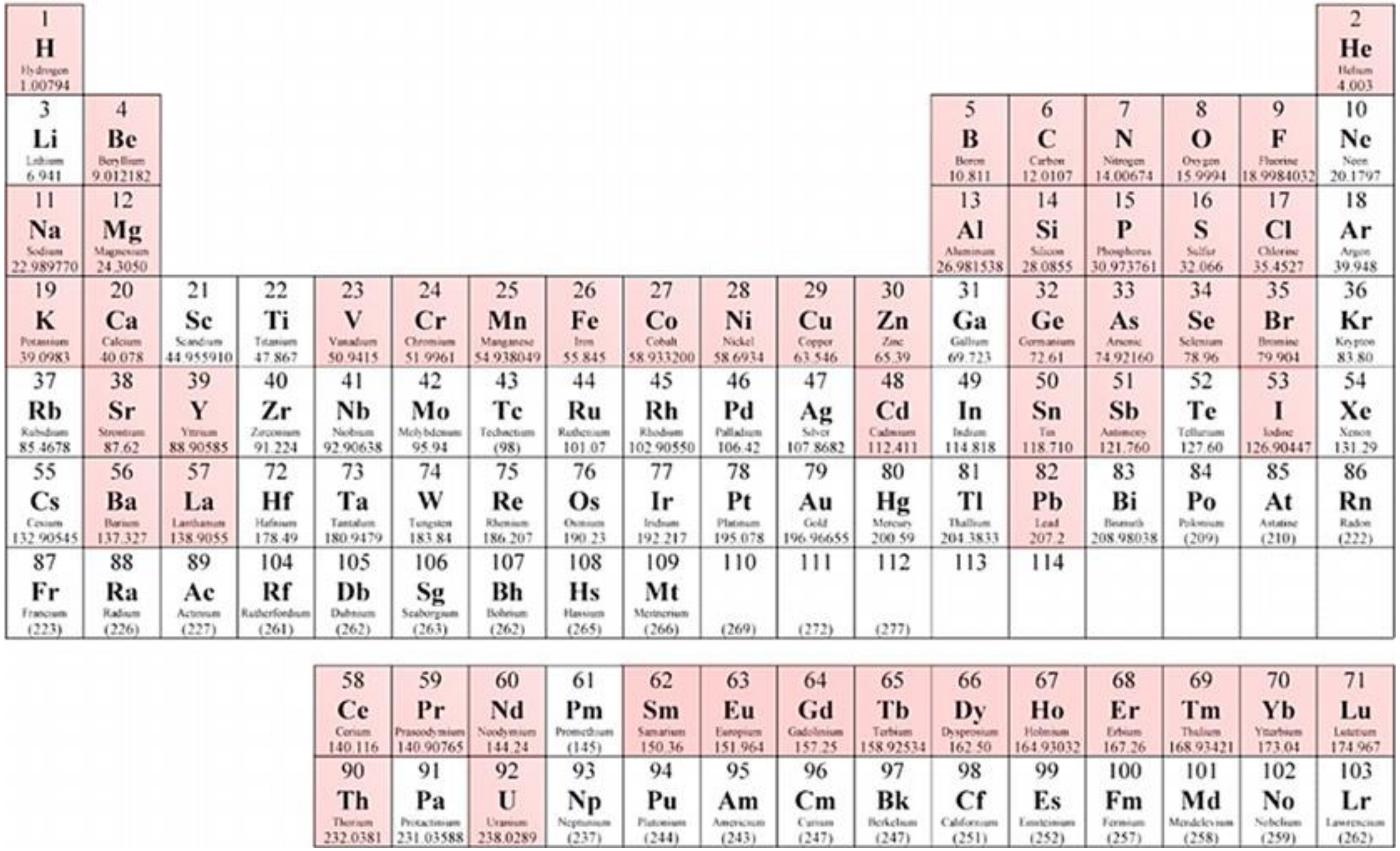
Phosphate based remediation strategies



Elements that can be incorporated into the apatite structure

Hughes & Rakovan (2015) *Elements*, **11**, 165–170.

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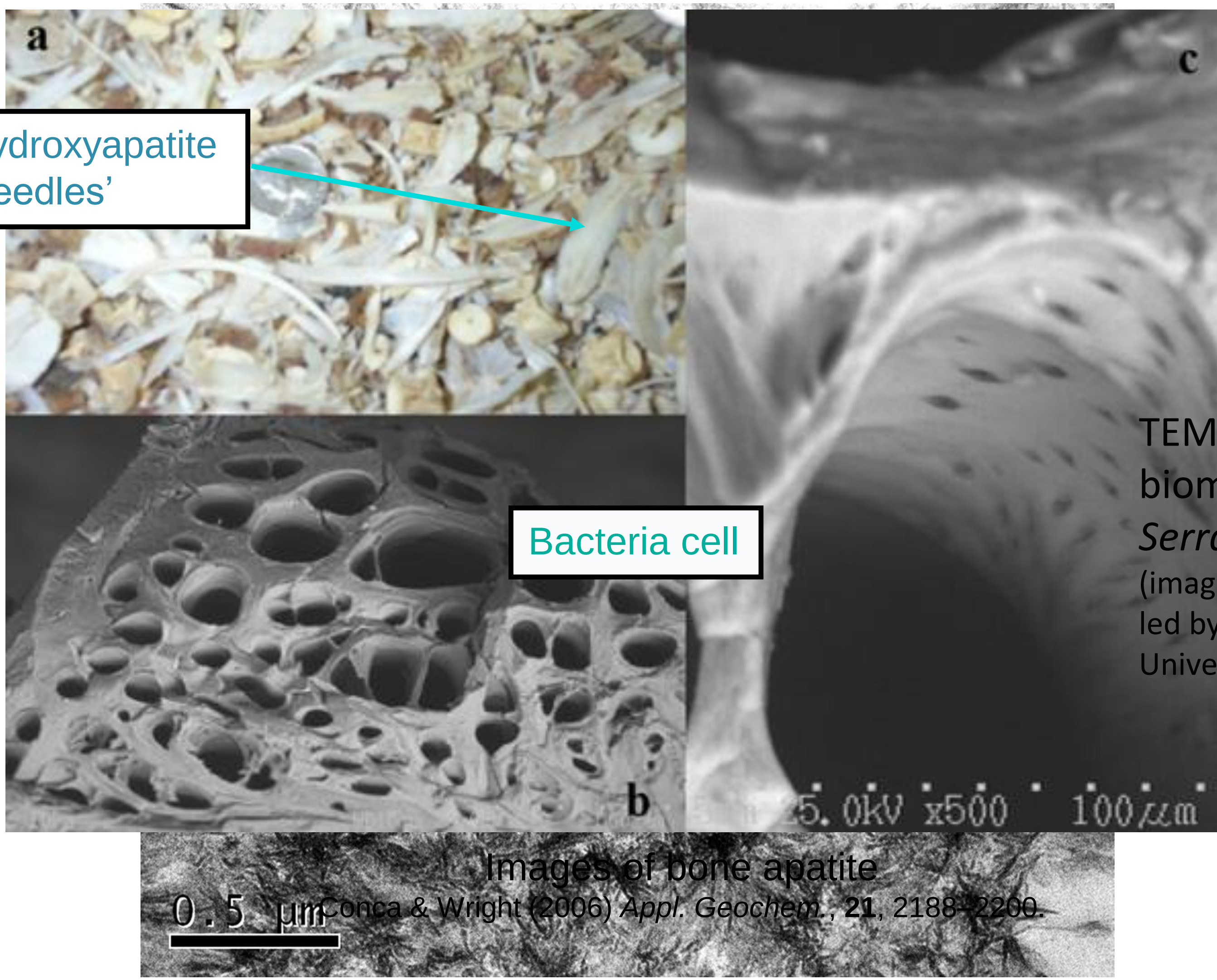
Phosphate biominerals



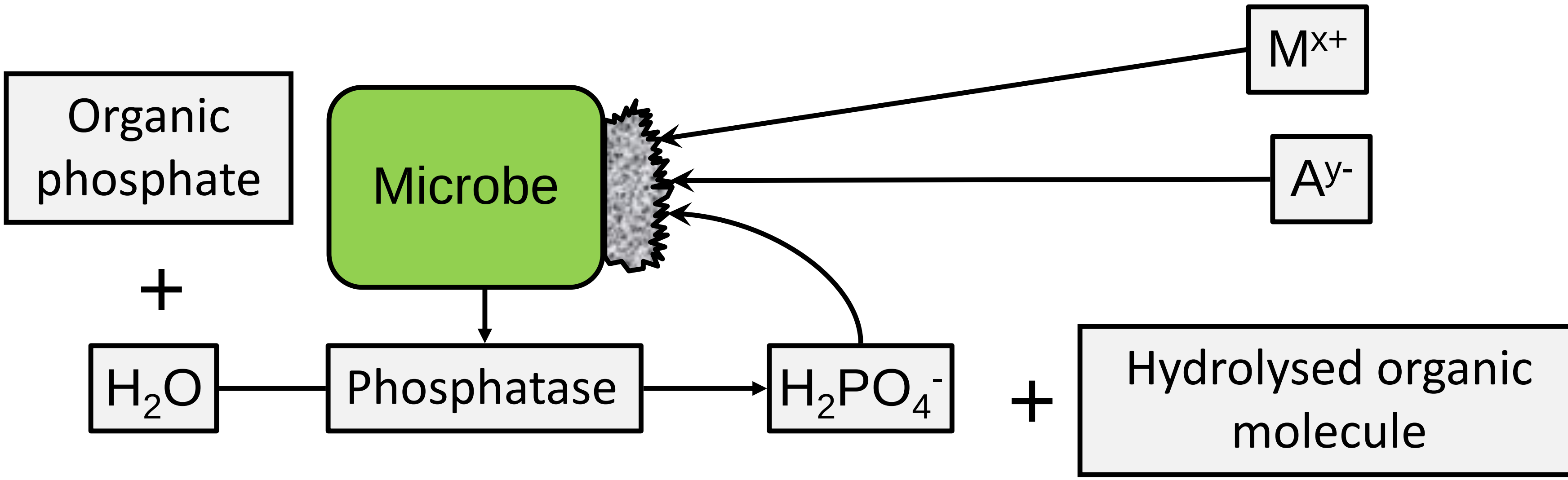
Images of bone apatite

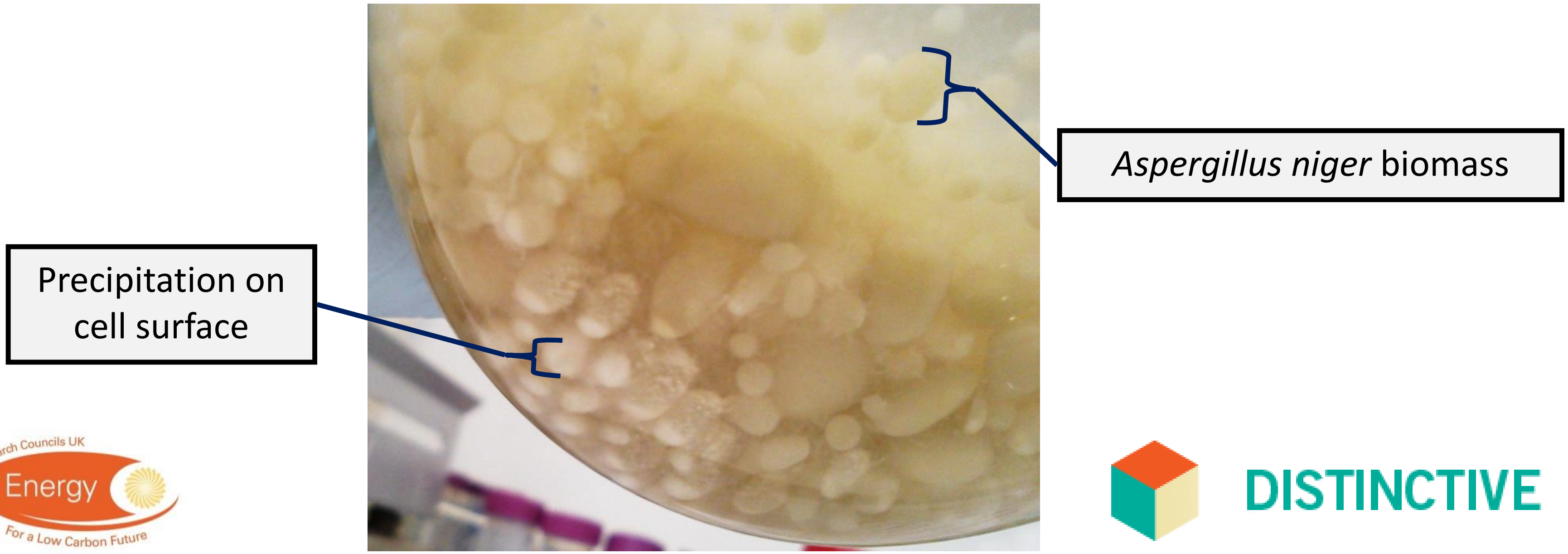
Conca & Wright (2006) *Appl. Geochem.*, **21**, 2188–2200.

TEM image of biomineral produced by *Serratia* sp. N14

(image recorded during work led by Dr. Handley-Sidhu at University of Birmingham)

Microbially induced phosphate biomineralisation





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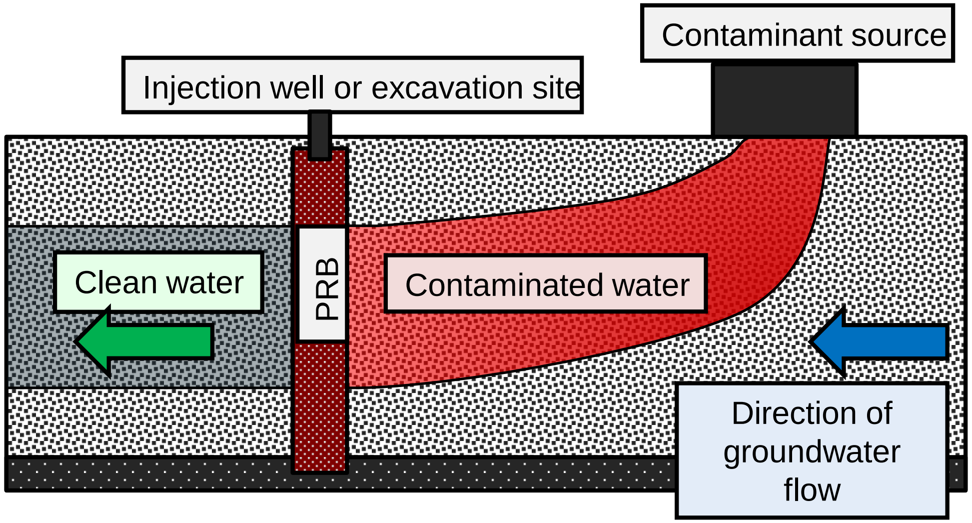
Previous research

Heat-treated bacteriogenic hydroxyapatite

A packed bed reactor system used in the precipitation of uranium phosphate (Macaskie *et al.* (2004) in Phosphorus in Environmental Technologies: Principles and Applications, 549–581)



Sketch of a permeable reactive barrier

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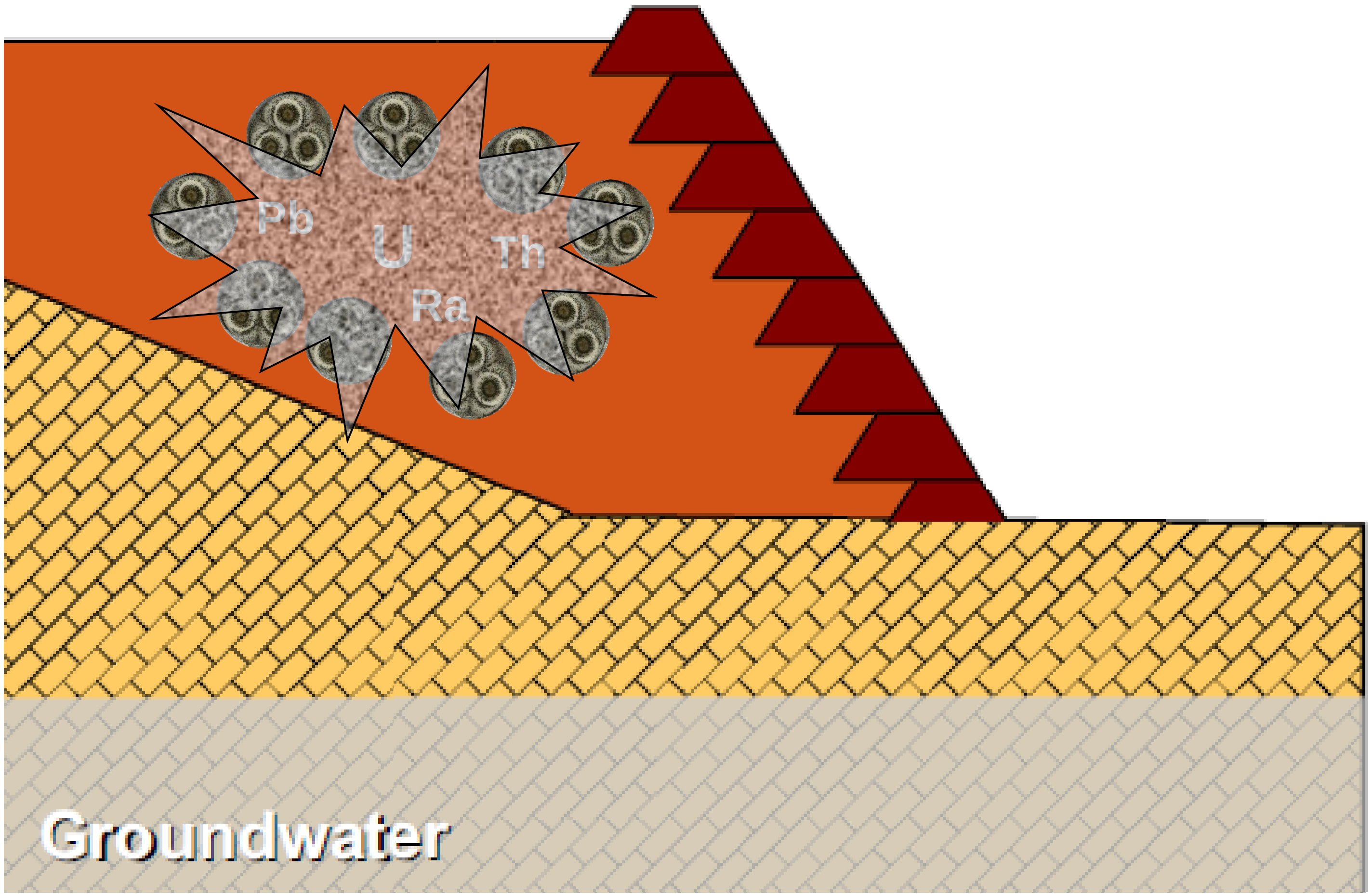
Aims and objectives



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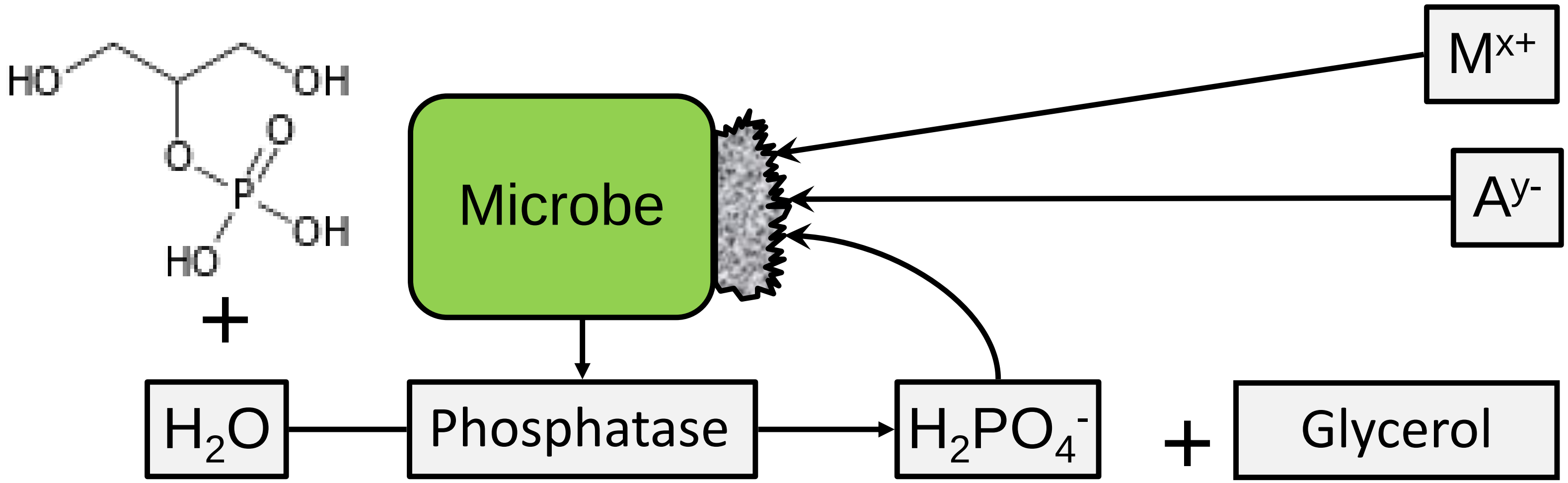
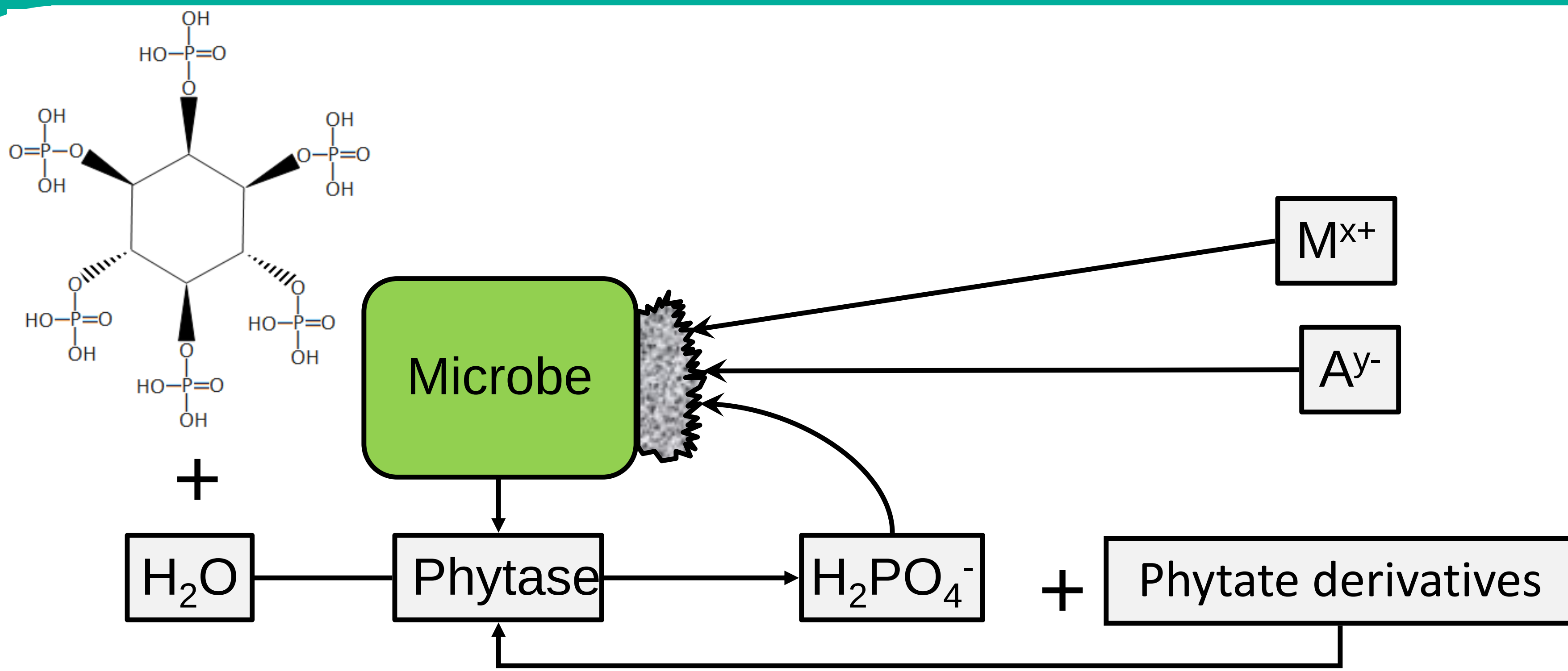
Aims and objectives

Glycerol 2-phosphate diagram from:
https://commons.wikimedia.org/wiki/File:Glycerol_2-phosphate.svg



Aims and objectives



As sequestering agent: Nash *et al.* (1998) *J. Alloys Compd.*

In biomineralisation: Paterson-Beedle *et al.* (2009) *Adv. Mater. Res.*
Paterson-Beedle *et al.* (2010) *Hydrometallurgy.*
Roeselers & Van Loosdrecht (2010) *Folia Microbiol.*
Newsome *et al.* (2015) *Environ. Sci. Technol.*
Liang *et al.* (2016) *Environ. Microbiol.*
Liang *et al.* (2016) *Appl. Microbiol. Biotechnol.*
Salome *et al.* (2017) *Geochim. Cosmochim. Acta.*

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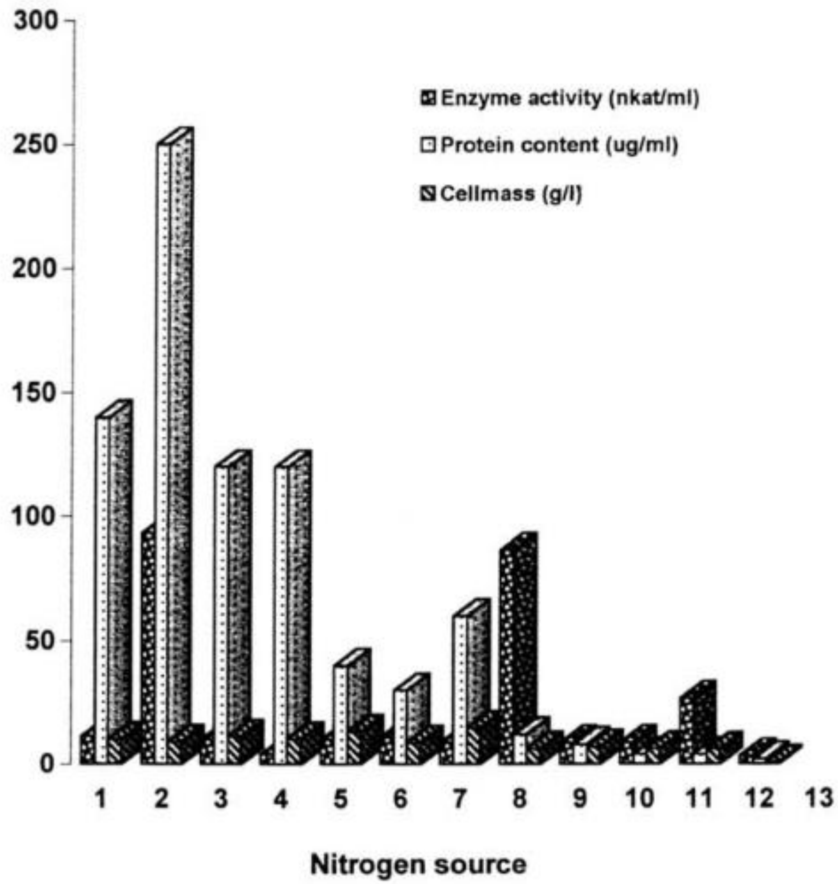
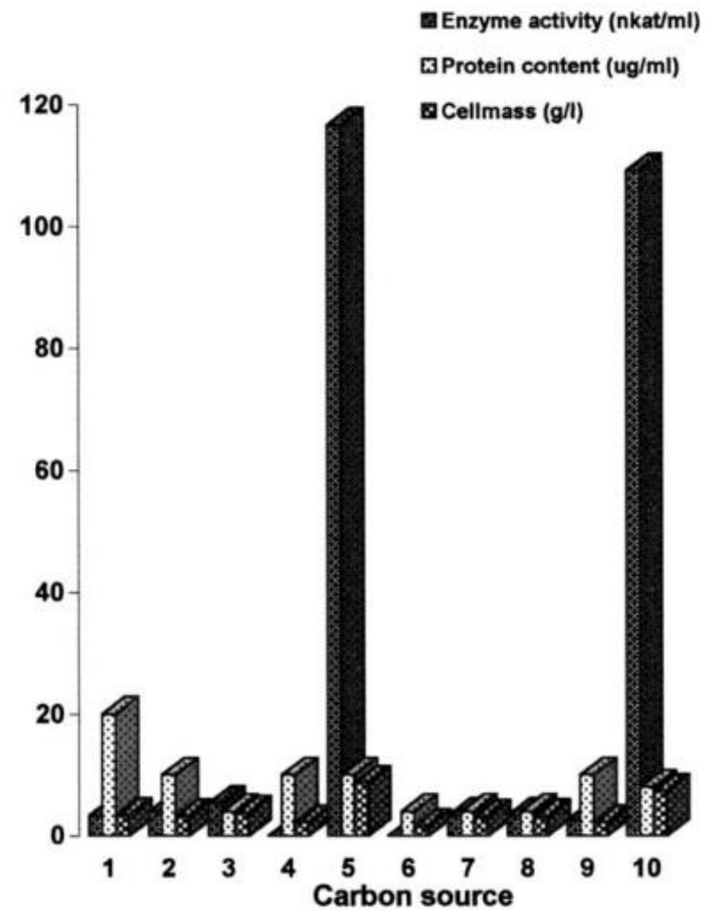
Important factors



1: yeast extract; 2: biopeptone; 3: soyapeptone; 4: tryptone;
5: tryptose; 6: yeast autolysate; 7: beef extract; 8: ammonium nitrate;
9: potassium nitrate; 10: ammonium chloride; 11: ammonium sulphate;
12: No Nitrogen source(only 1% starch & 3% glucose).



1: glucose; 2: sucrose; 3: maltose; 4: glycerol; 5: starch; 6: lactose;
7: sorbitol; 8: mannitol; 9: fructose; 10: glucose+starch (3 & 1 % resp.)

Vats & Banerjee (2002) *Process Biochem.*

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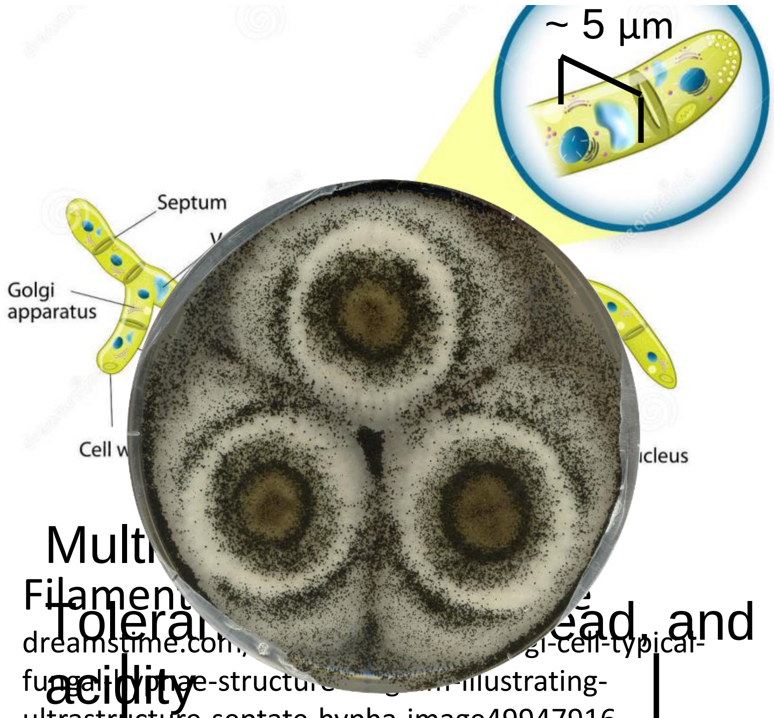
Choice of organisms

Aspergillus niger

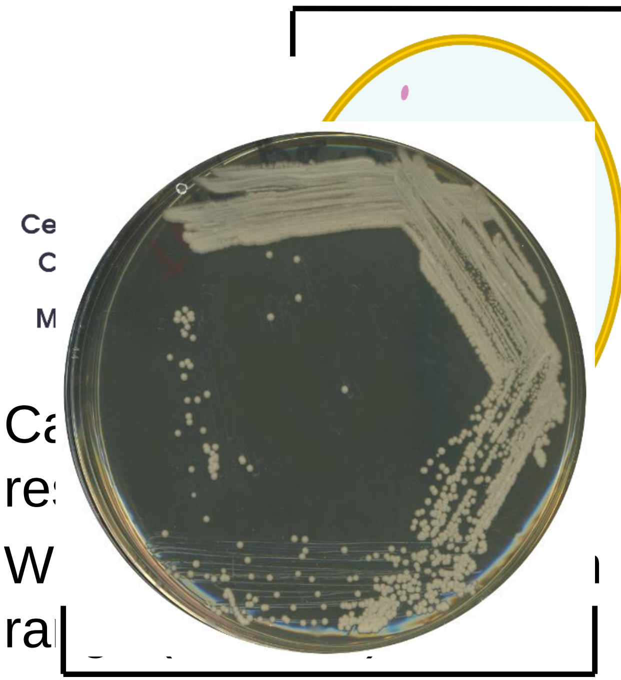


- Multi
Filament
- Toleral ... ead, and acidity

dreamstime.com/... gi-cell-typical-fungal-hyphae-structure ... illustrating-ultrastructure-septate-hypha-image49947916

90 mm

Blastobotrys adeninivorans



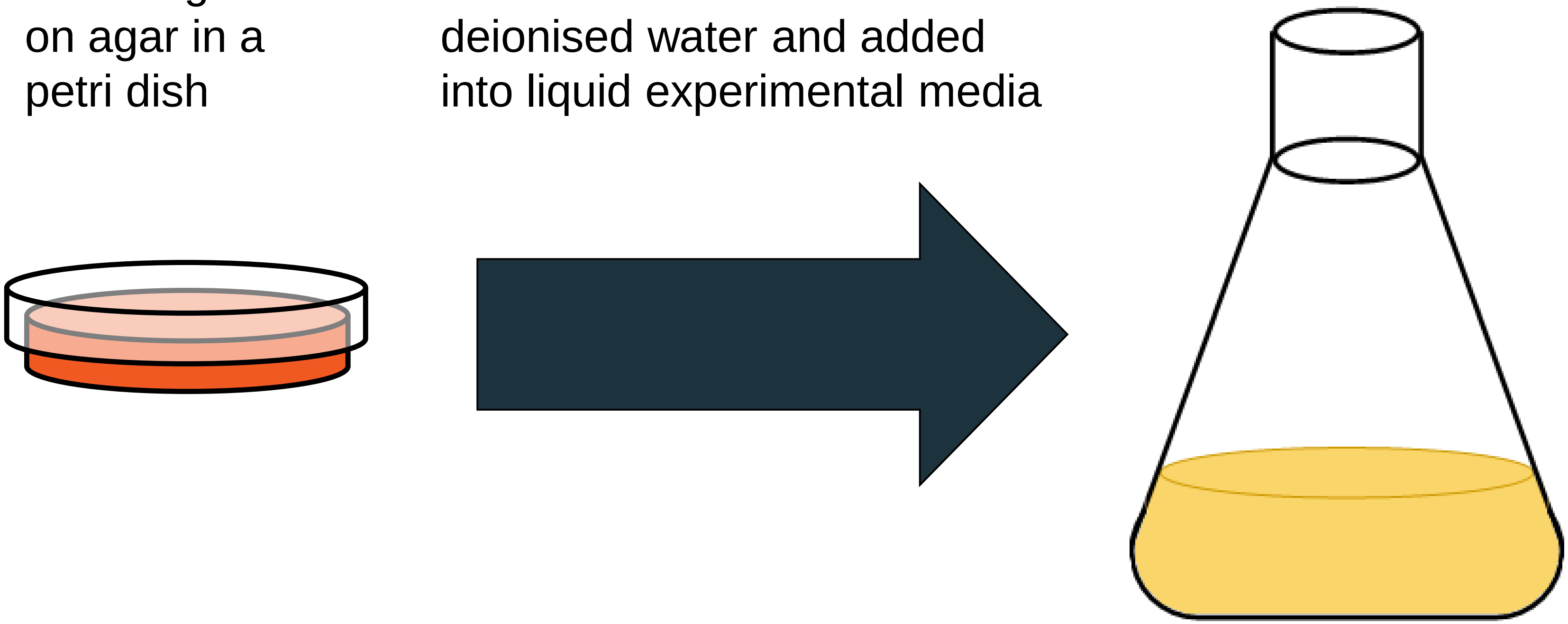
- Ca
res
- W
ra
- Salt-tolerant

90 mm

Experimental setup

Culture grown on agar in a petri dish

Cells harvested with sterile deionised water and added into liquid experimental media



Controls consisted of sterile experimental media

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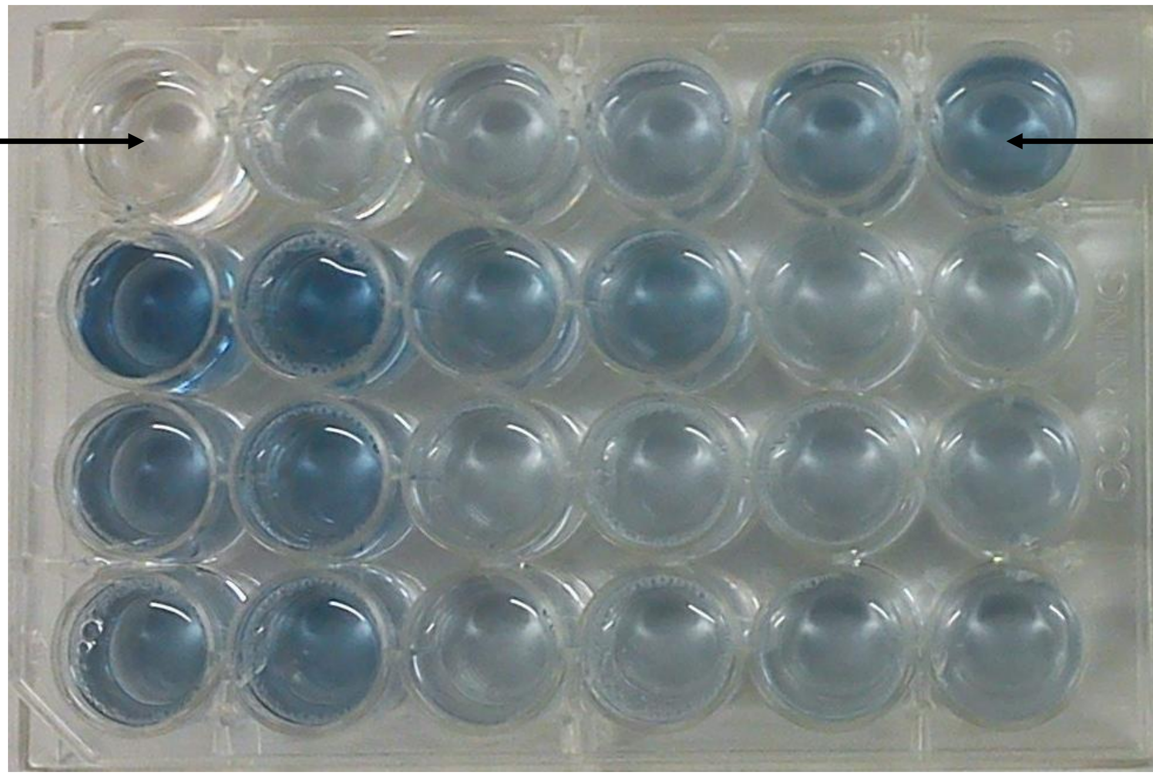
Experimental setup

Samples removed at various time points and phosphate detected colorimetrically at 700 nm and compared to a standard curve of known concentrations (Qvirist *et al.* (2015) *J. Biol. Methods*, **2**, e16.

0 mg/L phosphate

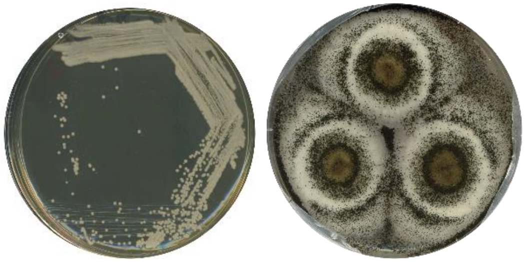


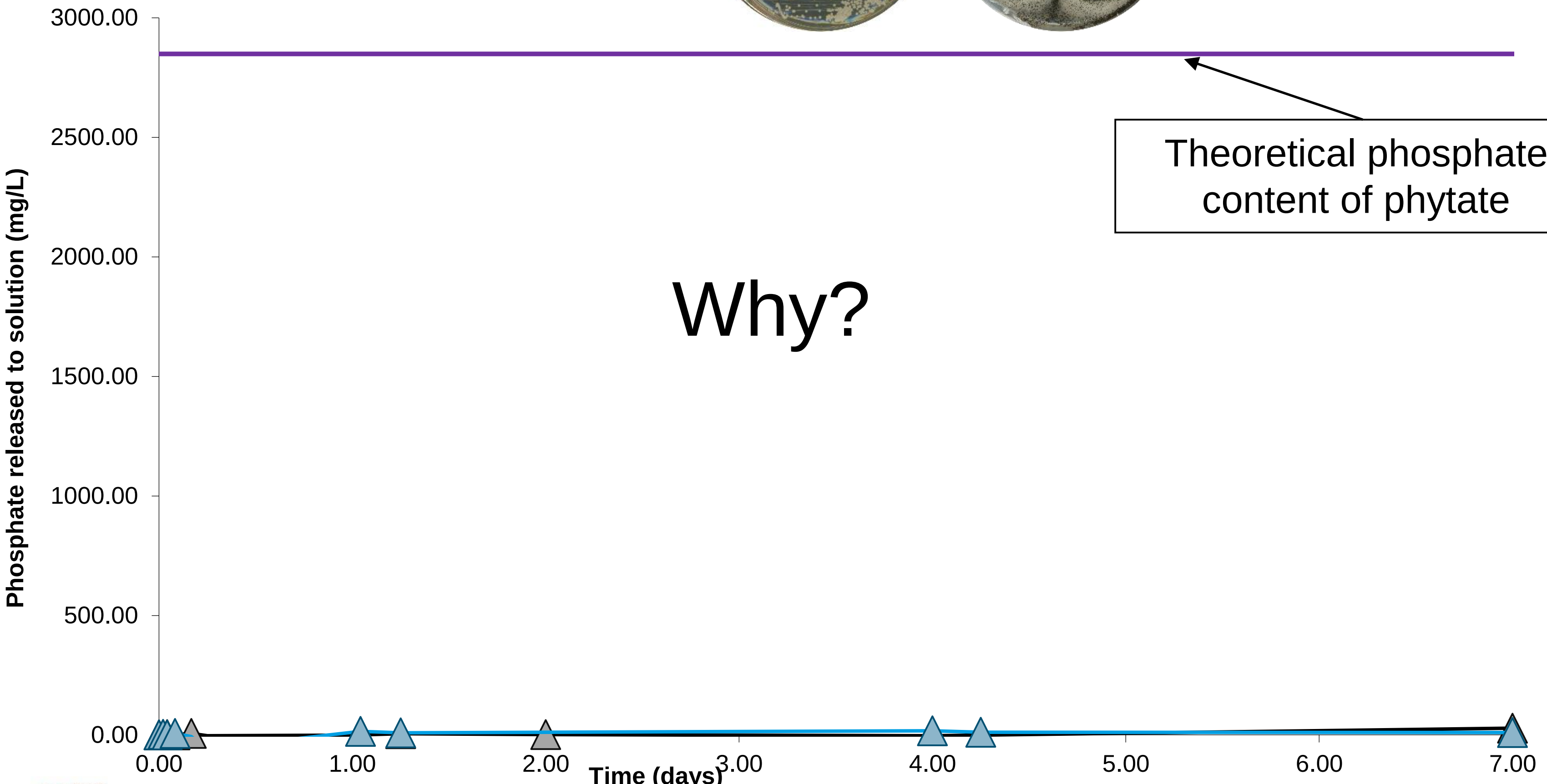
30 mg/L phosphate

Temperatures: ◆ 4 °C ■ 12 °C ▲ 20 °C ● 30 °C

Blastobotrys adeninivorans

Aspergillus niger





Why?

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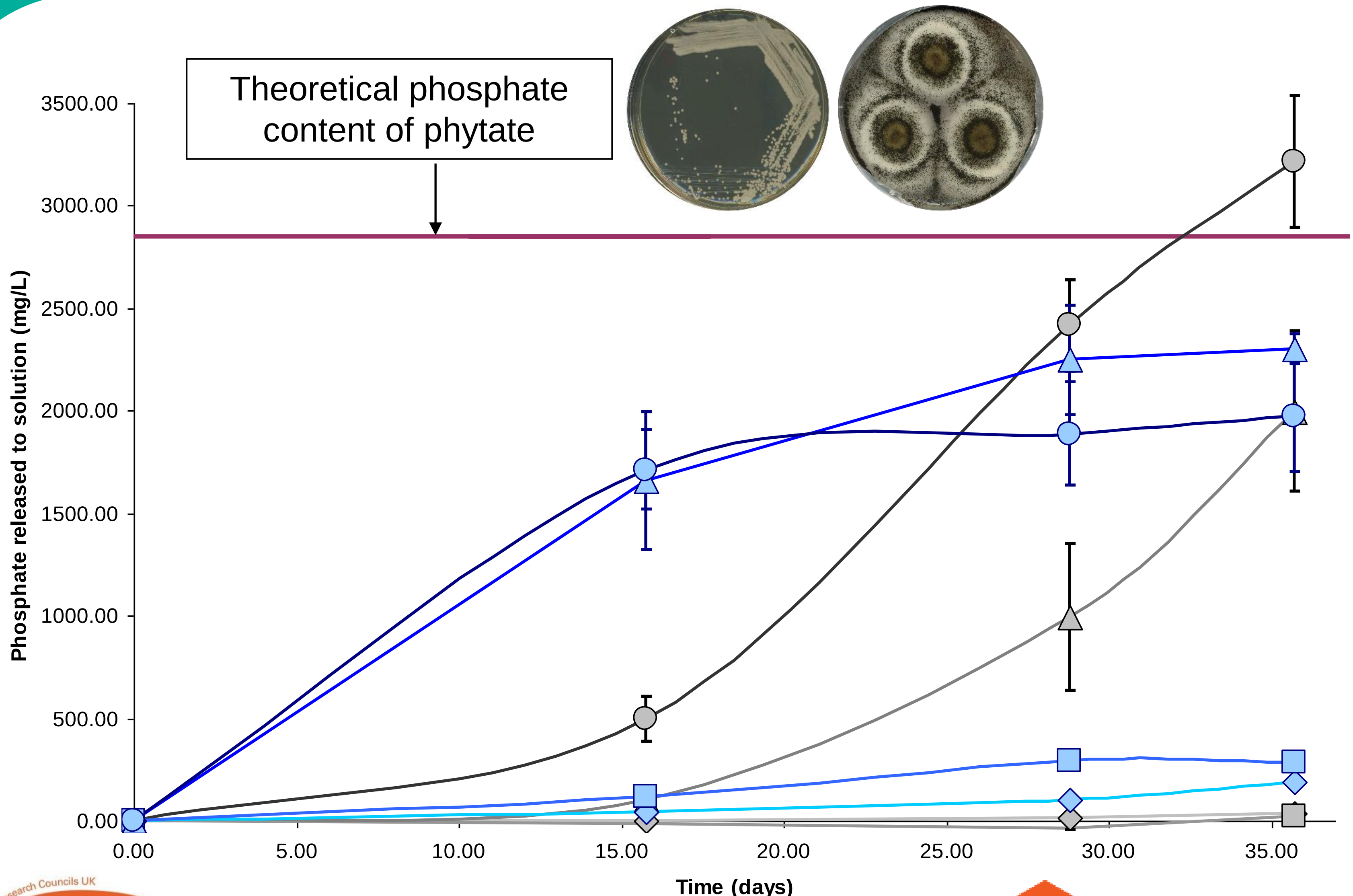
Temperatures: ◆4 °C ■12 °C ▲20 °C ●30 °C

■ *Blastobotrys adeninivorans*
■ *Aspergillus niger*



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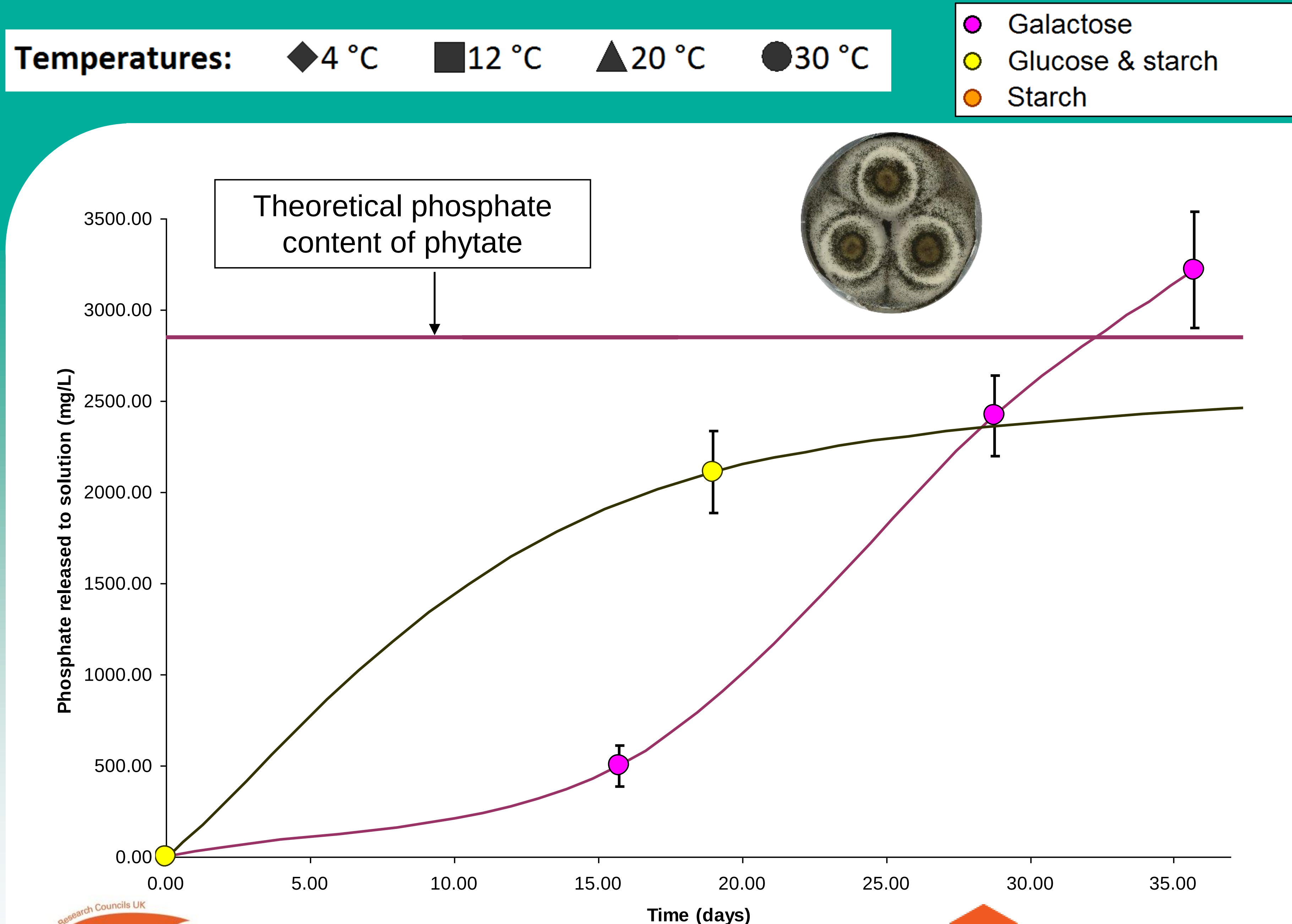

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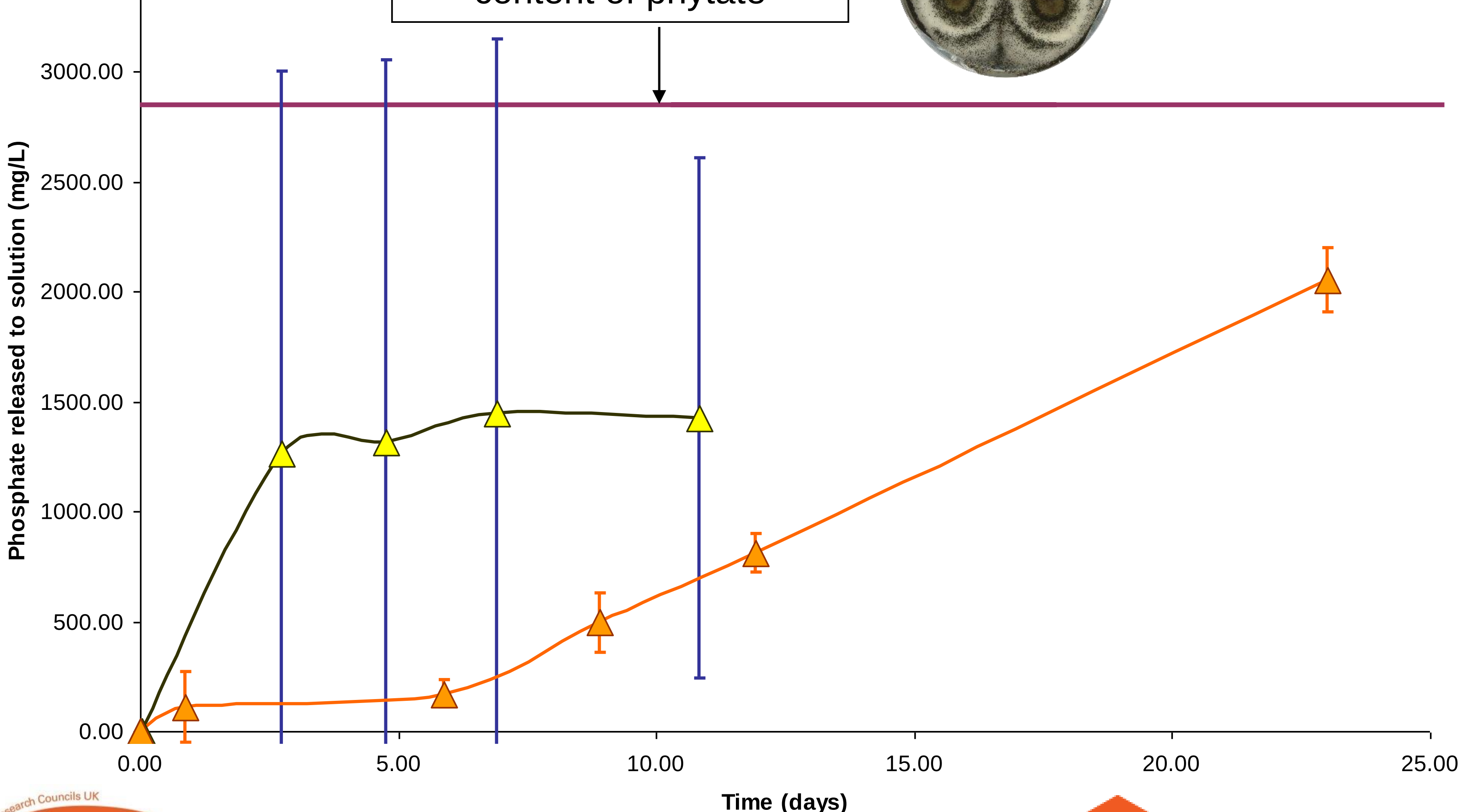
Temperatures: ◆ 4 °C ■ 12 °C ▲ 20 °C ● 30 °C

● Galactose
● Glucose & starch
● Starch



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Conclusions

- Carbon source not hugely important
- Temperature matters
- Time matters
- pH not hugely significant

Future direction

- Characterise biomineral precipitates
- Characterise uptake of relevant contaminants
- Begin tests within waste tailings microcosms

Acknowledgements

- Project supervised by Dr. Joanna Renshaw and Prof. Rebecca Lunn
- Funding provided by Mr. Ian Stalker through the University of Strathclyde alumni fund
- Also thanks to DISTINCTIVE for supporting travel funds to these meetings

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Geopolymers as chloride / moisture sensors and surface repairs for concretes in nuclear structures

Lorena Biondi
PhD student (2 nd year), CEE, University of Strathclyde

Supervisors: **Dr. Marcus Perry**, **Dr. Andrea Hamilton**

University of Strathclyde Glasgow

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Introduction

➢ **Structural integrity in nuclear context**

Structures in nuclear context:

- **Underpin safety-critical structures and radiation barriers**
- **Irradiated by ionizing radiation**
- **Usually coastal**
- **Made by reinforced concrete**

✓ **Radwaste storage buildings in UK:**

- **Passive cooling → air convection flow → No filters**

Sea waterspray dispersed in air → condensation on concrete surfaces

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Chloride and Moisture

Corrosion of steel rebars

Cracking and spalling of concrete

✓ **<u>Radwaste storage buildings in UK</u>:**

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Introduction

➢ **Chloride and moisture monitoring**

✓ **Existing methods:**

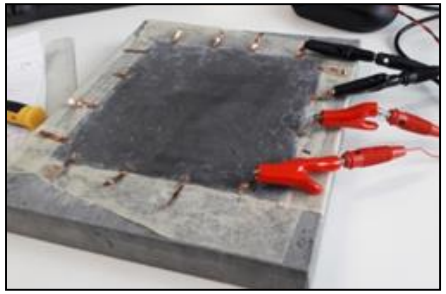
- **Chloride → Ion selective electrodes and Fiber optic sensors.**
- **Moisture → Humidity, electrical resistance and dielectric permittivity sensors.**

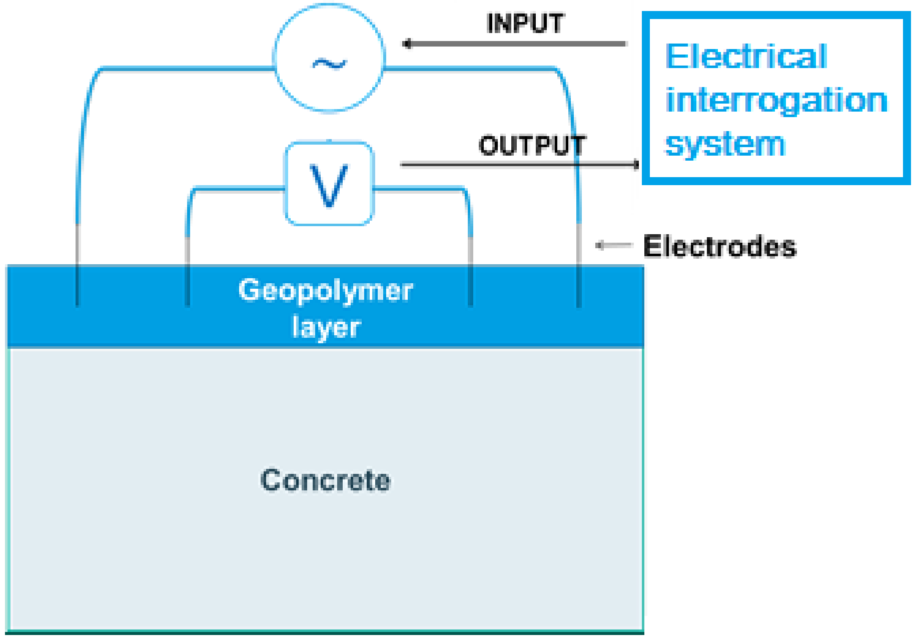
Disadvantages:

- **High cost;**
- **Not much flexible to apply to any surface and shape;**
- **Not sensitive to both chloride and moisture;**
- **Don't provide protection and repair to concrete.**

Overview of the project

- **Chloride and moisture monitoring: novel solution proposed**
  - ✓ **<u>Sensing/repair system</u>:**
    - **Fly ash geopolymer patch on concrete surface;**
    - **Embedded electrodes;**
    - **Electrical interrogation system.**





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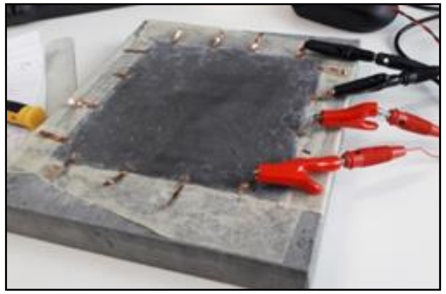

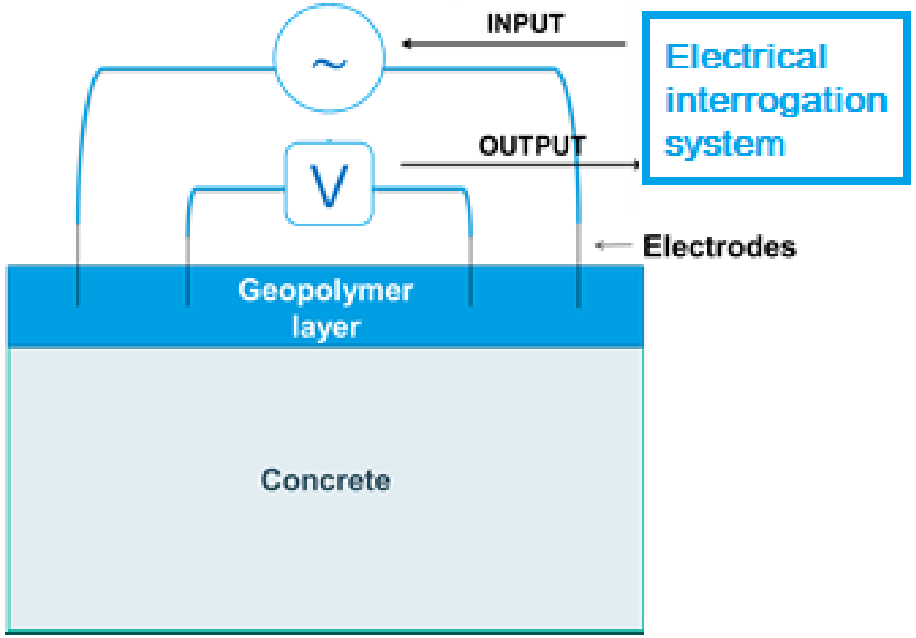

Advantages:

- **Affordable;**
- **Non-destructive;**
- **Sensitive to both chloride and moisture;**
- **Combined monitoring and maintenance technology.**

Overview of the project

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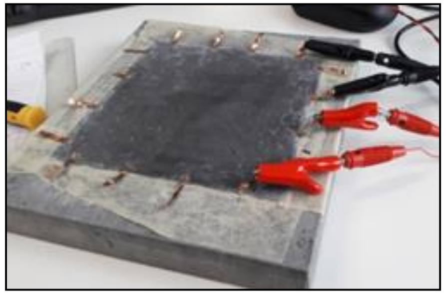

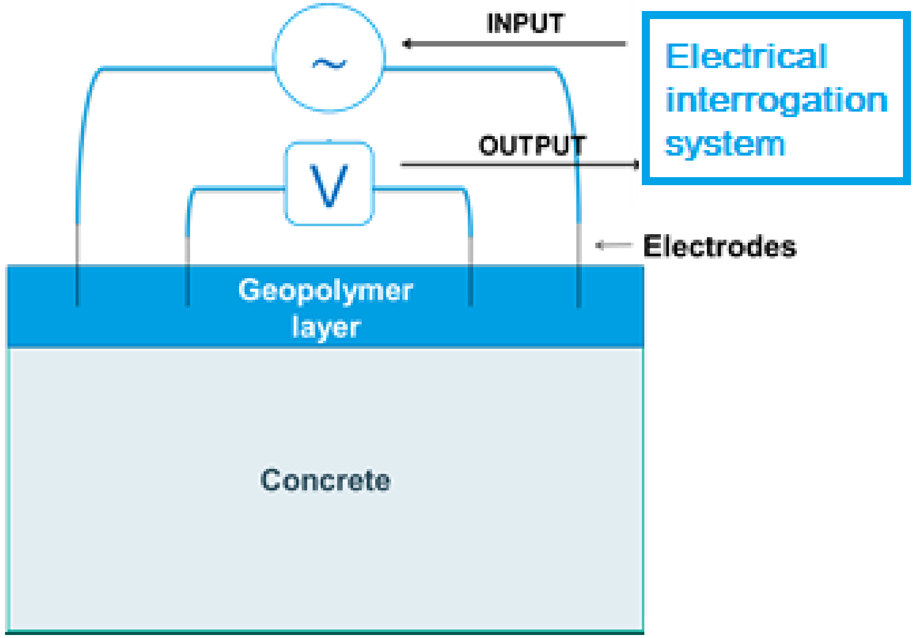

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Geopolymers ➡

- **Highly-adhesive binders;**
- **Durable;**
- **Chemically resistant;**
- **Electrically conductive.**

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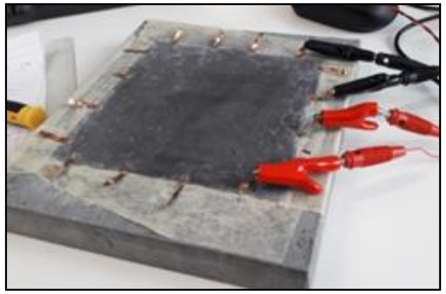

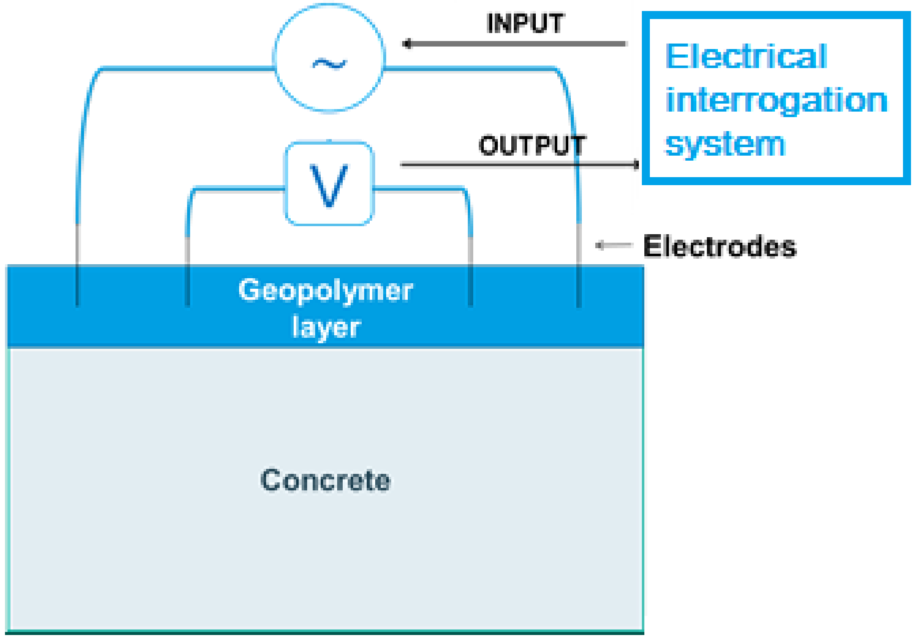

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Overview of the project

➢ **Chloride and moisture monitoring: novel solution proposed**

✓ **Electrochemical Impedance Spectroscopy (EIS):**

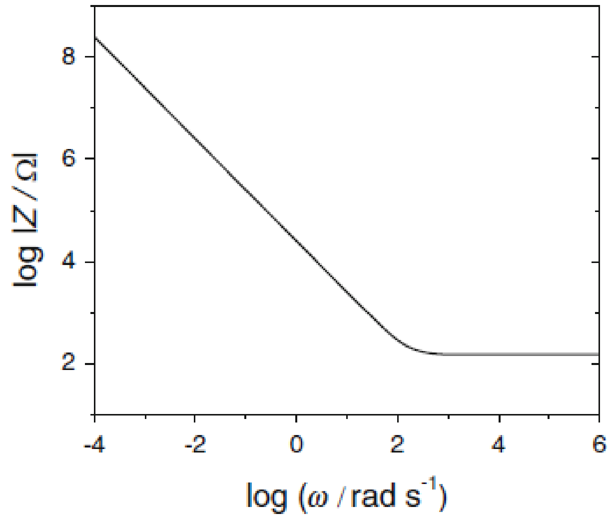
Advantages:

- **High information;**
- **Non-destructive;**
- **Different frequencies.**

$$Z = \frac{V_t}{I_t} = \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)}$$

Z = Impedance V = Potential I = Current

ω = Frequency φ = Phase t = Time



ΔZ :

- **Temperature**
- **Strain**

Previous studies

- **Concentration of chloride ions**
- **Moisture**

Object of study in this work

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Overview of the project

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↓

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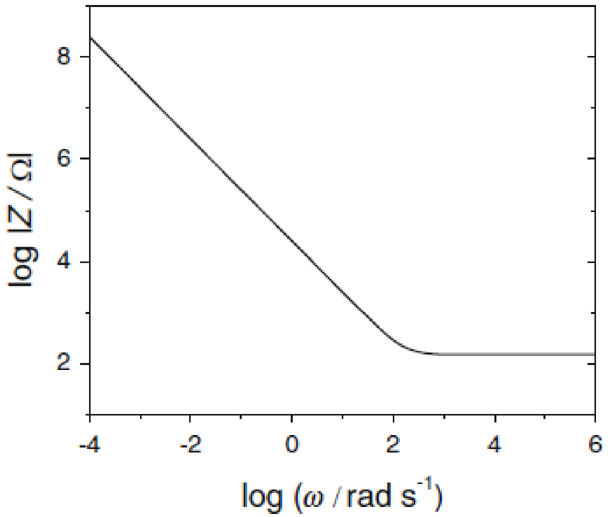

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Object of study in this work

Radiation

Interference?

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Overview of the project

- Objectives of the project

  - ✓ 1st year PhD: 1. Laboratory system manufacture: geopolymer patches on concrete specimens with embedded electrodes

    2. Laboratory preliminary tests and analysis: inspection of samples

  - ✓ 2nd year PhD: 3. Laboratory tests and measurements
    - Applying EIS analysis varying variables:
      - Chloride and moisture concentration;
      - Ionizing radiation.

  - ✓ 3rd year PhD: 4. Field trials measurement and data acquisition
    - Applying the sensing and repair system to:
      - Radwaste storage structure at Sellafield

        → Air corridor concretes

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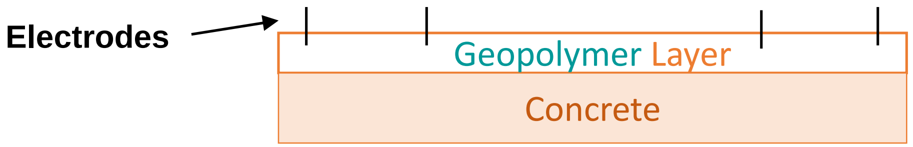
Overview of the project

➢ **Objectives of the project**

✓ **1st year PhD:** **1. Laboratory system manufacture**

- **Making the most suitable geopolymer binder;**
- **Putting it in a layer on concrete;**
- **embedding electrodes into the layer;**
- **Curing it at room temperature to an uncracked layer.**



2. Laboratory preliminary tests and analysis

- **Visual inspection;**
- **Calorimeter analysis;**
- **Setting time: Vicat Needle test;**
- **X-Ray Diffraction (XRD) analysis.**

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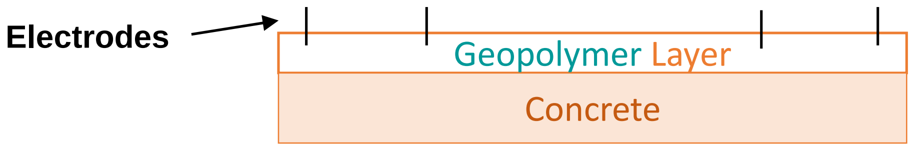

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Experimental work

- **Materials and methods:**

  ✓ **Making samples:**

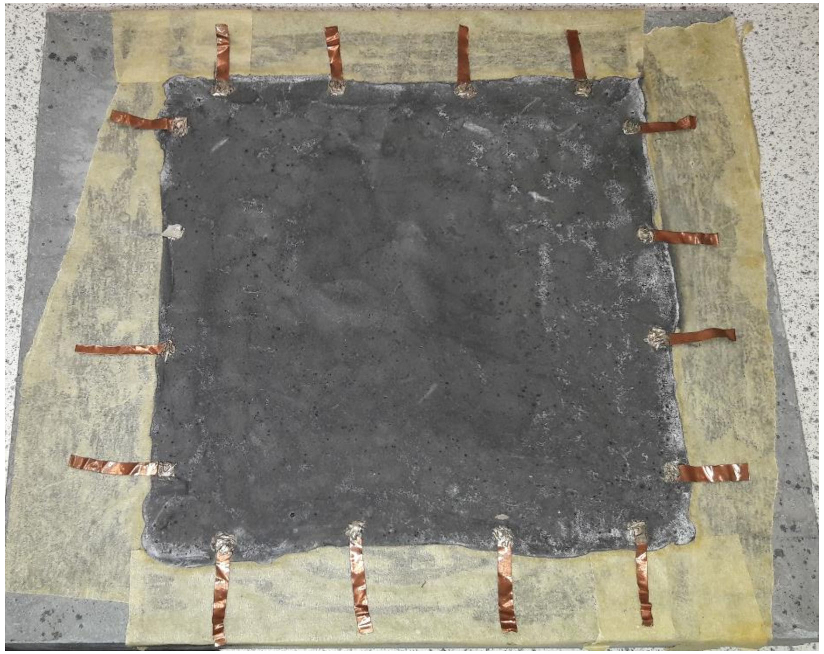
Samples: 1. Geopolymer binder + 2. Electrodes + 3. Concrete specimens

System samples components:

1. Geopolymer binder:
- Composition;
- Mixing.

2. Electrodes: copper electrodes (0.1 mm thick).

3. Concrete specimens:
- different ages:
  - Young: age < 3 months
  - Intermidiate: 6 months < age < 1.5 years
  - Old: age > 3 years



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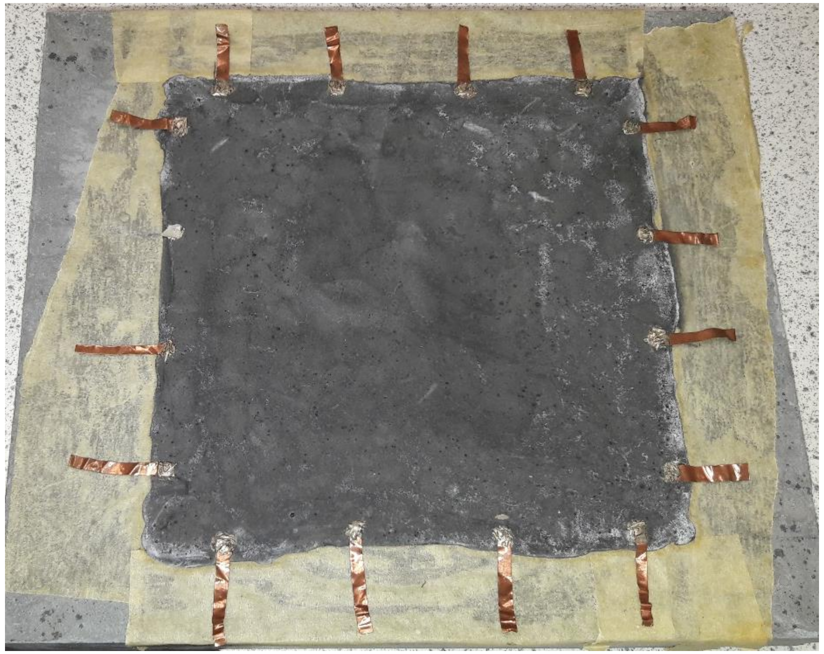

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Experimental work

- Materials and methods
  - ✓ Making samples:

Geopolymer binder composition = 68 wt% fly ash + 32 wt% alkaline solution

1. Fly ash

Fly ash	UK power station	Fineness category	LOI category	Calcium content	Si/Al
ScotAsh	Longannet, Scotland	N	B	Low (class F)	1.4
Cemex	West Burton, England	S	B	Low (class F)	2.1

N.B. Category N fineness > category S fineness

2. Alkaline solution

Component solution	Concentration/ composition	Wt%
Sodium Hydroxide (NaOH)	10 M	10 wt%
Sodium silicate (Na_2SiO_3)	63.7 wt% distilled water 8.5 wt% Na_2O 27.8 wt% SiO_2	24 wt%

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Experimental work

- **Materials and methods**
  - ✓ **Making samples:**

Geopolymer binder mixing

1. Manual mixing

Mixing time = 10 minutes

Some binder left resting:
From 1 hour to 5 hours

2. Authomatic mixing

Mixer speed = 500 min^{-1}

Mixing time =
From 10 minutes to 5 hours

3. Mixing conditions:

Temperature: 20°C

RH level: Intermediate (~50%)

Experimental work

- **Materials and methods**
  - ✓ **Making samples:**

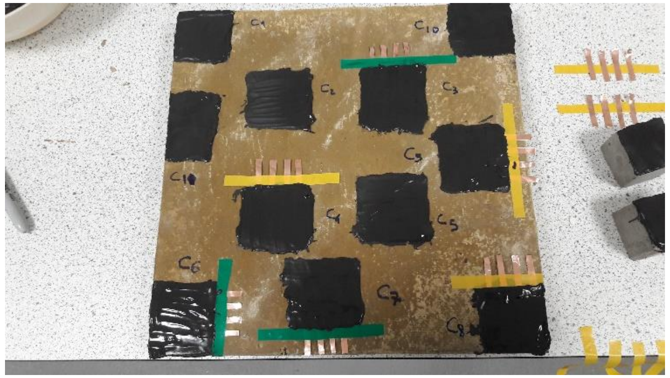
Samples curing conditions

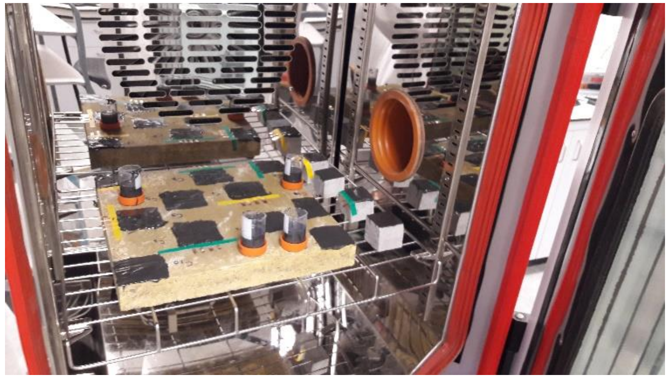
Temperature	RH level	Storage system
20°C	Intermediate (~50%)	Laboratory bench
20°C	High (~ 98%)	Enviromental chamber

Simulating:

→ The real average humidity field conditions

→ The worst humidity condition



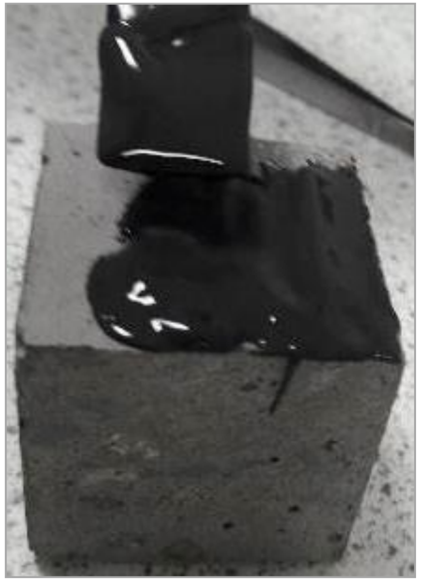


Experimental work

- Materials and methods
  - ✓ Making samples:

Putting geopolymer patches onto concrete surface

Mixing time	Resting time	Putting procedure
10 minutes	0 minutes	Spatula
10 minutes	1 hour	Spatula
10 minutes	4 hours	Spatula
1 hour	0 minutes	Spatula
4 hours	0 minutes	Spatula



Experimental work

- **Materials and methods**
  - ✓ **Analysis methods:**

Analysis method	Property analysed
Visual inspection	Cracks onto the surface
Isothermal calorimetry	Heat of reaction spectrum in dependance of time
Vicat Needle test	Setting time
XRD analysis	Mineral/amorphous composition

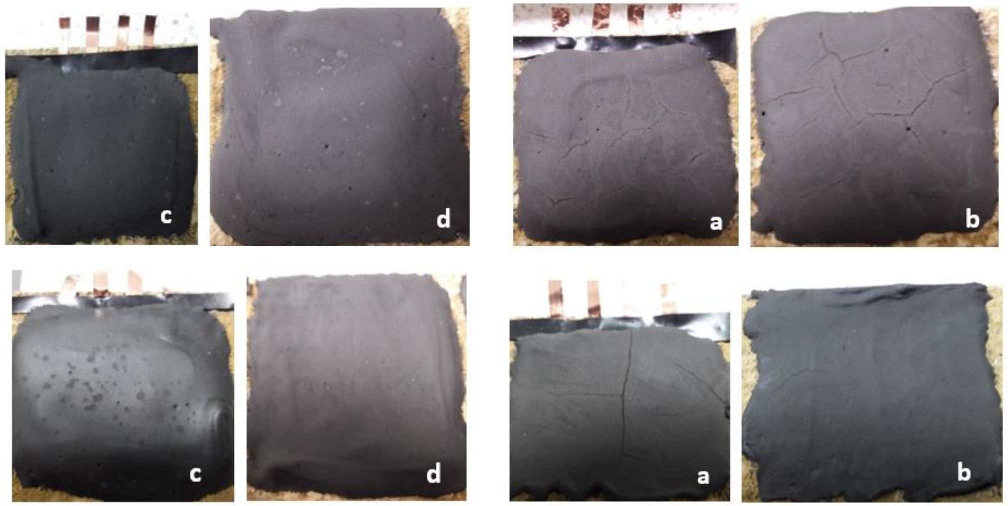
Experimental work

- **Results**
  - ✓ **Visual inspection**

ScotAsh fly ash geopolymers | **Cemex fly ash geopolymers**

Old After 10 min mixing

Old After 4 hours resting/ mixing



No cracks | **Cracks**

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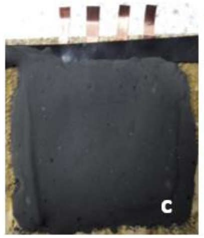
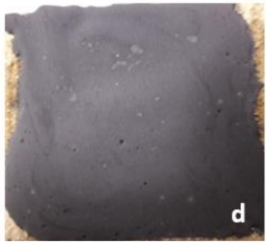
Experimental work

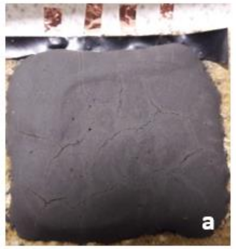
- Results
  - ✓ Visual inspection

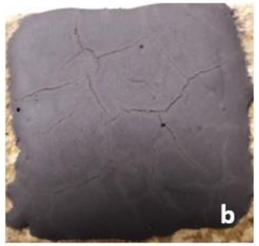
ScotAsh fly ash geopolymers | Cemex fly ash geopolymers

Old
After 10 min mixing

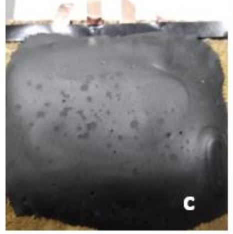


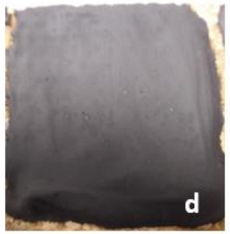


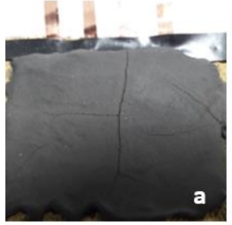


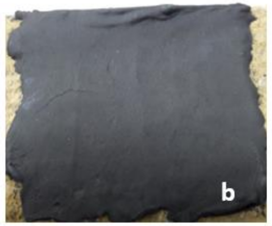


Old
After 4 hours resting/ mixing









No cracks | Cracks

Cemex fly ash geopolymers

Old
After 1 hour mixing

No cracks

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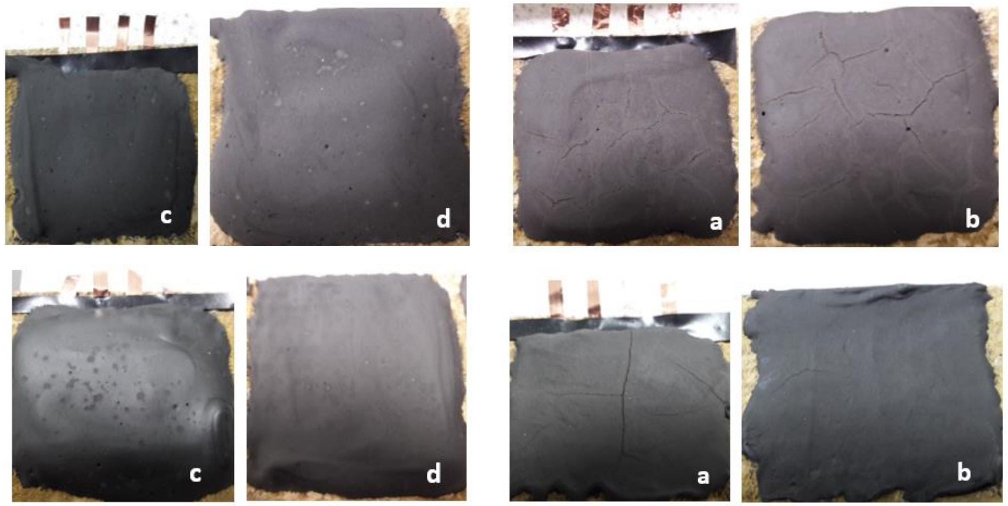
Experimental work

- **Results**
  - ✓ **Visual inspection**

	ScotAsh fly ash geopolymers	Cemex fly ash geopolymers
Old After 10 min mixing		
Old After 4 hours resting/ mixing		
	No cracks	Cracks



Cemex fly ash geopolymers

Old

After 1 hour mixing

Application on **vertical surfaces: few leaching!**

No cracks

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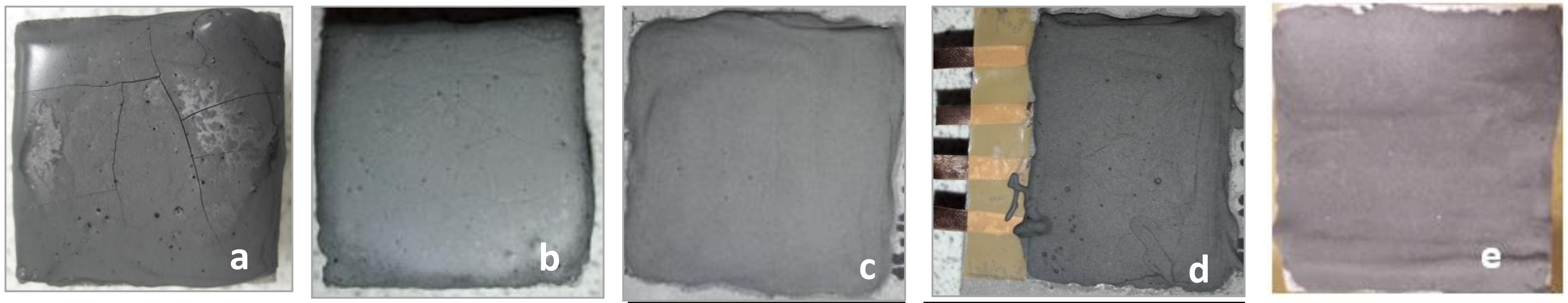
Experimental work

- **Results**
  - **Visual inspection:**

ScotAsh fly ash geopolymers

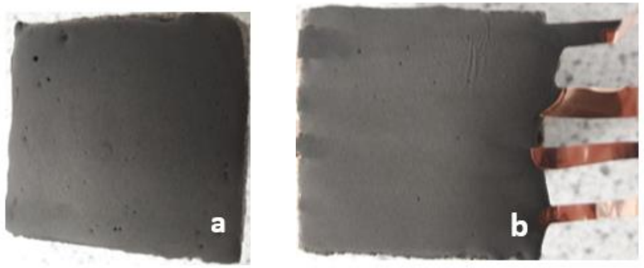


Young	Intermidiate	Old	Old + electrodes	Young
Cracks	Slight cracks	No cracks	No cracks	No cracks

← After 10 minutes mixing →

After 1 hour mixing

Cemex fly ash geopolymers



Young	Young + electrodes
No cracks	No cracks

After 1 hour mixing

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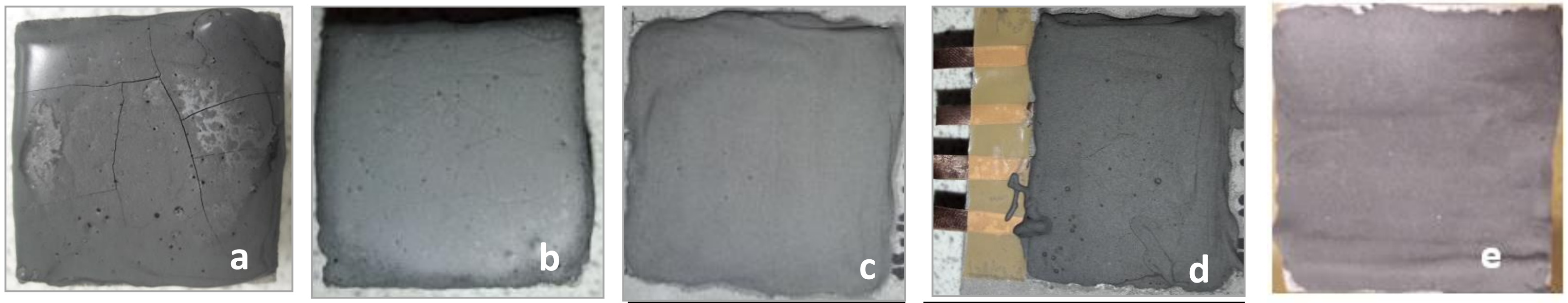
Experimental work

- **Results**
  - ✓ **Visual inspection:**

Dependance on the age of concrete or not?

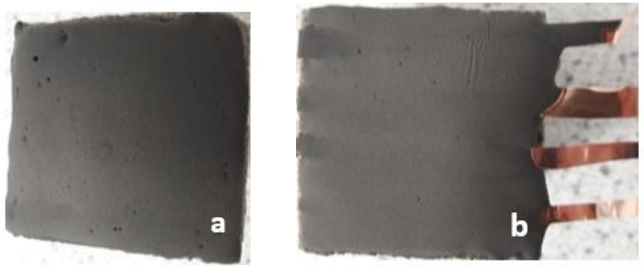
ScotAsh fly ash geopolymers



Young	Intermidiate	Old	Old + electrodes	Young
Cracks	Slight cracks	No cracks	No cracks	No cracks

← After 10 minutes mixing → | After 1 hour mixing

Cemex fly ash geopolymers



Young	Young + electrodes
No cracks	No cracks

After 1 hour mixing

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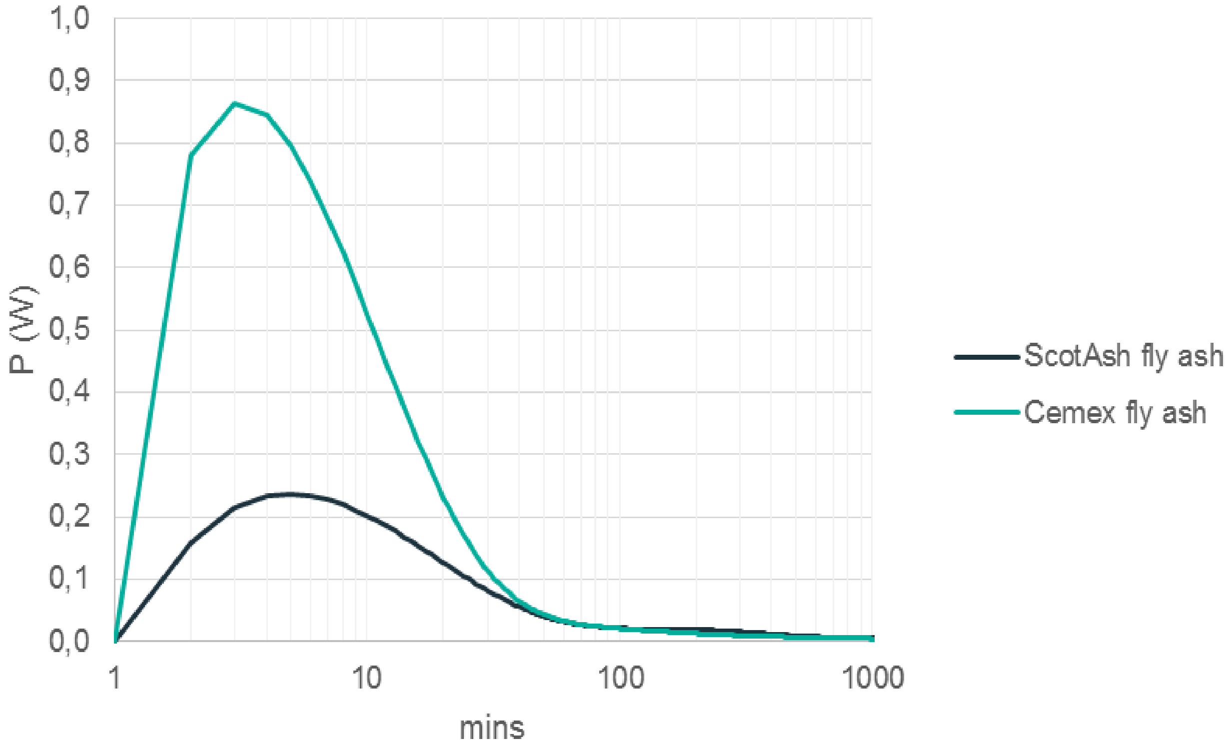
Experimental work

- **Results**
  - ✓ **Isothermal calorimeter analysis:**



- Main extent of reactions ~ after 1 hour
  - for both the types of fly ash
- Remarkable difference in heat of reaction:

Type of fly ash	Heat of reaction (first hour)
Cemex	>
ScotAsh	<

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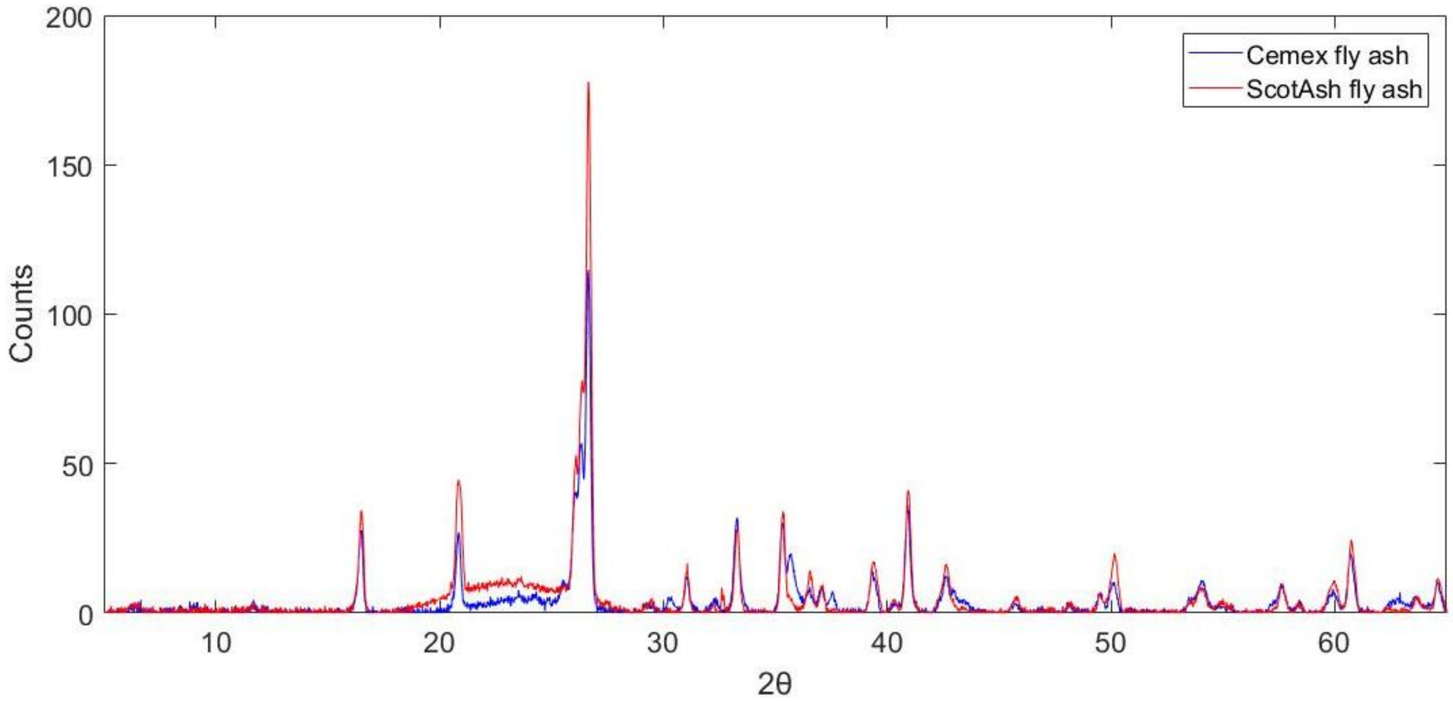
Experimental work

➢ **Results**

✓ **XRD analysis:**



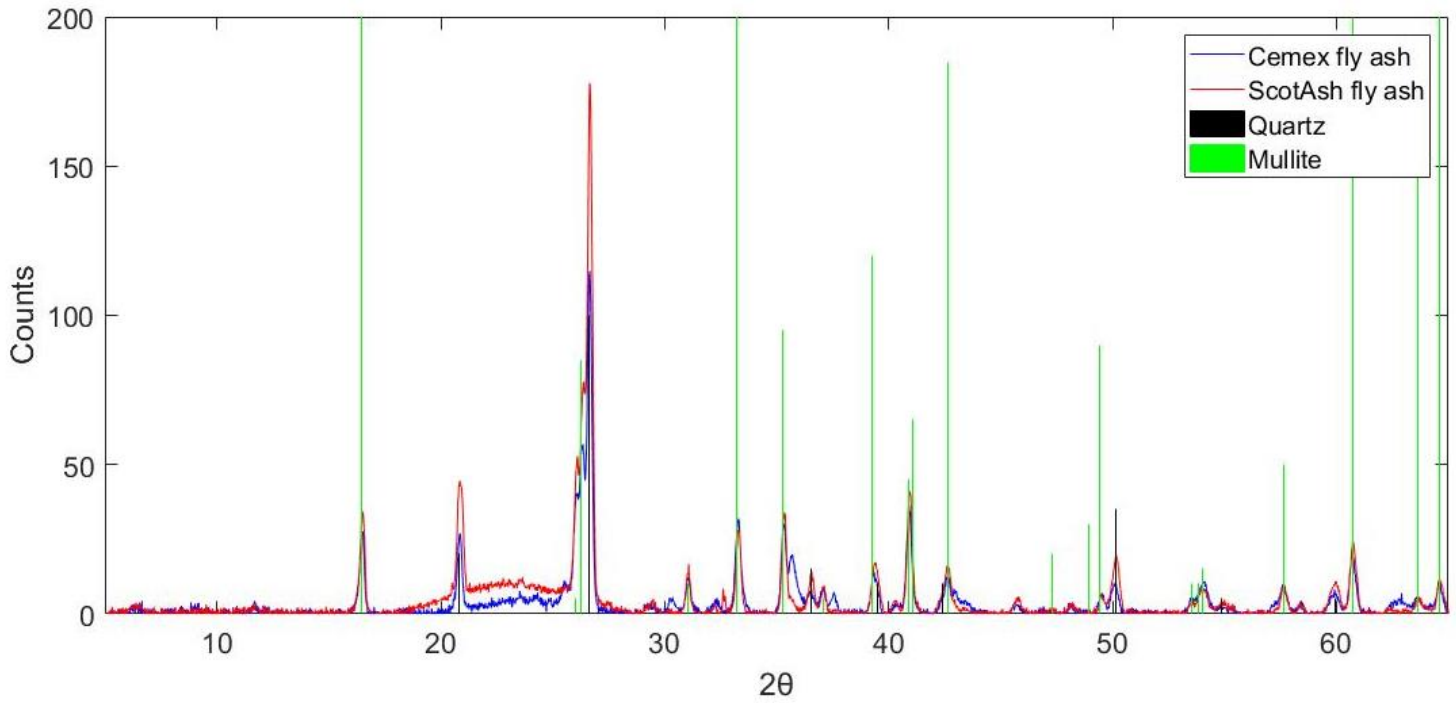
Type of fly ash	Amorphous content
Cemex	<
ScotAsh	>

➢ **Almost the same peaks**

Experimental work

- **Results**

  - ✓ **XRD analysis:**



Type of fly ash	Amorphous content
Cemex	<
ScotAsh	>

- **Almost the same peaks:**
  - ✓ **Quartz and Mullite**

Experimental work

➢ **Results**

✓ **Setting time:**

Vicat Needle test:

Fly ash geopolymer	Setting time
ScotAsh	36 hours
Cemex	5-6 hours

➡ **Faster!**

Experimental work

- **Results**

  - ✓ **Setting time:**

Vicat Needle test:

Fly ash geopolymer	Setting time
ScotAsh	36 hours
Cemex	5-6 hours

→ **Faster!**

Type of fly ash	Si/Al
Cemex	**>**
ScotAsh	**<**

→ **Slower!**

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Experimental work

- **Results**
  - ✓ **Setting time:**

Vicat Needle test:

Fly ash geopolymer	Setting time
ScotAsh	36 hours
Cemex	5-6 hours

→ **Faster!**

Type of fly ash	Particle fineness	Amorphous content
Cemex	>	<
ScotAsh	<	>

Type of fly ash	Si/Al
Cemex	>
ScotAsh	<

→ **Slower!**

Experimental work

- **Results**

  - ✓ **Setting time:**

Vicat Needle test:

Fly ash geopolymer	Setting time
ScotAsh	36 hours
Cemex	5-6 hours

→ Faster!

Type of fly ash	Particle fineness	Amorphous content
Cemex	>	<
ScotAsh	<	>

Type of fly ash	Si/Al
Cemex	>
ScotAsh	<

→ Slower!

Finer is the particle size → Better dissolution

Main component dissolute → Amorphous component

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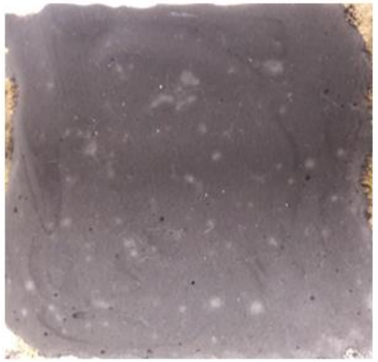
Experimental work

- Results
  - ✓ Efflorescence

Visual inspection



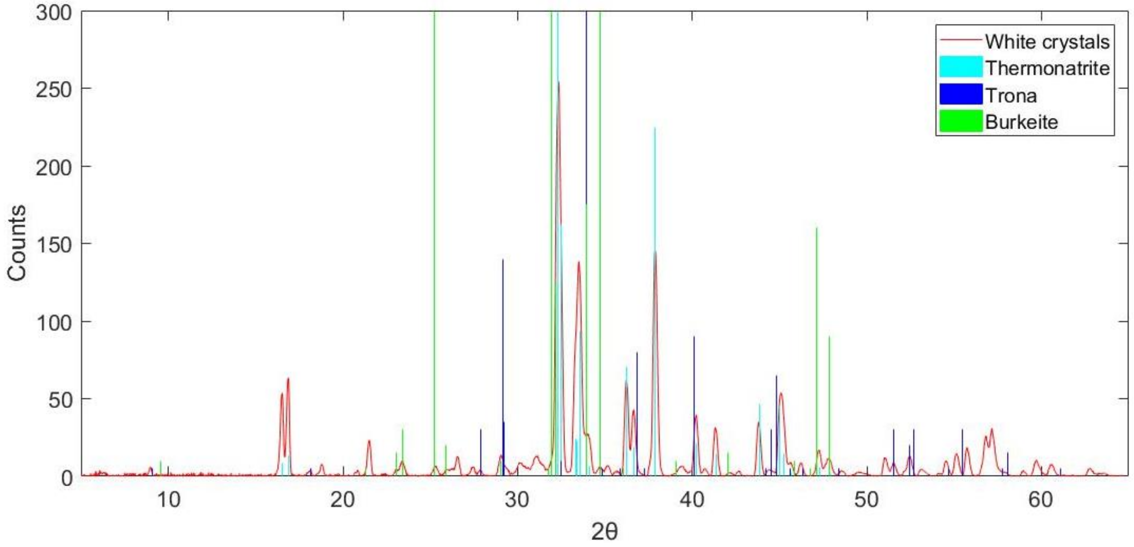
RH level = 50 %

White spots

RH level = 98 %

Crystals

XRD analysis



Thermonatrite = $Na_2(CO_3) \bullet (H_2O)$

Trona = $Na_3(HCO_3)(CO_3) \bullet 2(H_2O)$

Burkeite = $Na_6(CO_3)(SO_4)_2$

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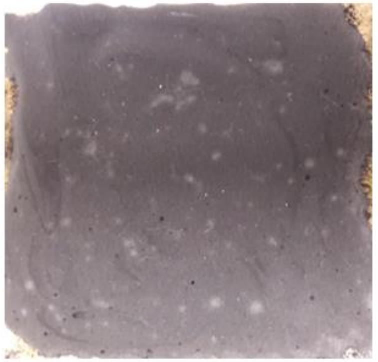
Experimental work

- **Results**
  - ✓ **Efflorescence**

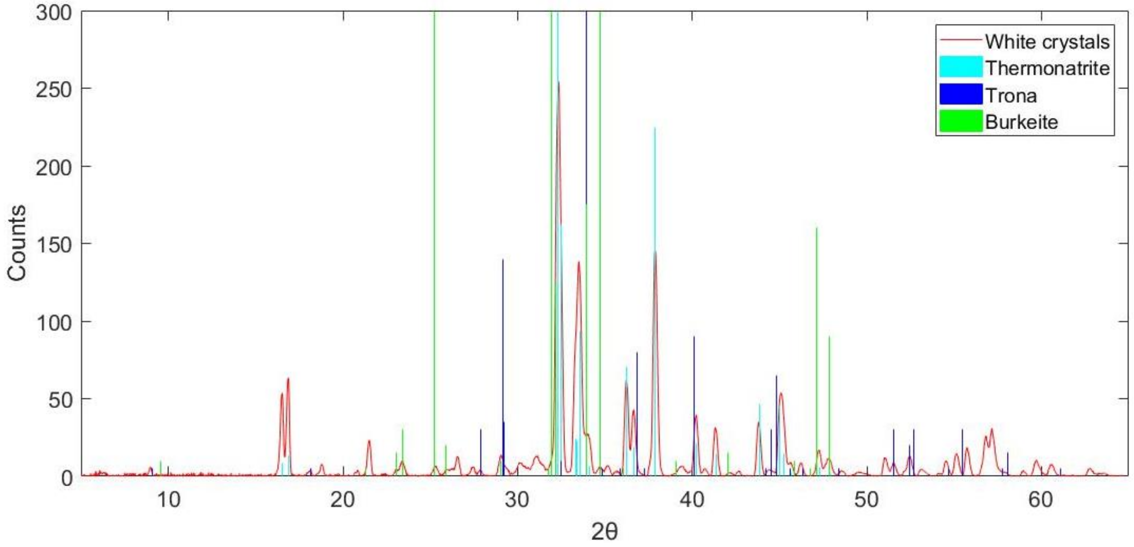
Visual inspection



RH level = 50 %	RH level = 98 %
White spots	Crystals

- Na excess
- High humidity
- CO_2

XRD analysis



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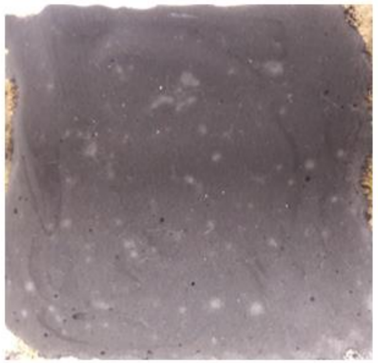
Experimental work

- **Results**
  - ✓ **Efflorescence**

Visual inspection



- Na excess
- High humidity
- CO_2

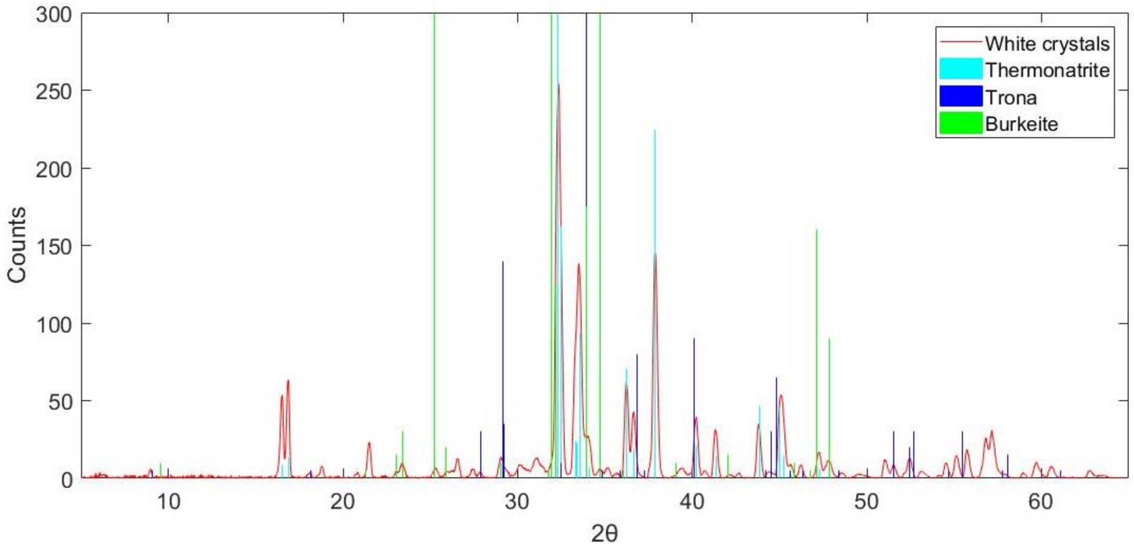
RH level = 50 %

White spots

RH level = 98 %

Crystals

XRD analysis



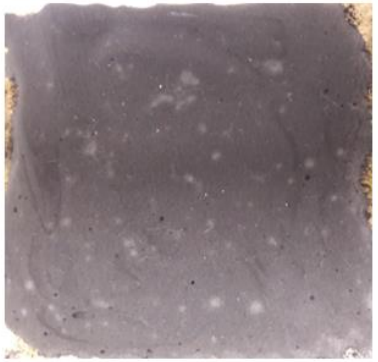
Issue for the sensing system?

Thermonatrite = $Na_2(CO_3)\bullet(H_2O)$
Trona = $Na_3(HCO_3)(CO_3)\bullet 2(H_2O)$
Burkeite = $Na_6(CO_3)(SO_4)_2$

Experimental work

- **Results**
  - ✓ **Efflorescence**

Visual inspection



RH level = 50 %

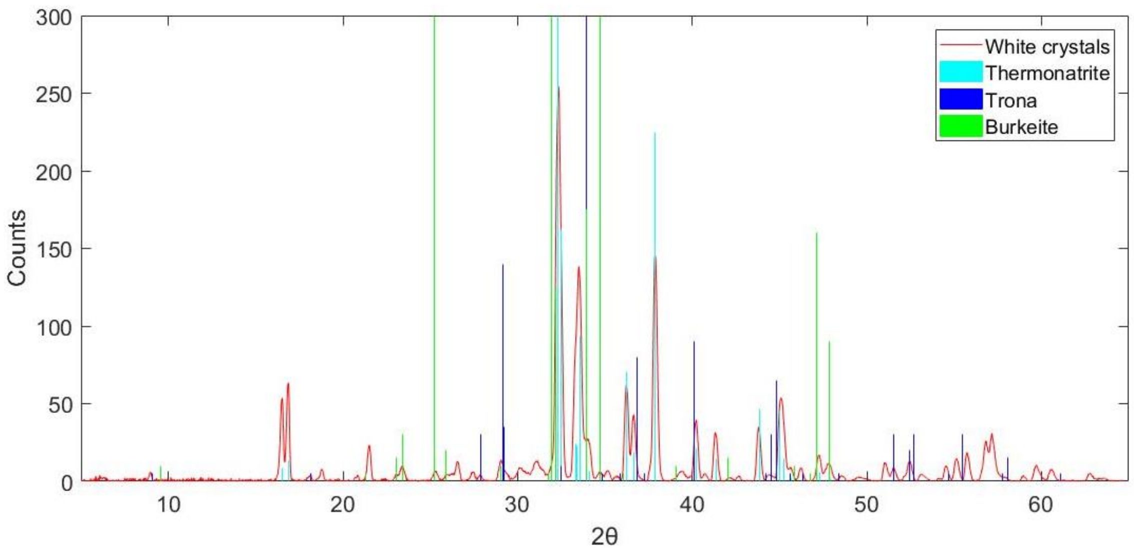
White spots

RH level = 98 %

Crystals

- Na excess
- High humidity
- CO_2

XRD analysis



Thermonatrite = $Na_2(CO_3)\bullet(H_2O)$
Trona = $Na_3(HCO_3)(CO_3)\bullet 2(H_2O)$
Burkeite = $Na_6(CO_3)(SO_4)_2$

Issue for the sensing system?

- **Don't know yet!**

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Conclusions

- **Optimistic results:**

  - Uncracked geopolymer patches → both onto young and old concretes specimens surface
    - Putting geopolymer binder onto concrete after a reasonable time from the initial mixing:
      - ✓ After the main extent of heat release reactions
      - ✓ Far enough from the setting time

        → about 1 hour
    - Better result after continous mixing than after a period of resting of the geopolymer binder
  - Possibility to reach a suitable (fast but not too fast) setting time with a category S of low calcium fly ash
    - No need to add any binder (such as fibers, calcium or cement)

Conclusions

❑ <u>Main issue → efflorescence</u>:

- At intermediate and high RH levels → worse for high RH level
- Due to Na excess, humidity content, CO_2
  - ➢ We can reduce it by:
    - ✓ Balancing the Na/Al ratio → we could reduce Na^+ inside the binder → sensing performance?
  - ➢ By the EIS analysis we will evaluate if it is an issue for the sensing system

❑ <u>Future work → applying the EIS analysis to the samples</u>:

- Evaluating the influence of the different parameters on the sensing system
- Modifying parameters in dependance of the EIS response
- Applying different values of Chloride concentrations at different RH levels → simulating field real conditions

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Thank you!

Thank you for your time!

Any questions

E-mail contact:
lorena.biondi@strath.ac.uk

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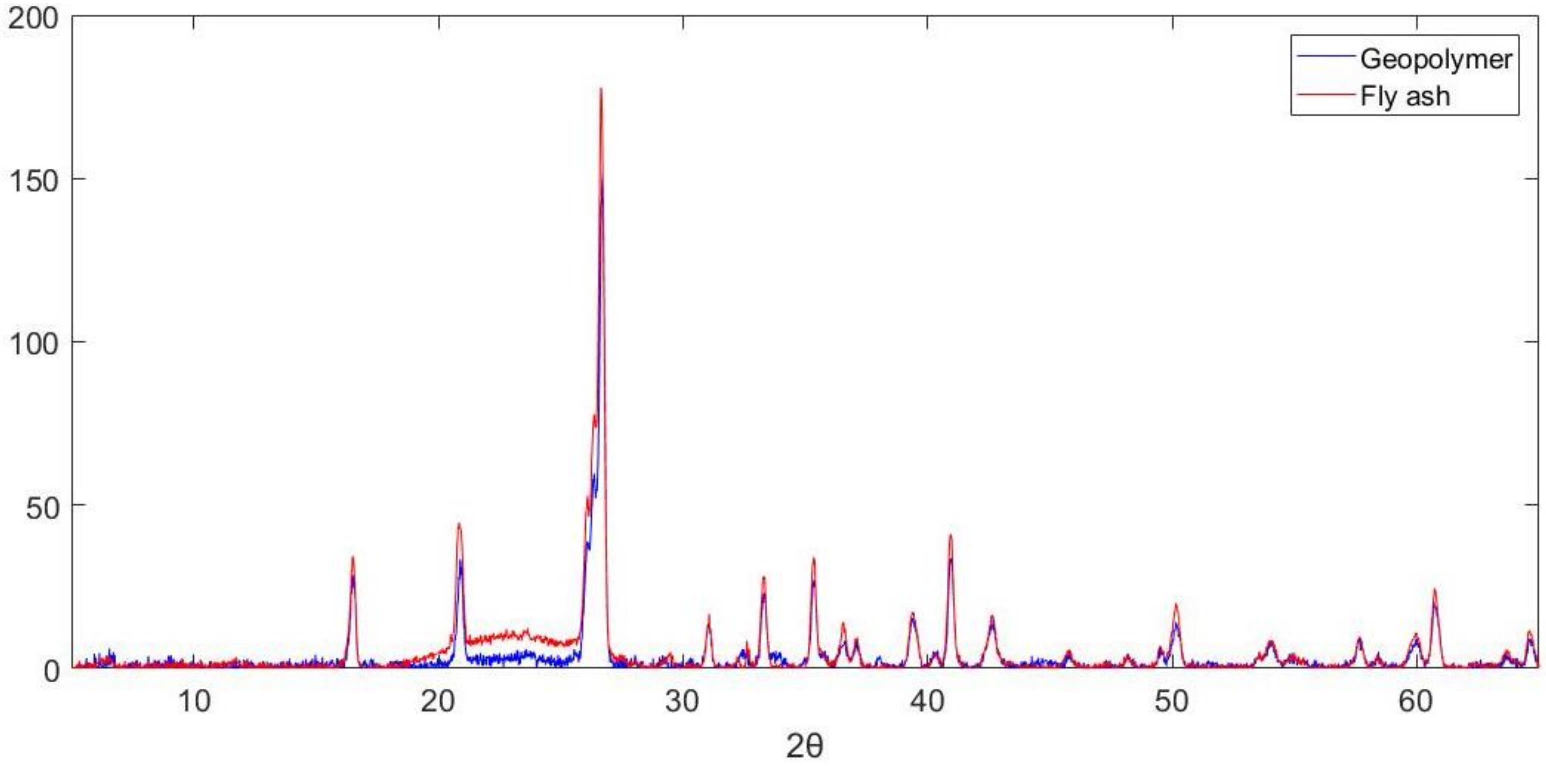
Experimental work

➢ **Results**

✓ **XRD analysis**



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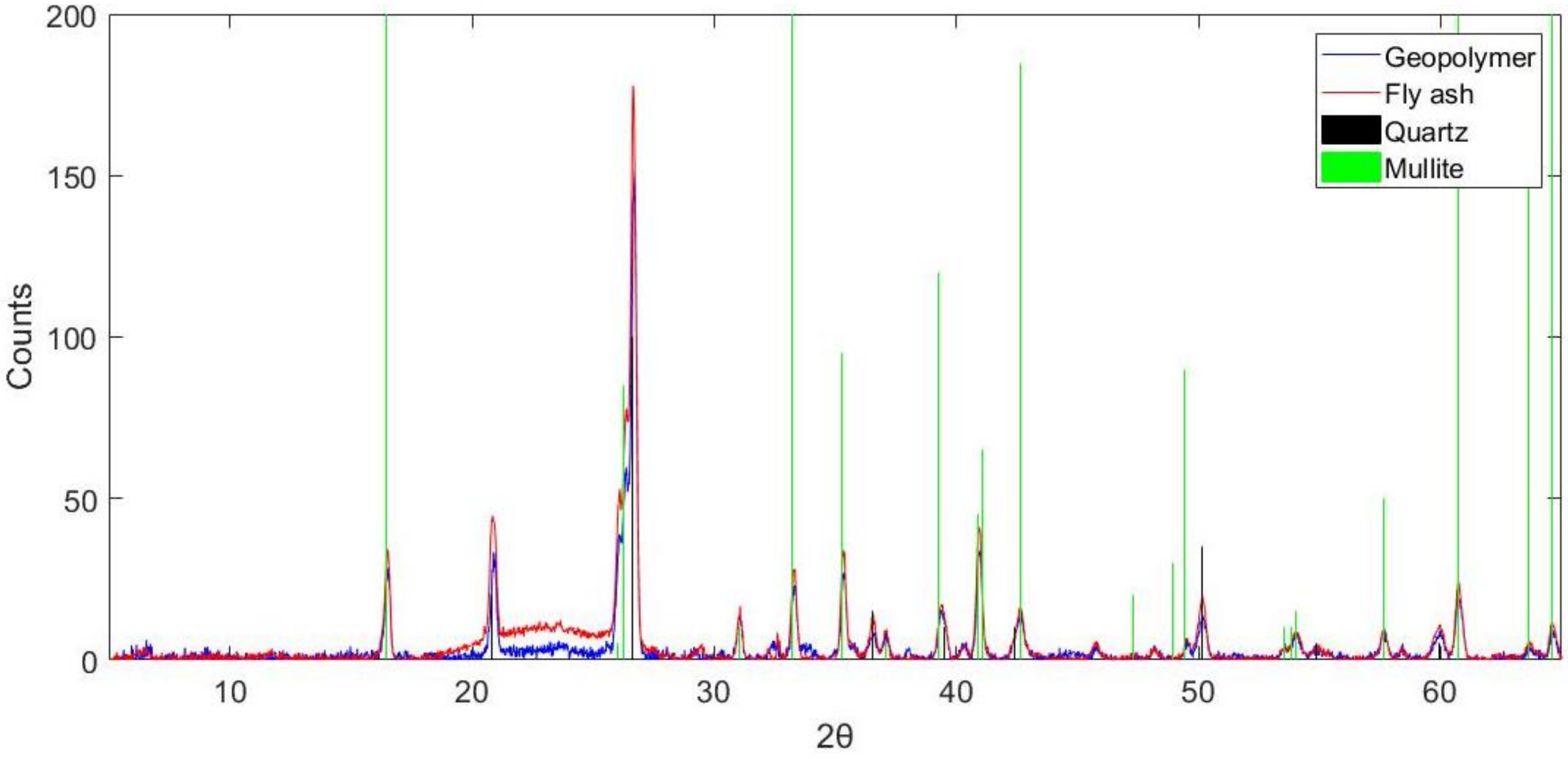
Experimental work

- **Results**
  - **XRD analysis**



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First Principles Simulation of Radiation Effects in Cement

RYAN KAVANAGH

J. KOHANOFF AND G.A. TRIBELLO

DISTINCTIVE THEME MEETINGS – THEME 4: STRUCTURAL INTEGRITY

rkavanagh04@qub.ac.uk

Talk Contents

1. Introduction - Why use Cement?
2. Cement minerals Studied
3. Results
4. Conclusions and Future Work

The Need for Decommissioning

Waste Category	Amount (April 2016)	Future Arisings	Lifetime Total
HLW	1960	-820	1150
ILW	99000	191,000	290,000
LLW	30100	1,320,000	1,350,000
VLLW	9345	2,860,000	2,860,000
Total	**132,000**	**4,360,000**	**4,490,000**

Figures reported in Volume m^3

The Advantages of “Nuclear” Cement

- Cement widely available. You can practically dig up the ingredients

- Easy to use and inexpensive – Much cheaper than appropriate glasses

- Produces both physical and chemical barriers for waste. High pH, can mould to any shape, physical trapping in pores...

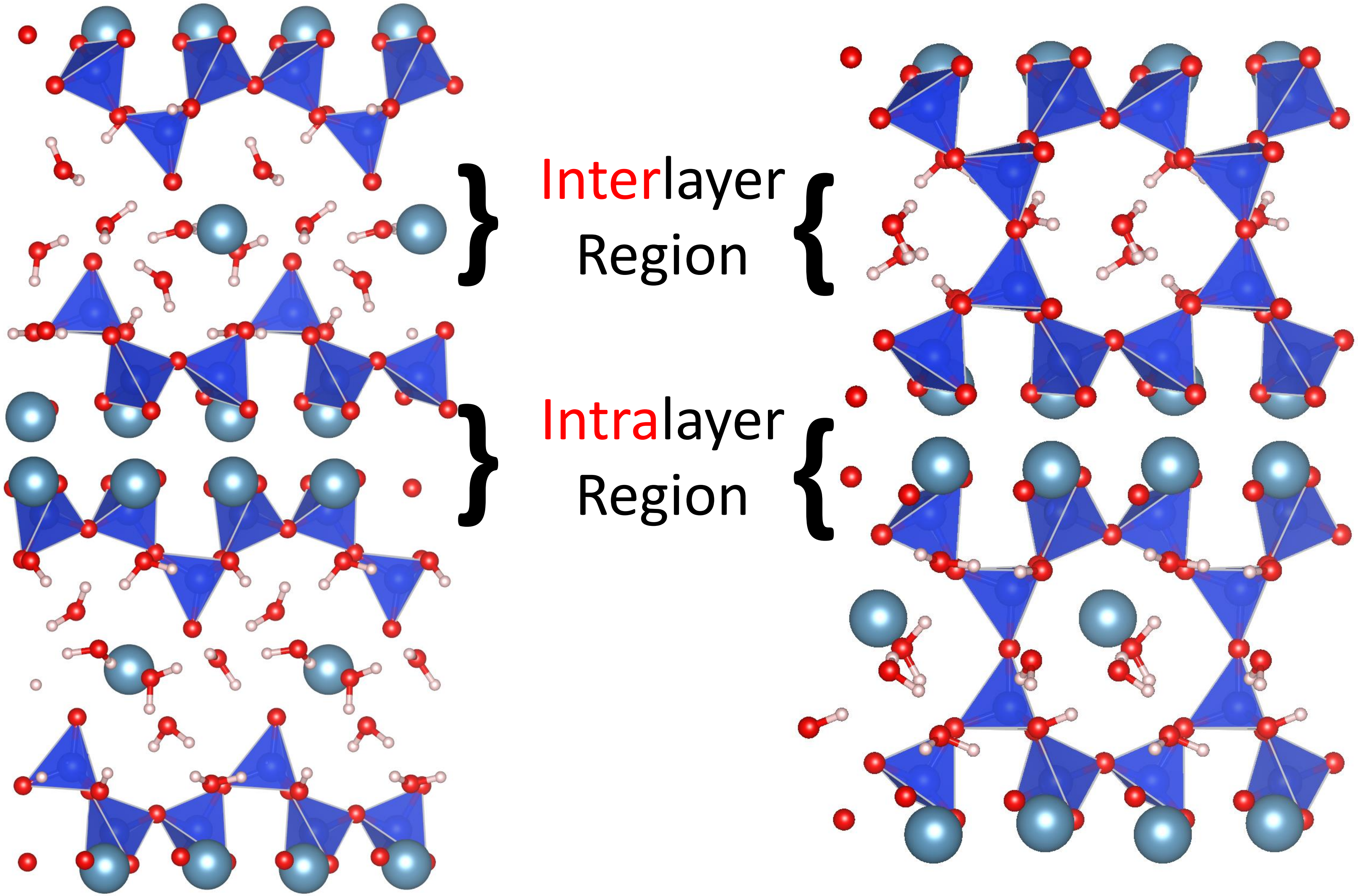
- Numerous “recipes” allow tailoring of properties – tuneable pH and chemistry

What is Cement?

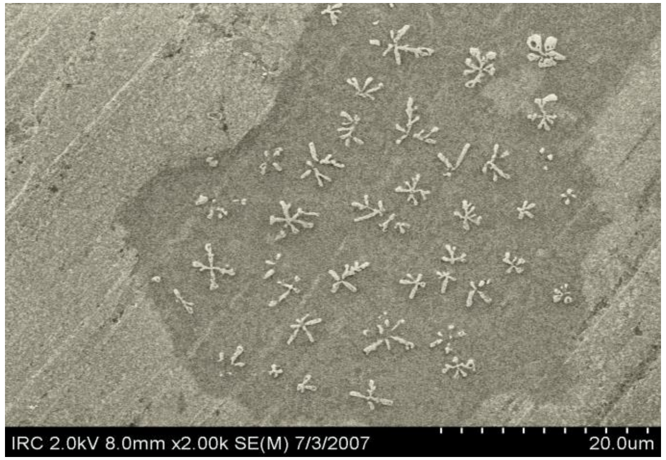
- Calcium Silicate Hydrate minerals
- Extremely variable composition and morphology – 2 “phases” widely believed
- Often even more complicated due to supplementary materials such as Blast Furnace Slag and Pulverized Fly ash

CSH (I)	CSH (II)
C/S Ratio between 0.67 and 1.4	C/S Ratio 1.5 or more
Poorly Crystalline “Tobermorite” Minerals	Poorly Crystalline “Jennite” Mineral

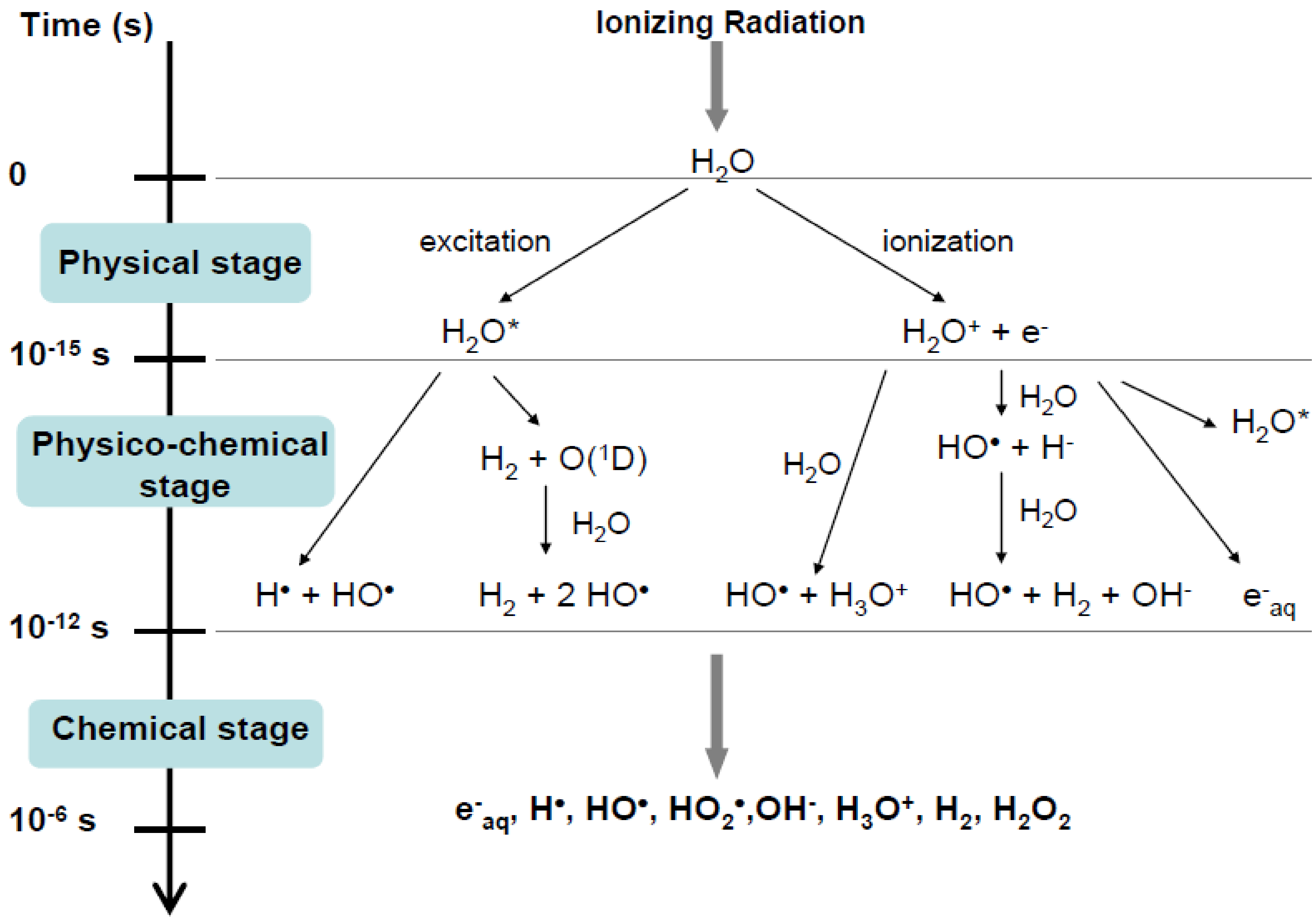
UK “White” Cement


Interlayer
Region
Intralayer
Region

Microcracking and Physical Damage

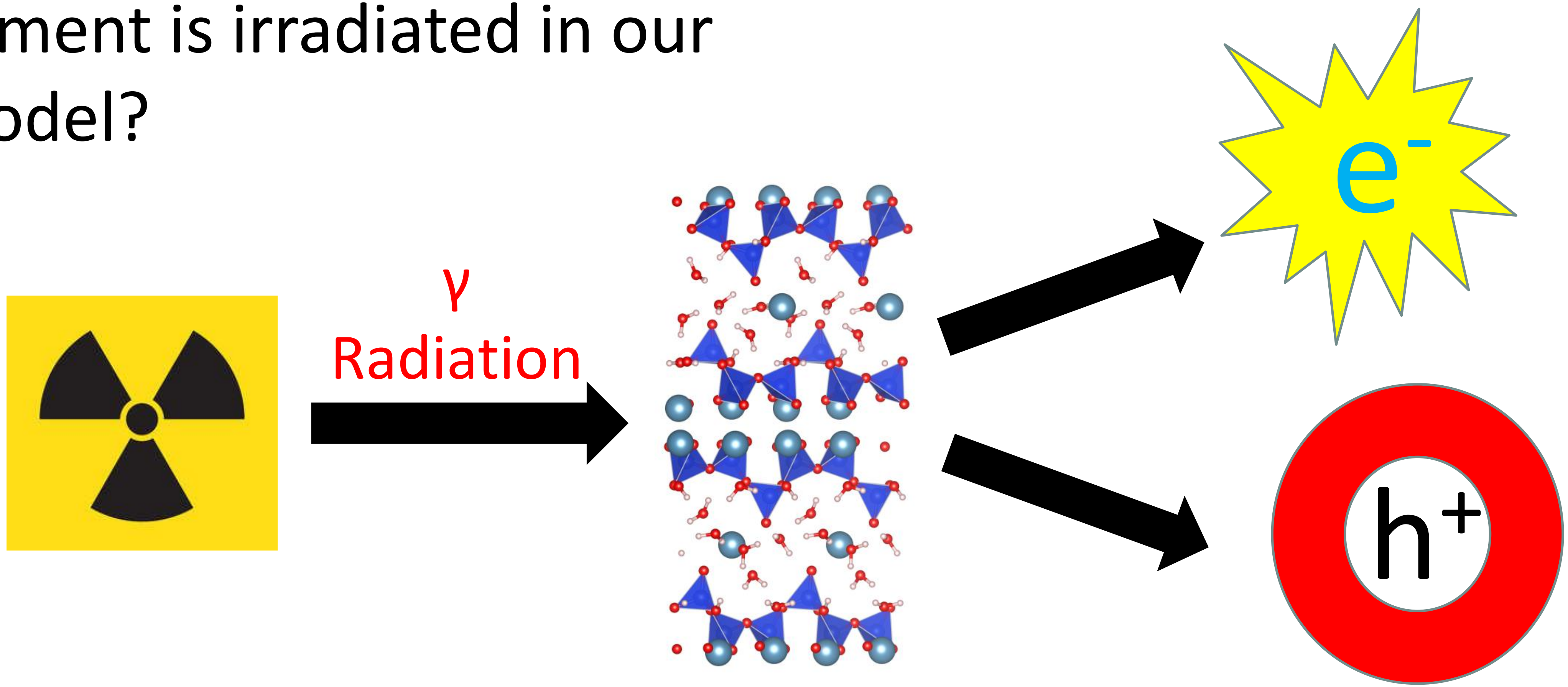


Carbonation, chlorination and chemical damage….

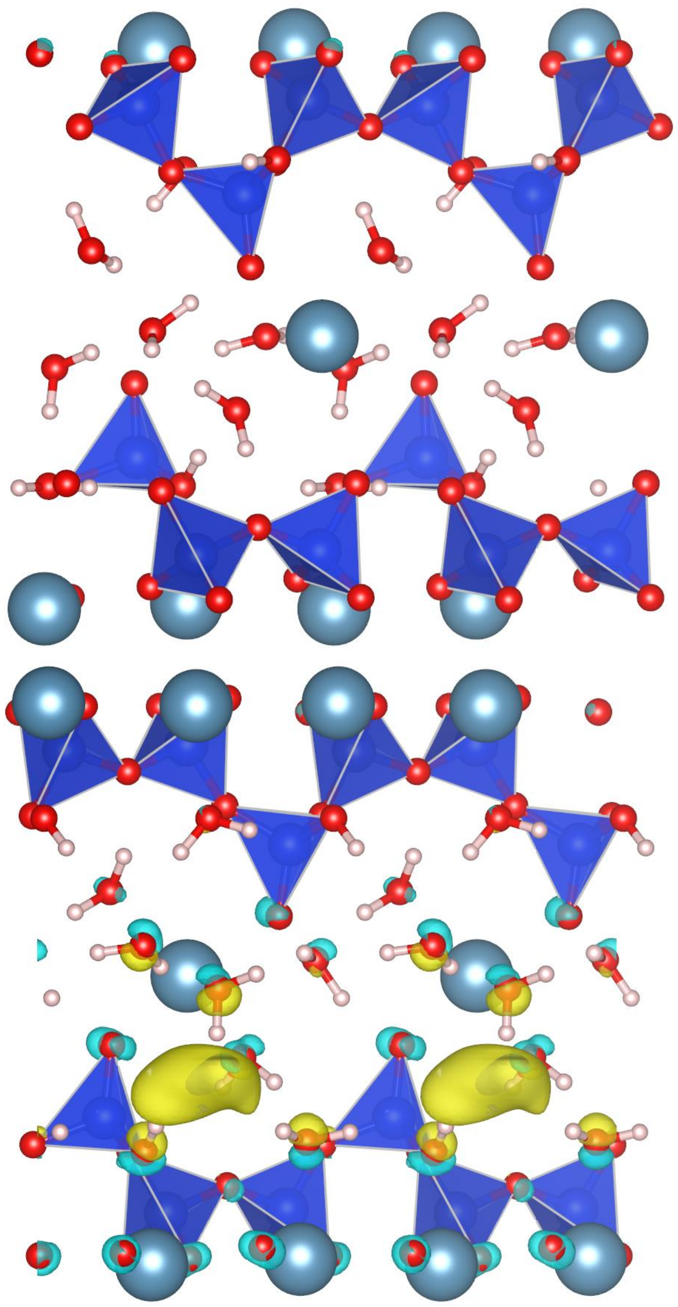


As well as a whole host of aqueous radiation chemistry due to the sludges and radionuclides!

What happens when the cement is irradiated in our model?

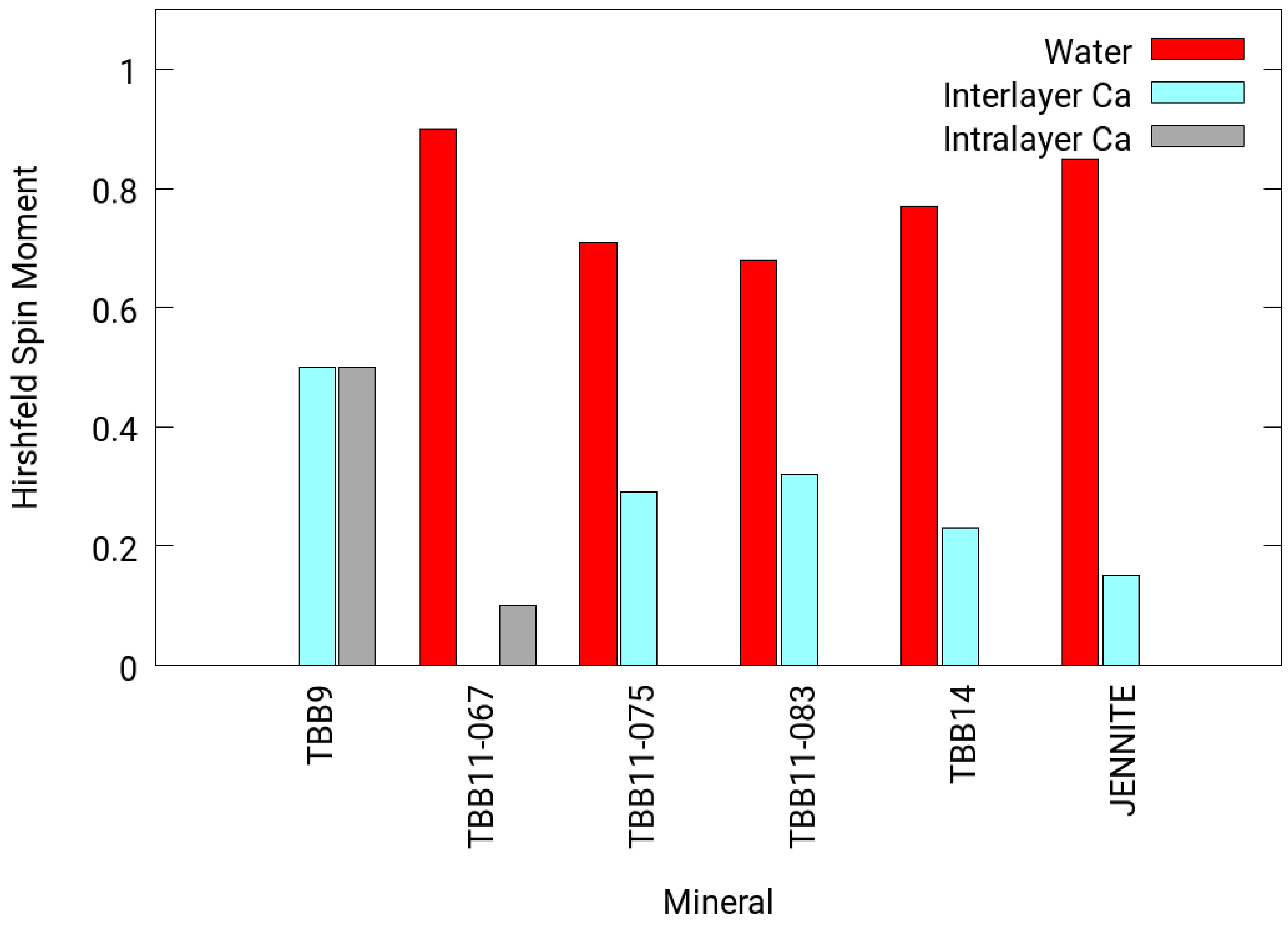


Other factors such as α/β radiolysis, ballistic collisions, and other products of irradiation such as excitons are not considered…

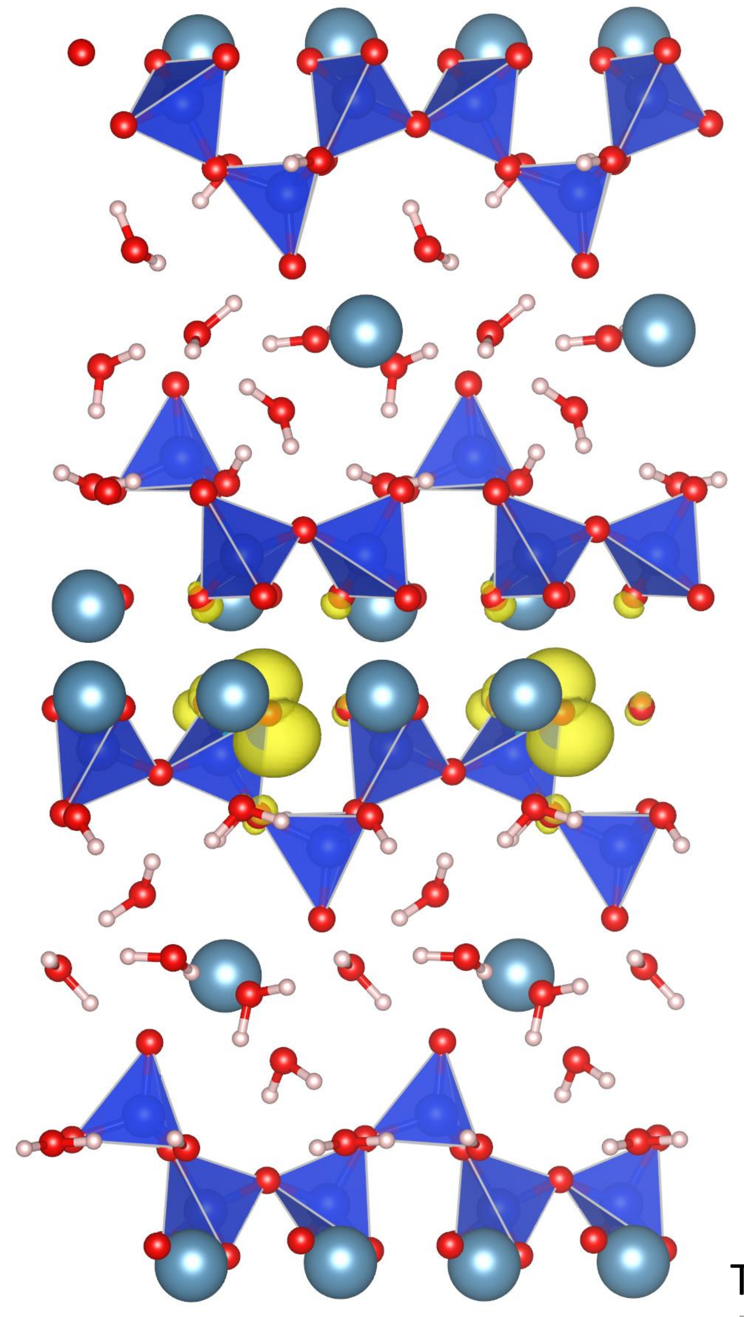


Excess Electrons tend to locate in the interlayer region where water and calcium ions are contained. Where there are interlayers that contain calcium and regions which don’t, the interlayer with calcium is favoured.

Tobermorite 14Å Excess Electron Isocontour. Drawn at 0.015 e/$Å^{-3}$



Water
Interlayer Ca
Intralayer Ca
Hirshfeld Spin Moment
0
0.2
0.4
0.6
0.8
1
TBB9
TBB11-067
TBB11-075
TBB11-083
TBB14
JENNITE
Mineral



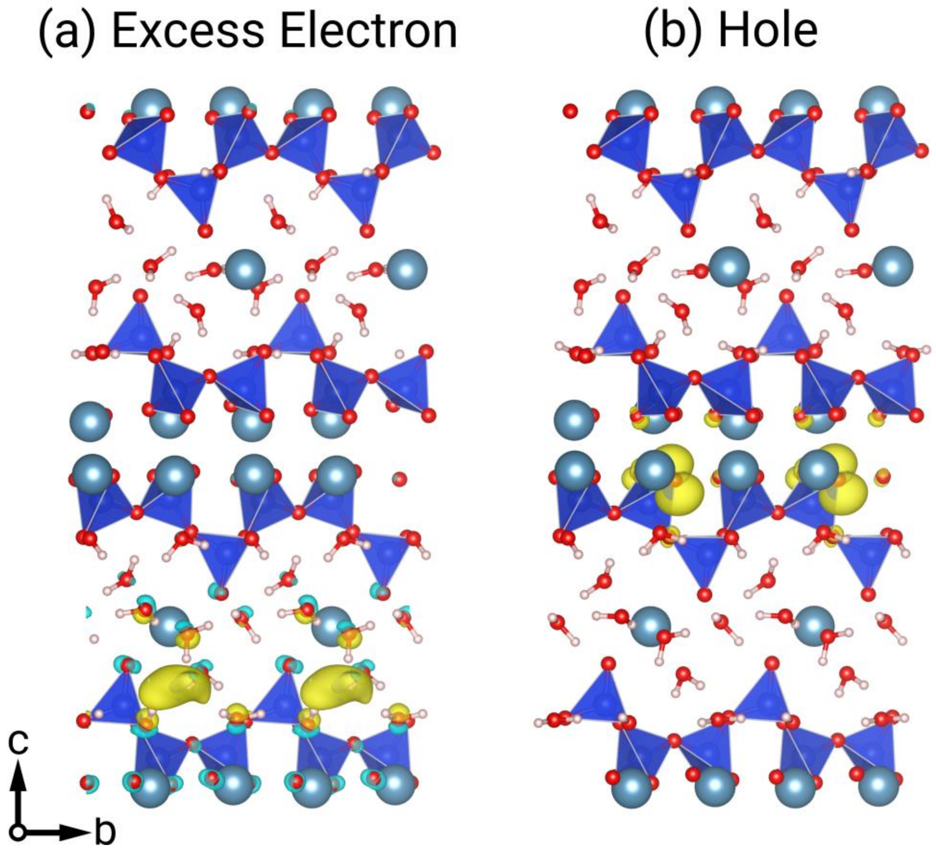
Holes tend to locate in the intralayer region on tetrahedral oxygen atoms. These silicate O˙ radicals are immobile and point towards the CaO polyhedral intralayer.

Tobermorite 14Å Hole Isocontour. Drawn at 0.015 e/Å^{-3}

Implications of Results

Excess electrons tend to locate in the Interlayer space where calcium is often surrounded by water. Calcium appears to “direct” the electron into these regions. As such, low calcium blends may reduce the amount of electrons trapped in cement. Like BFS, PFA and white cements!

Holes locate in the electron-rich CaO intralayer region. The oxygen atoms on which the hole locates usually only have one Si-O link and as such possess lone-pairs that are more “available” than other electrons in the system. These holes are benign – They are immobile and cannot react with the pore water to form radicals.



Cement and Concrete Research 100 (2017) 110–118

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Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Production of H_2 by water radiolysis in cement paste under electron irradiation: A joint experimental and theoretical study

Sophie Le Caër[a,*], Lucile Dezerald[b,c,d], Khaoula Boukari[e], Maxime Lainé[a], Sébastien Taupin[a,b,c], Ryan M. Kavanagh[f], Conrad S.N. Johnston[f], Eddy Foy[a], Thibault Charpentier[a], Konrad J. Krakowiak[g,b], Roland J.-M. Pellenq[b,c,e], Franz J. Ulm[b,c], Gareth A. Tribello[f], Jorge Kohanoff[f], Andres Saúl[e,*]

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[b] Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
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[e] Aix-Marseille University, CINaM-CNRS UMR 7325 Campus de Luminy, 13288 Marseille cedex 9, France
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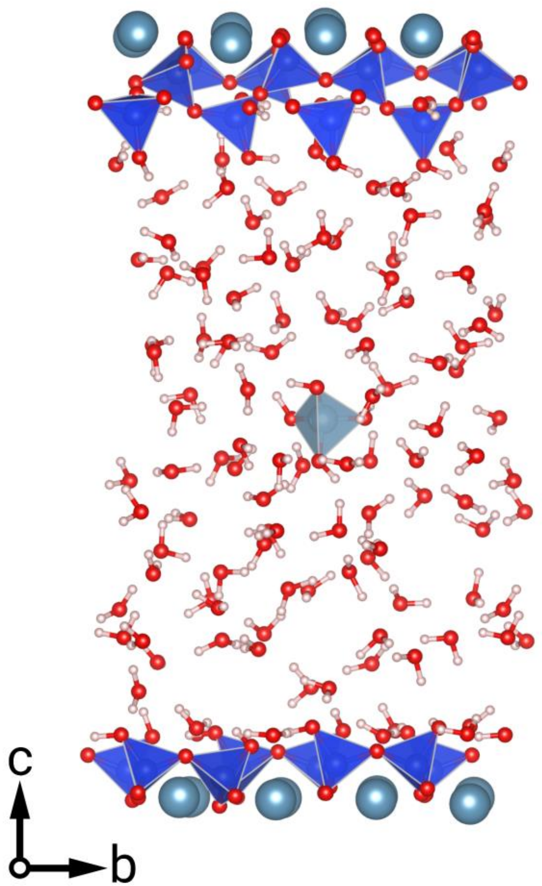
https://doi.org/10.1016/j.cemconres.2017.05.022

Future Work

- Investigating substitutions of elements of interest – Strontium, Caesium, Actinides…
- Do they have notable effects on the stability of the cement matrix?
- Will these elements become immobilized chemically or physically?



Thank You for Your Attention!

UKCP consortium and funded by EPSRC grant ref EP/K013564/1.

Methodology Summary

- Partial occupancies of Tobermorite 11Å and 14Å resolved using Quantum Espresso – The lowest energy variant was assumed to be the most stable. Tobermorite 9Å and Jennite were simply checked for stability.
- All minerals were transferred to CP2K for electronic defect calculations using the PBE and M06-2X functionals. This consists of adding or removing an electron into the simulation. (Altering charge to +1 and -1 respectively)
- PBE, a standard DFT GGA method was not found to provide adequate results, hence the use of the M06-2X hybrid functional. The addition of extra kinetic energy density terms allows "symmetry breaking" effects which provide more accurate results.

Methodology – Creating the Models

- Partial Occupancies in Tobermorite 11Å and Tobermorite 14Å calculated with Quantum ESPRESSO using the PBE functional.

- Kinetic Energy cutoff for Wavefunctions (ecutwfc) of 80 Ry and K.E. cutoff for charge density and potentials (ecutrho) of 640 for all calculations

- Ultra-Soft Vanderbilt Pseudopotentials with 3x3x1 k-point grid for tobermorite 11Å and 4x4x1 grid for tobermorite 14Å

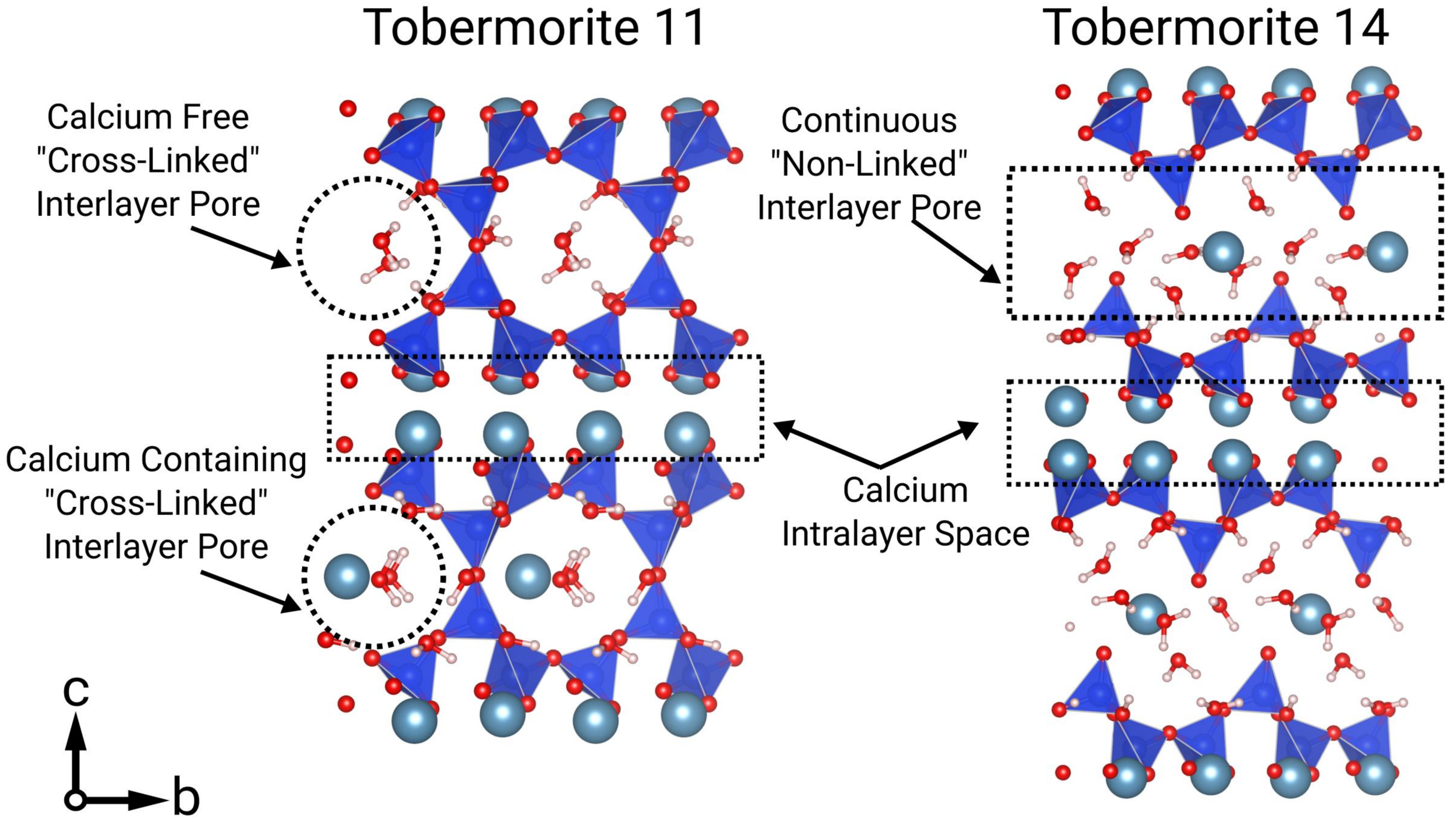
Methodology 2 – Electronic Defects

- All subsequent calculations performed in CP2K opensource electronic structure code. PBE and M06-2X meta-GGA functionals employed (i.e. kinetic energy density dependency terms)

- Unit cells optimized at 0, +1 and -1 charges to simulate the effects ionizing radiation.

- Calculations employed the Gaussian Plane Wave (GPW) approach in the QUICKSTEP module with Gaussian-centered molecularly optimized (MOLOPT) basis sets at the TZVP level and a plane wave cutoff of 800 Ry throughout. GTH Norm-Conserving pseudopotentials as standard.

- M06-2X calculations used 54% HFX as standard for the functional and CP2K ADMM basis sets with a truncated interaction potential used to reduce cost.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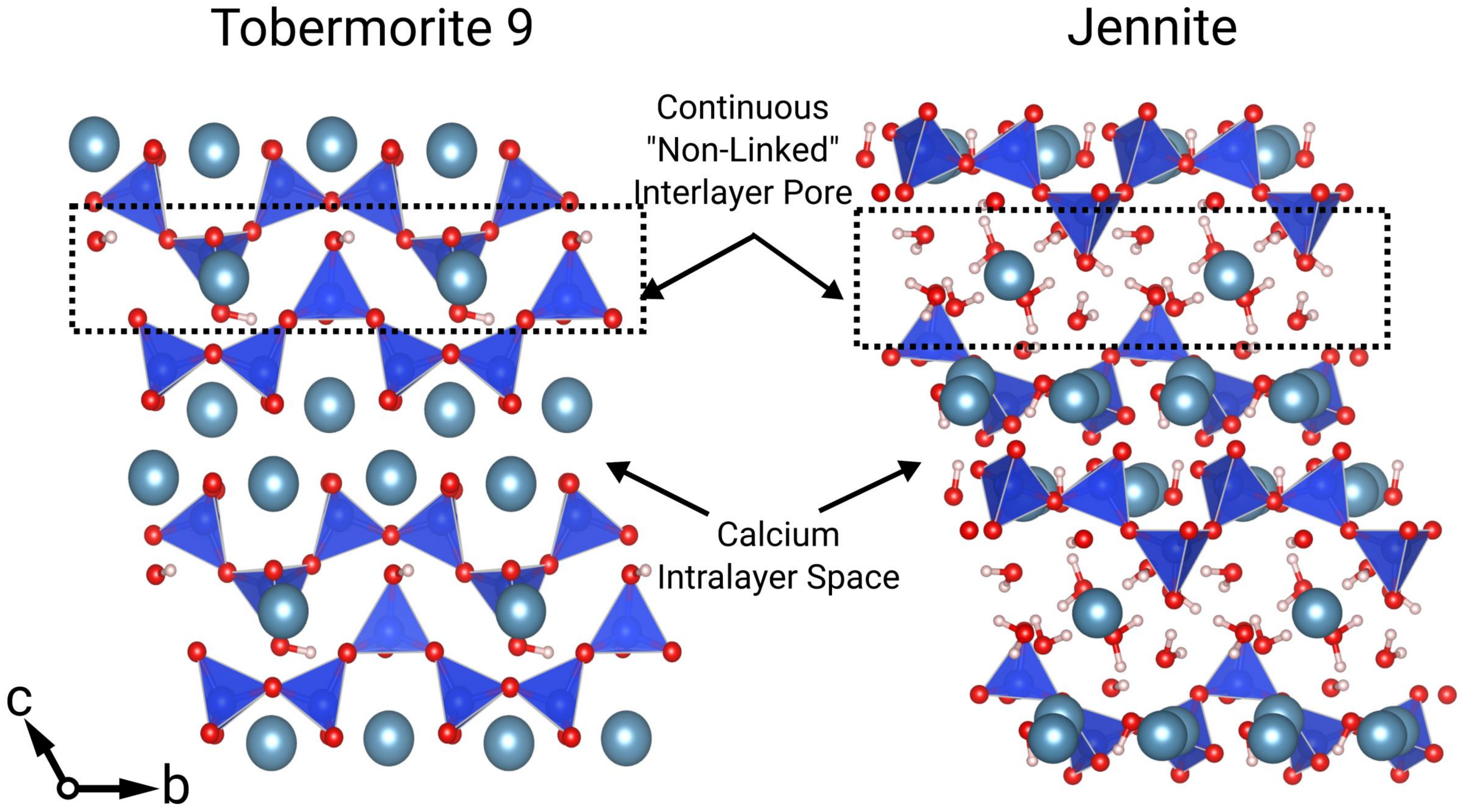
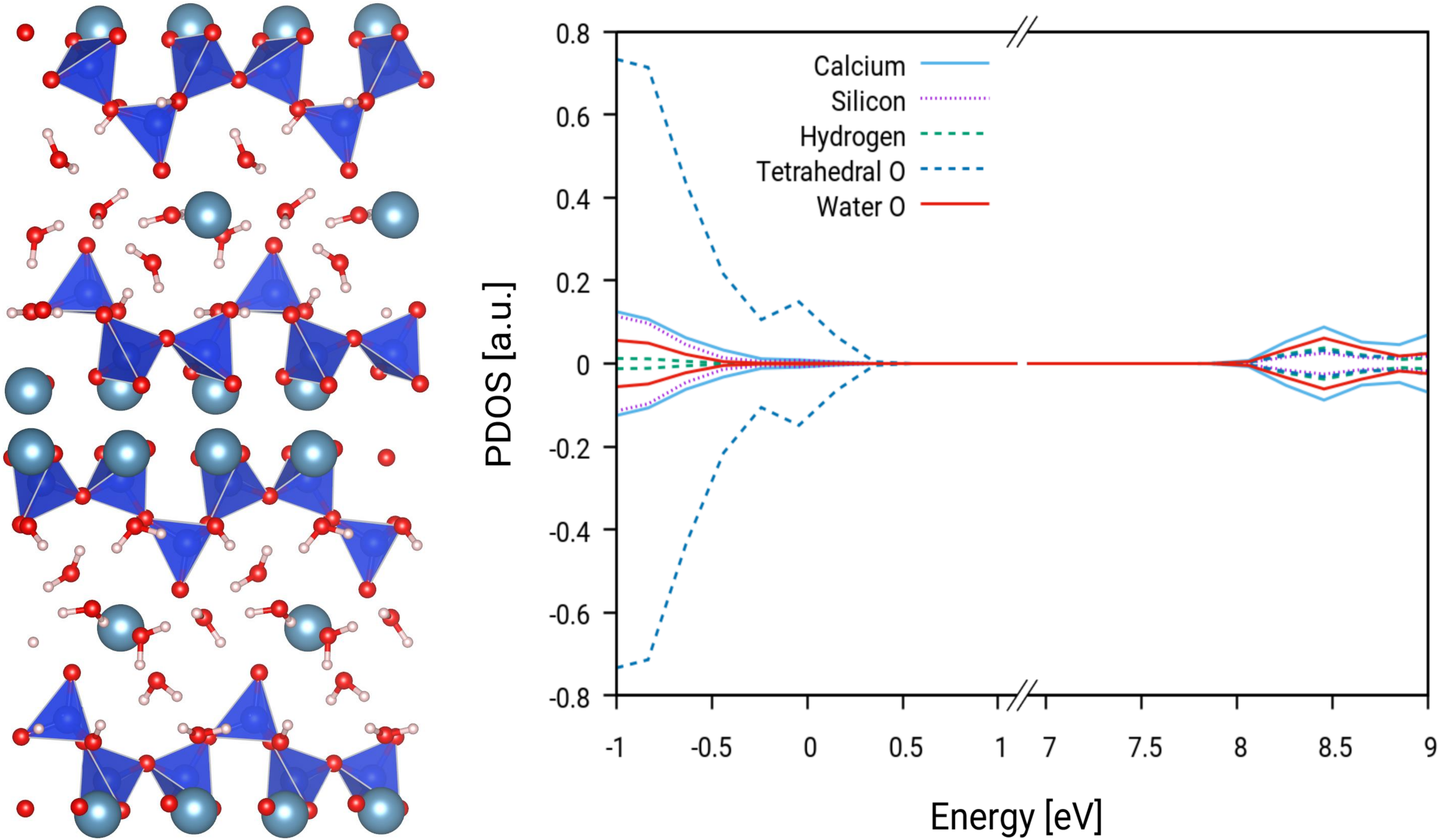
Tobermorite 14
Calcium Free
"Cross-Linked"
Interlayer Pore
Continuous
"Non-Linked"
Interlayer Pore
Calcium Containing
"Cross-Linked"
Interlayer Pore
Calcium
Intralayer Space
c
b


Tobermorite 9
Jennite
Continuous
"Non-Linked"
Interlayer Pore
Calcium
Intralayer Space
c
b



Calcium
Silicon
Hydrogen
Tetrahedral O
Water O
PDOS [a.u.]
Energy [eV]
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-0.5
0
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7.5
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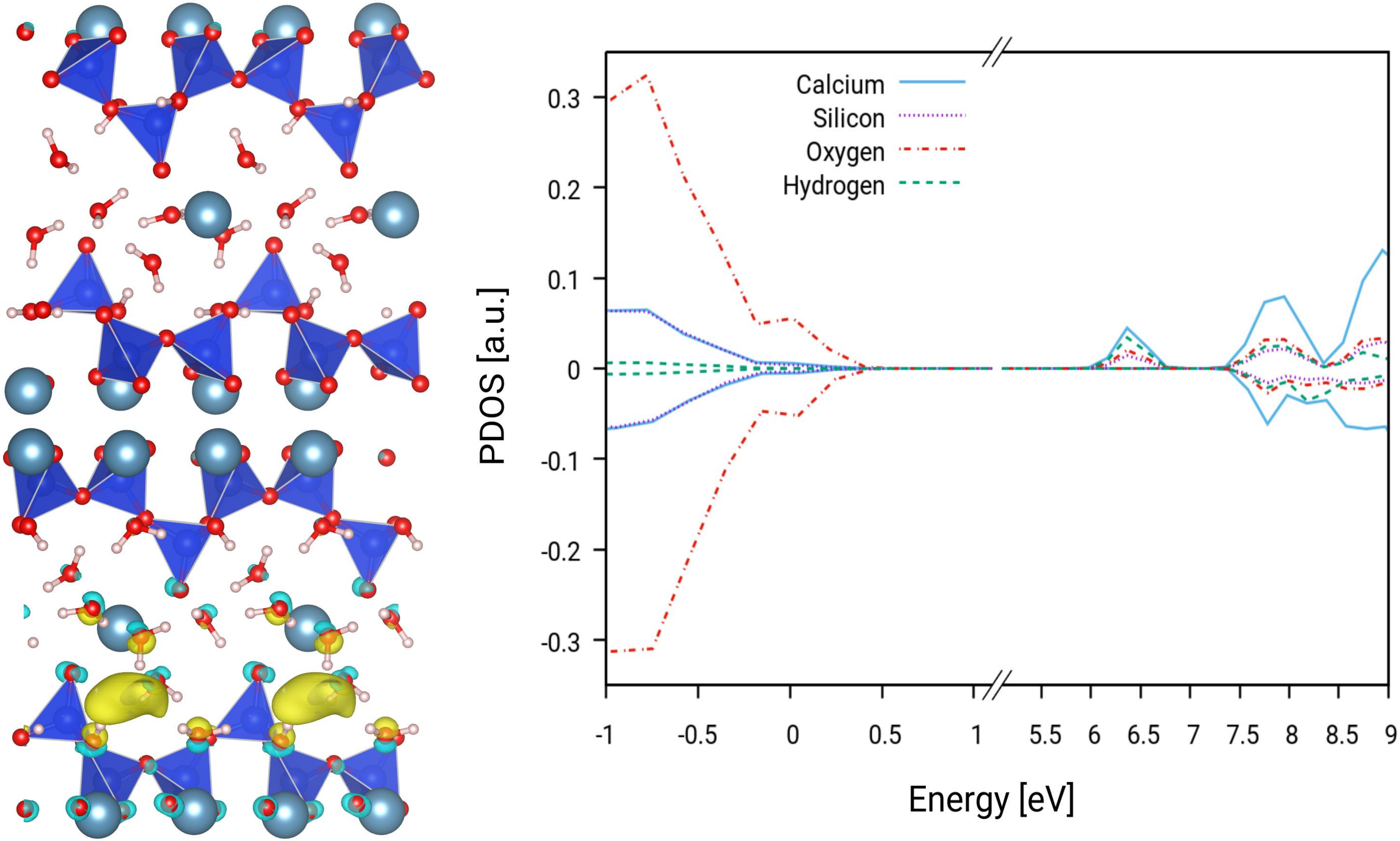
8.5
9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Silicon
Oxygen
Hydrogen
PDOS [a.u.]
Energy [eV]
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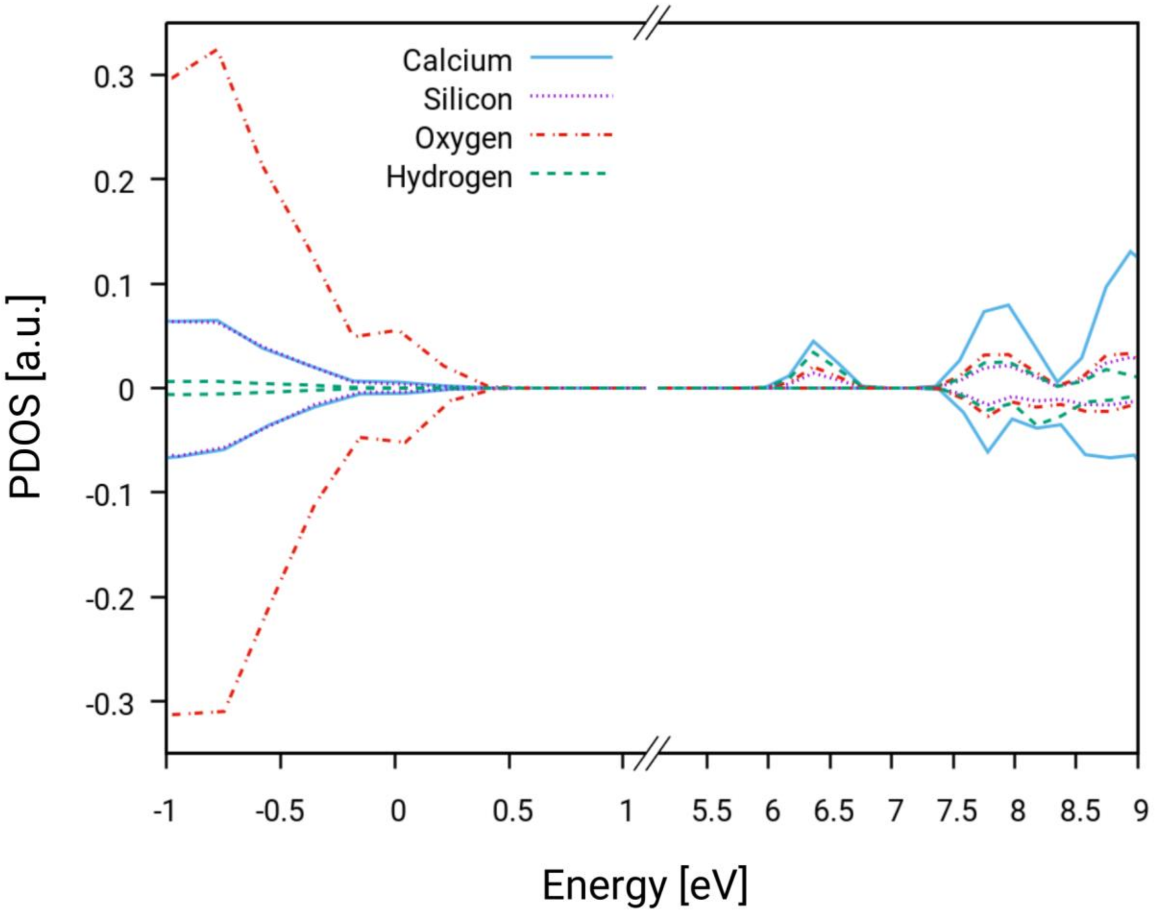
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Oxygen
Hydrogen
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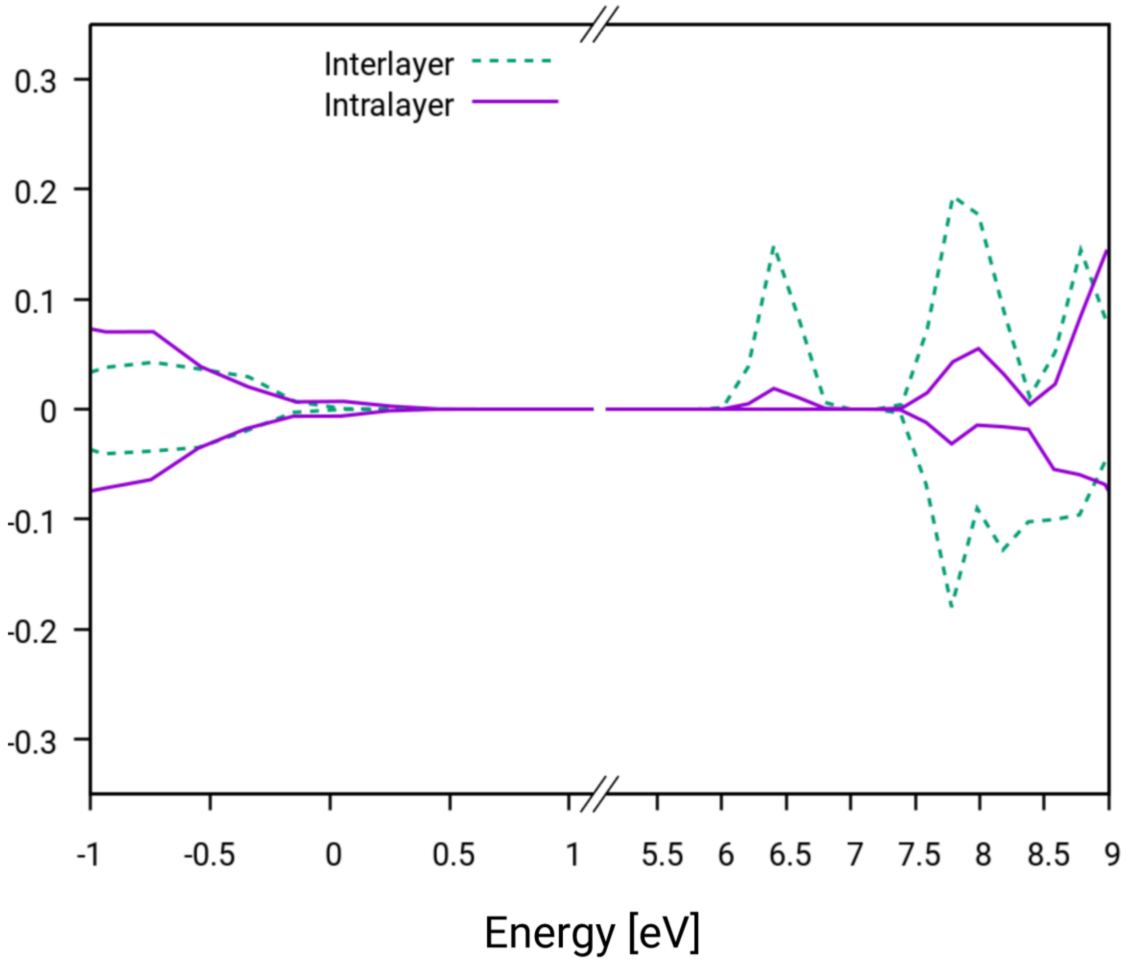
Energy [eV]

Interlayer
Intralayer
0.3
0.2
0.1
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-0.2
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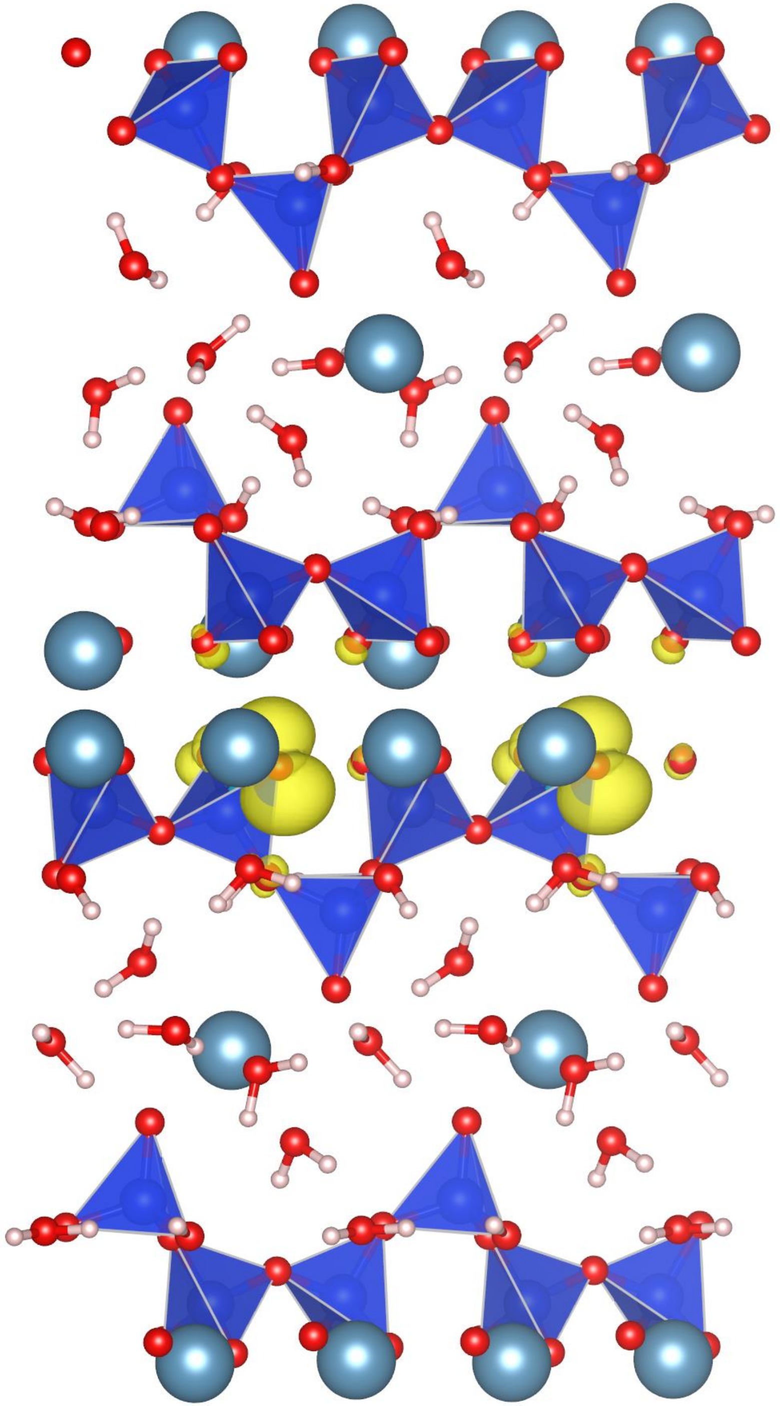
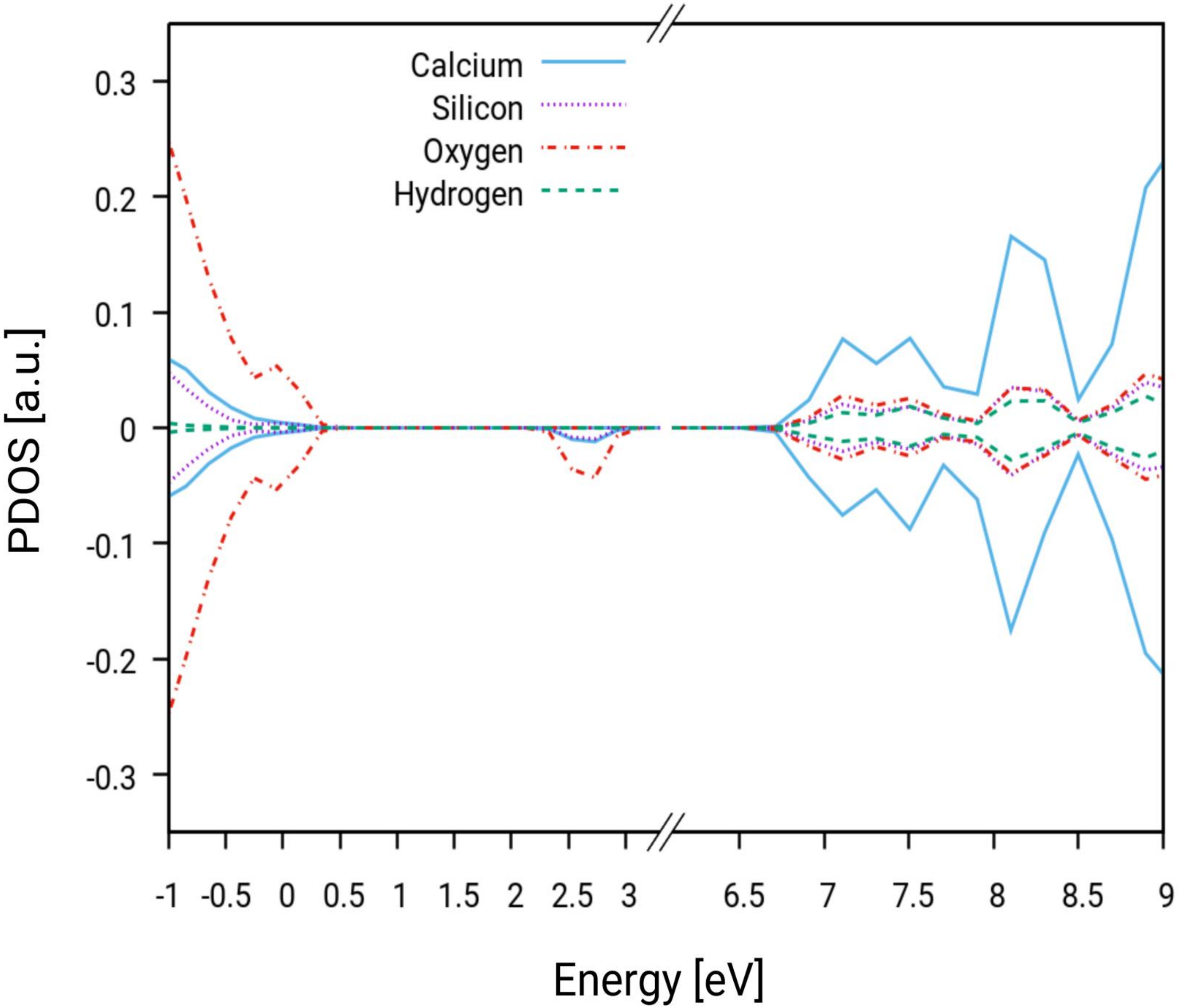
Energy [eV]





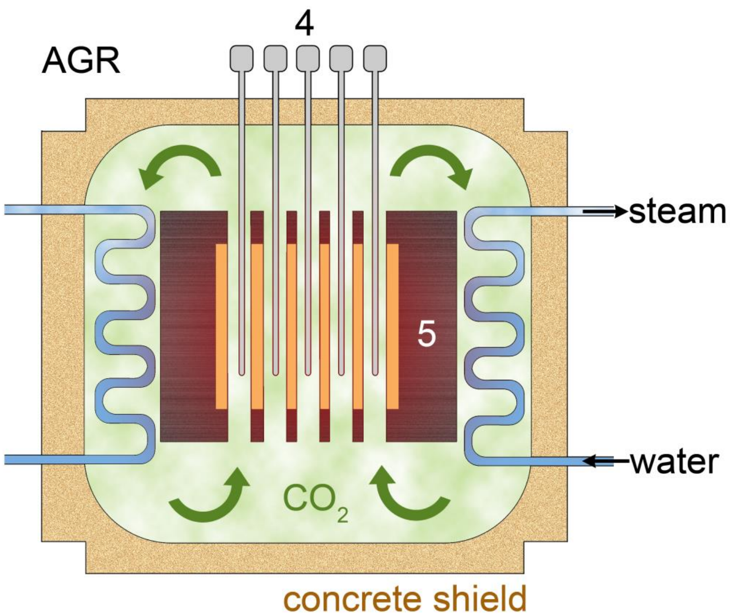
Calcium
Silicon
Oxygen
Hydrogen
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
PDOS [a.u.]
-1
-0.5
0
0.5
1
1.5
2
2.5
3
6.5
7
7.5
8
8.5
9
Energy [eV]

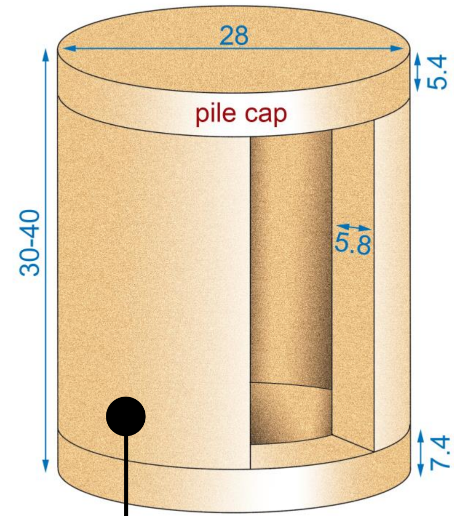
Fibre optic monitoring of nuclear concrete pressure vessels

Marcus Perry, Iain McKeeman, Grzegorz Fusiek,
Pawel Niewczas, Michael Johnston, Sadaat Khan

Prestressed concrete barriers

University of Strathclyde Engineering





PCPV

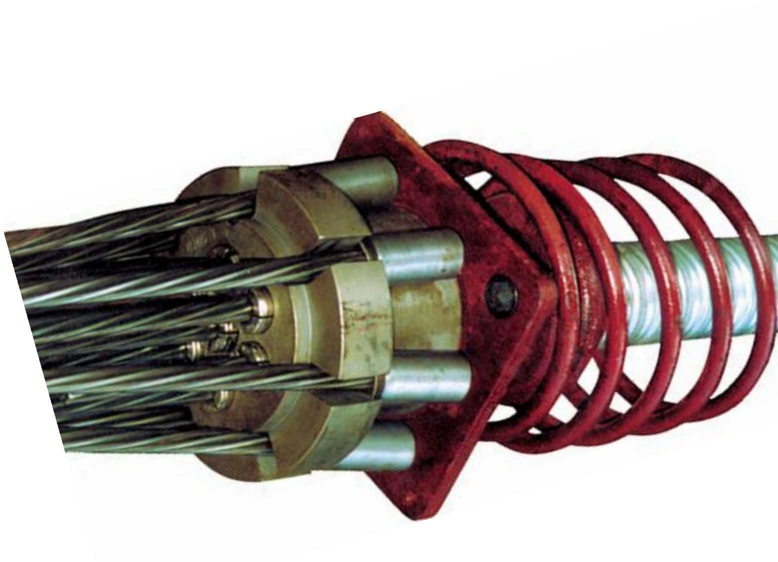
Adequate levels of prestress?

What is prestress?

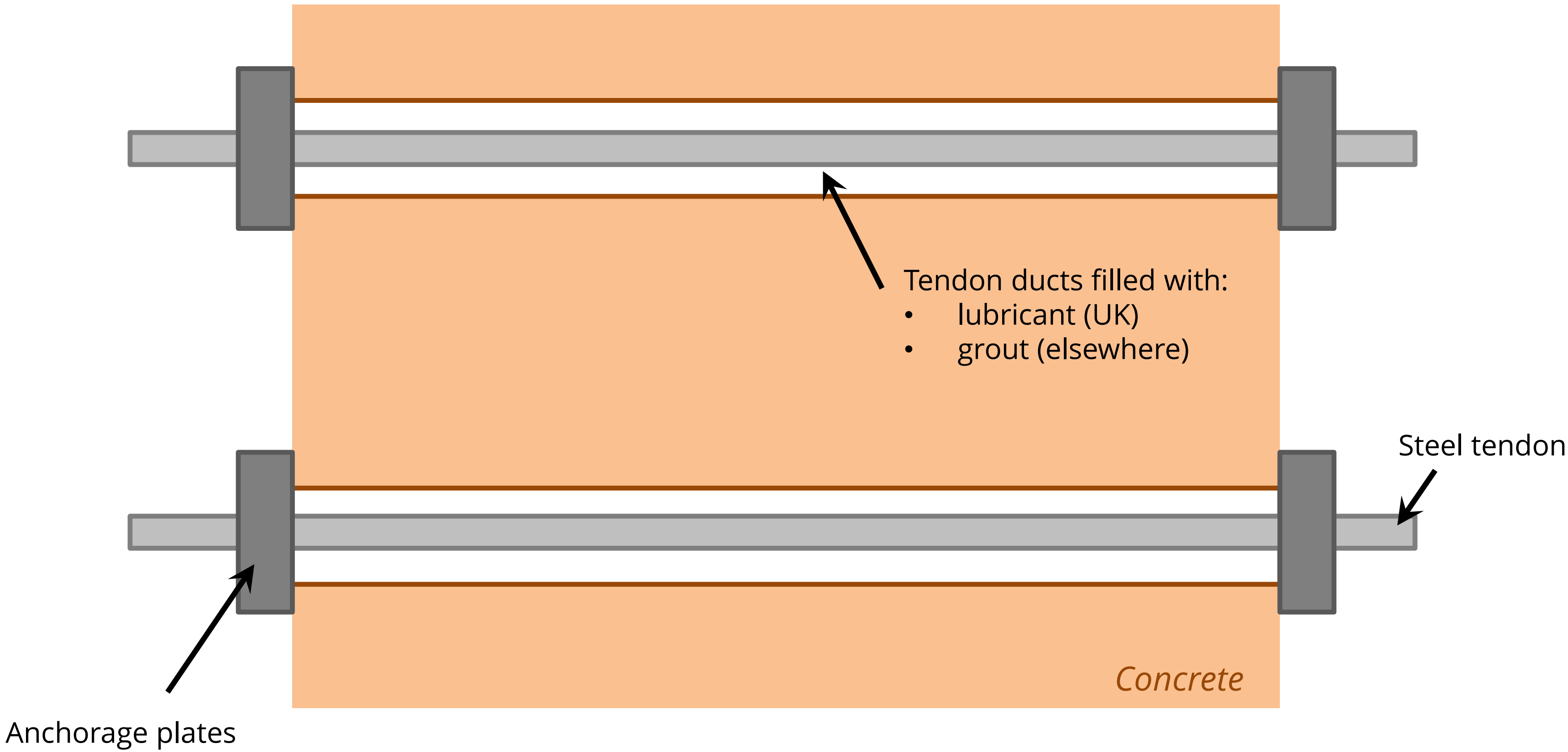
Prestress is what keeps concrete under compression
Prevents tensile stress: concrete does not cope well with tension

7 steel wires make
prestressing strands

7 strands make
prestressing tendons



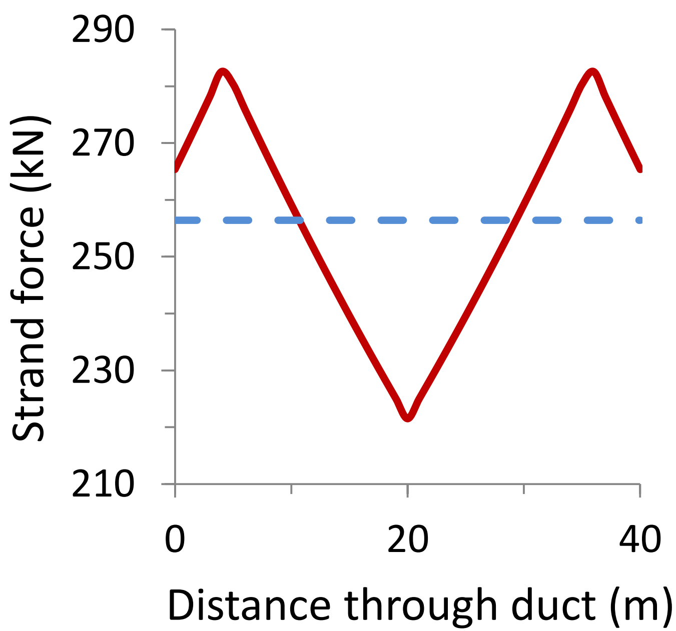
What is prestressing?

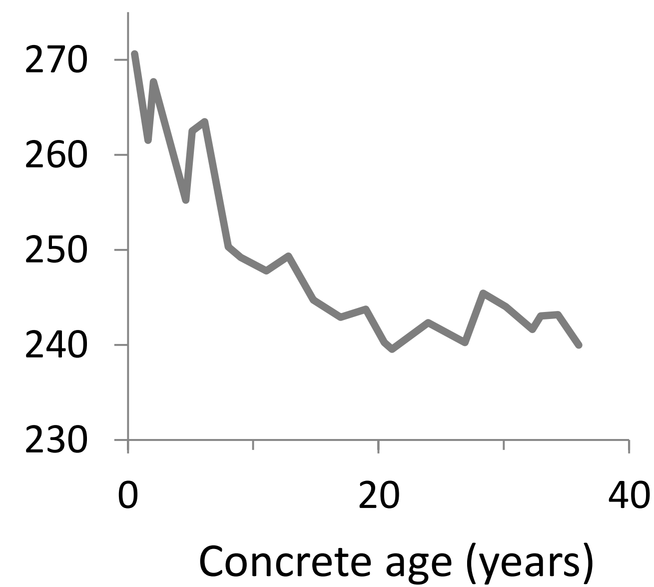


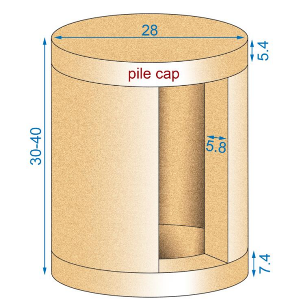
Prestress losses

Friction
Anchorage slip
Elastic shortening

Creep
Shrinkage
Stress Relaxation





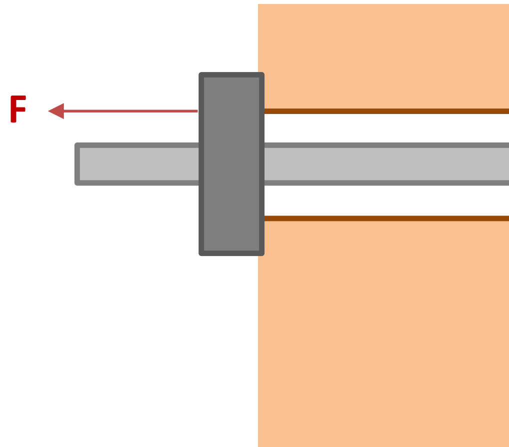


PCPV

Prestress loss measurement

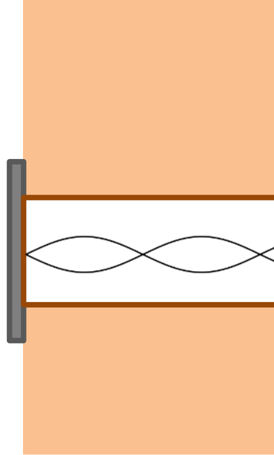
Lift-Off inspections

- 1-2 % tendons checked 1.5 - 5 years
- Reliable measurements of average tendon load
- No information on load distribution over the tendon's length
- Some reactors require outage
- Time consuming, expensive, hazardous



Vibrating-wire strain gauges (VWSGs)

- Verify lift-off inspections
- Degrade with time/use
- Can't add to the VWSG population (installed at construction)



Project aim and objectives

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Can we improve prestress monitoring?

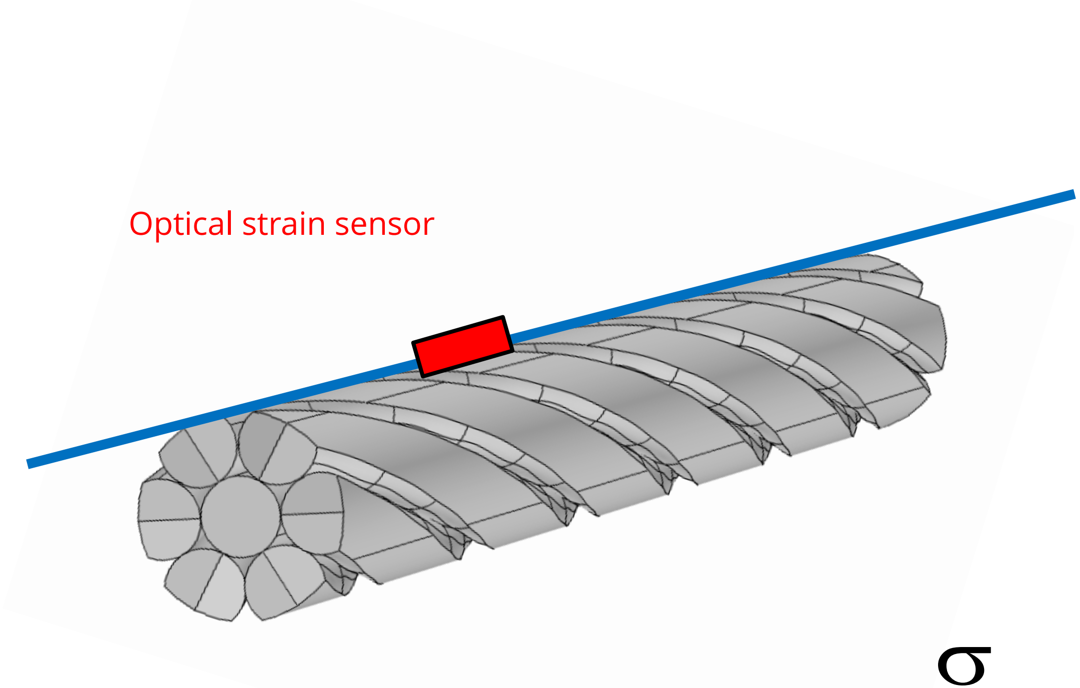
What do I mean by improve?

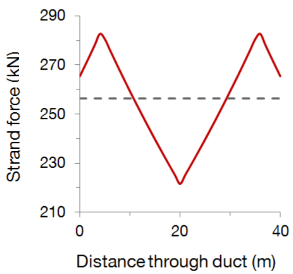
- Rate: frequency of prestress check
- Density: number of strands / tendons monitored
- Resolution: minimum force change detectable
- Distribution: obtain force profiles along strands

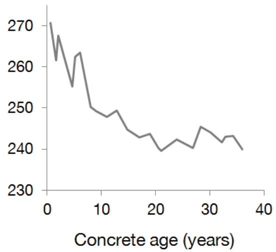
Why do this?

- Verify lift-off inspections:
  - Monitoring & maintenance phase of decommissioning
  - Improved technology / prestress loss models for next-gen reactors
- Allow prestress measurement when lift-off isn't possible (grouted systems)
- Early-warning system: faster response to risks
- Remote monitoring: reduce costs and risks of lift-off

Optical fibre solution





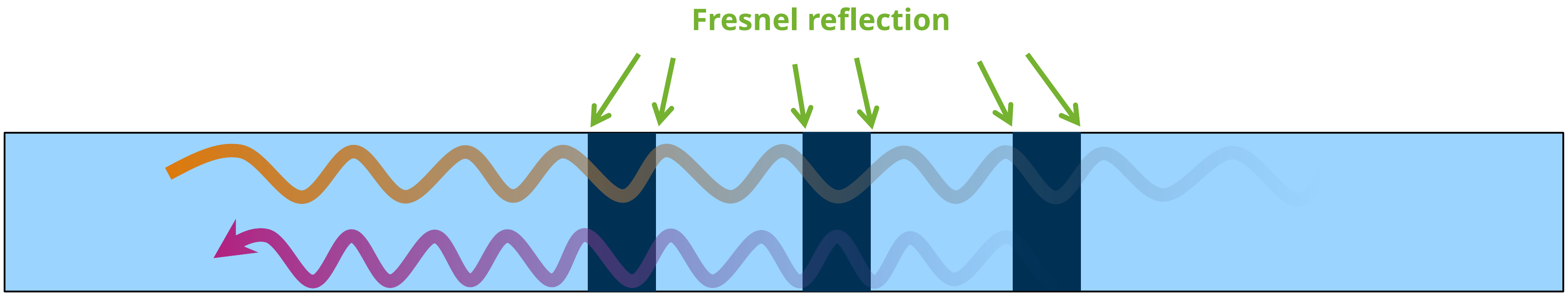


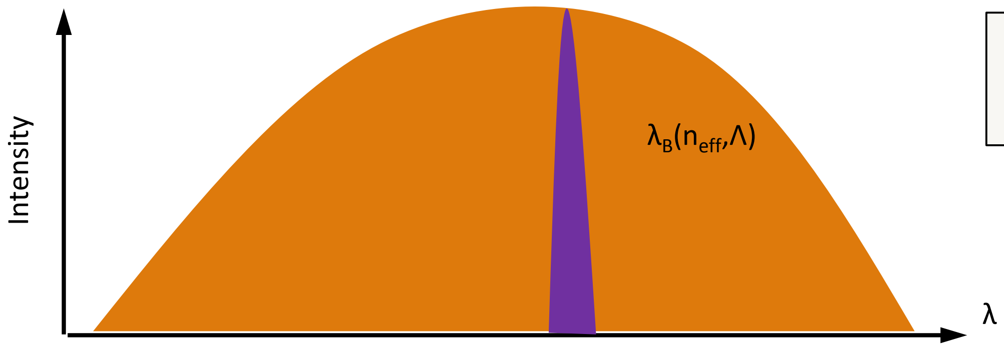
$$\varepsilon = \frac{\sigma}{E} = \frac{F}{AE}$$

200 GPa

223 mm^2

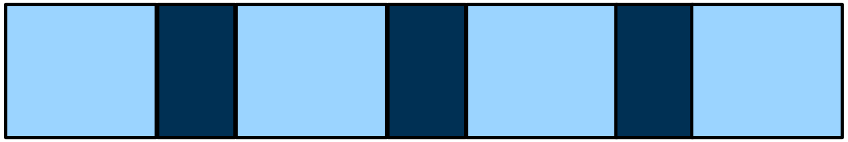
Fibre Bragg gratings



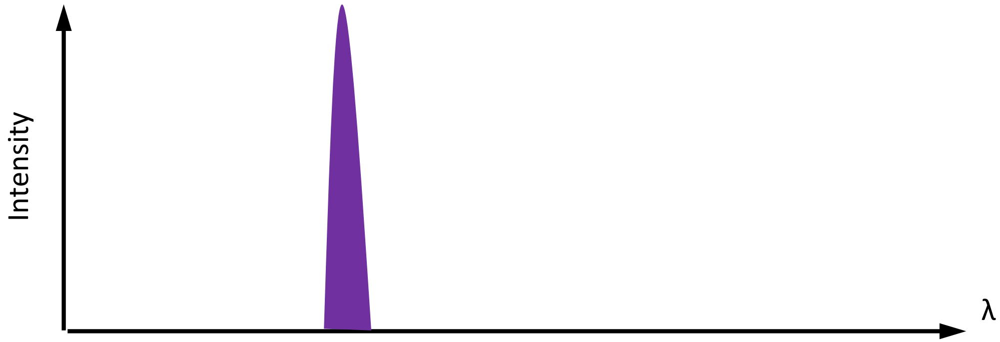


Note:
$n_{eff}(\varepsilon)$
$\Lambda(\varepsilon)$

FBG strain sensor



λ_B = 1550 nm λ_B = 1556 nm



Optical vs electronic sensing

	Electronic	FBG
Size (profile)	Small	1-dimensional
Marginal cost	£	£
Fixed cost	£	££
Max Temp.	100 °C	1200 °C
Strain resolution	1-10 με	Sub 1 με
Serial Multiplexing?	No	Yes
Environmental Resistance	Chemical, radiation	Chemical, radiation, EMI
Addressing	2-way (circuit)	1-way

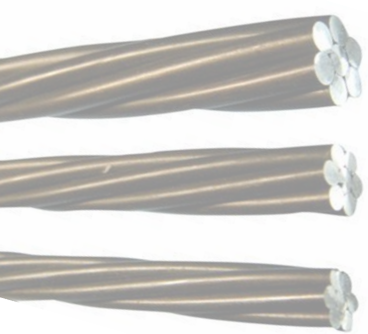
Project objectives

1) Fabricate FBG strain sensor and packaging that meet radiation-hardness requirements

2) Come up with an attachment method to make “smart strands”

3) Have the smart strands survive and measure prestressing (80% UTS steel: 200-300 kN)

4) Design interrogation system that meets strain resolution requirements



Radiation induced attenuation

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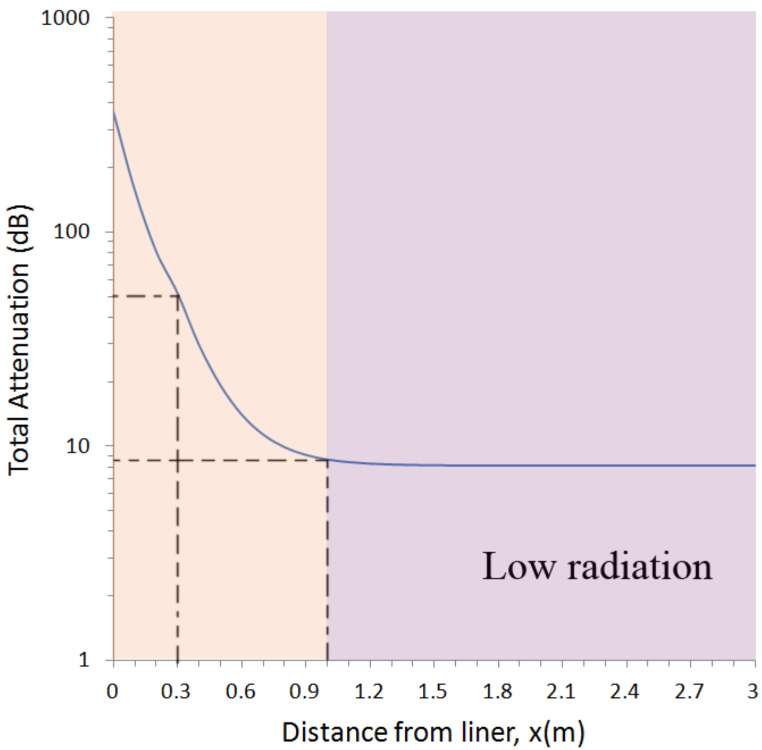
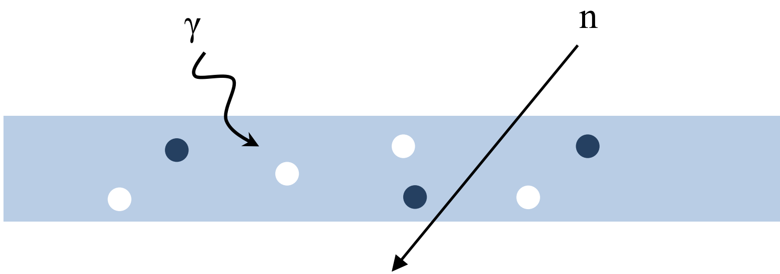


Neutron-gamma radiation: defects in glass (absorption) and compaction (scattering)

Fast neutrons create voids (scattering)

Irradiated polymer coats leach hydrogen into fibre: “water damage”



DOI: 10.1109/JSEN.2012.2214030

Sensor attachment methods

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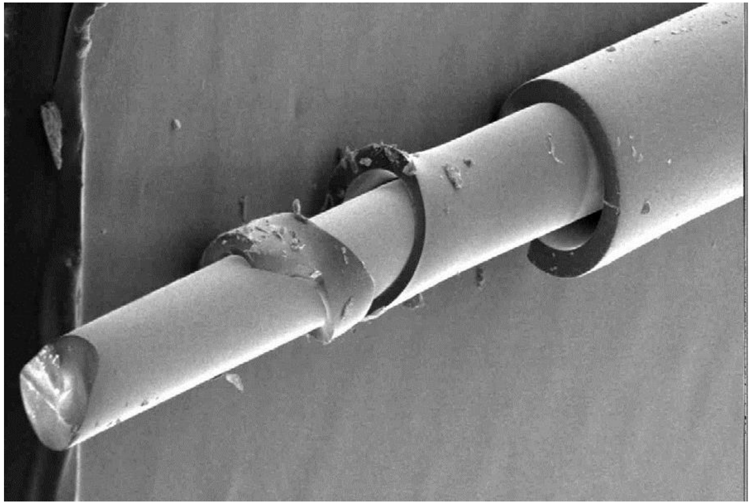
Attachment Method	Pros / Cons
Epoxy	Simple, lacks mechanical /radiation resistance, creep under high load, aggressive pre-treatments
Embed into fibre-reinforced polymer (FRP) strand	Standards?, shear strength, behaviour different to steel, radiation resistance?
Embed into concrete	Drilling, install during construction
Surface-mount to concrete walls	Internal prestress?, more suitable for crack monitoring
Brazing (high-temperature soldering)	Good strength, reduced creep, causes thermal damage, no polymers = high rad resistance
Resistance spot-welding	Low thermal damage, fibre itself can't be spot-welded (must be packaged)

Solution:
i) Manufacture metal-packaging for the FBG sensor (brazing), then;
ii) spot-weld the packaged sensor to the strand

Fibre coating

Problem: commercially available FBG sensors are polymer coated

- Not hermetic (water-corrosion)
- Limited mechanical and chemical resistance
- Degrade and leach hydrogen under neutron radiation
- Unsuitable for brazing



Capillary encapsulation

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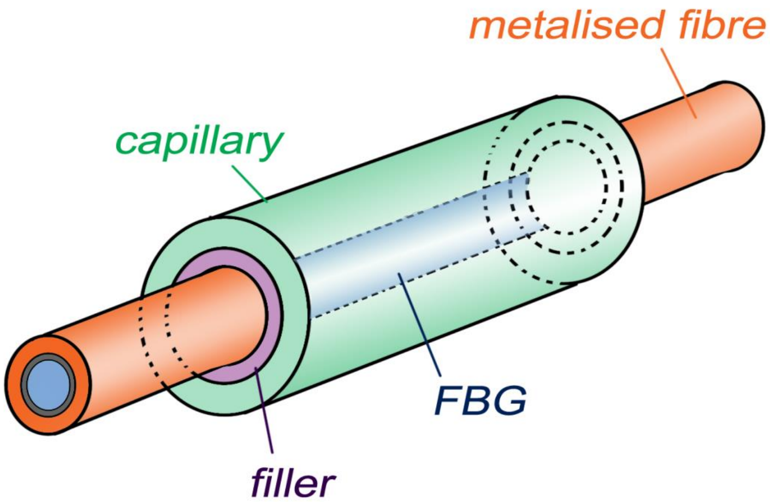
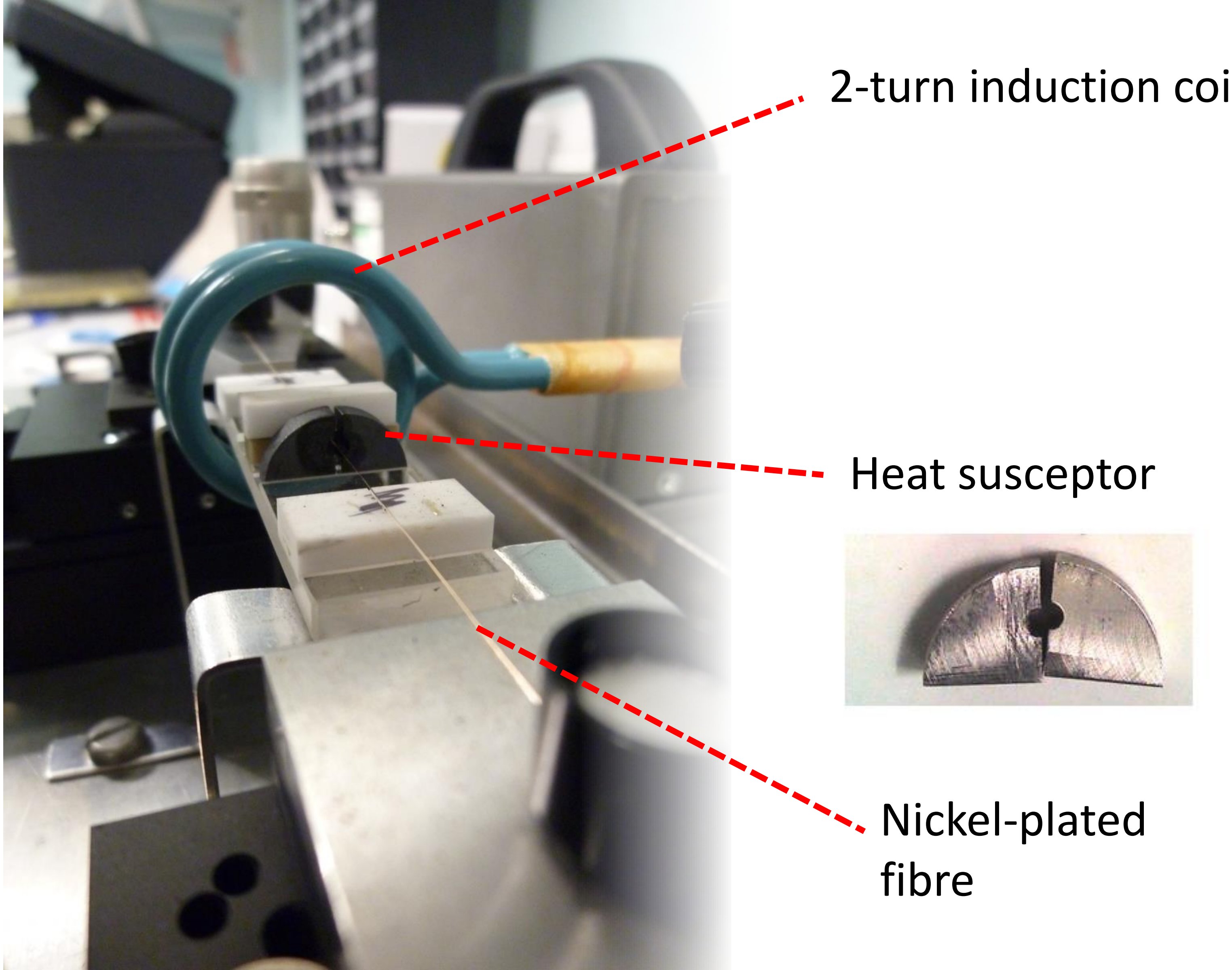
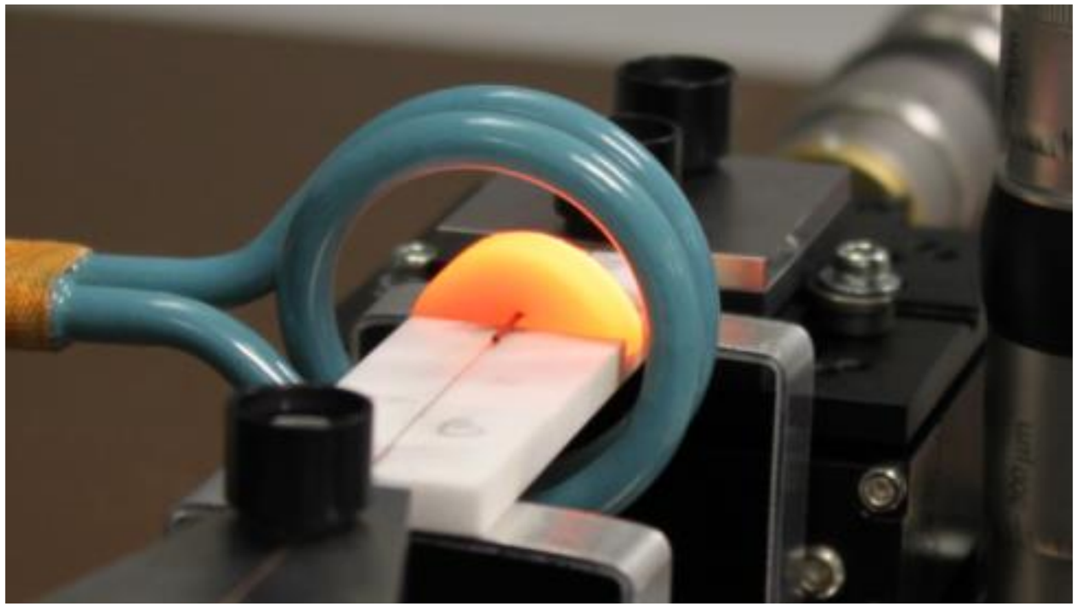


MECHANICAL:	Guides and transfers strain to FBG
CHEMICAL:	Hermetic, alkaline resistant
RADIATION:	No reaction, no leaching


2-turn induction coil
Heat susceptor
Nickel-plated
fibre



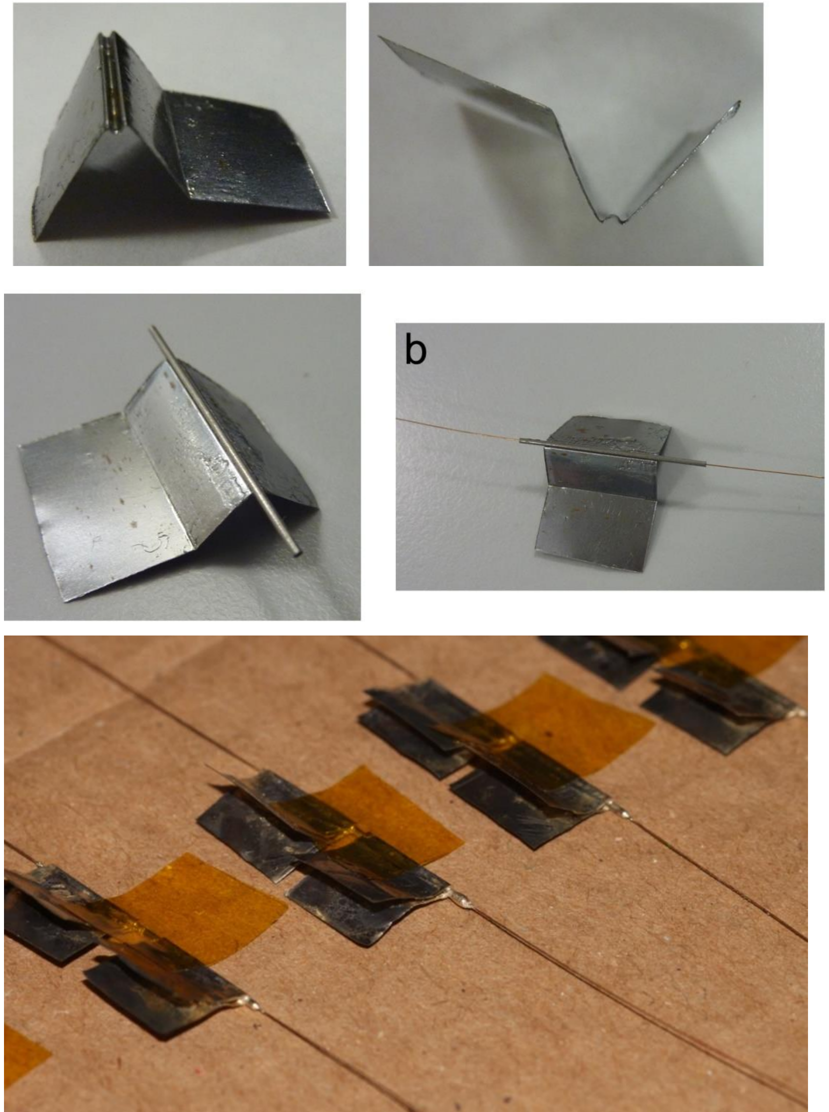
Reference sensors

Strain, ε	Temperature, T	Radiation, γ
Grating length	Thermal expansion	Compaction
Strain-optic effect	Thermo-optic effect	

Sensor: $$\Delta\lambda_{B1} = f(\varepsilon) + g(T) + h(\gamma)$$

Reference: $$\Delta\lambda_{B2} = g(T) + h(\gamma)$$

Correction: $$\Delta\lambda_{B1} - \Delta\lambda_{B2} = f(\varepsilon)$$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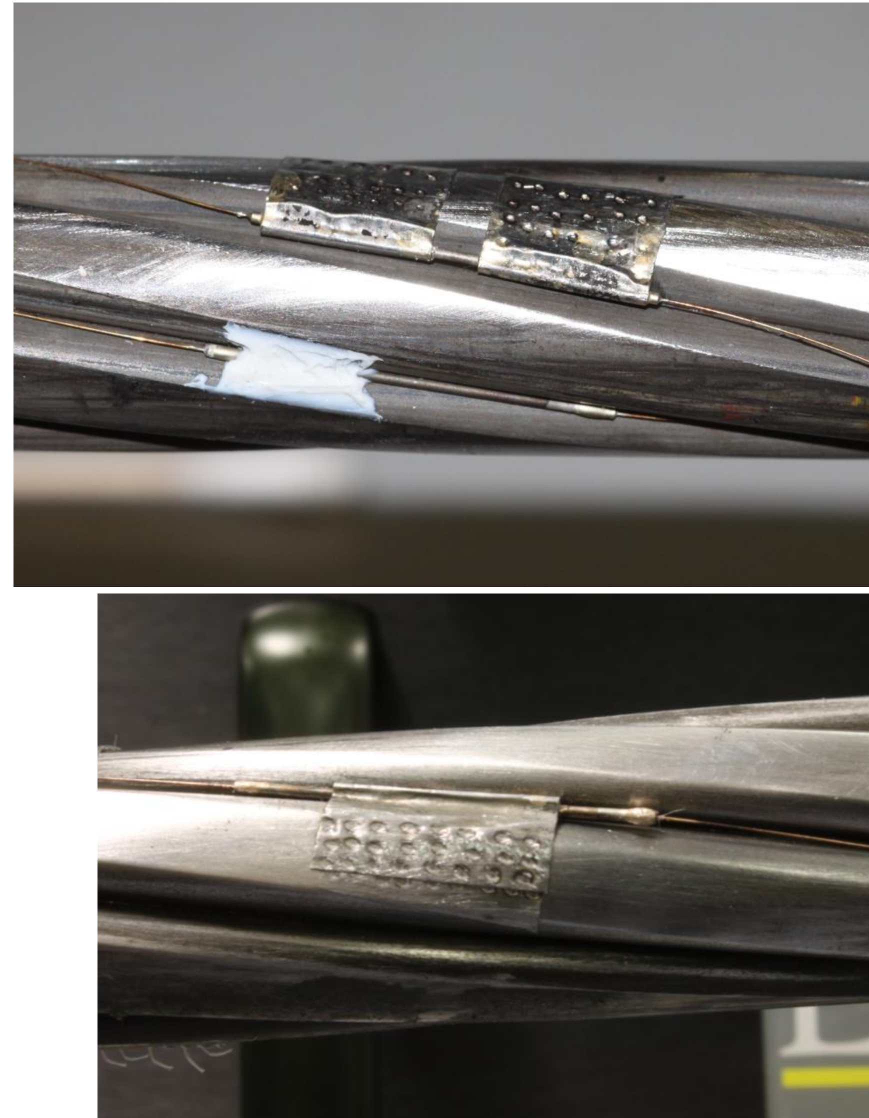
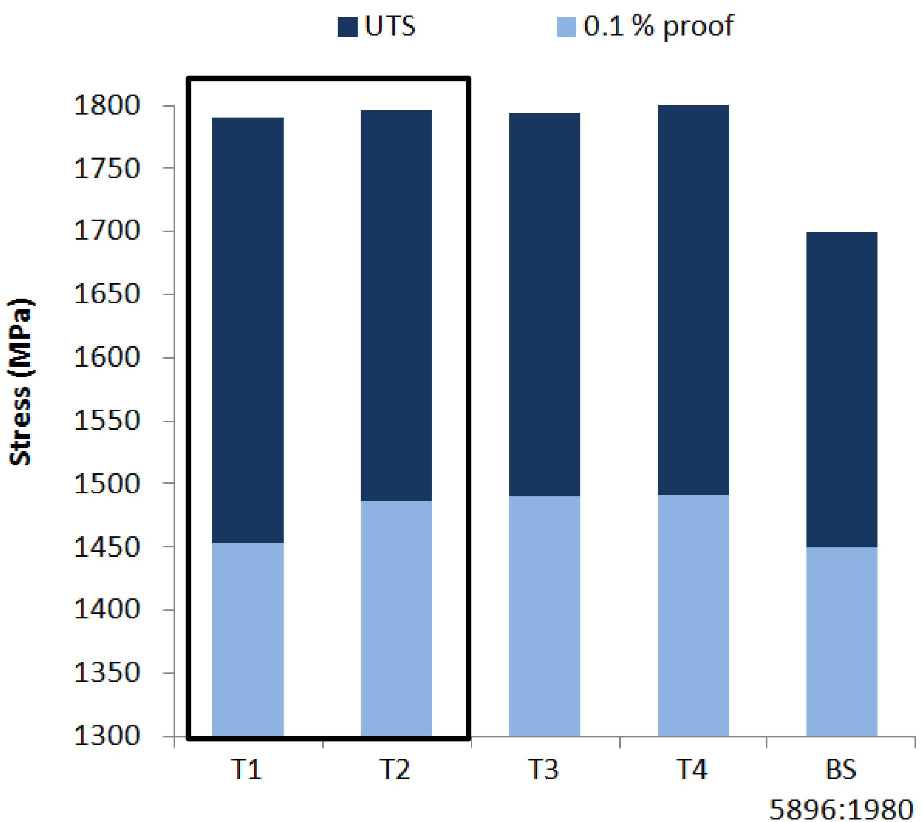
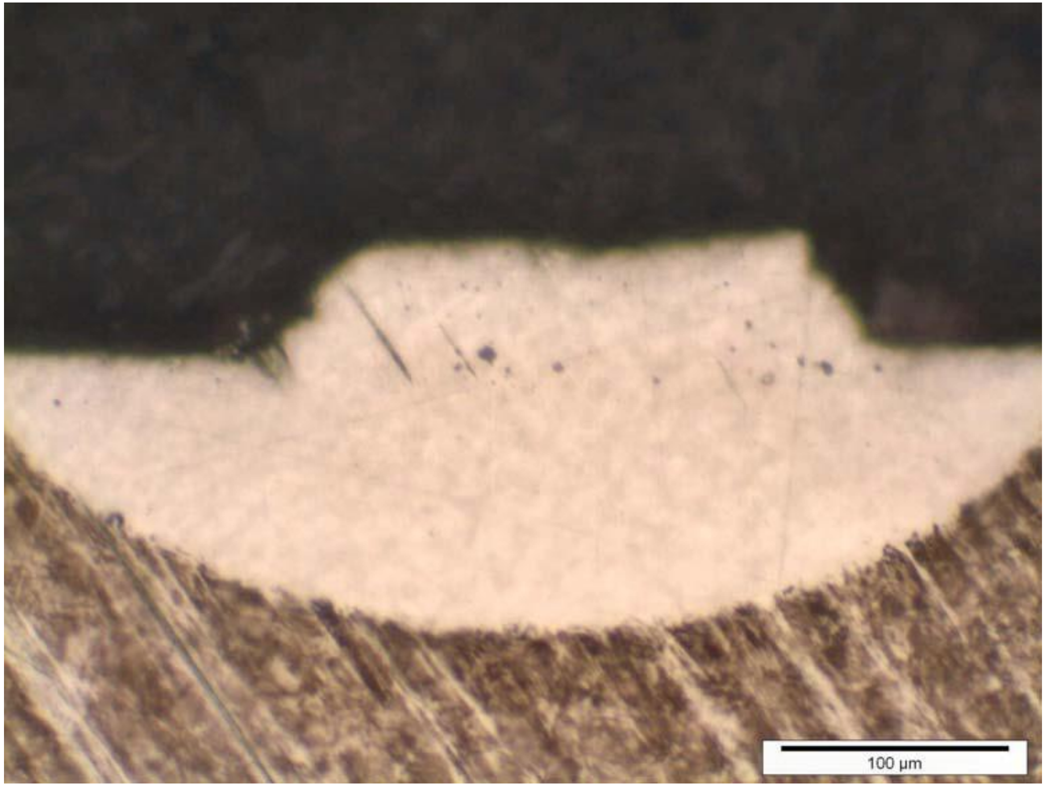


Welding: effect on strand

Destructive testing of strands with / without welded sensors attached



Martensite growth



Spot-welded regions are martensitic (brittle, small steel crystals) down to 0.1 mm
Standards say: <1mm is acceptable damage

Strain characterisation

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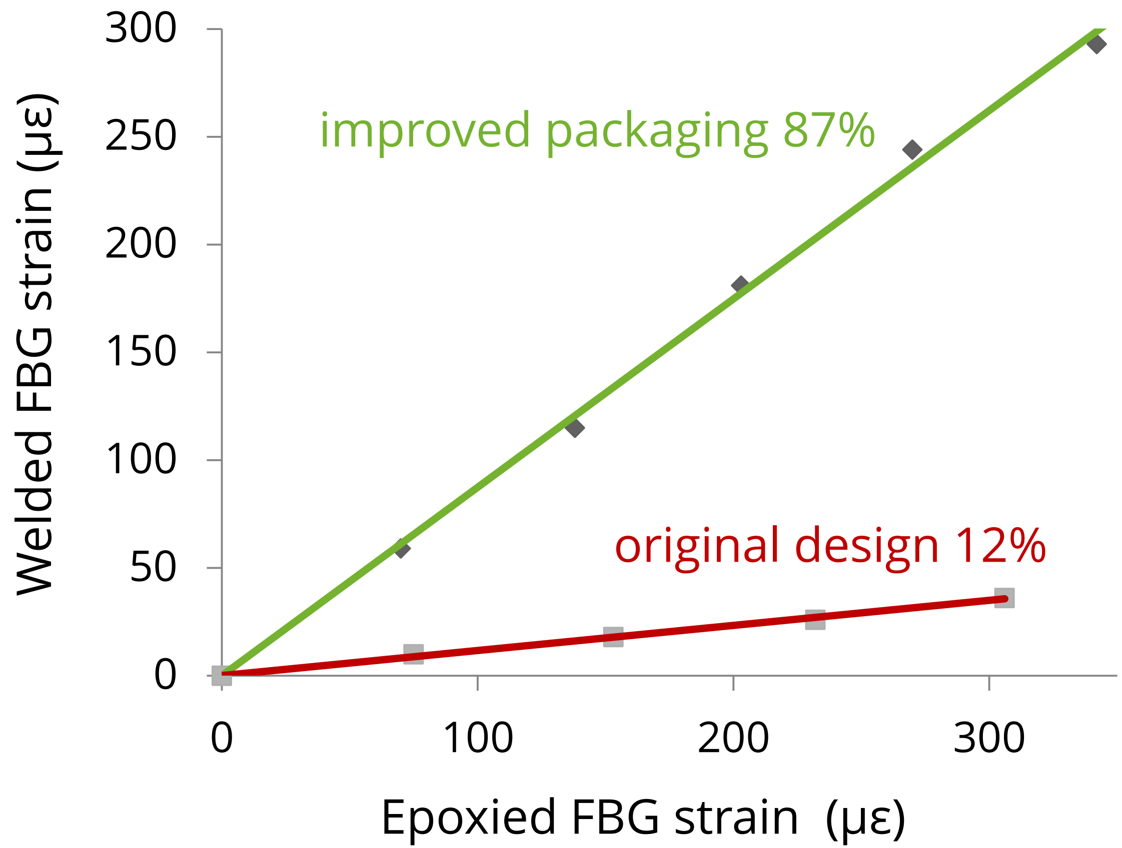
Strain characterisation

Compare welded and epoxied FBG sensors: find the strain transfer



Temperature characterisation

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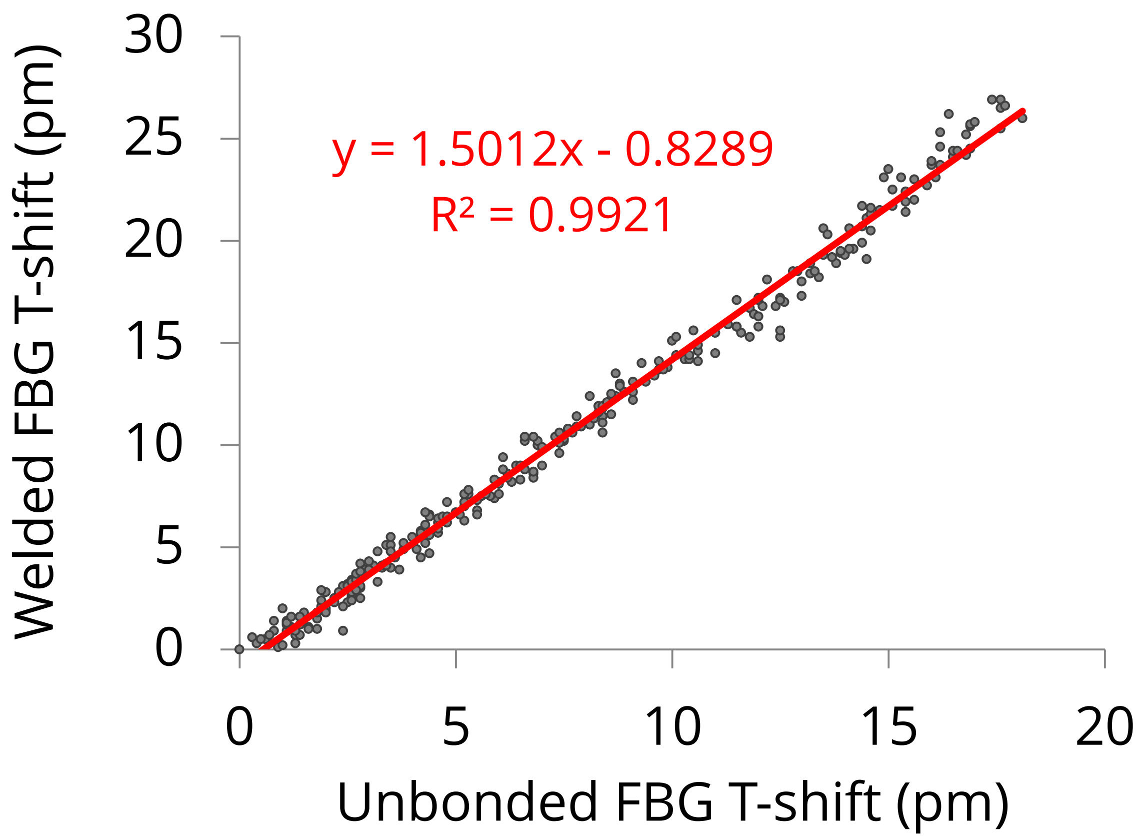
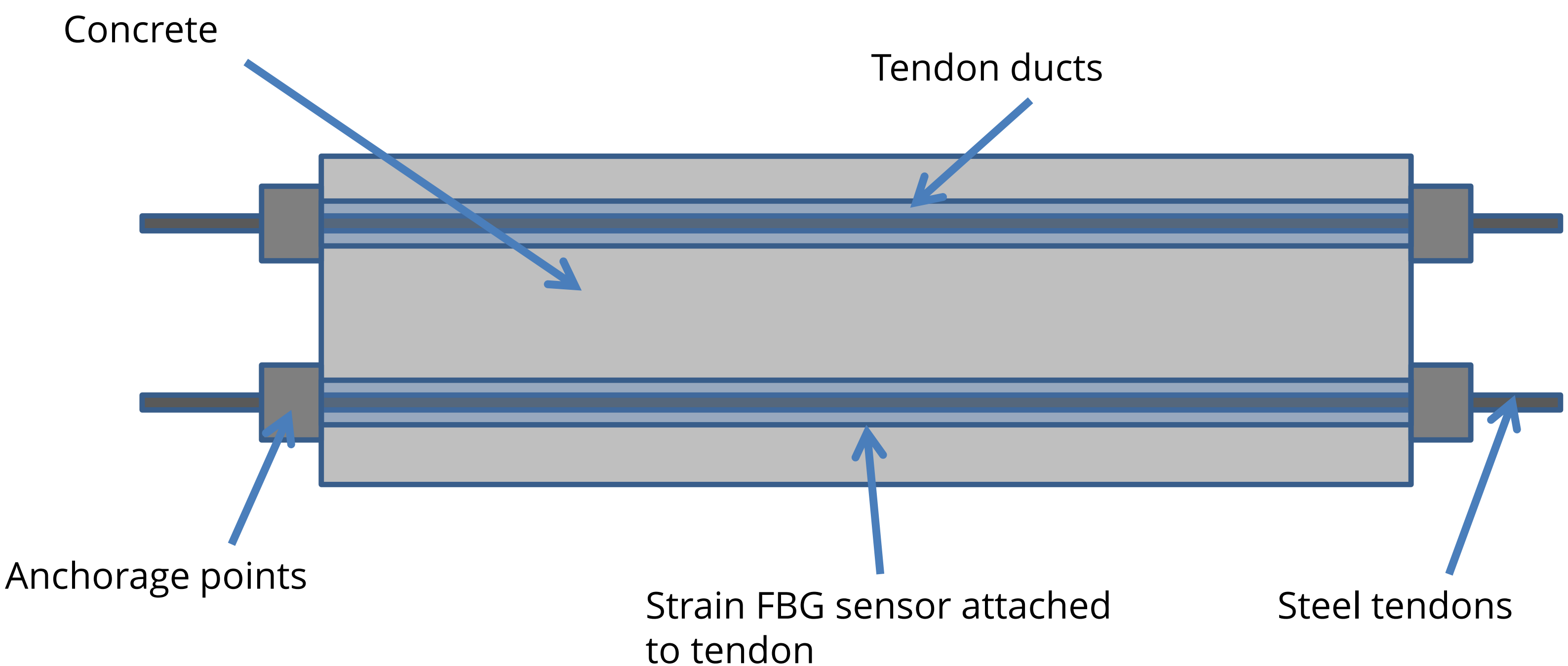
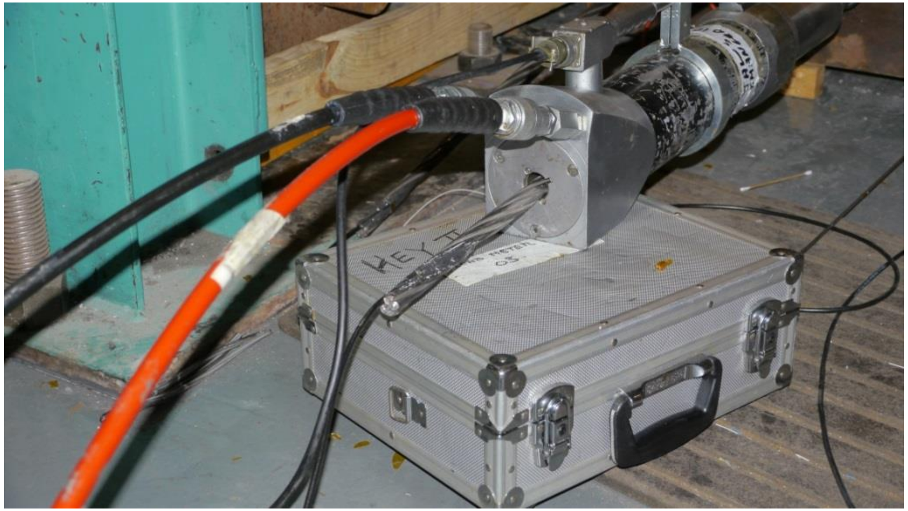
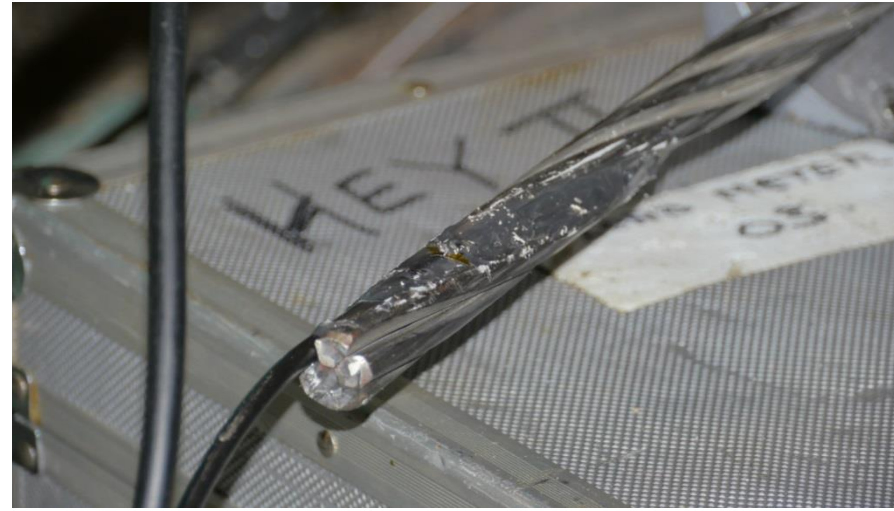
Thermal expansion also causes strain

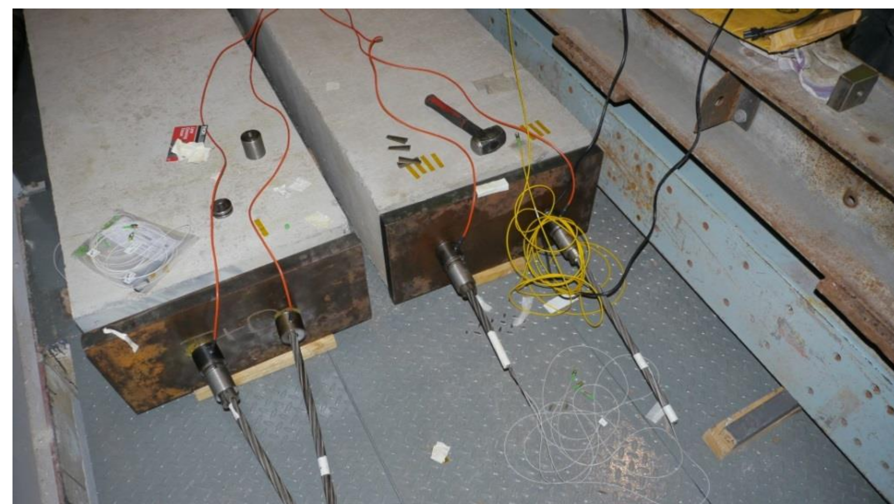


Scale up the tests







Long-term: temperature

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Long-term measurements

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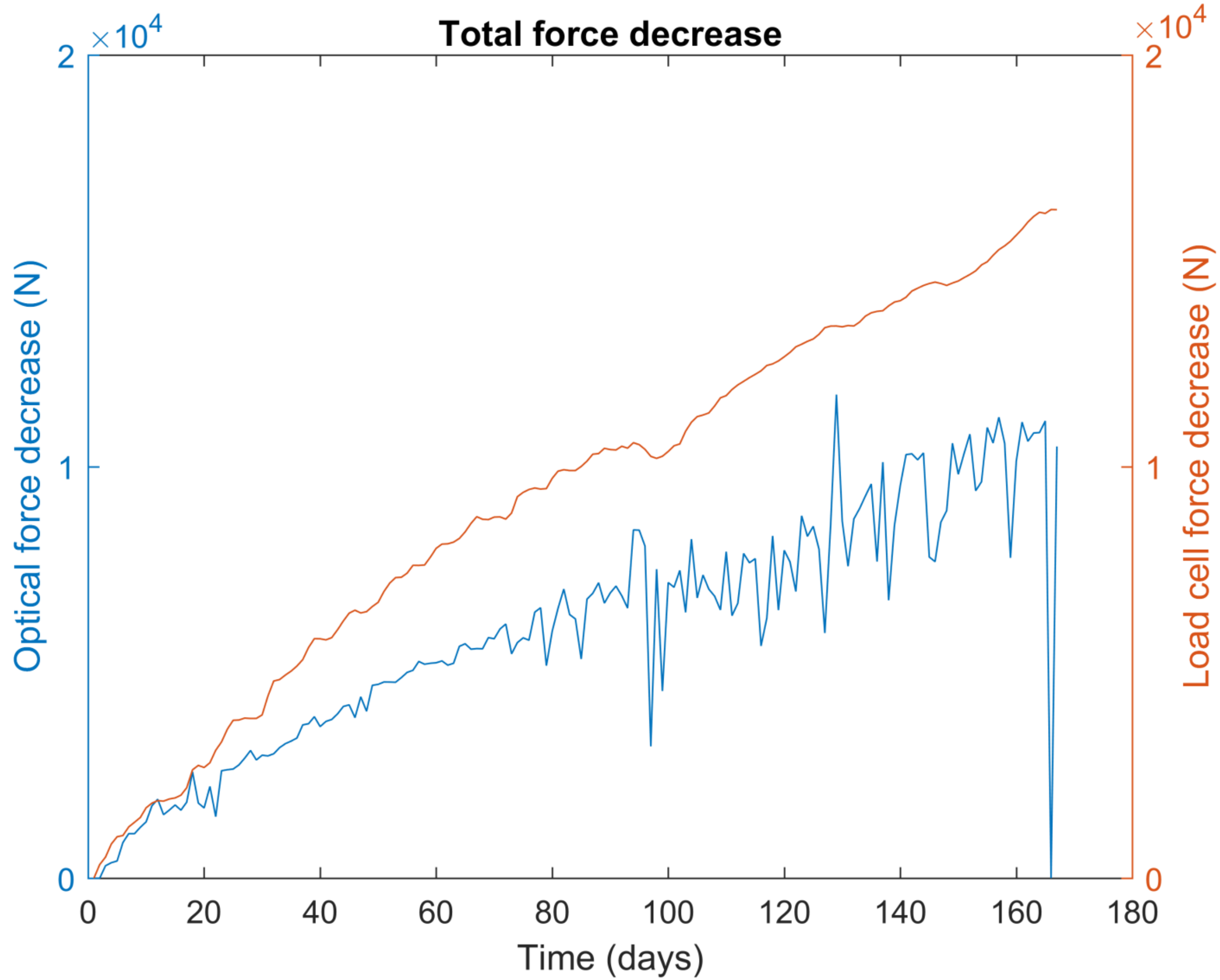
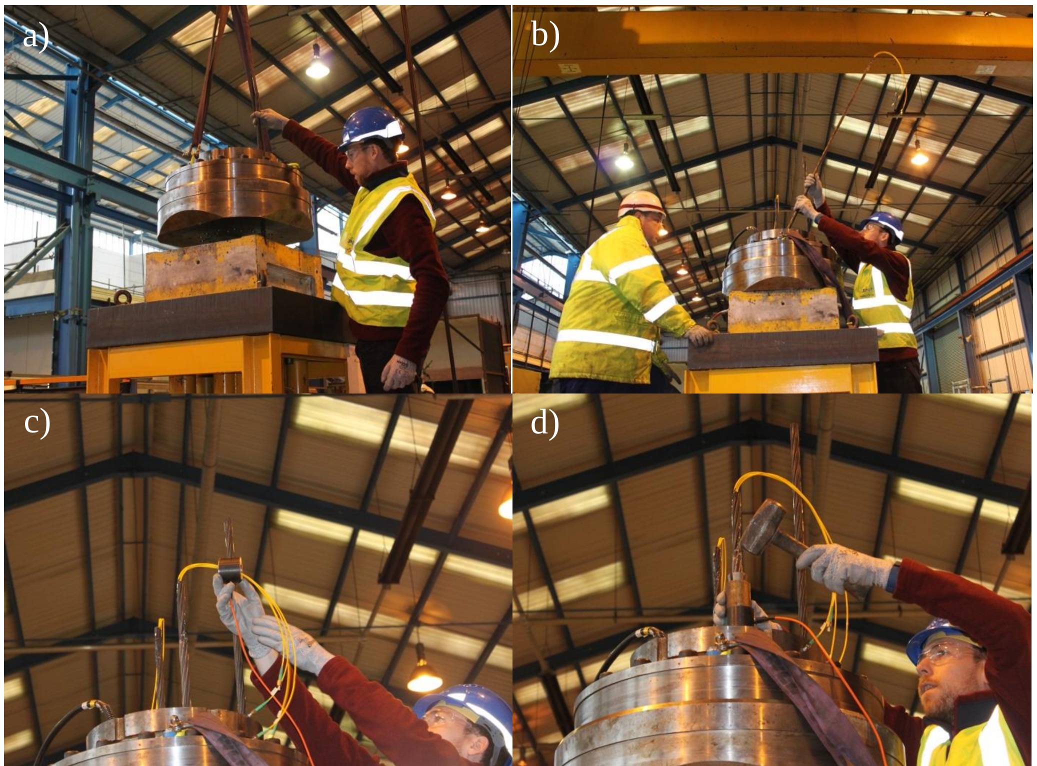
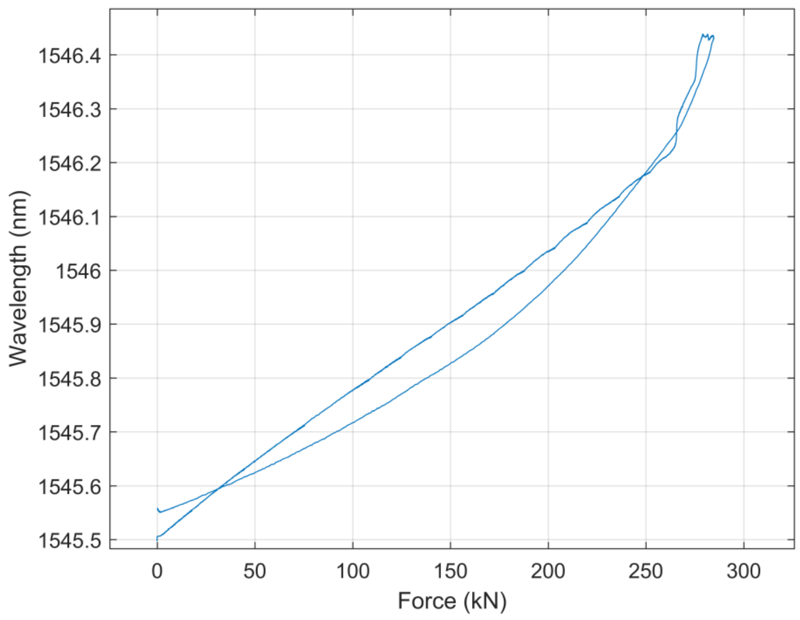


Second trial

VINCI

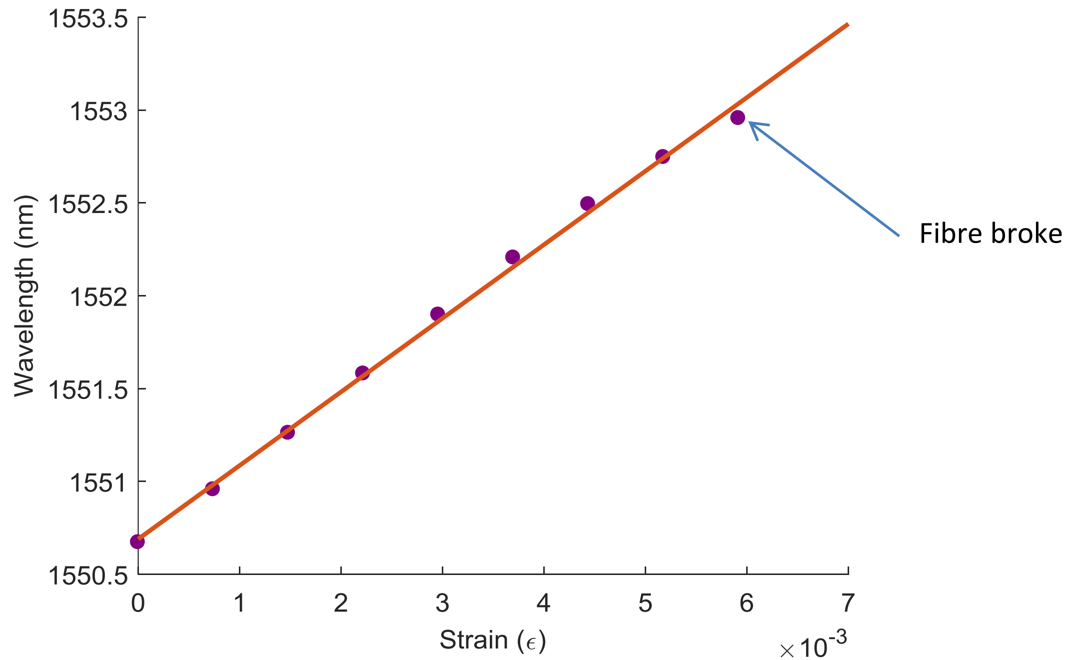


Typical response



- Survival up to 250-300 kN
- Inter-wire friction and wire slippage
- Sensor packaging relaxation

Design improvements



Optical vs manual inspection

	Lift-Off Inspection	FBG Strain Sensing
Measurement type	Force	Strain
Spatial Resolution	1 locations per strand	10 locations per strand
Tendons Checked	1 %	>1 %
Check Freq	1.5-5 yrs	1 s
Time per Check	1 week	<1 s
Risk to contractors during check	Intermediate	Low
Personnel Required	>2	0 (automatic)
Reactor Shutdown?	Yes / No	No
Fixed Cost	<£10k	£50k
Marginal cost	>£100k	£0

Future work

University of Strathclyde Engineering

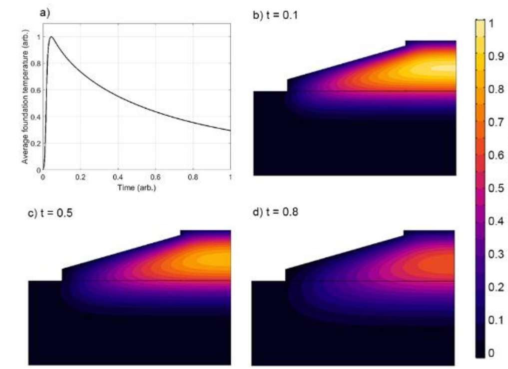
- Multiple sensors: account for strand bending and wire slip / friction
- Creep under prolonged stress, temperature cycling
- Influence of high radiation doses
- Formalise installation procedures

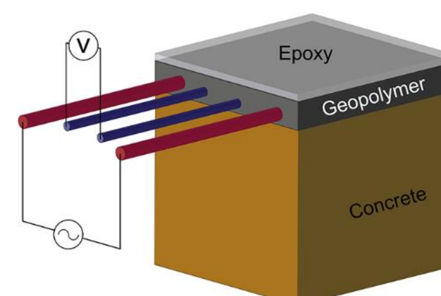
Civil Automation Group

Department of Civil & Environmental Engineering, University of Strathclyde

Remote installation, sensing and analysis of…

Measurement	Application Examples
Strain, displacement, cracking	Waste storage, reactor: fuel channel diameter, refuelling resistance, and penetration cross-sections; concrete cracks, pile cap deflection, building foundations, waste storage
Temperature and pressure	Gas leakage, standpipe/fuel decay storage, PVCS water flows and gas flow
Acceleration and tilt	Broken fan-blades, seismic activity, crane wobble, standpipe monitor
Electric field	Interference, current, voltage
Chemical contamination	Chlorides, moisture, humidity, CO_2 /water leakage, oil analysis, soil analysis
Radiation	Flux at standpipes / fuel decay stores / nuclear waste





Monitoring technologies: robotics, smart materials, sensors and models