TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

Lancaster University

NATIONAL NUCLEAR LABORATORY

GAME CHANGERS

Hybrid Instruments

Preliminary studies of an advanced blind-tube apparatus for characterisation of underground sources

PhD student: Soraia Elisio (Engineering Department, Lancaster University)
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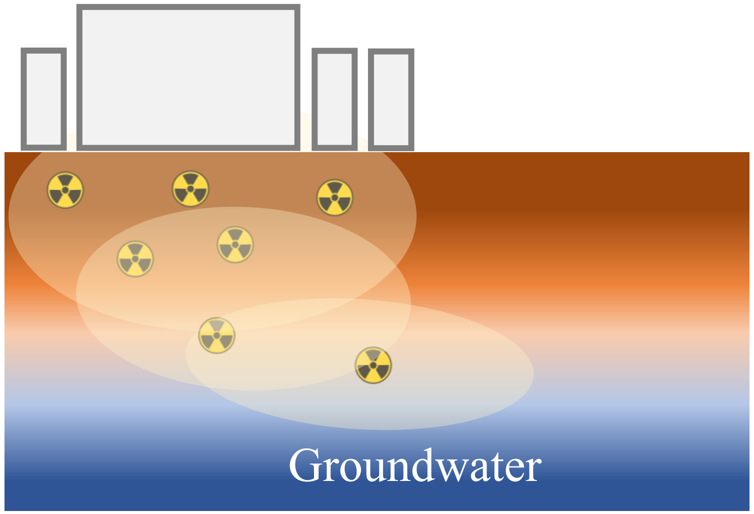
Industrial supervisors:
James Graham (Central Laboratory, National Nuclear Laboratory Ltd.)
Frank Cave (Hybrid Instruments Ltd.)

Energy

For a Low Carbon Future

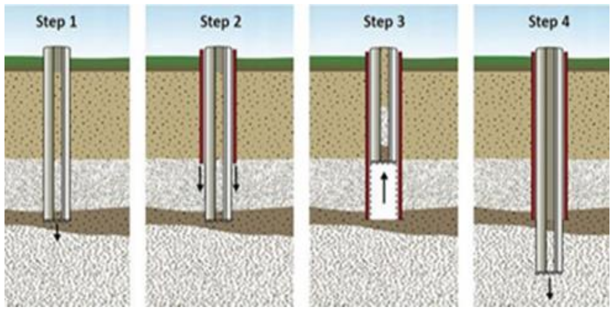
Content

- The problem…
- The challenge…
    1. Infrastructure and deployment constraints
    2. In-ground assets
    3. Radiological issues
- Monitoring Programs at Licensed Sites
- Down-hole radiometric logging systems
- Radiometric logging probe
- The blind-tube test bed
- Detector performance
- Future work



Monitoring Programs at Licensed Sites

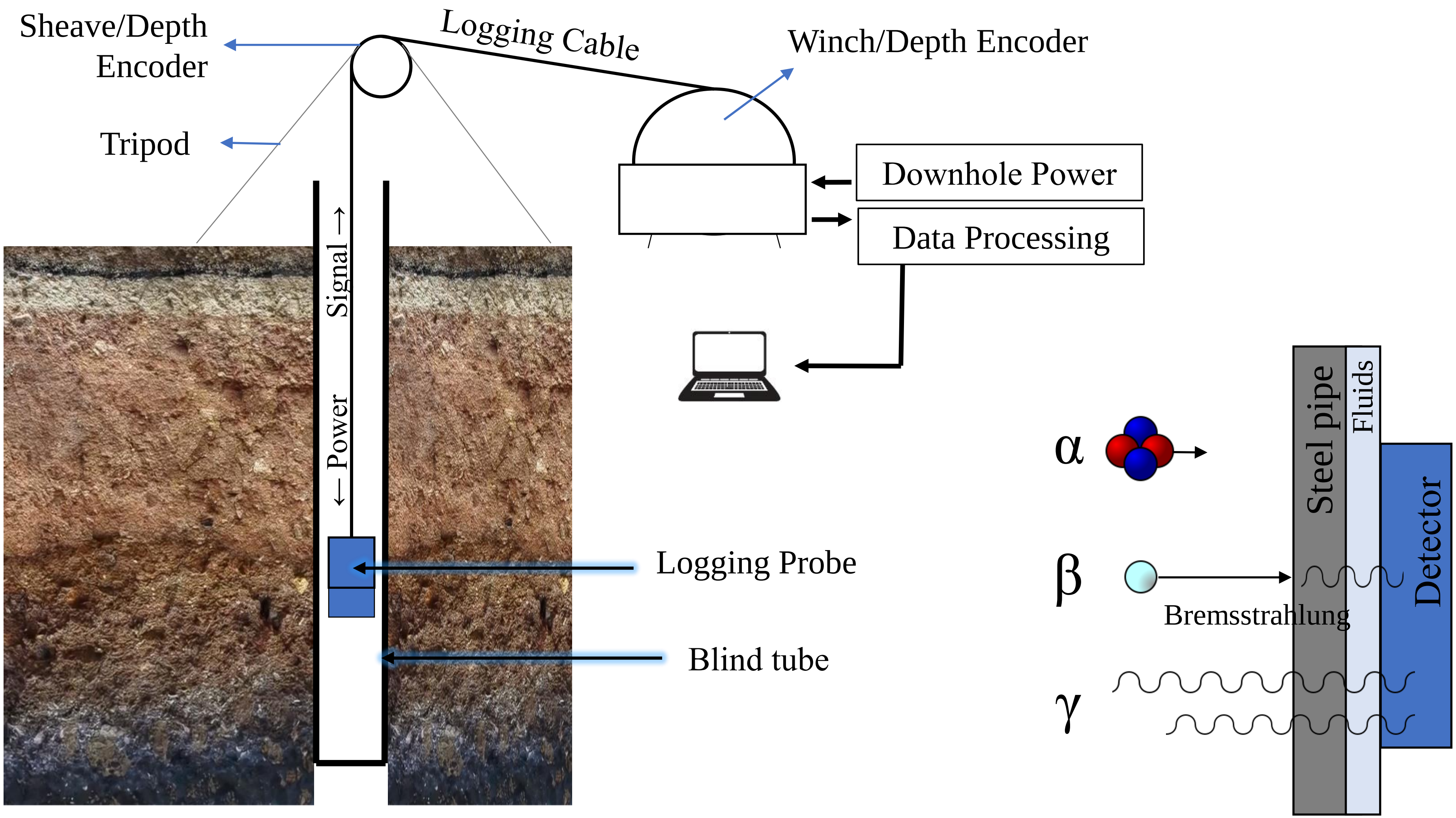
Soil sampling



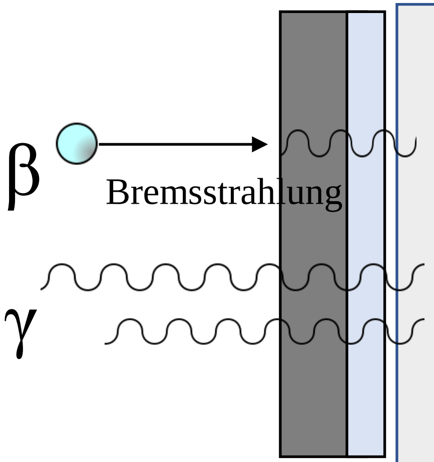
Groundwater sampling

Taken from *Groundwater monitoring at Sellafield: Annual data review, 2016*

Down-hole radiometric logging systems



Radiometric logging probe



Sensing element

e.g.
GM counter
NaI:Tl
HPGe
CdZnTe

Signal conditioning

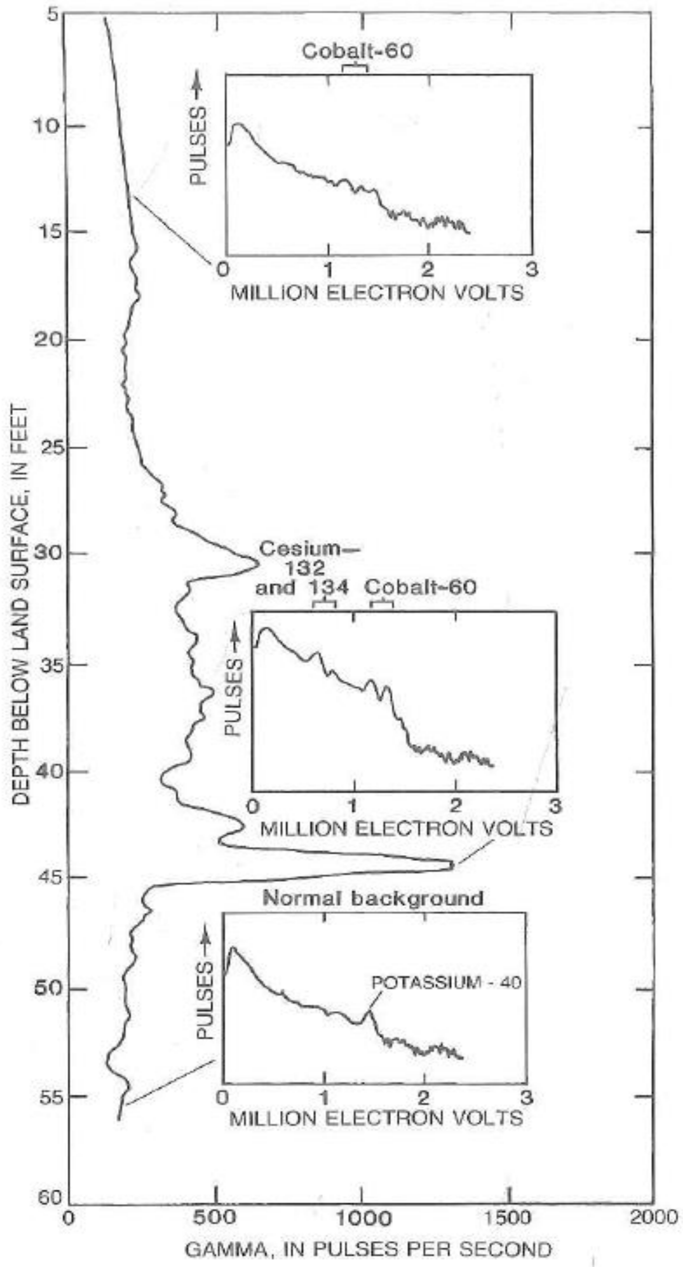
e.g. Preamplifier

Signal processing

e.g. Analog and Digital
Pulse height analysis

Visualisation of data

Counts versus depth
Spectra display



Gamma log at Maxey Flats site (Keys, 1997)

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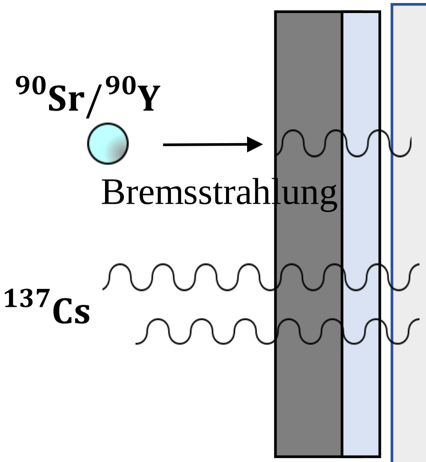
Radiometric logging probe

CASE STUDY

MSSS



Sensing element

$CeBr_3$ scintillation crystal

↓

Signal conditioning

PM6660-SiPM
+ Preamplifier

↓

Signal processing

↓

Visualisation of data

Counts versus depth
Spectra display

Ø10 x 9 mm $CeBr_3$ detector

Commercialized by Scionix (Netherlands)

1. Good γ-ray detection efficiency

$Z_{eff} = 46$ $\rho = 5.2 gcm^{-3}$

2. Good energy resolution

4 % @ 662 keV

3. High count-rate capability

$\tau = 17\ ns$

4. High radiation hardness

Dose up to 100 kGy

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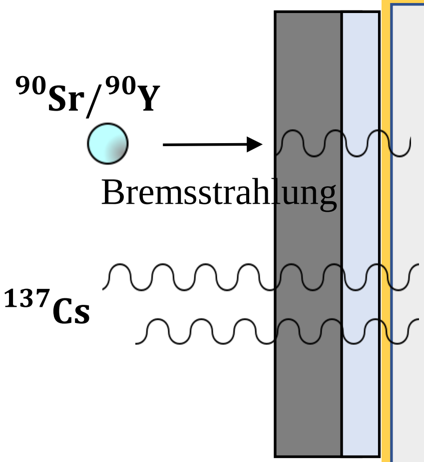
Radiometric logging probe



Sensing element

$CeBr_3$ scintillation crystal

Signal conditioning

PM6660-SiPM
+ Preamplifier

Signal processing

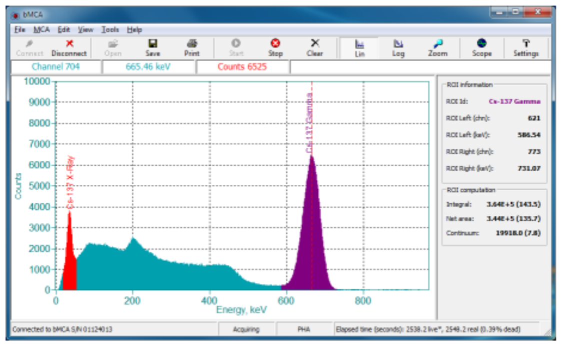
Digitizer MCA

Visualisation of data

Counts versus depth
Spectra display

TOPAZ-SiPM digital MCA

Commercialized by BrightSpec NV



bGAMMA

γ-ray spectroscopy software

Commercialized by BrightSpec NV

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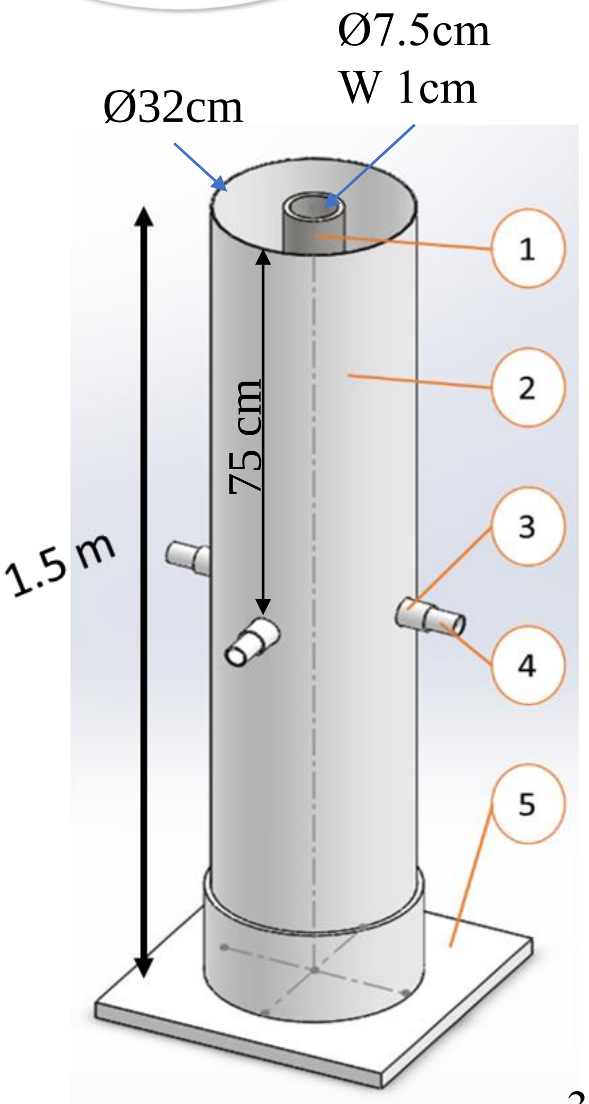
The blind-tube test bed



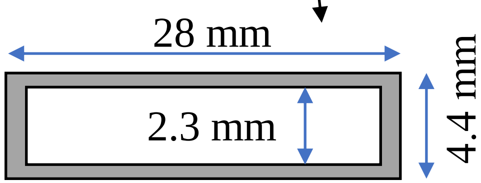
1. Carbon steel tube
2. Plastic sand retaining tube
3. Plastic ‘void’ tube
4. Plastic tubes to hold disk point sources
5. Base support

Ground content:

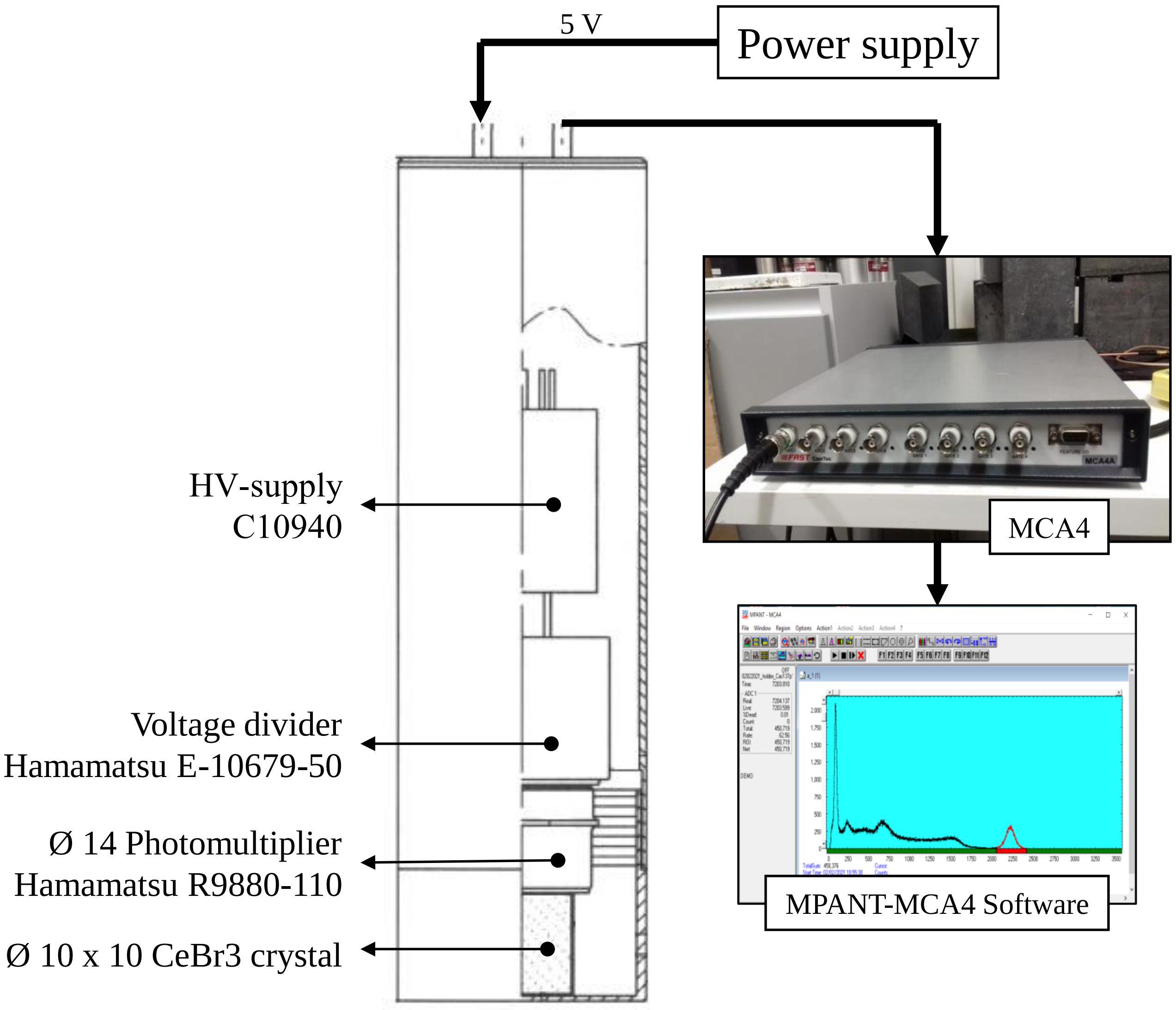
sand

Source holder + plastic capsules:

h: 110 mm



Detector performance



A. Preliminary desk studies:

A1. Spectral performance

A2. Angular dependence of response

A3. Detector response in practice of source holder (and capsules) use.

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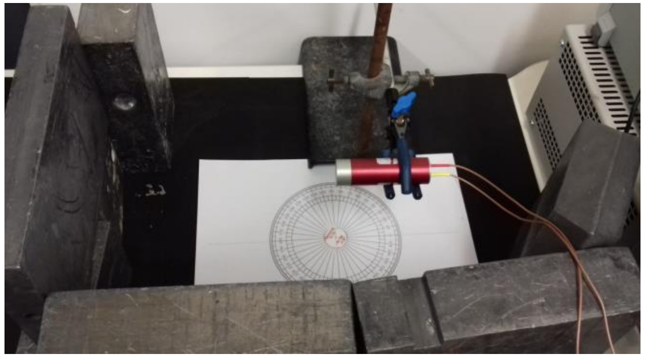
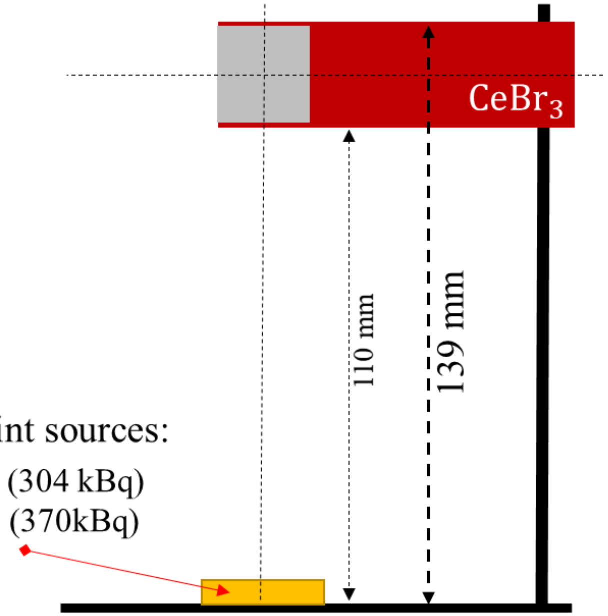
A1. Spectral performance

Experimental setup

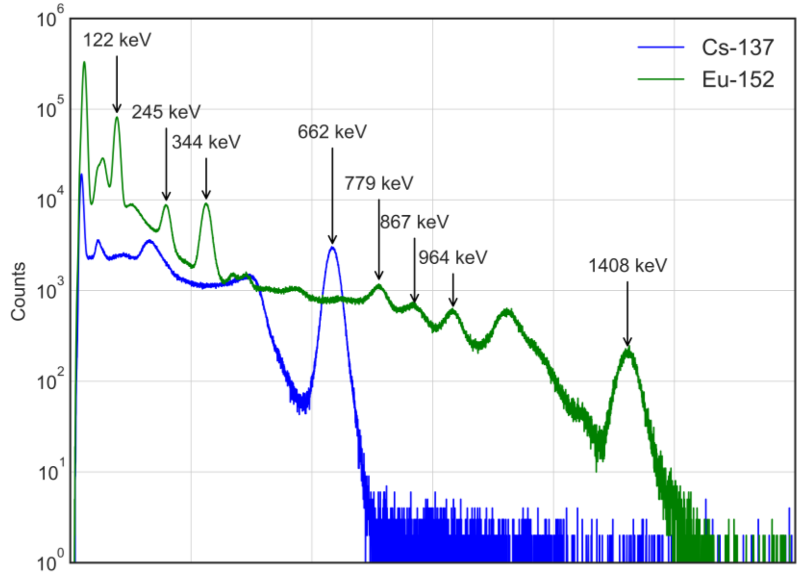


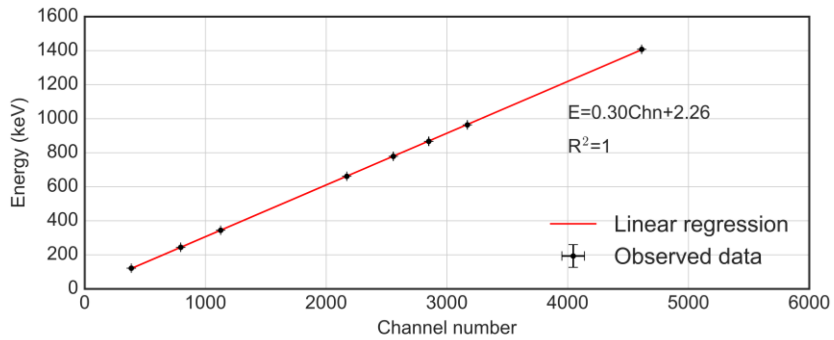


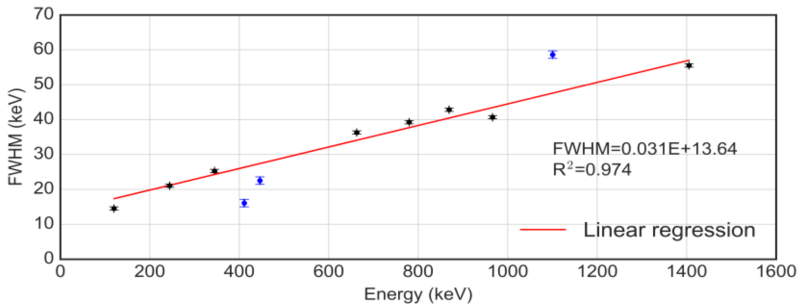
Disk point sources:

Cs-137 (304 kBq)

Eu-152 (370kBq)







energy resolution
5.2% @ 662 keV

photopeak efficiency
0.002% @ 662 keV

multiple peaks

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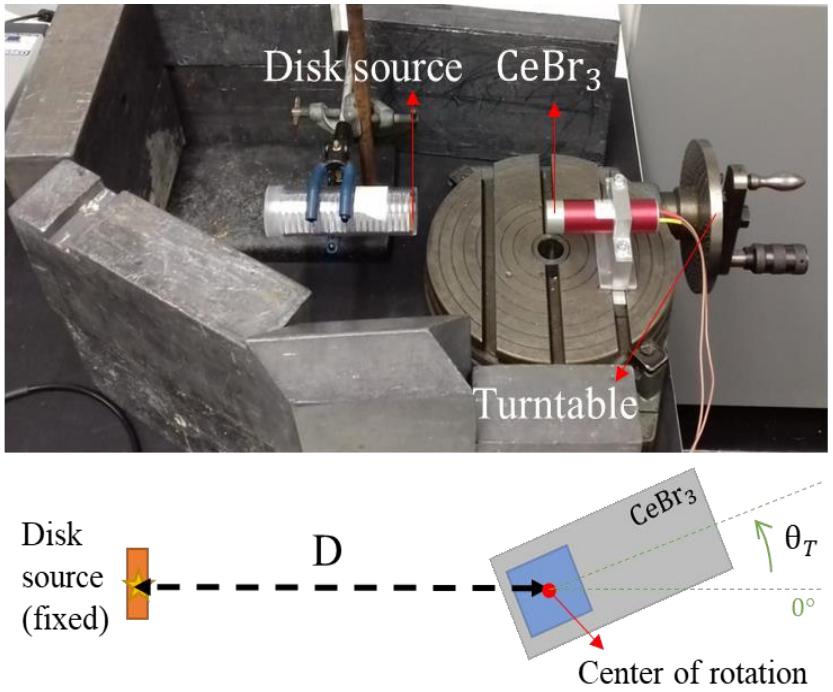
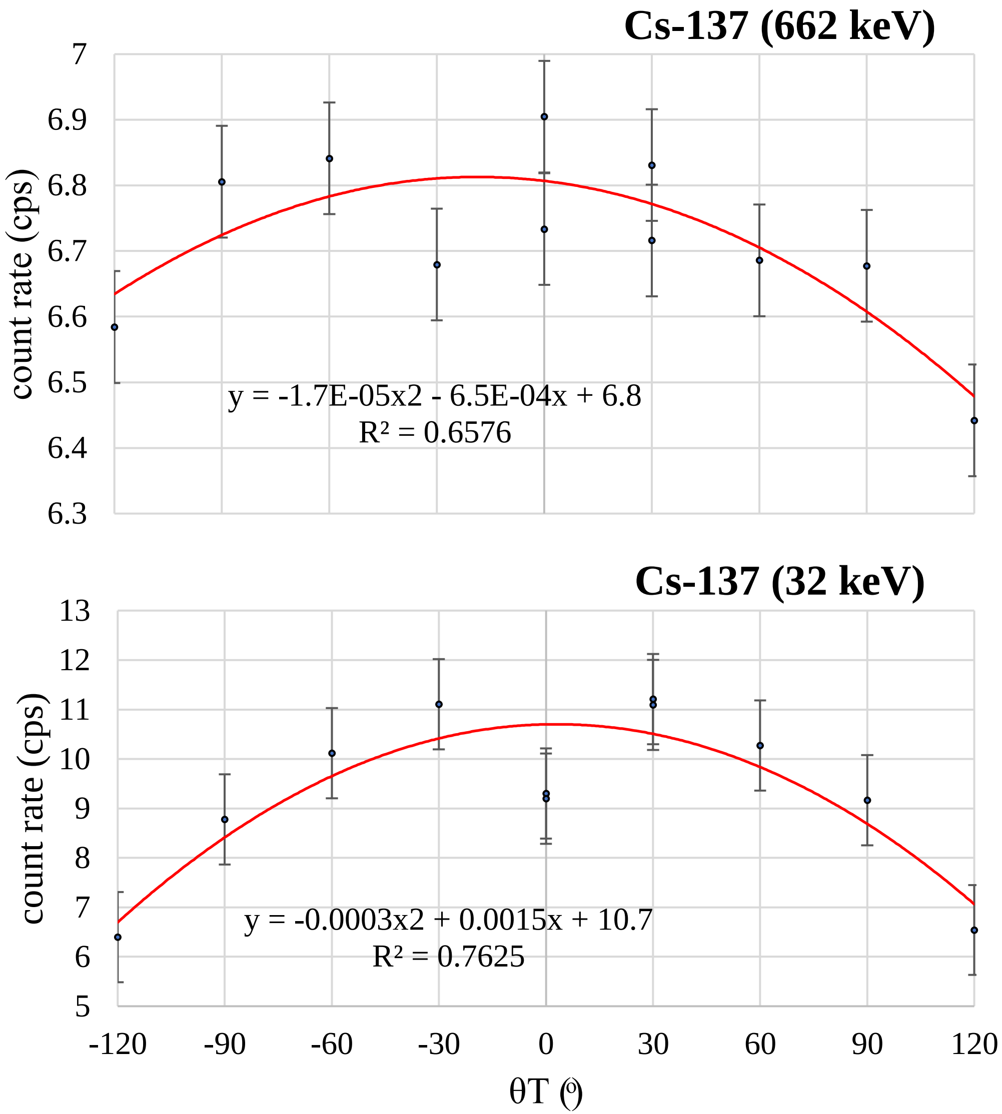
A2. Angular dependence of response

Experimental setup



$D = 105 \pm 2$ mm



+ variation on peak position of about 2%

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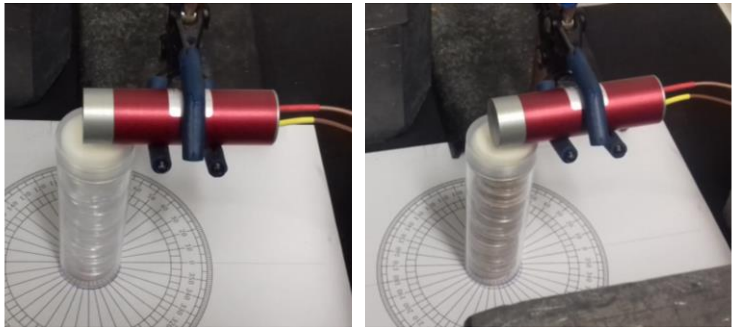
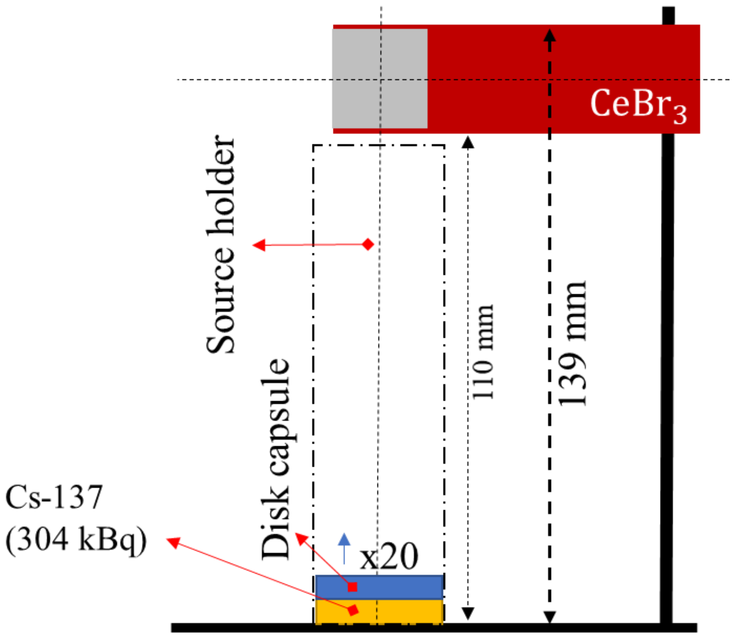
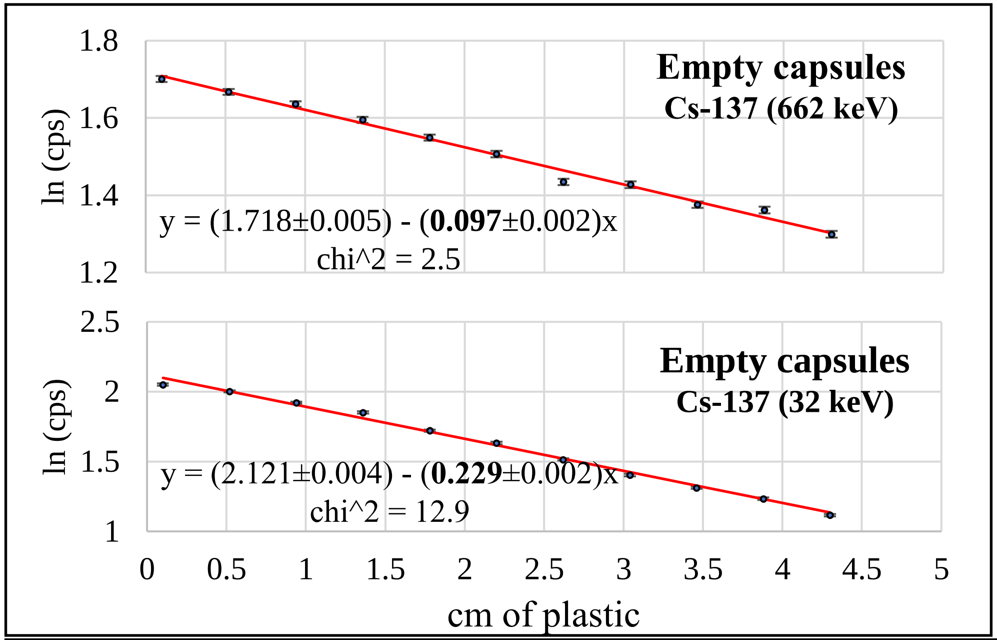
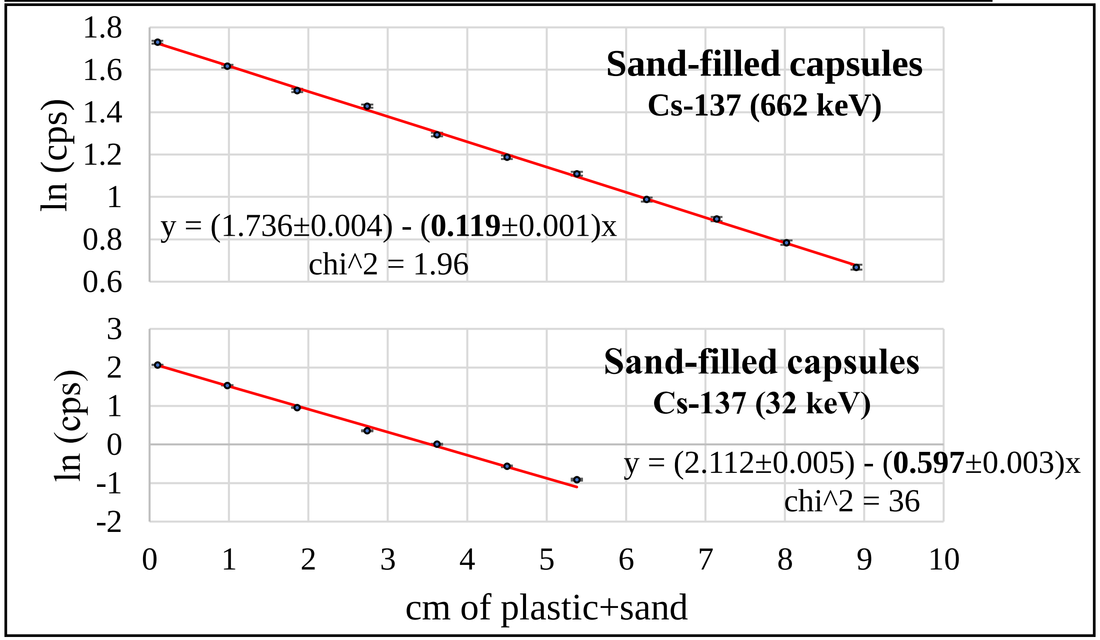
A3. Practice with source holder + capsules

Experimental setup









+ variation on peak position of

3%

10%

50%

20%

Future work

A. Radiological tests

- Blind tube test bed
- High dose environment

→ Gamma-ray detection (Cs-137)
Bremsstrahlung detection (Sr-90)

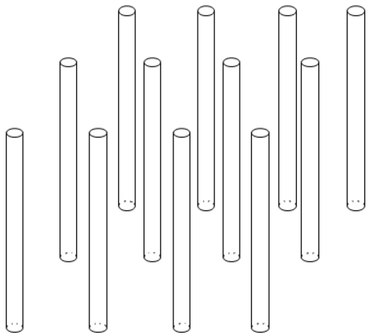

+


B. Simulations Geant4

C. Temperature dependence, waterproofing, vibration tests, etc

D. Extension of a single detector to a blind tube string network -> 3D underground mapping

1 m^3 Tank soil



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PhD student Soraia Elisio
e-mail : s.elisio@lancaster.ac.uk

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Characterisation and monitoring using in-ground assets

Thank you

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The Application of Electrokinetics for Remediation of Difficult to Measure Radionuclides

Shaun Hemming

University of Southampton

TRANSCEND Theme Meeting 2
17/05/21

Energy
For a Low Carbon Future

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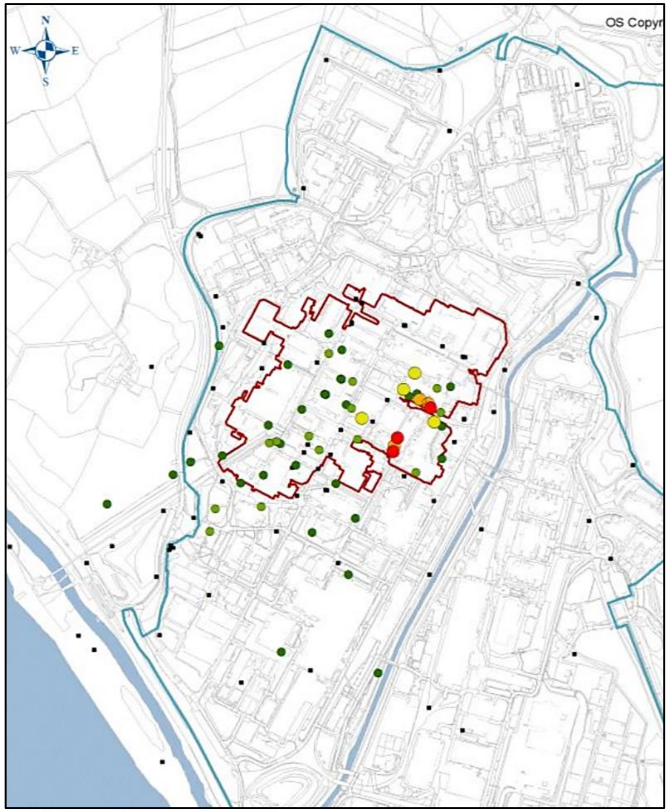
Sellafield, UK



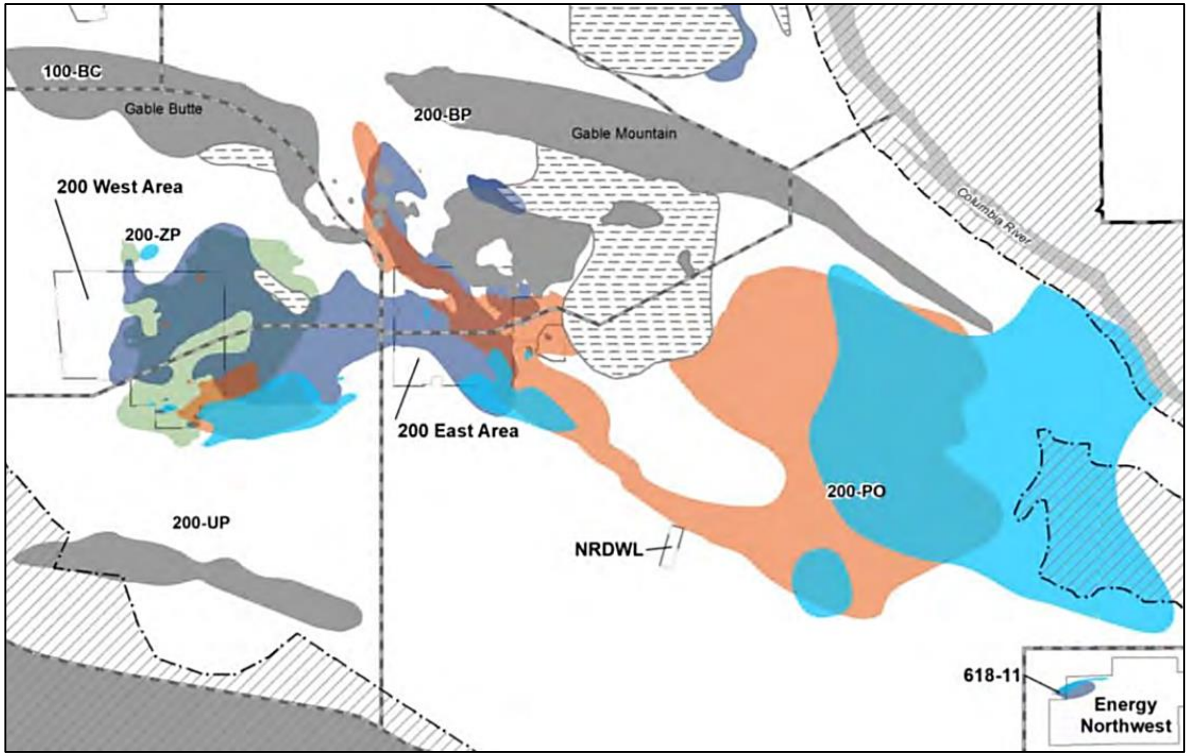
Carbon-14 Bql[-1]

- <LOD
- LOD - 10.00
- 10.01 - 100.00
- 100.01 - 1000.00
- 1000.01 - 10000.00
- 10000.01 - 45000.00

1 km

Groundwater Monitoring Annual Data Review 2016, Sellafield Ltd, 2017

Hanford, USA

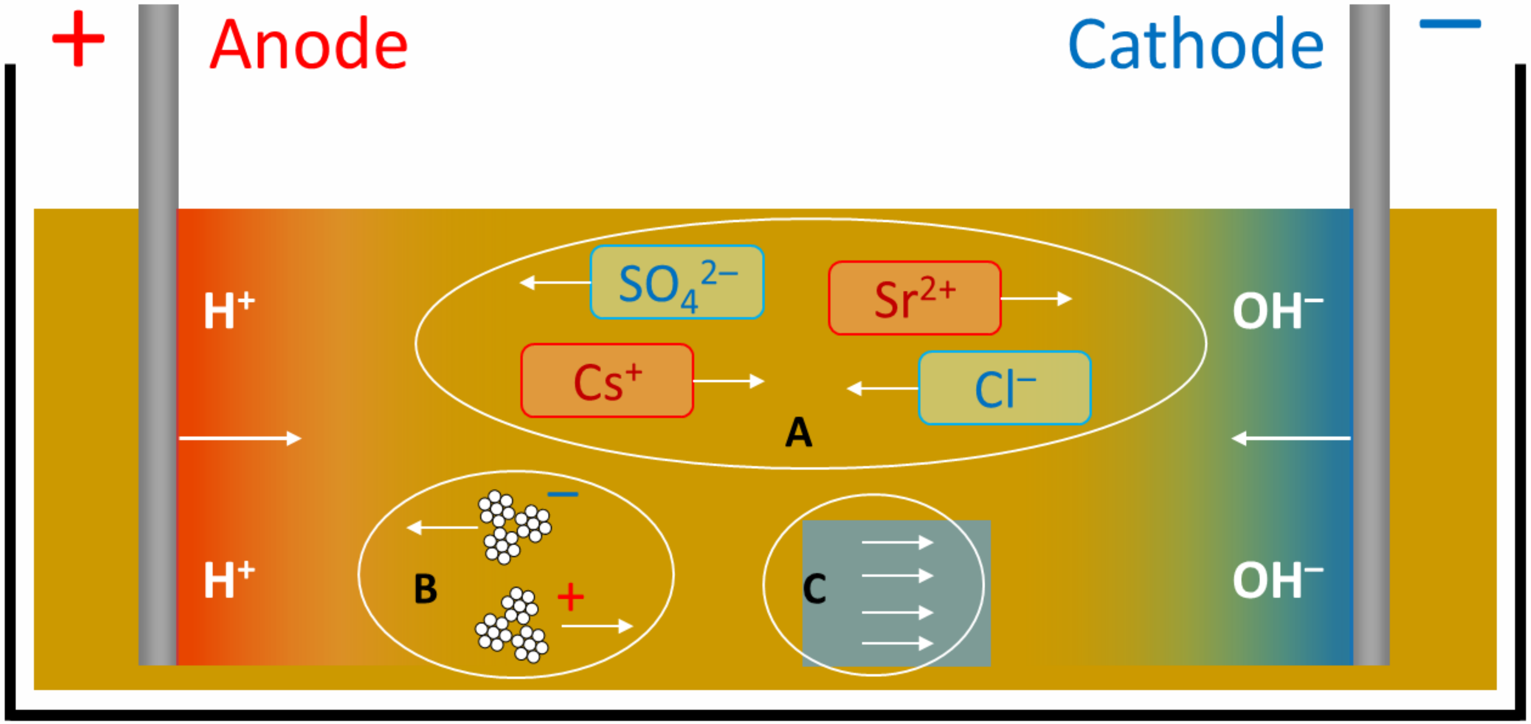


- Carbon Tetrachloride (5 µg/L)
- Iodine-129 (1 pCi/L)
- Nitrate (45 mg/L)
- Tritium (20,000 pCi/L)
- Former Operational Area
- Groundwater Interest Area Boundary
- Basalt Above Water Table
- Ringold Mud Unit Above Water Table
- Hanford Site Boundary
- Hanford Reach National Monument
- Hanford Operations Area

5 km

Hanford Site Groundwater Monitoring Report for 2019, USDOE, 2020

Electrokinetics



$H_2O \rightarrow 2\,H^+ + \frac{1}{2}\,O_2\,(\uparrow) + 2\,e^-$

$H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2\,(\uparrow)$

Experiments

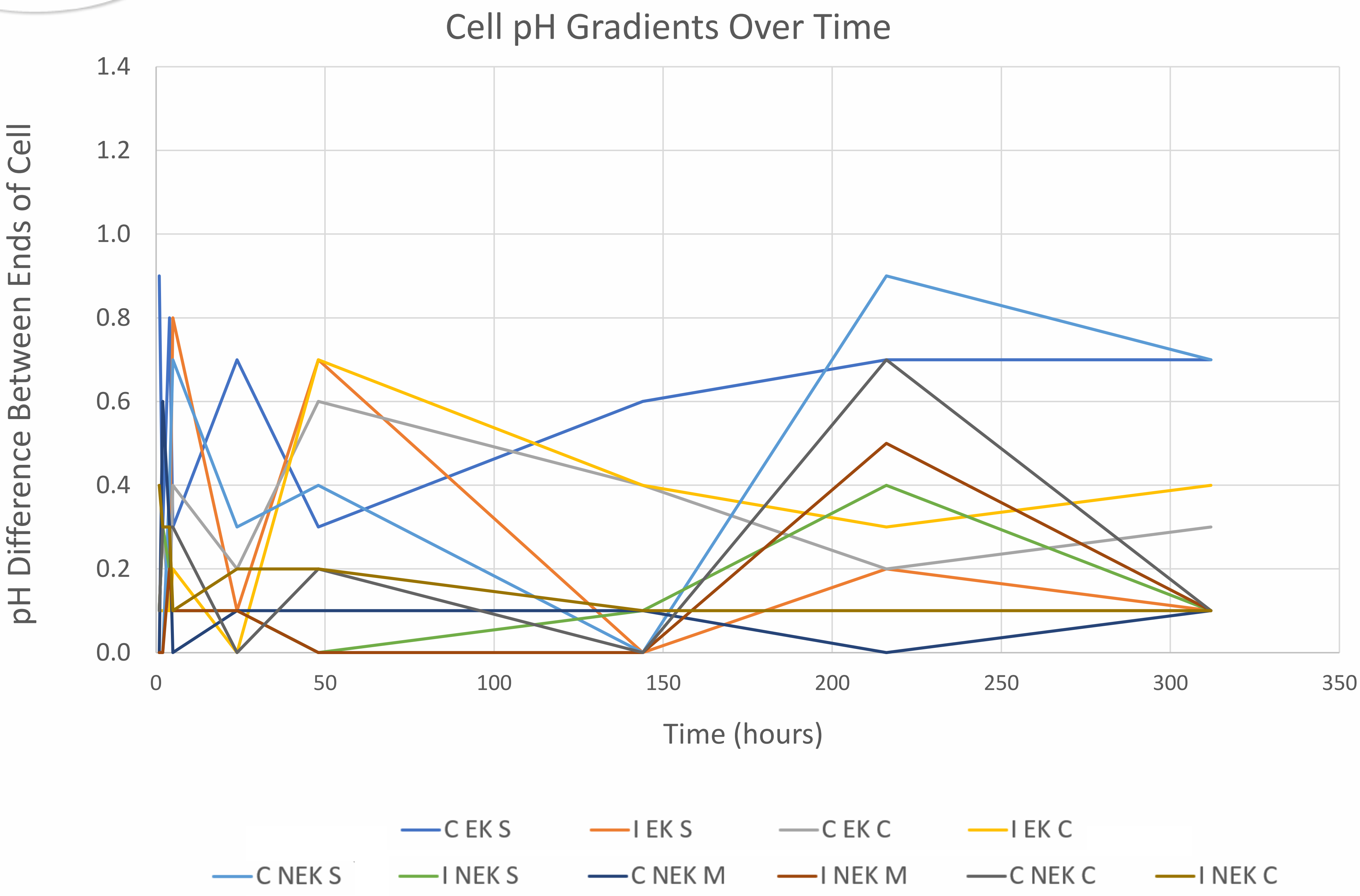
Contaminants:

- $H^{13}CO_3^-$
- $I^- + IO_3^-$

Materials:

- Sellafield sand
- Sellafield sand + compost barrier
- Sellafield sand + compost mix
- Sellafield GW Simulant


I EK M
C EK
C EK S
I EK S


Cell pH Gradients Over Time
pH Difference Between Ends of Cell
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
Time (hours)
C EK S
I EK S
C EK C
I EK C
C NEK S
I NEK S
C NEK M
I NEK M
C NEK C
I NEK C

Predictions:

- Sand only: nearly all carbon and iodine will migrate
- PRB and compost mix: all carbon will migrate but iodine migration will be more limited?
- Carbon will exist primarily as HCO_3^- along with minor component of CO_3^{2-} and CO_2
- Iodine will exist as both I^- and IO_3^- but the latter may be dominant at close proximity to the anode

Next Steps

- Water sample analysis
- Sediment analysis
- Repeat experiments with a pH gradient present

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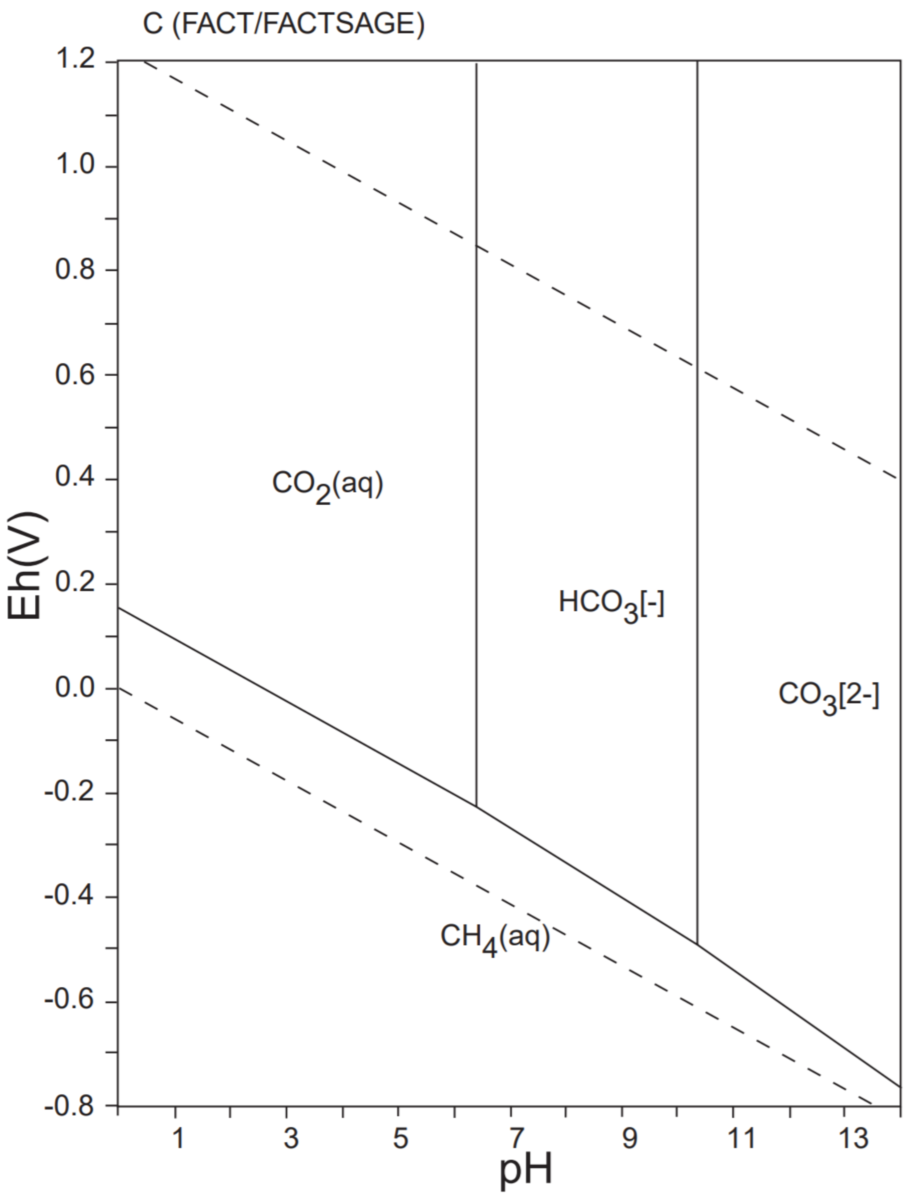
Any questions?

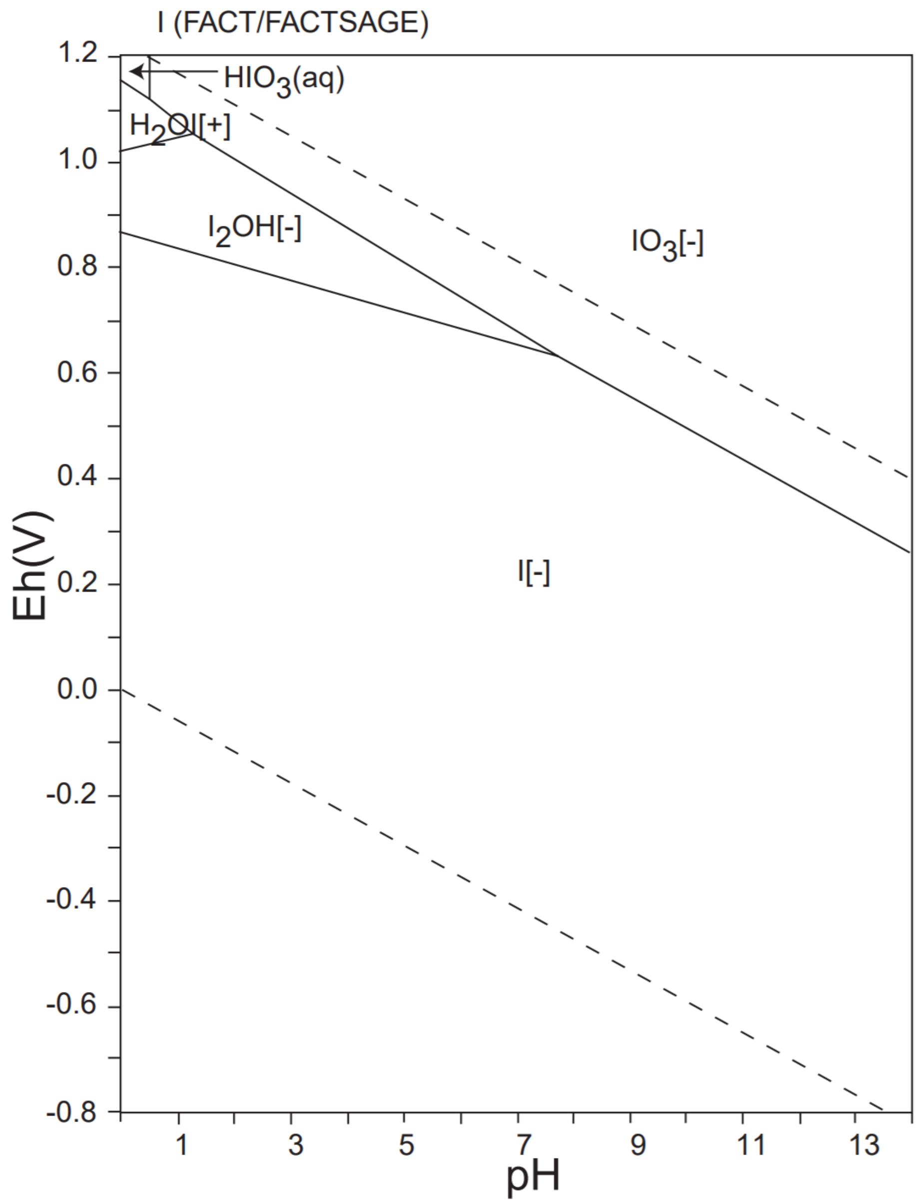
s.d.hemming@soton.ac.uk

UNIVERSITY OF Southampton

GAU Radioanalytical Laboratories

INSPIRE


C (FACT/FACTSAGE)
CO2(aq)
HCO3[-]
CO3[2-]
CH4(aq)
Eh(V)
pH
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
1
3
5
7
9
11
13


I (FACT/FACTSAGE)
HIO3(aq)
H2OI[+]
I2OH[-]
IO3[-]
I[-]
Eh(V)
pH
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
1
3
5
7
9
11
13

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Assessing the strength of biomineral strategies for concrete repairs

Thanos Karampourniotis, University of Strathclyde

Theme 2: Site Decommissioning and Remediation

email: athanasios.karampourniotis@strath.ac.uk

Supervisors:

Professor Rebecca Lunn[1] , Dr. Enrico Tubaldi[2], Dr. Grainne El Mountassir[3]

[1,2,3] Department of Civil and Environmental Engineering, Faculty of Engineering, University of Strathclyde, Glasgow, United Kingdom

17 May 2021

University of Strathclyde Glasgow

cavendish nuclear

Energy For a Low Carbon Future

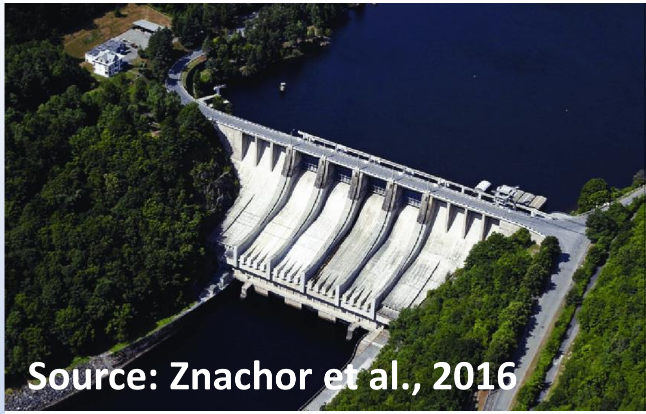
CONCRETE IN MODERN SOCIETY

What is concrete?

Concrete is a structural material consisting of a hard, chemically inert particulate substance, known as aggregate (usually sand and gravel), that is bonded together by cement and water. ***(Source:*** *Britannica)*

Why is it important?

Approximately 4.4 billion tonnes of cement and 33 billion tonnes of concrete are produced each year, making concrete the second most consumed material in the world, after water.
(Sources: *Mehta and Monteiro, 2014*
The American Society of Mechanical Engineers)



Slapy Reservoir, Czech Republic

Wind Turbines, Gaildorf, Germany

Santiago Calatrava's auditorium Tenerife, Spain

Burj Khalifa, Dubai, United Arab Emirates

THE ENVIRONMENTAL IMPACT OF MASS CONCRETE PRODUCTION

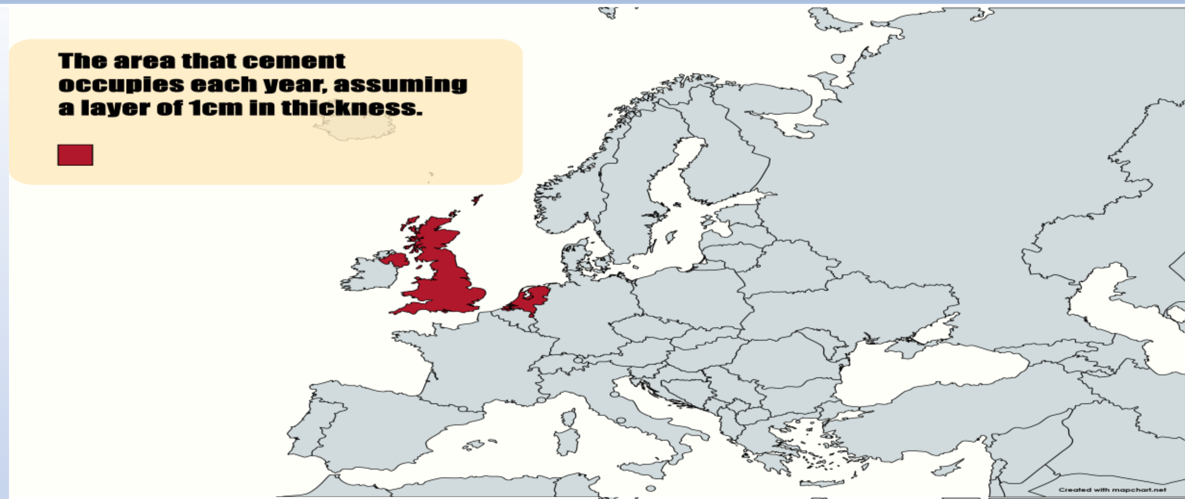
The problem

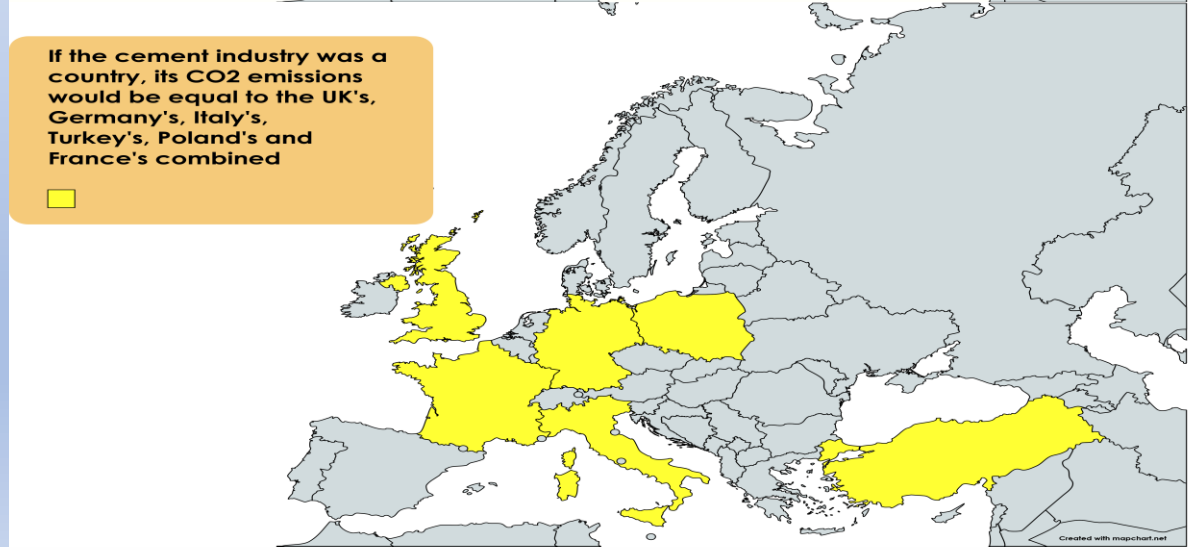
- Worldwide concrete production is estimated to be responsible for 8.6% of all anthropogenic CO_2 emissions. (**Source:** Miller et al., 2016)

- Global cement production is expected to rise from 4.4 billion tonnes to 5.5 billion in 2050 due to further urbanization, increasing the amount of CO_2 emissions. (**Source:** Chatham House, 2018)

A possible solution

More attention should be given to effectively repairing and maintaining the existing structures and infrastructure.





Created on www.mapchart.net

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DURING THE DECOMMISSIONING PROCESS

- Most of the UK's nuclear power stations are decades old and in need of maintenance during the decommissioning process, to ensure both their safety and functionality.
- For instance, the Hunterston B and Hinkley Point B nuclear power stations in Scotland and England respectively, remain operational since 1976 and are scheduled for closure by 2023. (**Source:** assets.publishing.service.gov.uk)
- The deterioration of concrete assets on these sites should be attended to effectively.

Hunterston B nuclear power station, Scotland, **Source: news.sky.com**

Hinkley Point B nuclear power station England, **Source: world-nuclear-news.org**

TRADITIONAL CONCRETE-REPAIR MATERIALS

Epoxy resins

- Epoxy resins have a much greater coefficient of thermal expansion than concrete, something that can cause high shear stresses at the interface between the materials when temperature changes. As a result, cracks begin to form in the interface.
- They need constant periodic care and maintenance, making them in many cases uneconomical.

Source: safetyshop.com

Cement mortar

- Cement mortar consists of big particle size grains, resulting in poor penetration, making it ineffective when treating micro-cracking.

Source: polycote.com

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RESEARCH AT THE UNIVERSITY OF STRATHCLYDE

Microbially Induced Carbonate Precipitation

A novel concrete repair method that takes advantage of the mineralization properties of certain types of bacteria like *S. Pasteurii* where together with a calcium source can form calcium carbonate ($CaCO_3$) crystals on their surface.

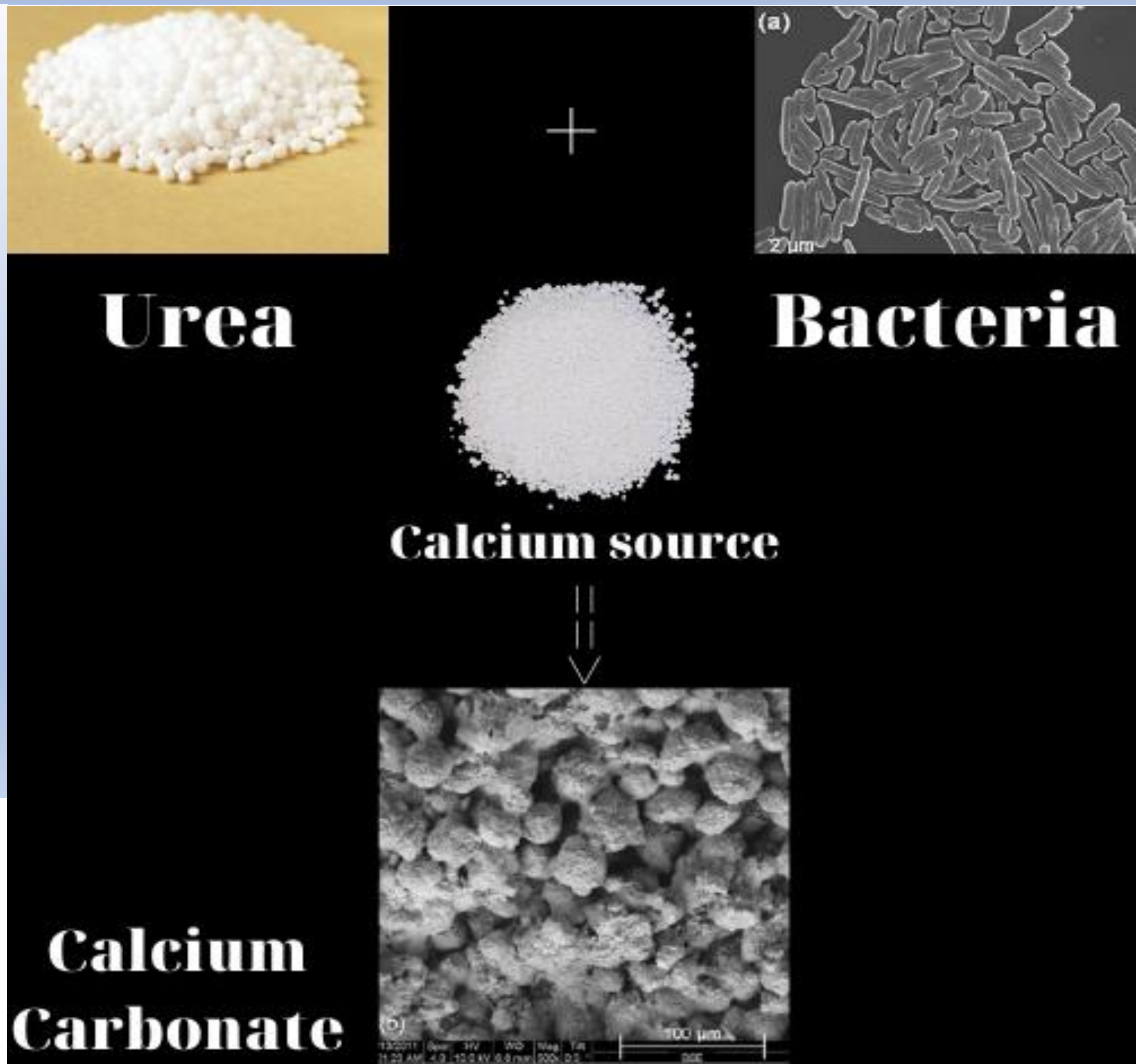
$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + H_2CO_3$

$2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^-$

$H_2CO_3 + 2OH^- \leftrightarrow HCO_3^- + H_2O + OH^-$

$HCO_3^- + H_2O + OH^- \leftrightarrow CO_3^{2-} + 2H_2O$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (s) (calcite precipitation)



17 May 2021

MICP HAS GIVEN PROMISING RESULTS TO

- Soil strengthening
- Sealing fractured rock
- Increasing fractured rock's shearing resistance
- Leakage reduction from carbon sequestration reservoirs
- Permeability reduction
- Enhancing the compressive strength of cement mortar

THE AIM AND OBJECTIVES OF THIS PHD ARE

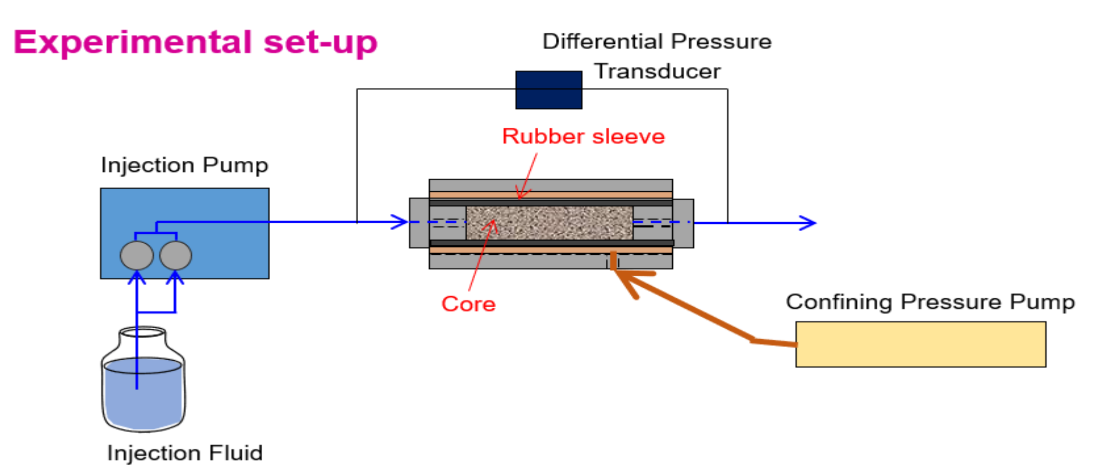
AIM

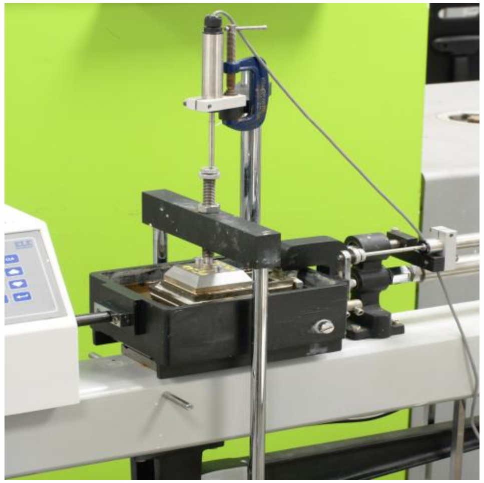
- To repair concrete structures in nuclear sites so that they are fully functional and safe for the duration of the decommissioning process.

OBJECTIVES

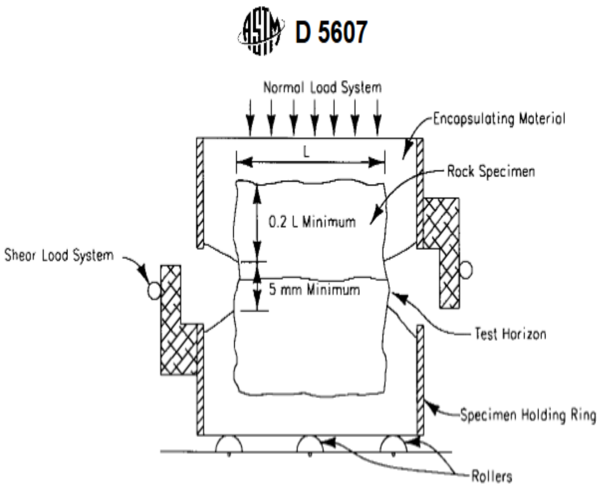
- To develop a modelling strategy, conduct experiments to validate it and show it can predict the mechanical behavior of MICP-treated concrete.
- To optimize the repair strategy which is investigated.

GRANITE CORES TREATMENT AND SHEAR TESTING





Direct shear box



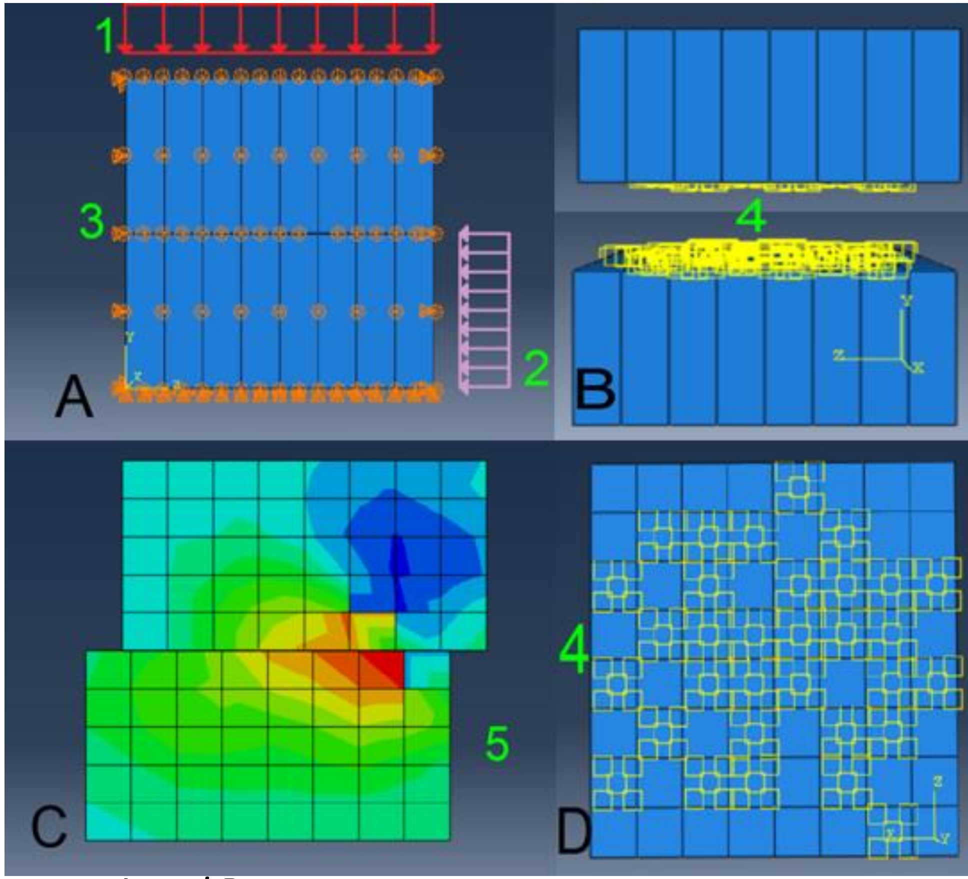
Schematic test setup

Calcite crystals bridged the fracture
after the MICP treatment was implemented

Source: Tobler et al., 2018

THE FINITE ELEMENTS MODEL CREATED

1) Vertical load on the top face of the half-core
2) Displacement rate on the second half-core
3) Horizontal fracture
4) Calcite distribution on half-cores' surfaces
5) Displacement

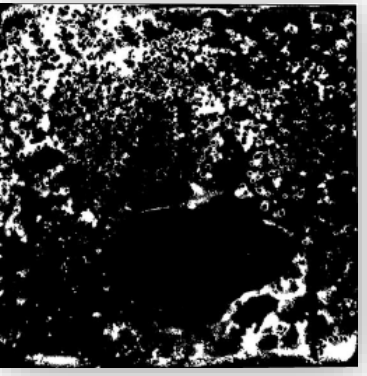


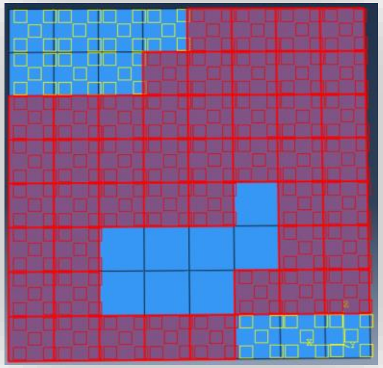
Images A and B: Loading and boundary conditions on the rock core, consisting of two rock sections (top and bottom half). *Y-Z axes view*

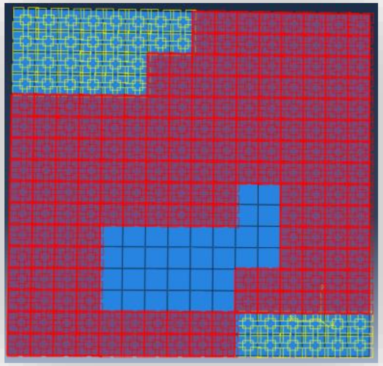
Image C: Shear stress distribution and displacement. *Y-Z axes view*

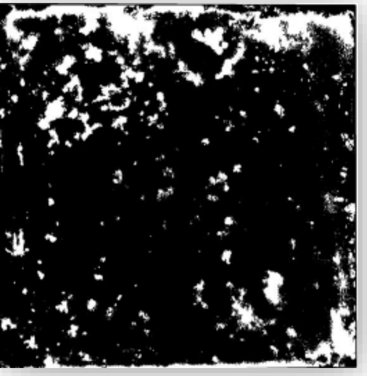
Image D: Simulating calcite (yellow patches) as a cohesive component in different geometrical patterns on the rock's surfaces. *X-Z axes view*

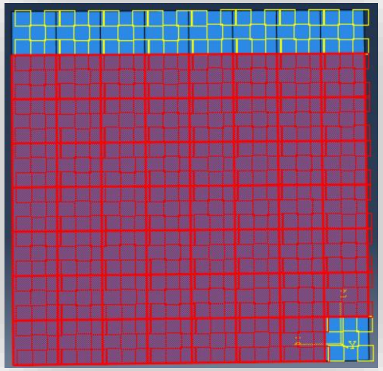
MODELING THE CONNECTED REGIONS OF THE HALF-CORES

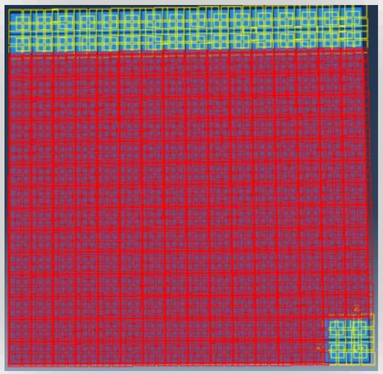

X-CT Image, FG2 Core


64 elements Model, FG2 Core


256 elements Model, FG2 Core


X-CT Image, FG4 Core


64 elements Model, FG4 Core


256 elements Model, FG4 Core

Yellow elements:

Cohesive behavior assigned

FG2 Core: 0.50 MPa

FG4 Core: 0.73 MPa

Red elements:

Frictional behavior assigned

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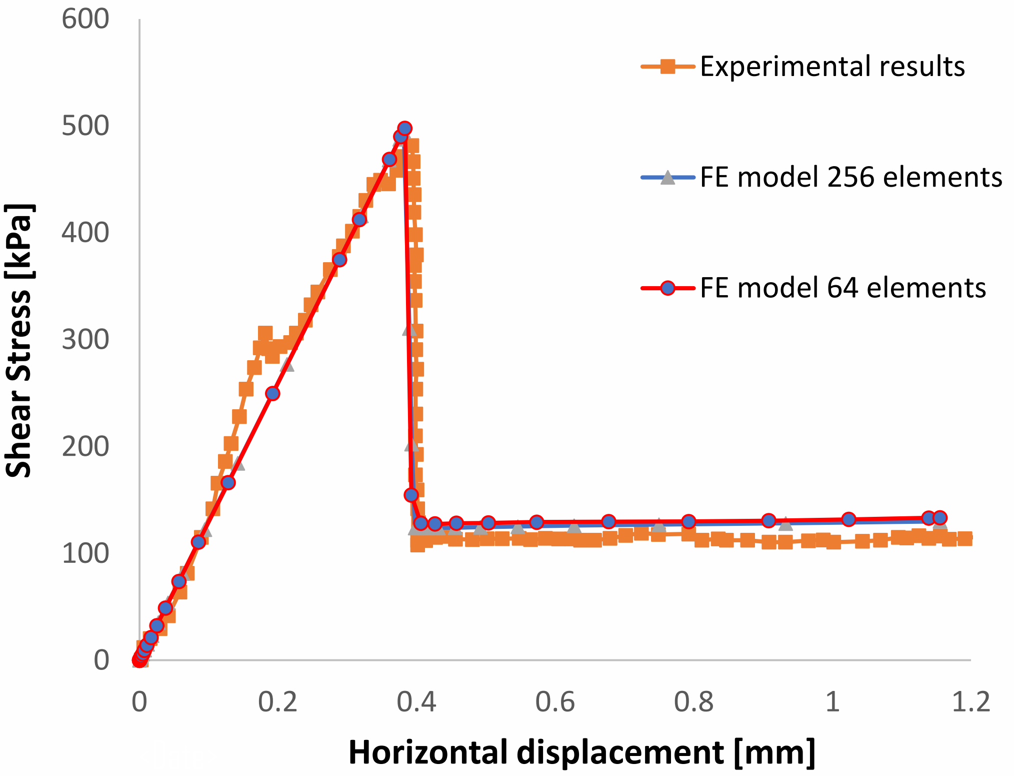
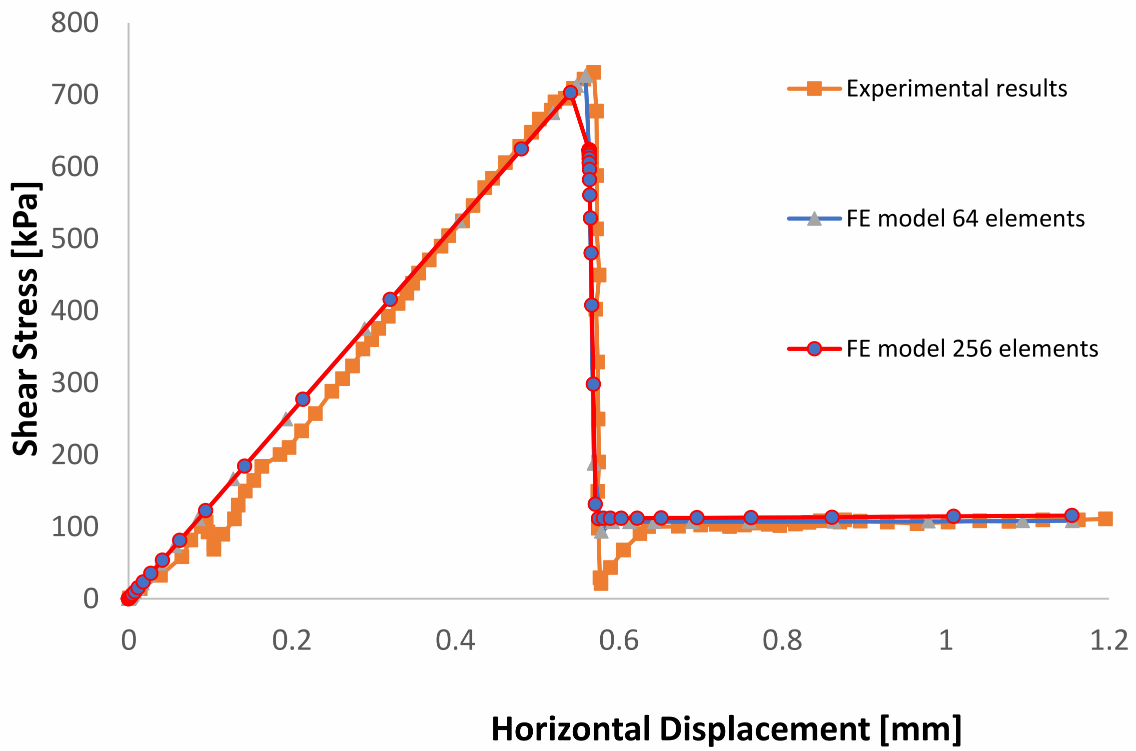
CALIBRATION OF THE MODEL - MESH DEPENDENCY

FG2 Core

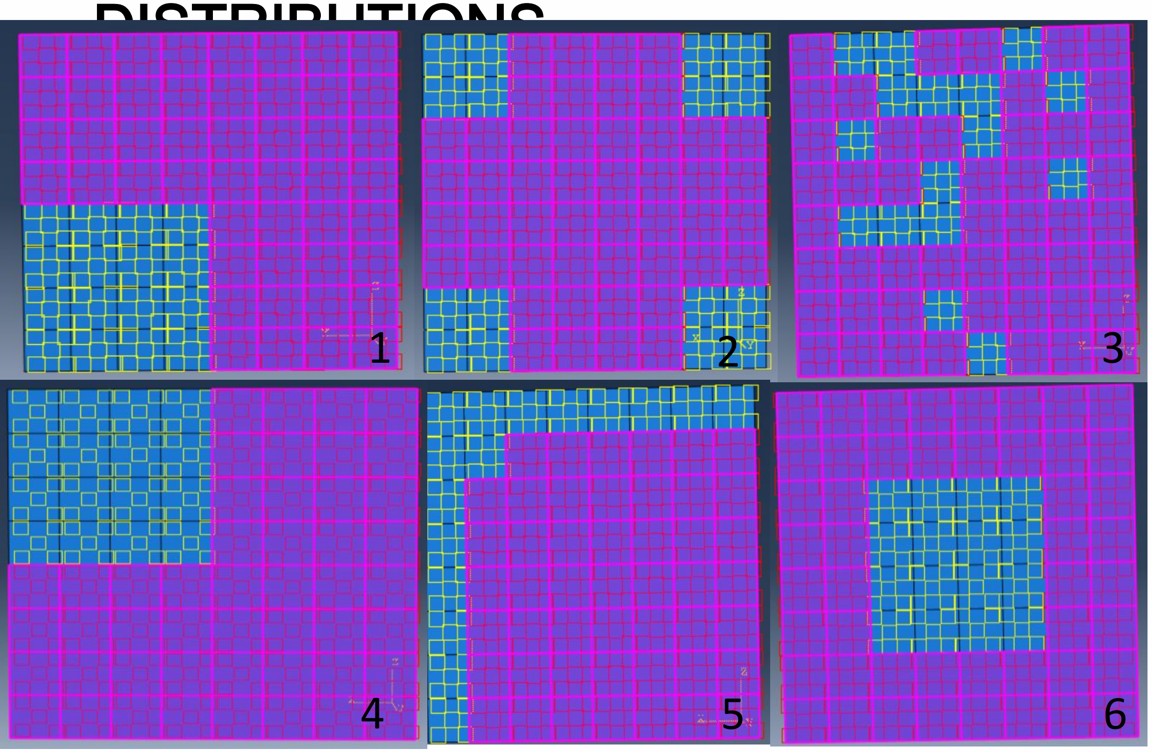


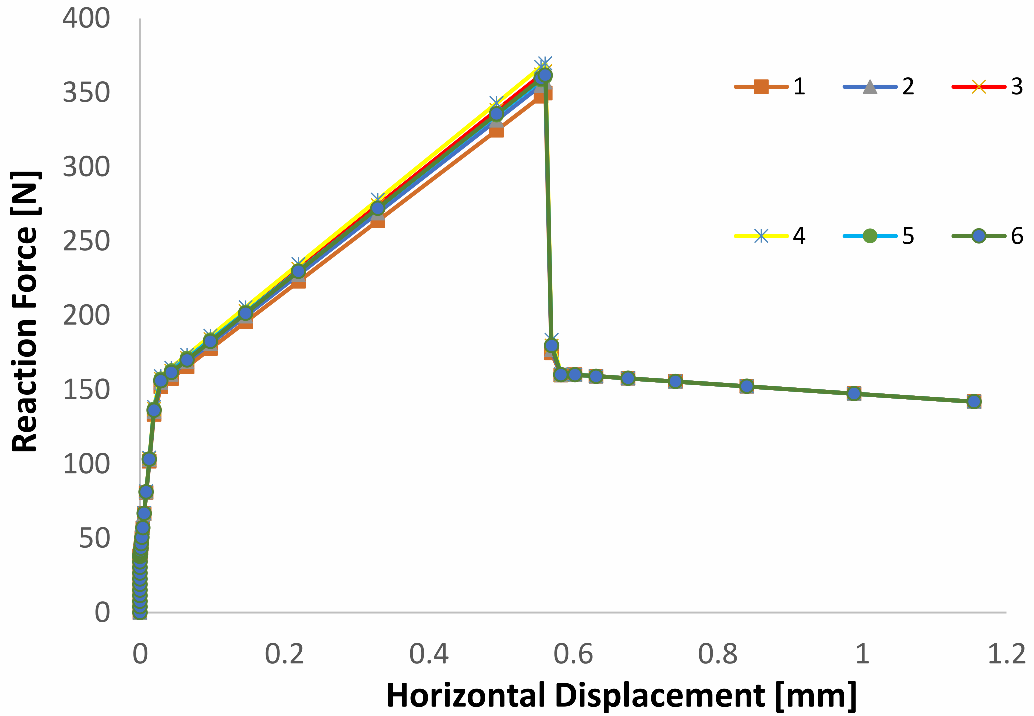
FG4 Core



CALCITE DISTRIBUTION STRATEGIES

DIFFERENT CALCITE DISTRIBUTIONS



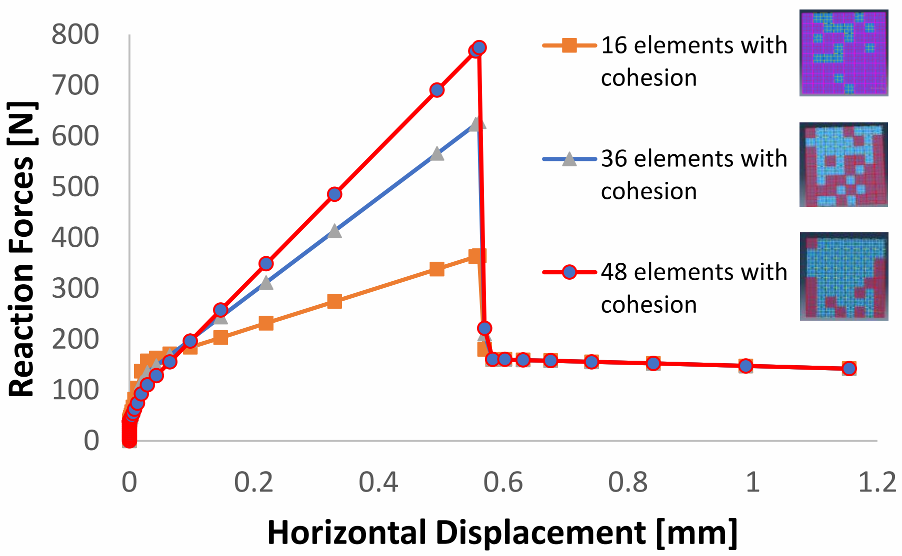


Yellow elements: Cohesive behavior assigned

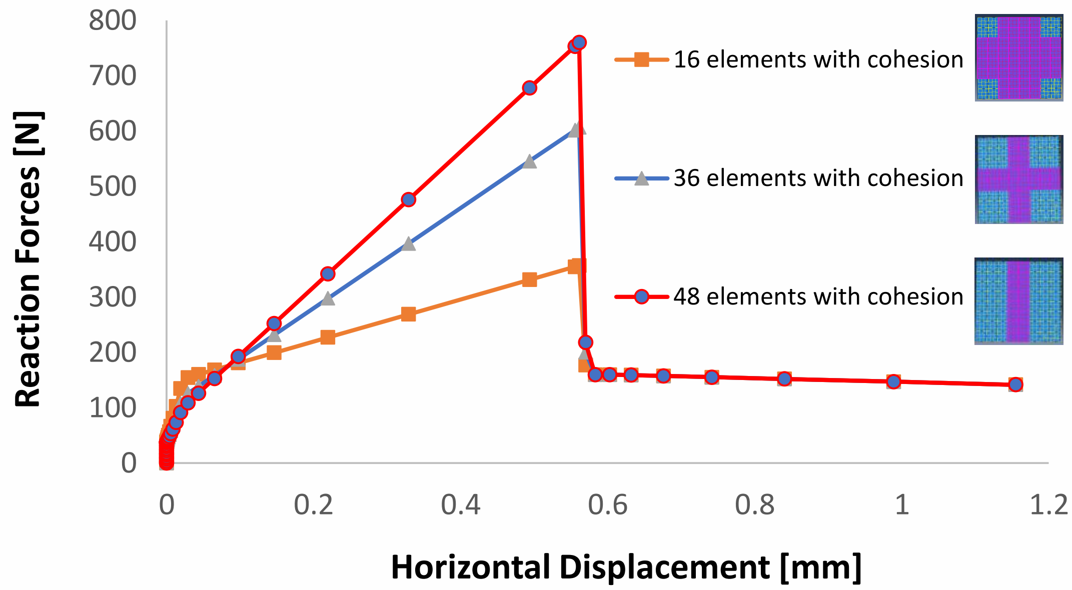
Purple elements: Frictional behavior assigned

THE INFLUENCE OF INCREASING THE NUMBER OF BRIDGING ELEMENTS ON STRENGTH

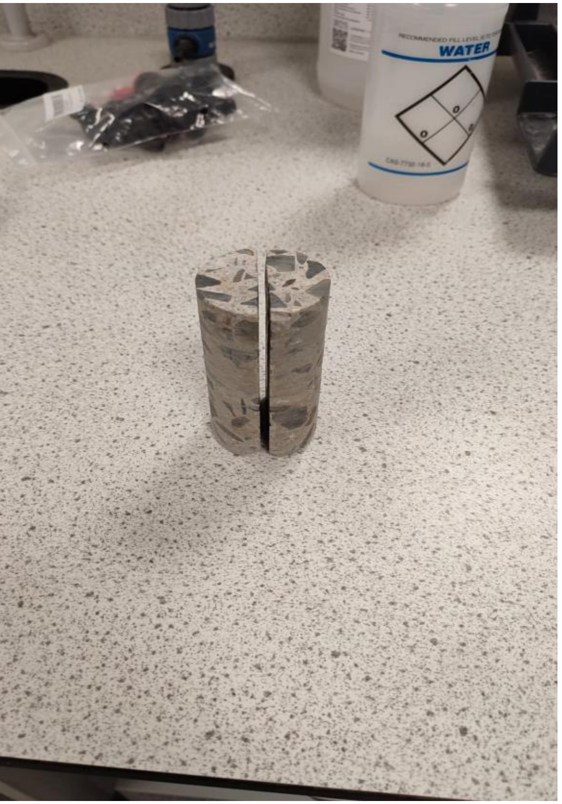
"Random distribution" of calcite models



"Pillars distribution" of calcite models



EXPERIMENTAL SETUP



The separated half-cores

0.5mm diameter glass beads on the half-core's surface

The half-cores wrapped together with membrane layers

EXPERIMENTAL SETUP

Rigid clear tube acting as core holder

Peristaltic pump

EXPERIMENTAL SETUP

After having the wrapped half-cores immersed in colloidal silica

15 minutes after having introduced colloidal silica

After removing the top layer of membrane

CONCLUSIONS

- A Finite Elements Model has been developed and calibrated against experimental data.
- According to the sensitivity analyzes that took place, the model shows that there is relatively little effect on the geometry of the calcite and that strength is largely governed by the size of the contact area.
- Microbially Induced Carbonate Precipitation treatments will be implemented to old artificially-cut concrete cores and then subjected to shear tests to confirm the efficiency of the already developed Finite Elements Model.

FUTURE WORK

- Concrete specimens with various fracture widths will be treated with MICP.
- Concrete specimens with rough (and thus closer to real condition cracking) rather than smooth fracture surfaces will be treated.
- The effect of the created flow paths due to the spatial distribution of calcite on the efficiency of the repair will be investigated.
- Different mechanical tests will be conducted to determine whether the same behavior will be observed.

Thank you

Predicting Gamma Dose Rates from Underground Contaminated Structures with Limited Information

Luke Lee-Brewin: l.lee-brewin@surrey.ac.uk

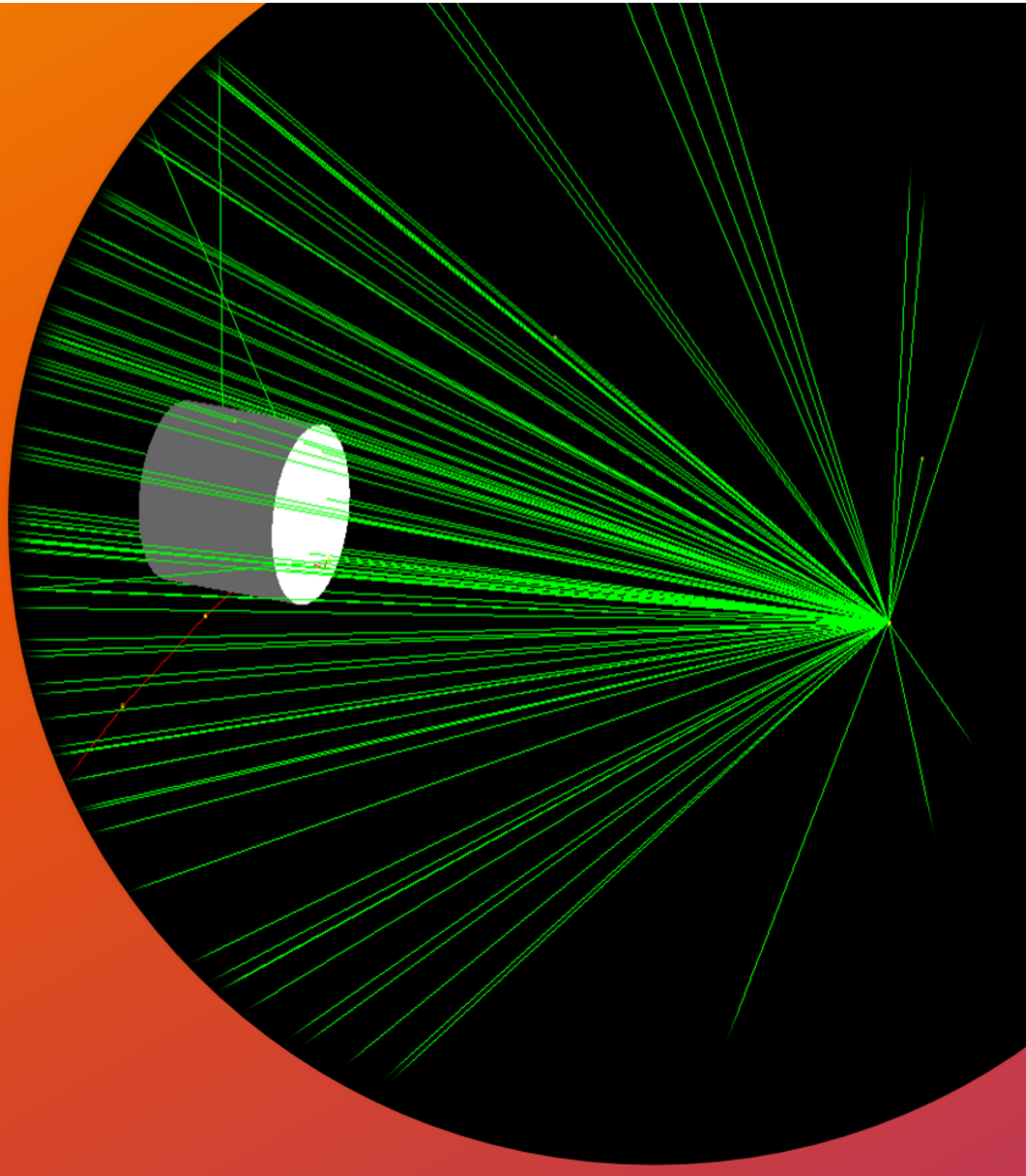
University of Surrey

TRANSCEND Virtual Meeting

17/05/2021

Project Overview

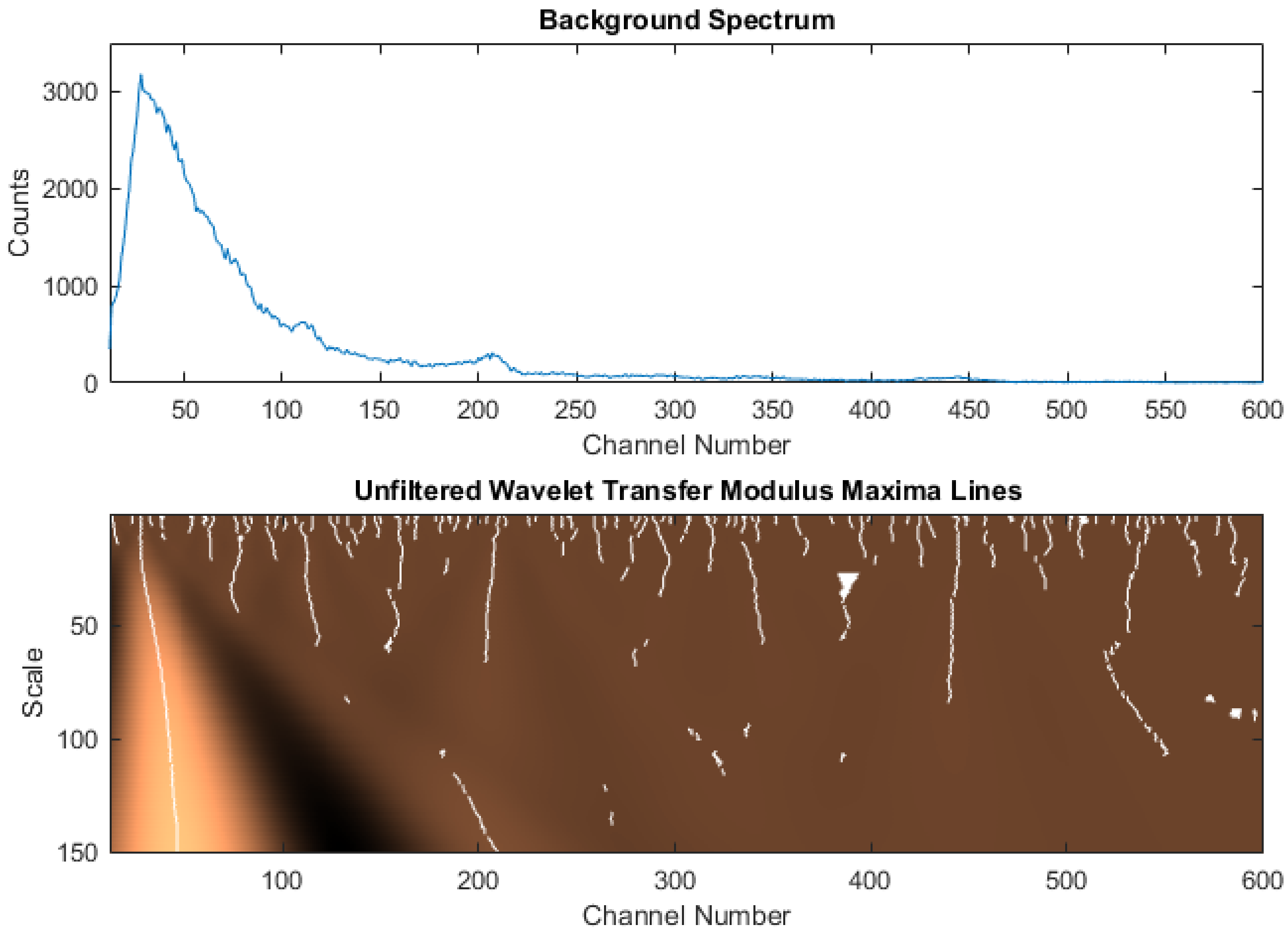
- Identify radioisotopes present within low SNR gamma signals
- Several Methods of Signal Analysis Explored:
  - Wavelet Analysis
  - Principal Component Analysis
  - Neural Networks



Wavelet Analysis

Wavelet analysis provides a method of identifying the locations of low signal to noise ratio photopeaks in gamma spectra

This method works by assessing how gaussian a distribution is rather than how tall the photopeak is making it independent of count time.



Information is extracted from the scalogram (the bottom image) by determining the local maxima within the heatmap. These are the white lines.

High frequency events (such as noise) are shows towards the top of the scalogram where as lower frequency events (photopeaks) are the longer lines extending into the higher scales.

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Wavelet Analysis

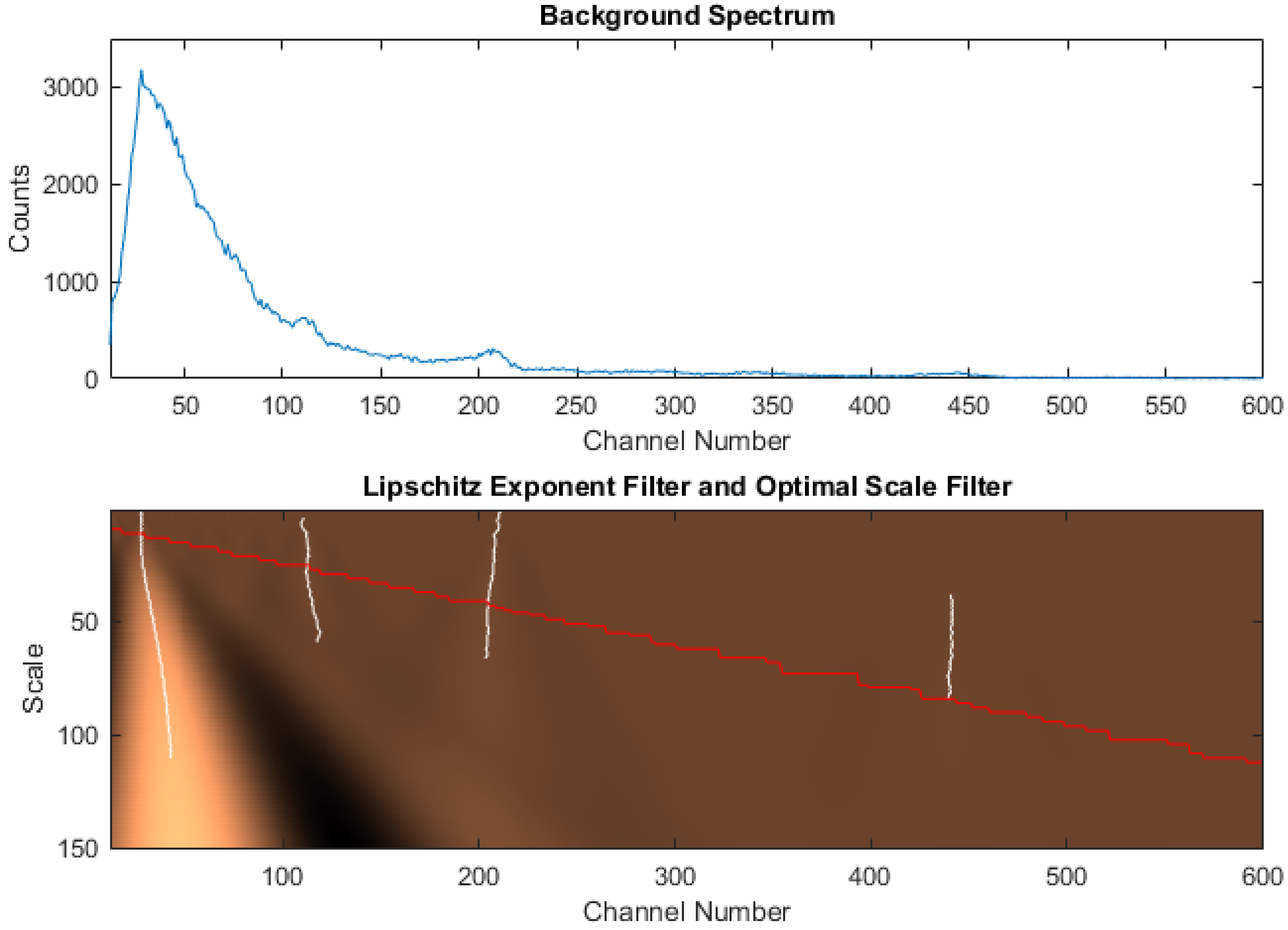
Spectrum info

Detector: NaI

Count Time: 1h

Nearby Sources: Cs137 and Eu152 approx. 2m away in lead containers.

White lines are filtered to remove any that cannot correspond to photopeaks.



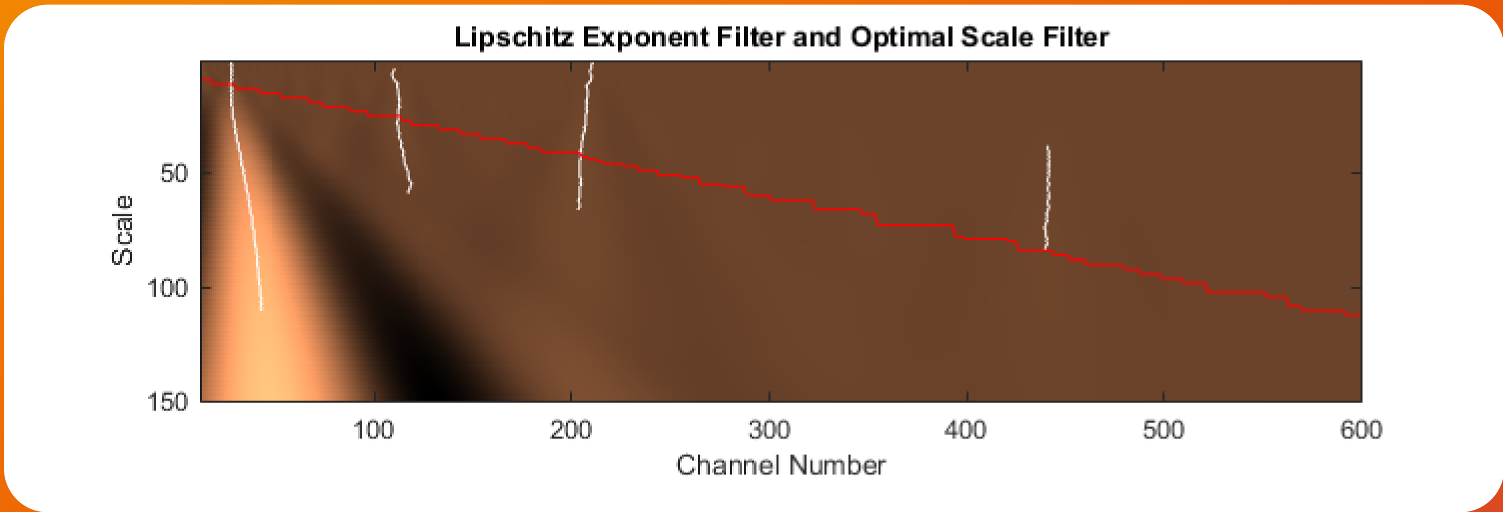
Lipschitz Filter

Measures differentiability of the line. Gaussians are differentiable therefore any line that isn't cannot be a photopeak

Optimal Scale Filter

Red line shows the energy resolution vs energy converted into scale vs channel number. Any line wholly above the red line corresponds to a feature too thin to be a photopeak

Analysis



Line 1:

Energy: ~30-70 keV

Source: Background X-rays

Line 2:

Energy: ~350 keV

Source: ^{152}Eu left in safe

Line 3:

Energy: ~670 keV

Source: ^{137}Cs left in safe

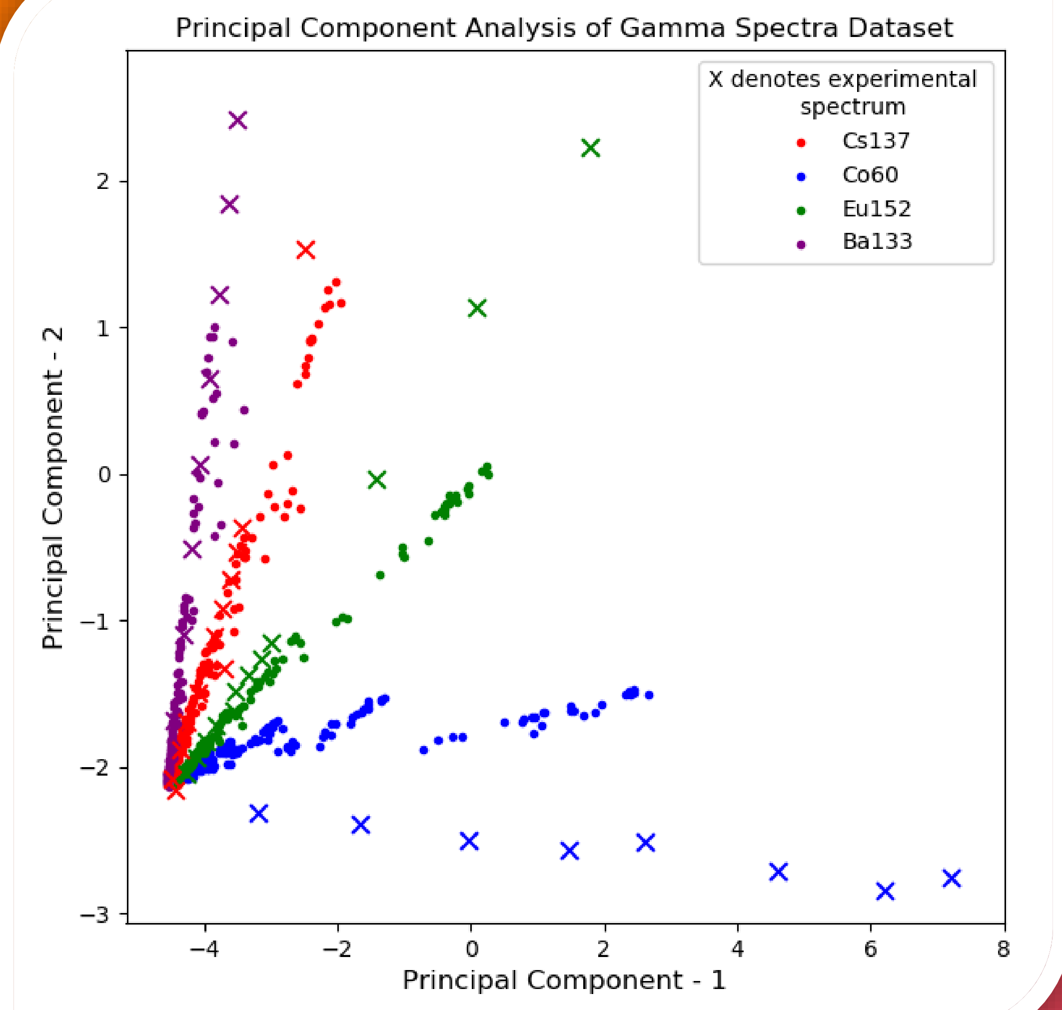
Line 4:

Energy: ~1450 keV

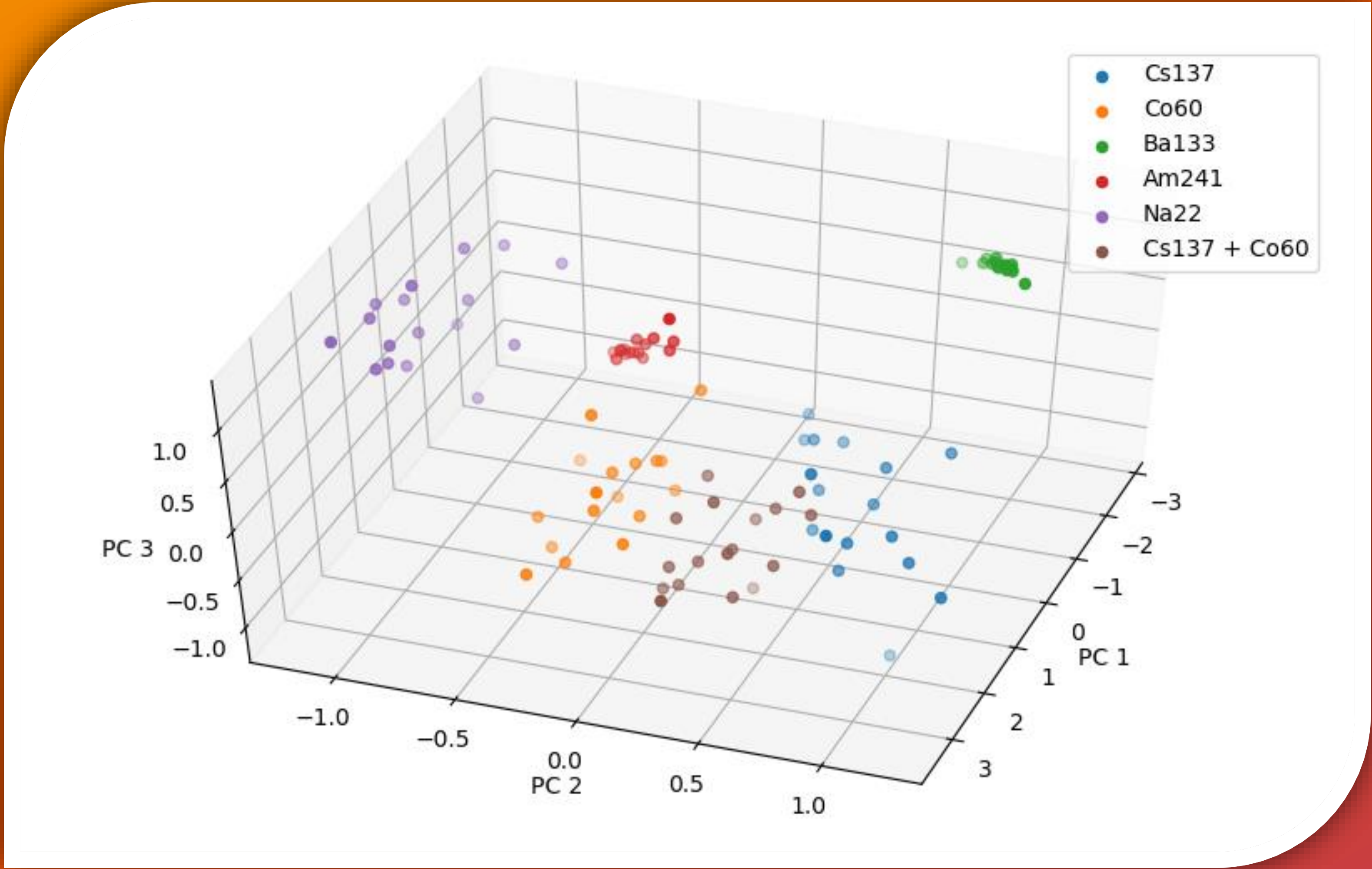
Source: Background ^{40}K

Principal Component Analysis

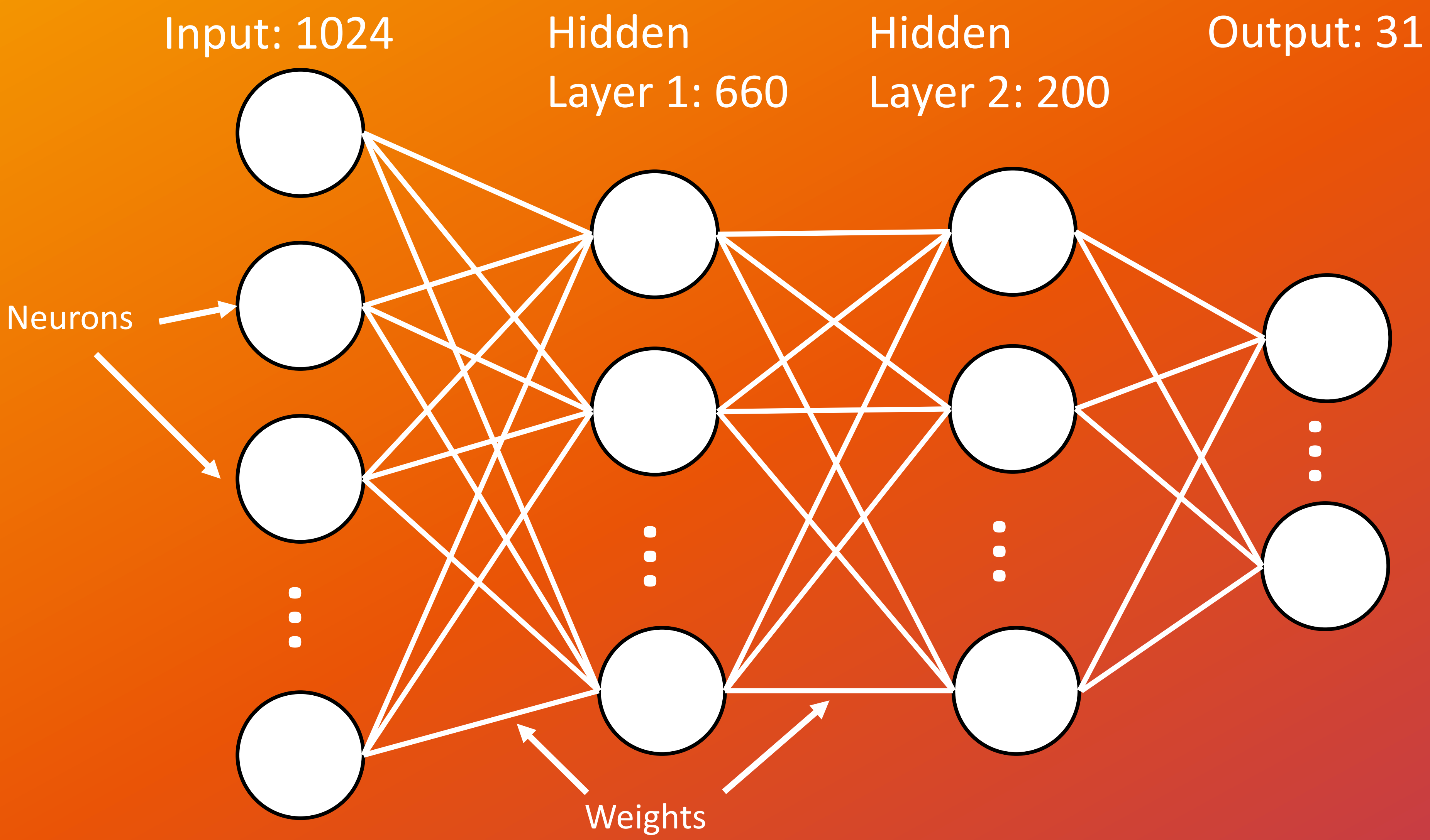
- Algorithm designed to reduce dimensionality of a dataset
- Gamma spectra can be reduced to 2 or 3 “principal components” and analysed
- So far used to check quality of simulated datasets
- Can be used to identify isotopes – bad at multi-isotope identification without additional help



Principal Component Analysis



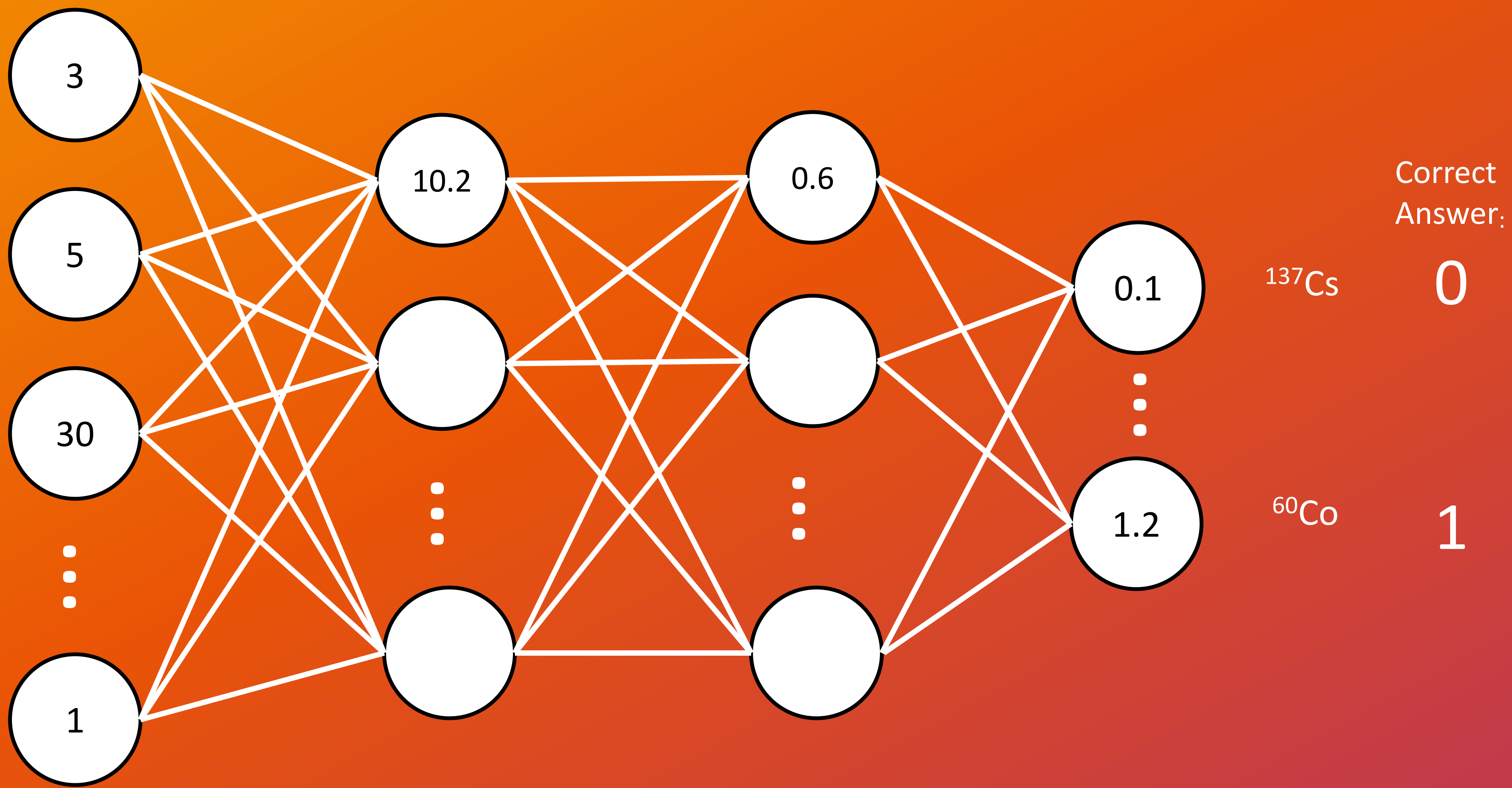
Neural Network



Neural Network

Gamma Spectrum

Each number of counts in a channel goes into 1 neuron



Training Set: Resampling

^{137}Cs	^{133}Ba	^{60}Co	^{241}Am	^{22}Na
18 Spectra Collected	18 Spectra Collected	18 Spectra Collected	18 Spectra Collected	18 Spectra Collected

^{137}Cs + ^{133}Ba

^{133}Ba + ^{60}Co

^{60}Co + ^{241}Am

^{241}Am + ^{22}Na

Initial set of 90 spectra are resampled into 6200

So far, 3 sets of 90 spectra have been created with different levels of shielding for 18600 spectra

Isotopes:

Training Sets

Isotopes	Activities / kBq
^{241}Am	369.86
^{137}Cs	129.77
^{60}Co	179.25
^{133}Ba	219.52
^{22}Na	76.92

Testing Sets

Isotopes	Activities / kBq
^{241}Am	398.90
^{137}Cs	200.13
^{60}Co	189.68
^{133}Ba	112.34
^{22}Na	93.89

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Testing Sets:

1. Different isotopes used with different activities
2. Fully experimental spectra, no resampling, all combinations collected
3. Initially tested in same shielding environments as training set
4. Finally, tested on new shielding environments to see how network handles new environments

Results

Lead Castle
Accuracy: 96.77% (30/31)

	Prediction	Answer
1	Am241	Am241
2	Ba133 Am241	Ba133 Am241
3	Cs137 Ba133 Am241	Cs137 Ba133 Am241
4	Co60 Ba133 Am241 Na22	Co60 Ba133 Am241 Na22
5	Cs137 Co60 Ba133 Am241 Na22	Cs137 Co60 Ba133 Am241 Na22
6	Cs137 Ba133 Am241 Na22	Cs137 Ba133 Am241 Na22
7	Co60 Am241	Co60 Am241
8	Co60 Ba133 Am241	Co60 Ba133 Am241
9	Cs137 Co60 Ba133 Am241	Cs137 Co60 Am241
10	Cs137 Am241	Cs137 Am241
11	Cs137 Co60 Ba133 Am241	Cs137 Co60 Ba133 Am241
12	Am241 Na22	Am241 Na22
13	Ba133 Am241 Na22	Ba133 Am241 Na22
14	Co60 Am241 Na22	Co60 Am241 Na22
15	Cs137 Am241 Na22	Cs137 Am241 Na22

Shielding	Size of Testing Set	Accuracy
Lead Castle	31	96.77%
Lead Pot at 20cm	15	100.0%
20cm No shielding	31	100.0%
Lead Pot at 10cm	15	100.0%

Accuracy is measured as the percentage spectra the network has predicted with no false positives or negatives

Conclusions

PCA

- Good visualisation up to 3 dimensions
- Fast, basic analysis possible without expert knowledge
- New data can't be added once PCA has been performed
- Multi-isotope identification requires more than 3 dimensions

Wavelets

- Excel at low signal to noise ratio photopeak detection
- Struggles with overlapping peaks (at the moment)
- Expert knowledge required to read scaleogram

Neural Networks

- Provides initial prediction in easy to read format
- Can be expanded to provide confidence level in prediction and recommend additional analysis
- Can be adapted to take in wavelet or PCA data

Acknowledgements

Supervisors: Caroline Shenton-Taylor:

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David Read: d.read@surrey.ac.uk

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Thank you

Modifying Colloidal Silica Grout for Nuclear Decommissioning Applications

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TRANSCEND Theme 2 Meeting, 17th May 2021

University of Strathclyde Engineering

University of Glasgow | School of Chemistry

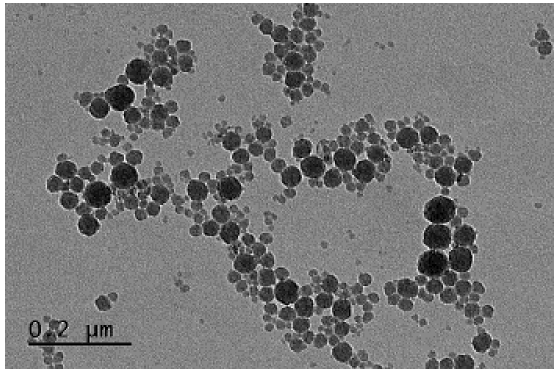
NATIONAL NUCLEAR LABORATORY

NDA

SRPe Scottish Research Partnership in Engineering

Outline

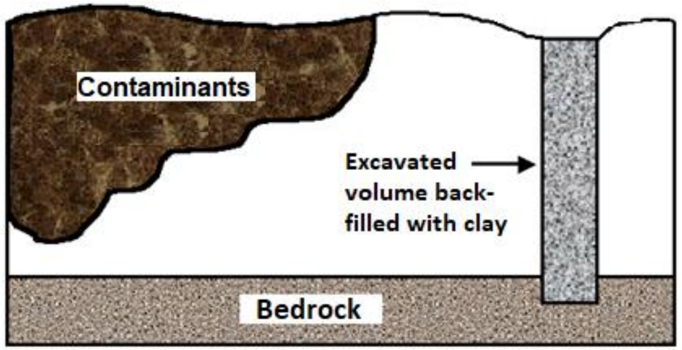
- **Introduction**
  - **Hydraulic barriers** in **nuclear decommissioning**
  - **Permeation grouting**
  - **Colloidal silica** grout
  - My project: chemically modifying **colloidal silica**
- **Background**
  - What chemically is **colloidal silica**?
  - Modifying **silica** using **polymers**
- **Experiments on 3 polymers**
- **Conclusion**
  - Summary
  - Next steps



Introduction

Hydraulic Barriers in Nuclear Decommissioning

- **At legacy nuclear sites, containment can be poor…**
  - Contaminants in direct contact with soil - **unlined trenches**
  - **Cement** containment structures compromised over time



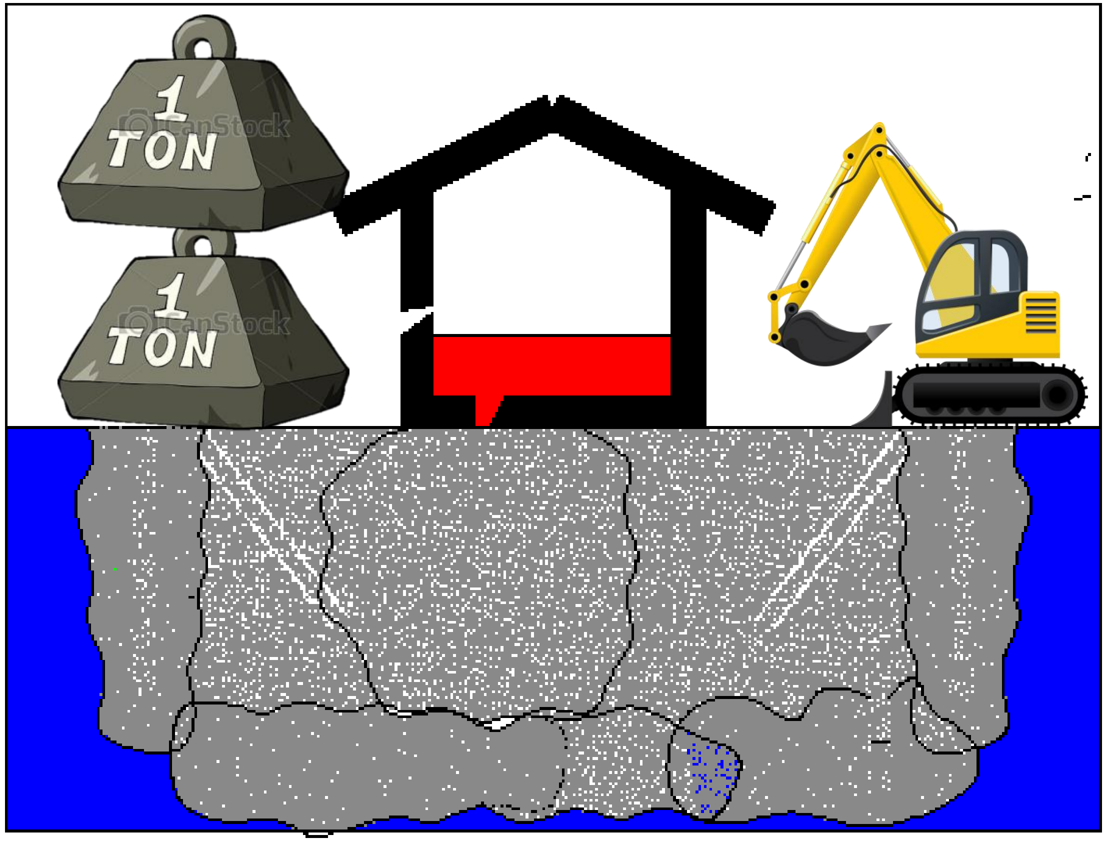
- Employ **sub-surface hydraulic barriers**:
  - Shore up structures, secure contaminants
  - Conventionally **clay-based**, installed by **excavation**
    - expensive
    - time consuming
    - Increases radiation exposure of workers
  - **Can inject liquid grout instead…**

Introduction
Permeation Grouting

University of Strathclyde Engineering

- **Permeation grouting**
  - **Low pressure** injection of **low viscosity** grout to fill free ground porosity
  - **Non-disruptive to ground**

- Create vertical + horizontal barriers
- Grout bulk space
- Increases strength/density of soil
  - Resistance to compression, settling



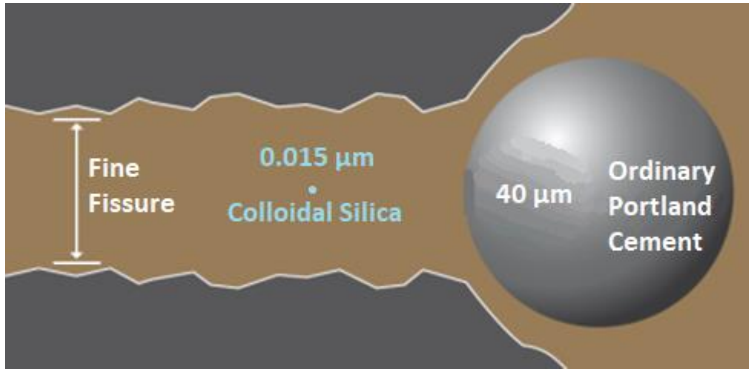
Contaminated site

Introduction

Colloidal Silica Grout

Colloidal silica permeation grout:

- **Water-like initial viscosity**
- **Precisely controllable gel-time** (mins to days)



- **Nano-scale** particle size
  - Fill smallest fissures
- **Non-toxic**, **inert**

- Gel has **extremely low hydraulic conductivity** K=1E-9 m/s
- **Inexpensive**
  - Comparable to concrete

- **Sorption of radionuclides** (Cs-137, Sr-90)

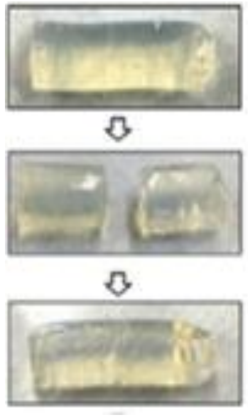
Introduction

My Project: Chemically Modifying Colloidal Silica

- **Colloidal silica** – Highly promising permeation grouting material.
  - **Can it do even more…?**

- My project: **chemically modify** silica grout:
  - Further improve hydro-mechanical properties
  - Tailor for specific environments
  - Open up to new applications
    - Encase waste containers for transport
    - Radiation shielding

- Work so far: combining **silica** with **polymers** and **polymer hydrogel**
  - Super-materials from biomedicine

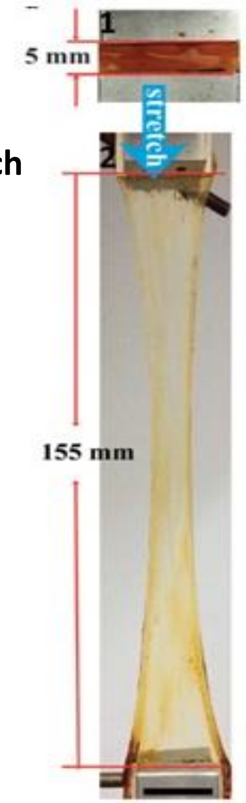


Original

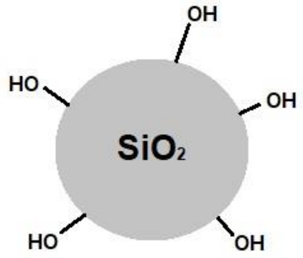
Cut

Heal on contact

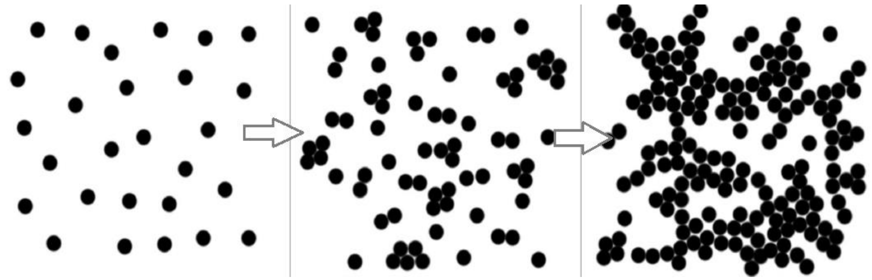
Stretch



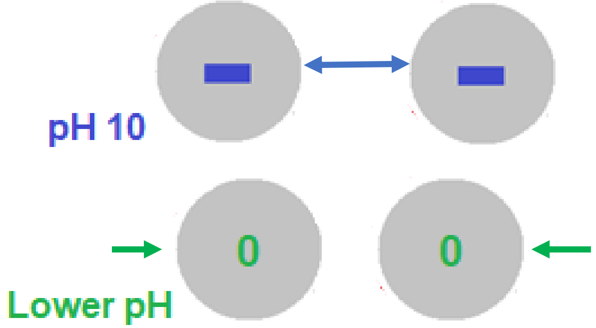
Background
What is colloidal silica?



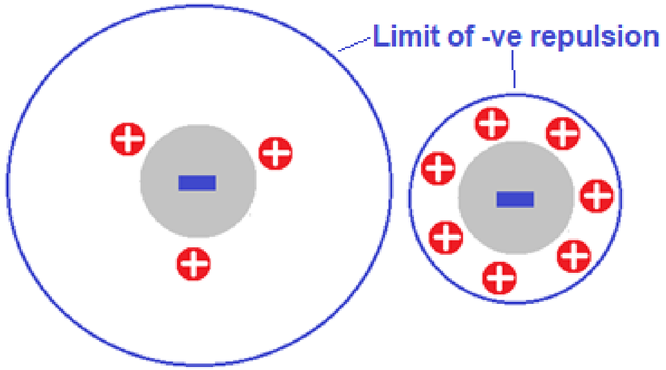
- **Suspension of silica nano-particles**
  - Particles tend to stick together
    - Permanent chemical bonds form
  - Build up into a network => **hydrogel**



- Particles have **–ve charge** that increases with pH
  - **Solution kept at pH ~10**
    - Repulsion between particles sufficient to prevent gelation



- Gelled by mixing with salt solution
  - **+ve ions** stick to silica particles
  - Screens –ve charge, allowing gelation



Background

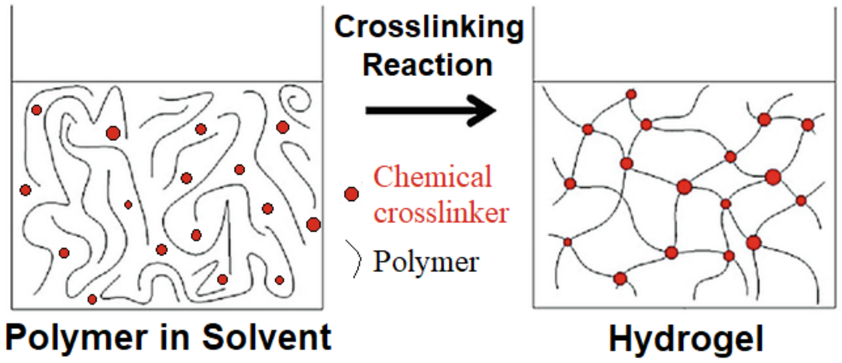
Colloidal Silica Gelation

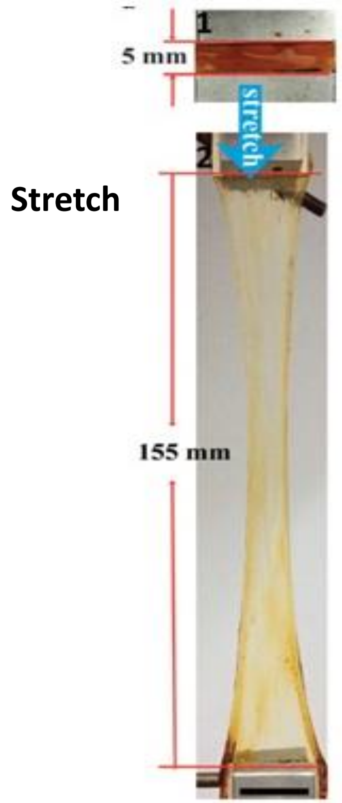
Gelation adjustable using…

- **Silica concentration**
- **Ionic strength**
- **Temperature**
- **pH**

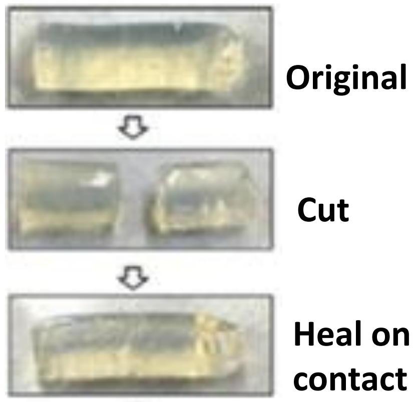
Background
Polymer Hydrogels

- Networks of hydrophilic **polymers** in water
- **Crosslinked** through either…
  - Permanent **chemical** reaction
  - Transient **physical** interaction





- Used in biomedical research for:
  - Tissue engineering/replacement, cell scaffolding
  - Excellent, highly-customisable properties:
    - **Super-strength**
    - **Re-healability**
    - **Super-flexibility**



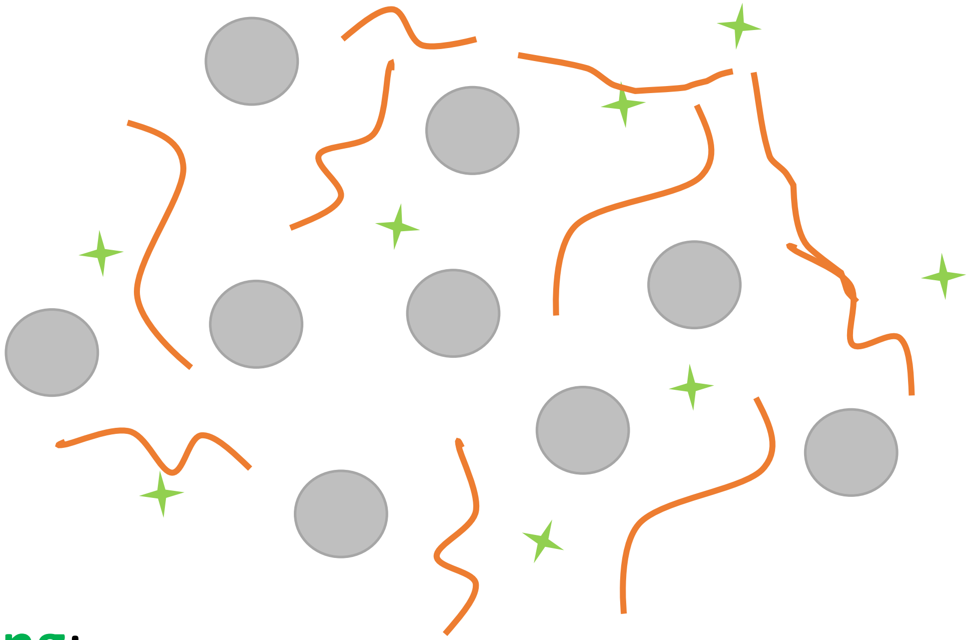
Background

How to Combine Silica & Polymer Hydrogels

○ Need:

- Simultaneous silica & **polymer** gelation
- 2 **independent**, **interpenetrating** networks

=> a **double network.**



○ Must find a **polymer gel** which…

- **Doesn't interfere with silica gelation**
- Is **cheap**
- **Gels in situ**

For **permeation grouting**:

- **Low enough initial viscosity** for injection
- **Gels underground**

Experimental

- 3 candidate polymers investigated:
  - **Polymer 1**
  - **Polymer 2** + crosslinker
  - **Polymer 3**

- Here, interesting **polymer** and **silica**/**polymer** hybrid gels are discussed

- Gels produced by either…

1. Simply adding **polymer** to **colloidal silica** gel

OR

2. **Crosslinking** the **polymer** into its own gel with **colloidal silica** present

   - Working towards a **double-network**

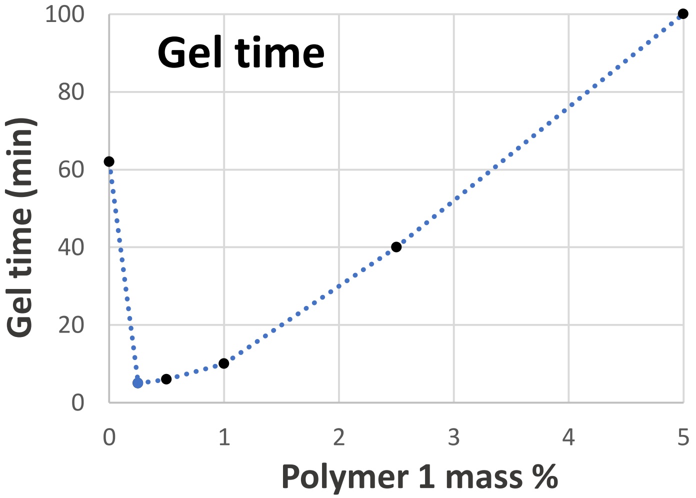
Experimental
Polymer 1

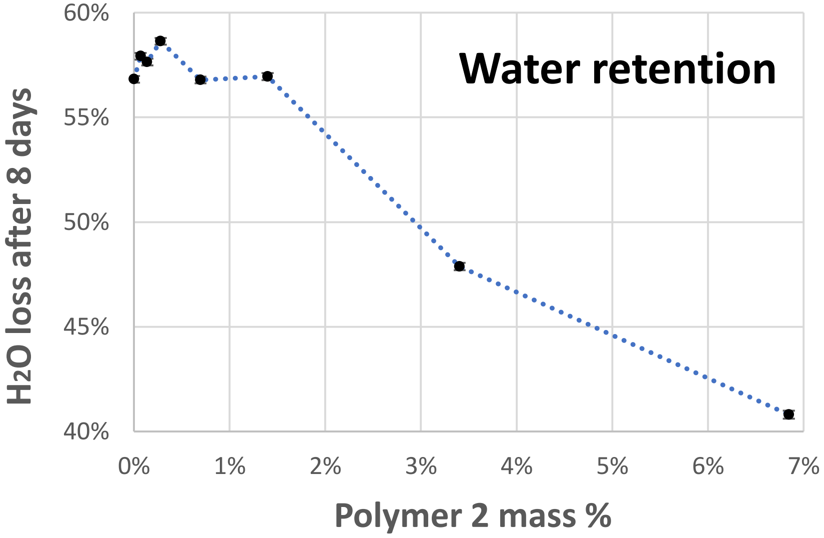
1. Adding polymer 1 to colloidal silica produces 2 gel variants depending on polymer concentration:

- **Low conc.**
  - Gives **plasticity, mouldability.**
  - **Cracks heal** upon applying pressure
  - White colour
  - Rapid gelation
- **High conc.**
  - **Increased water retention**
  - Weakened structure
  - Delayed gelation

Control **Low conc.** **High conc.**

Oven drying





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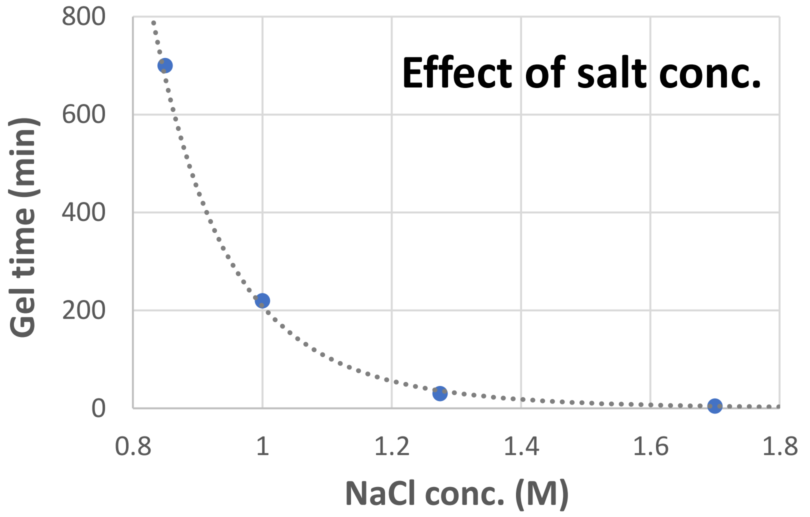
Experimental

Polymer 1

○ Effect depends on **pH + salt concentration**

- Only occurs upon mixing with salt solution (for pH 10)



2. Techniques for gelling polymer 1 on its own deemed unsuitable

Experimental

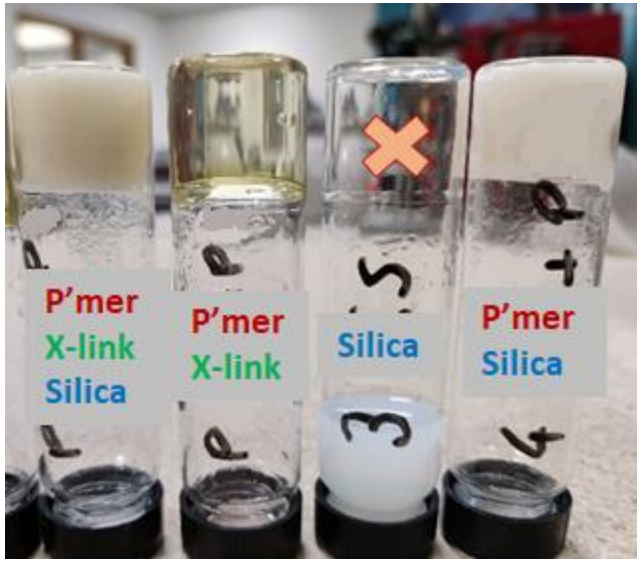
Polymer 2

2. Gels using a **chemical crosslinker**

- **Polymer 2** makes **very good gels**:
  - Stronger, more flexible than controls
- Can instil **silica** into **polymer 2** gel
  - **Double-network** produced?
  - Does **silica** improve **polymer 2 gel** properties?

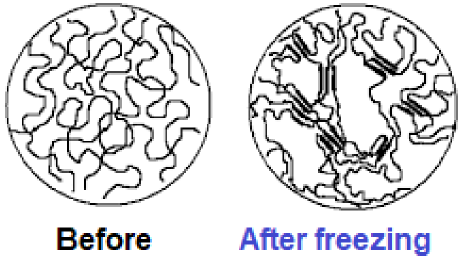
More work needed

- Gelation dependent on **molecular weight**
  - **High: viscosity too high** for permeation grouting
  - **Lower: gelation very slow** at soil temperature



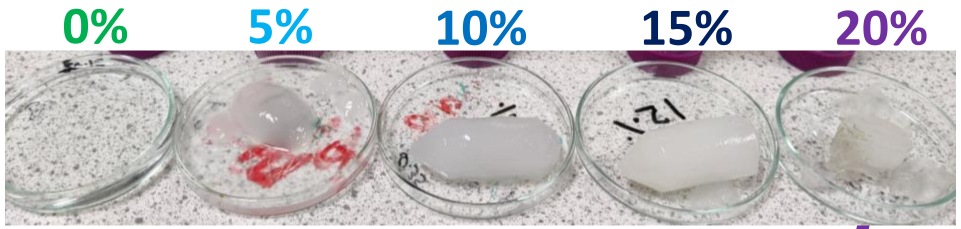
- Other applications:
  - Encasing wastes which generate **high temps**

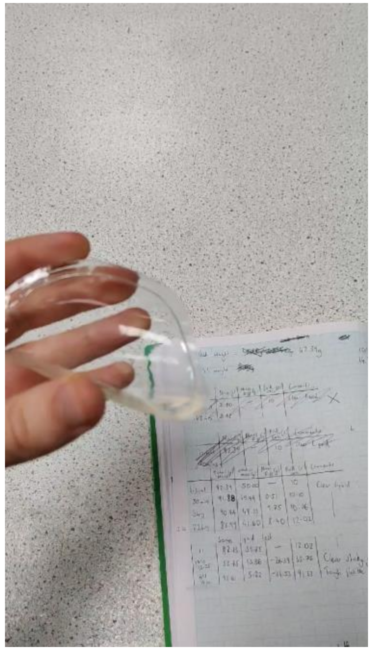
Experimental
Polymer 3



2. Forms **self-crosslinks** on **drying** or **freeze-thaw** cycling

- **Polymer 3** gives **super-tough, flexible gels**





Drying

- **Freeze-thaw**
  - Strength depends on:
    - **Polymer 3** concentration
    - # of **freeze-thaw** cycles
  - Can be frozen underground by **injecting liquid nitrogen**
    - Ground freezing already employed for **hydraulic barriers**
  - **Polymer 3** has strong interaction with **silica** – hard to mix

Freeze-thaw

More work needed

Conclusion

Summary

○ Colloidal Silica

- **Highly promising permeation grouting material**
- Considered for **hydraulic barrier** application in **nuclear decommissioning**
- My Project: **modify** silica **grout** to improve/tailor properties

○ Polymer hydrogels

- Excellent, customisable properties
- Combine them with silica in **double-network** gels?

○ Experimental Work

- **Polymer 1**
  - 2 gels produced depending on **polymer** conc.
    - **Low conc.**: mouldable, crack resistance
    - **High conc.**: water retention, weakened structure
- **Polymer 2** + crosslinker
  - **Strong, flexible gel**
  - Can instil **silica**: **double-network** produced?
  - Likely unsuitable for **permeation grouting**
- **Polymer 3**
  - Gels on **drying** or **freeze/thaw** cycling
  - **Super-tough, flexible gel**
  - Difficult to mix with silica

Conclusion

Next Steps

University of Strathclyde Engineering

○ **Short term**

- Analyse properties and structure of the gel variants produced using…
  - Rheology
  - Mechanical tests
  - Hydraulic conductivity tests
  - SEM
  - X-ray tomography
- Confirm if **double-networks** have been produced, and the properties of such gels
- Communicate with industry partners to identify nuclear applications for these gels

○ **Long term**

- Modify **colloidal silica** particles via eg. coating with aluminium
  - Further improve radionuclide sorption
- Study **colloidal silica**, **polymer hydrogel**, and hybrids as **radiation shielding**
  - Gels are 70-95% water
  - Rigid, can fit moulds
  - Easily vitrify silica to create a manageable wasteform
  - No movement or leaking as with water
  - Can embed radiation absorbers

References

[1,2] Zhao M, Liu G, Zhang C, Guo W and Luo Q 2020 *Appl. Sci.* **10** 15

[3] Sögaard C, Funehang J and Abbas Z 2018 *Nano Convergence* **5** 6

[4] Lin C-C and Metters A T 2006 *Adv. Drug Deliv. Rev.* **58** 1379-1408

[5] Wang Q and Gao Z 2016 *J. Mech. Phys. Solids* **94** 127-147

[6] Han L *et al.* 2017 *NPG Asia Materials* **9** e372

[7] https://www.youtube.com/watch?v=469C8l_wDeg&ab_channel=FluidDynamics

[8] Bercea M, Morariu S and Rusu D 2013 *Soft. Mater.* **9** 1244

Thank you for listening

Transformative Science and Engineering for Nuclear Decommissioning

Electrokinetic Remediation and *in-situ* iron barrier generation

Dr. Jamie Purkis

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University of Southampton

TRANSCEND Theme Meeting (virtual)
Monday 17th May 2021

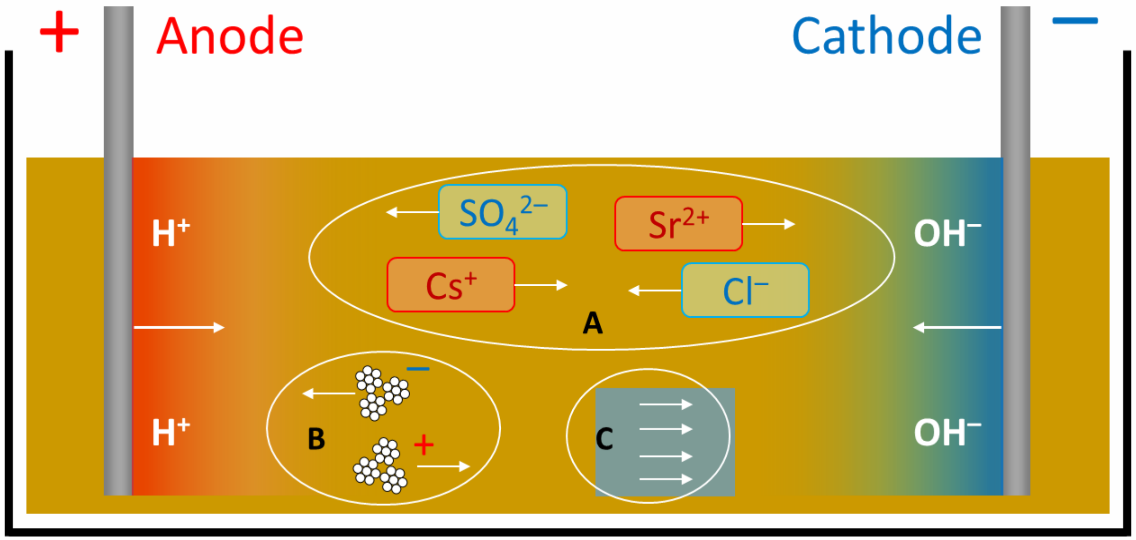
Energy
For a Low Carbon Future

Electrokinetic Remediation, EKR

electro kinetic

Electrical — **movement (of ions, …)**

- Soil/groundwater/concrete
- Electromigration (**A**)
  → *movement of ions*
- Electrophoresis (**B**)
  → *movement of particles*
- Electro-osmosis (**C**)
  → *movement of water*



*$H_2O \rightarrow 2\,H^+ + ½\,O_2\,(\uparrow) + 2\,e^-$
E^0 = - 1.229 V

*$H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2\,(\uparrow)$
E^0 = - 0.828 V

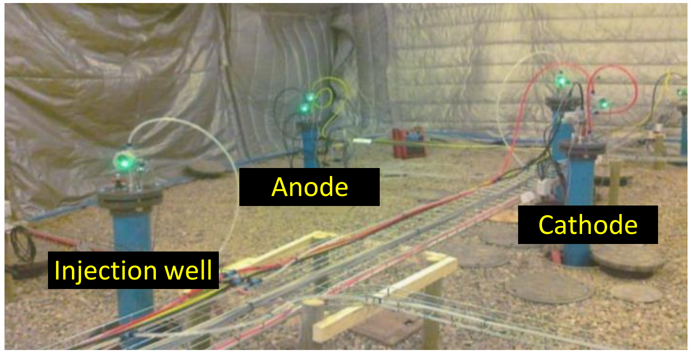
**vs.* standard hydrogen electrode (SHE)

Transformative Science and Engineering for Nuclear Decommissioning

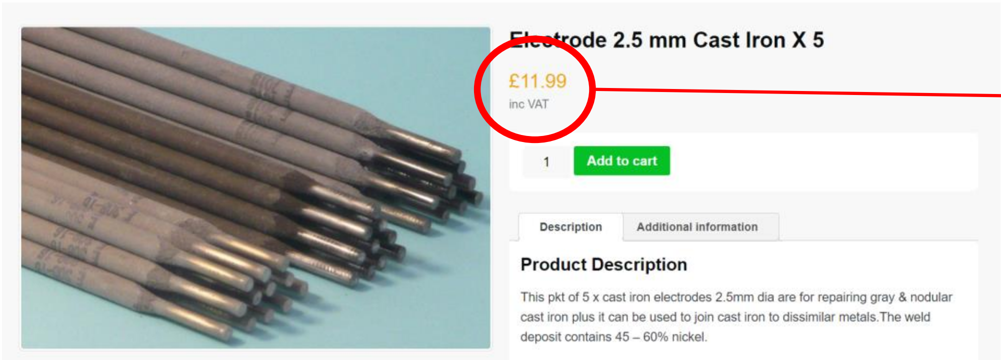
Advantages of EKR

- ***In-situ*** **(or *ex-situ*)**

  Worker safety



- **Cheap**



£11.99
inc VAT

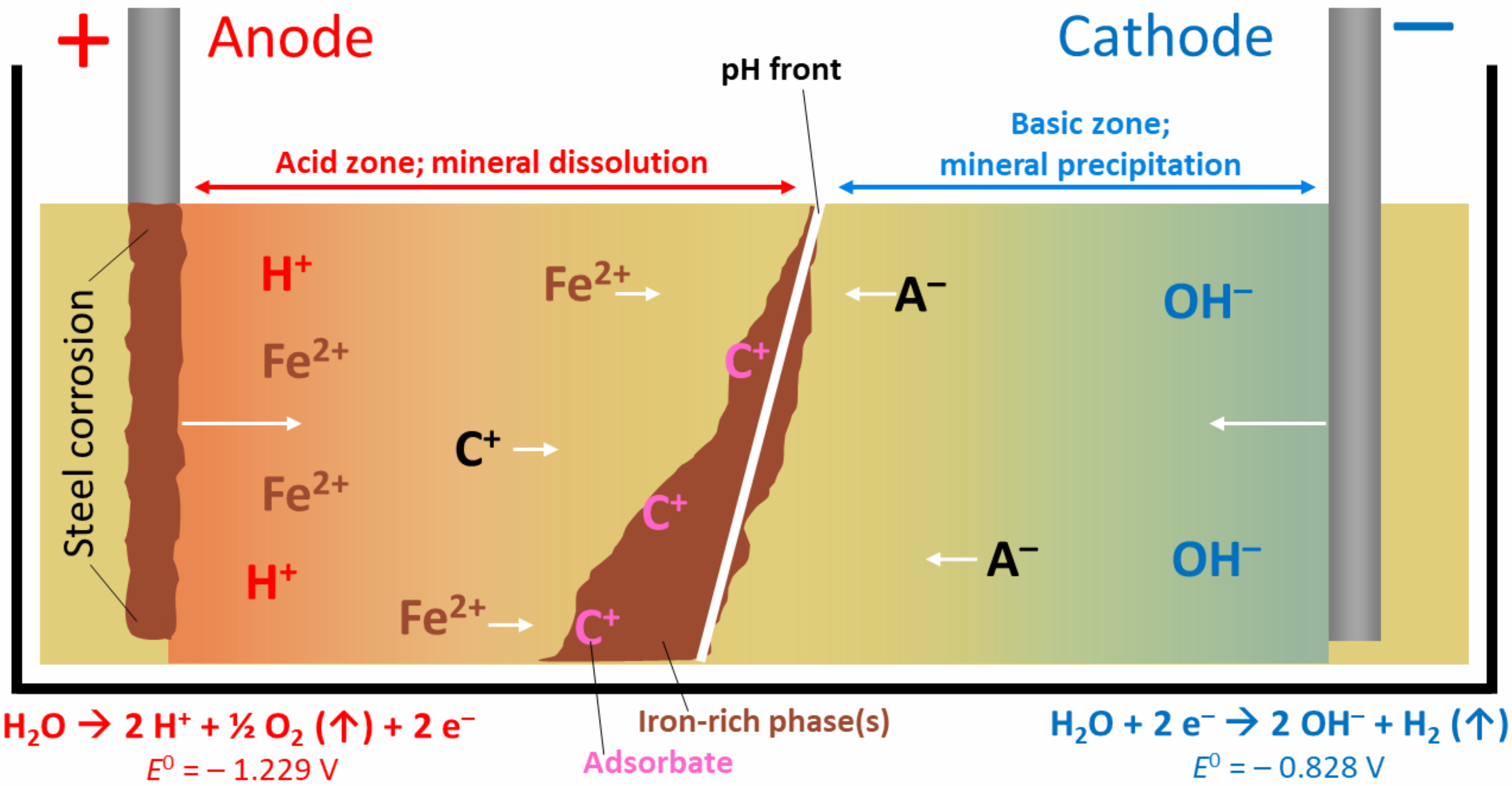
(+ next day delivery)

- **Adaptable**

Electrode material
Electrode placement
Electrolyte
Voltage

Additives
Duration
(In-)organic + radionuclide
Combination (EKR-Bio…)

Ferric Iron Remediation and Stabilisation (FIRS)



Previously demonstrated at scale (1m +) in silica sand by NNL and will shortly appear in press:
Purkis *et al.*, manuscript under review (J. Haz. Mater.). Data are *vs*. SHE

Case Study – FIRS

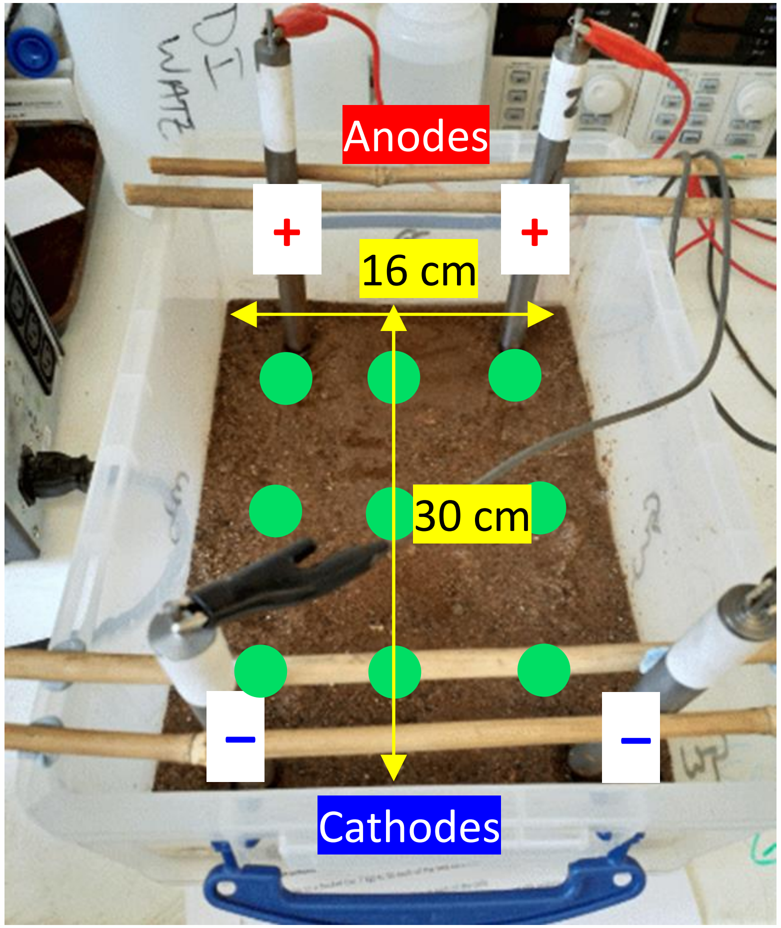
In-situ barrier growth in real materials?

1. Sellafield Sand/Groundwater (GW)
2. Sellafield Clay/GW
3. Sellafield Sand/Seawater (SW)
4. Sellafield Clay/SW

Steel electrodes, 0.5 V/cm

Monitor

- Barrier over time
- pH
- Changes before/after
- (Sorptive properties)



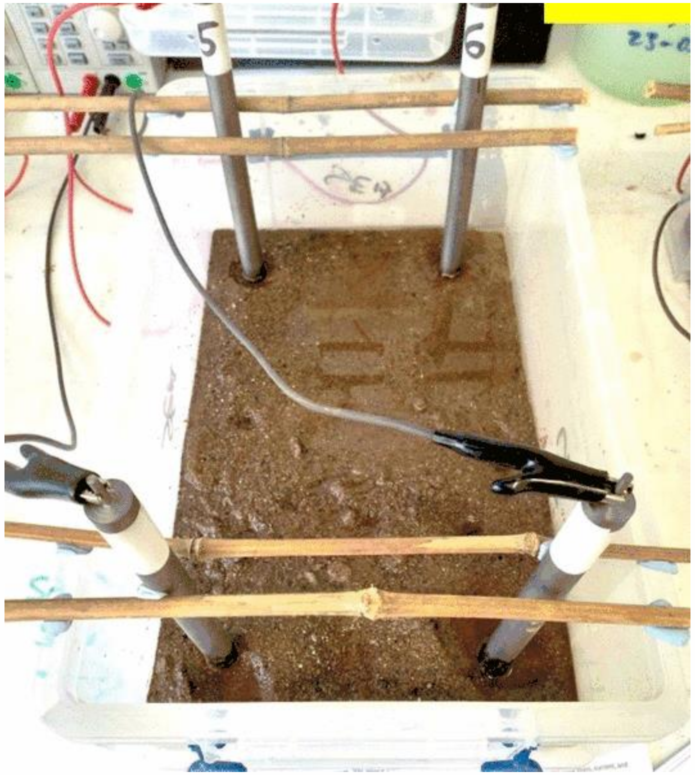
pH sampling point

Purkis *et al.*, manuscript under review (J. Haz. Mater.)

Case Study – FIRS

1. Barrier over time **2. pH over time** **3. Permeability** **4. SEM** **5. Mössbauer**

Clay with GW electrolyte



Sand with SW electrolyte
(GIF starts at day 0)

Iron barrier thicker and forms faster in SW electrolyte

Different composition?

Purkis *et al*., manuscript under review (J. Haz. Mater.)

Case Study – FIRS

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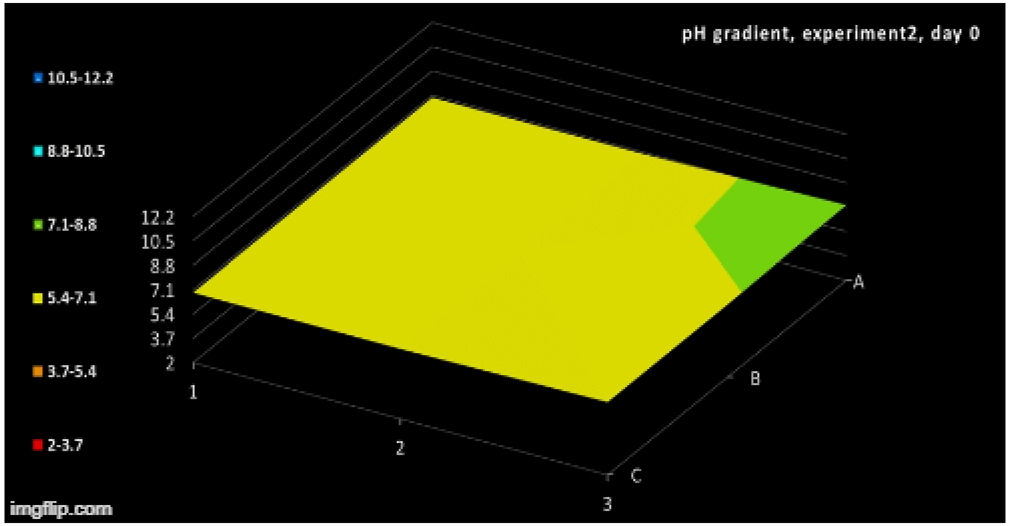
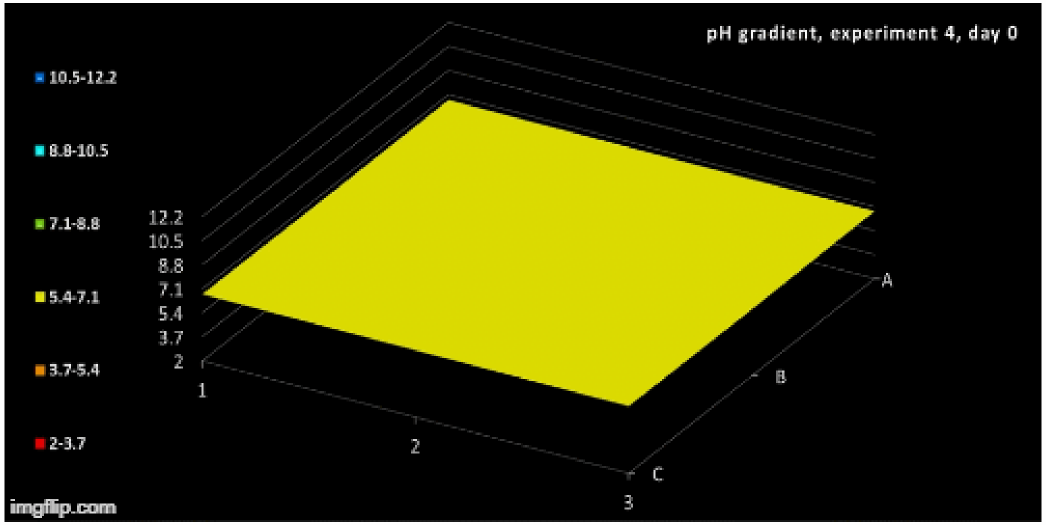
1. Barrier over time | **2. pH over time** | **3. Permeability** | **4. SEM** | **5. Mössbauer**



Clay/GW (shown to day 20)



Sand/SW (shown to day 21)

GW has lower ionic strength; weaker pH gradient forms (and forms slower) than SW

Purkis *et al*., manuscript under review (J. Haz. Mater.)

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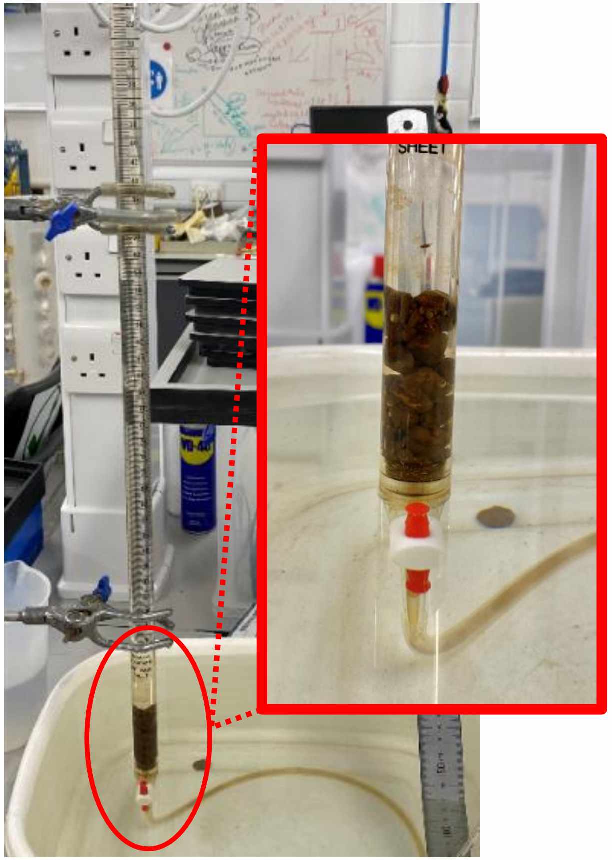
Case Study – FIRS

1. Barrier over time | 2. pH over time | **3. Permeability** | 4. SEM | 5. Mössbauer

Sand/SW



SAND	in m/s
Parent	*1.1 x 10^{-3}*
GW	2.4 x 10^{-4}
SW	1.6 x 10^{-4}

CLAY	in m/s
Parent	*1.3 x 10^{-10}*
GW	3.2 x 10^{-8}
SW	4.6 x 10^{-7}

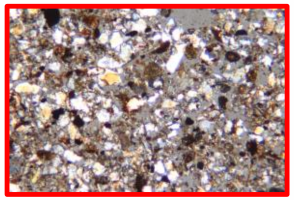
Sand = ↓ permeability
Clay = ↑ permeability

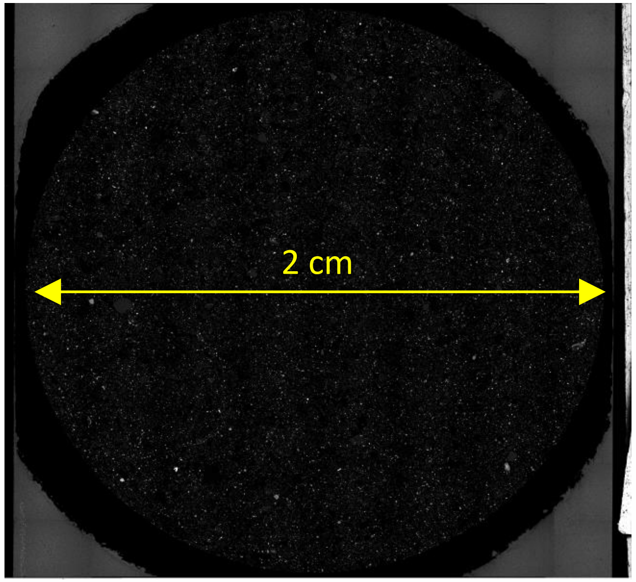
Purkis *et al.*, manuscript in preparation

We acknowledge Prof. William Powrie and Mr. Jeerapat Sang-Iam (UoS) for data collection (BS EN ISO17892)

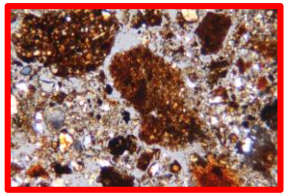
Case Study – FIRS

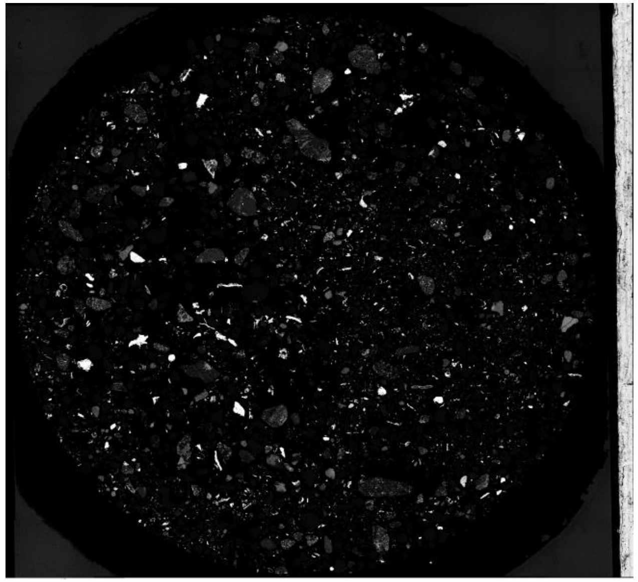
1. Barrier over time **2. pH over time** **3. Permeability** **4. SEM** **5. Mössbauer**





Clay/GW





Clay/SW

SEM on thin sections of iron barrier material (+ microscopy)
High contrast (white areas; back-scattering) $\propto$ high [iron]

Differences in iron phase formation between GW/SW electrolyte

Work ongoing

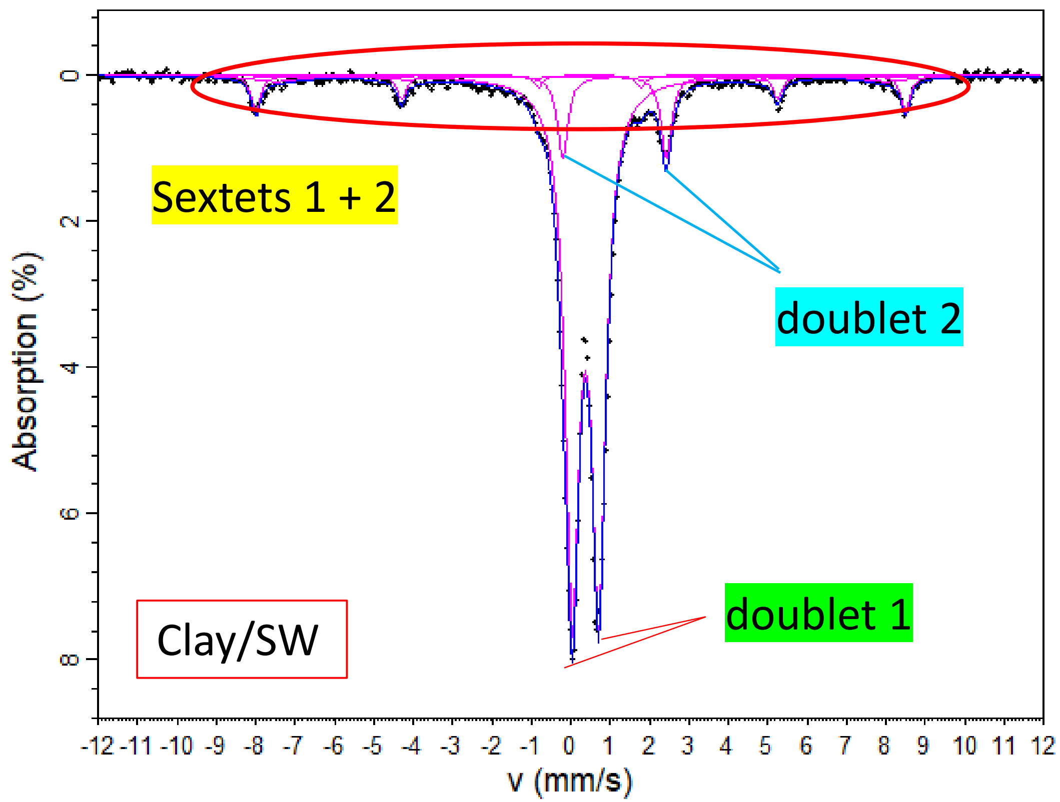
Purkis *et al*., manuscript in preparation; thanks to Dr. Richard Pearce (UoS)

Transformative Science and Engineering for Nuclear Decommissioning

Case Study – FIRS

1. Barrier over time **2. pH over time** **3. Permeability** **4. SEM** **5. Mössbauer**

Mössbauer Spectroscopy (ongoing)



- Doublet 1 – likely Fe(III); oxide; O_h geometry
- Doublet 2 – likely Fe(II); oxide/hydroxide; likely O_h geometry
- Sextets – likely Fe(III); possibly (α-)Fe_2O_3 + ? *haematite*

Likely mix of iron oxides and oxyhydroxides, Fe(II) and Fe(III)

Work ongoing

Purkis *et al.*, manuscript in preparation.

We acknowledge Prof. Paul Bingham and Dr. Alex Scrimshire (Sheffield Hallam) for data collection and interpretation

Wider Context?

i / ii
Properties of
Substrate **Contaminant**

Electrical conductivity?
Particle size?
Permeability and porosity?
Cation exchange capacity?
Redox chemistry?
Adsorption?
pH and buffering capacity?
Size and speed of contaminant plume?
Effect of biota?
Groundwater flow?
Hydraulic head?
Temperature?
Additives?
Ionic mobility?

iii
Electrical inputs and electrodes

Voltage?
Current?
Electrode placement?
Electrode separation?
Electrode material?
Corrosion resistance?
Strength of pH gradient generated?
Energy consumption?
Electrolyte?
Dead zones?
Borehole engineering?
Electrode installation?
Depth?
Renewable *vs.* fossil fuel?

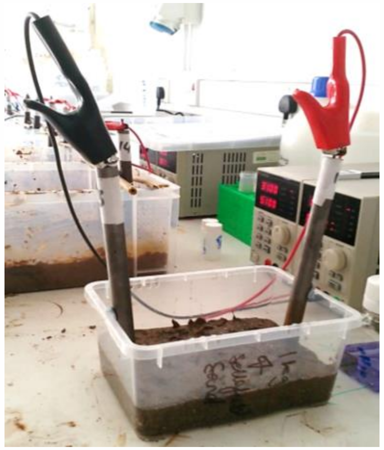
iv
Cost and sustainability issues

Duration?
Batch *vs.* continuous?
Labour costs?
Source of materials?
Electricity pricing?
Cost saving by remediating?
Safety?
Electrode value?
In-situ vs. ex-situ?
Use of machinery?
Material disposal costs?
Material and labour transport?
Insurance?
Material storage pending remediation?
Possibility to achieve wider socio-economic and environmental benefits?

Purkis *et al.* J. Haz. Mater., 2021, 413, 125274

Conclusions, Further work, and Thanks

- EKR: *in-situ*, cheap, flexible
- Limited at scale
- Combined approaches
  FIRS: iron barriering
  (Si grouting – ongoing)
- Characterise iron barriers?
  ongoing (XRD, XRF…)

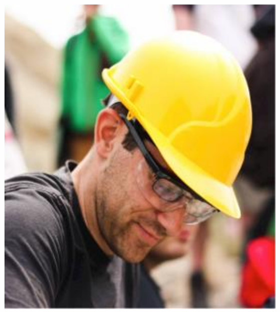


GAU Radioanalytical Laboratories

UNIVERSITY OF Southampton

NATIONAL NUCLEAR LABORATORY

NDA



Sellafield Simulant GW:

$MgSO_4$ = 250 mg

$KHCO_3$ = 55 mg

$CaCl_2.2H_2O$ = 472 mg

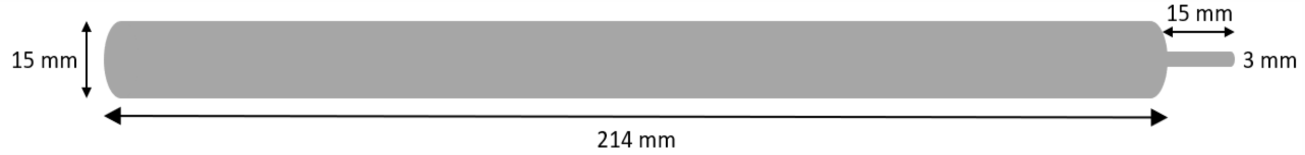
$NaHCO_3$ = 470 mg

$Ca(NO_3)_2$ = 185 mg

$SrCl_2$ = 167.5 mg

0.1 M HCl = 30 mL

in 5 L of DI water



J. Graham, *MSSS GEMS Phase 2: Characterisation of Soils and Strontium Sorption Batch Testing*, Report NNL 13224, National Nuclear Laboratory, NNL, 2015.

Advanced Nuclear Research Centre

Biotechnology for Treatment and Repair of Concrete Nuclear Infrastructure

Ronald J Turner, James M Minto, Emmanuel Salifu, Gráinne El Mountassir, Rebecca J Lunn

Centre for Ground Engineering & Energy Geosciences
Civil & Environmental Engineering

Introduction

Significant volumes of concrete infrastructure can be found on UK Civil Nuclear sites, and also more broadly within the built environment as a whole

Many degradation mechanisms, including salt water, freeze-thaw cycles, variable temperatures, and exposure to radiation

Introduction

The reduction of permeability is key to minimising the corrosion of the rebar, and is desirable in other contexts too

Limits ingress of damaging chemical compounds

Minimises carbonation and resultant damage of reinforcing materials

Decreases flux of any radioactive air and liquids present

Civil & Environmental Engineering
Centre for Ground Engineering & Energy Geosciences

Existing repair methods for concrete

Cement mortars as repair

Large grain size, won't seal small aperture cracks (and small parts of big cracks), poor penetrability

Epoxy resins

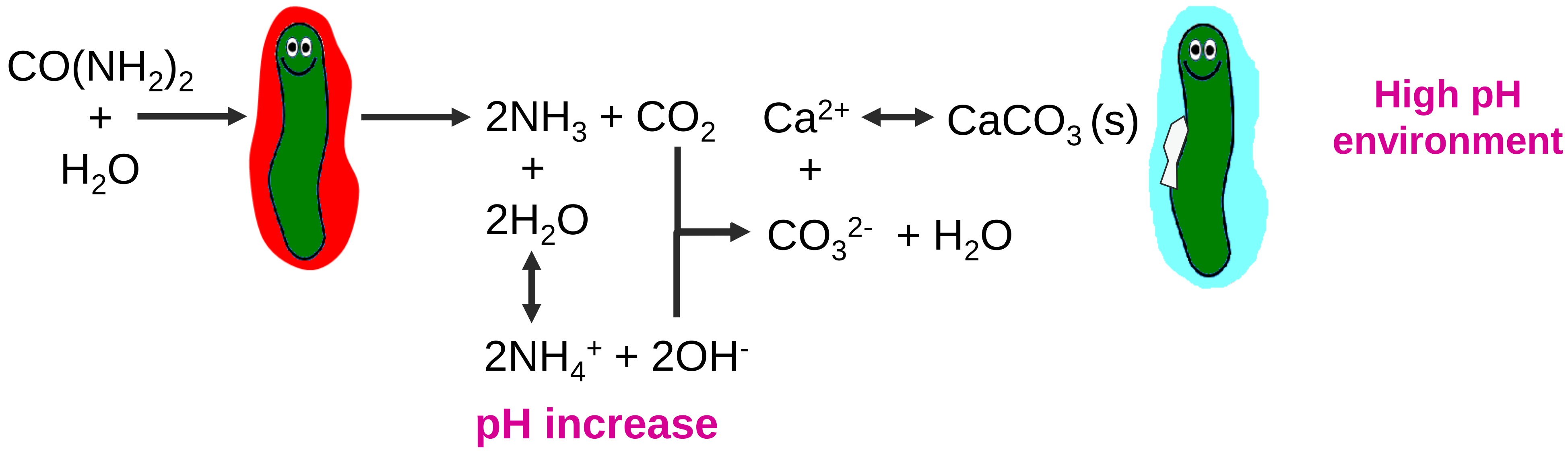
Thermal expansion coefficient different to concrete, cracks at interface, delamination

Civil & Environmental Engineering
Centre for Ground Engineering & Energy Geosciences

What is Calcite Biomineralisation?

The enzyme-mediated generation of calcium carbonate (calcite) from urea and calcium precursors

Bacterial ureolysis using ***Sporosarcina pasteurii***



Bacterially generated Calcite for Concrete Repair

Concrete is a mixture of (un)hydrated calcium silicates, calcium hydroxide, and calcium carbonate (+ aggregate and iron rebar). Used in many nuclear infrastructure applications, both structural and non-structural.

Bacterially generated calcite may be able to ‘plug up’ the fracture network and so reduce permeability, and could even contribute to some strength re-gain

This could increase the lifespan of concrete structures undergoing decommissioning, and is particularly relevant to steel-reinforced concretes which are susceptible to chloride attack/chloride ingress

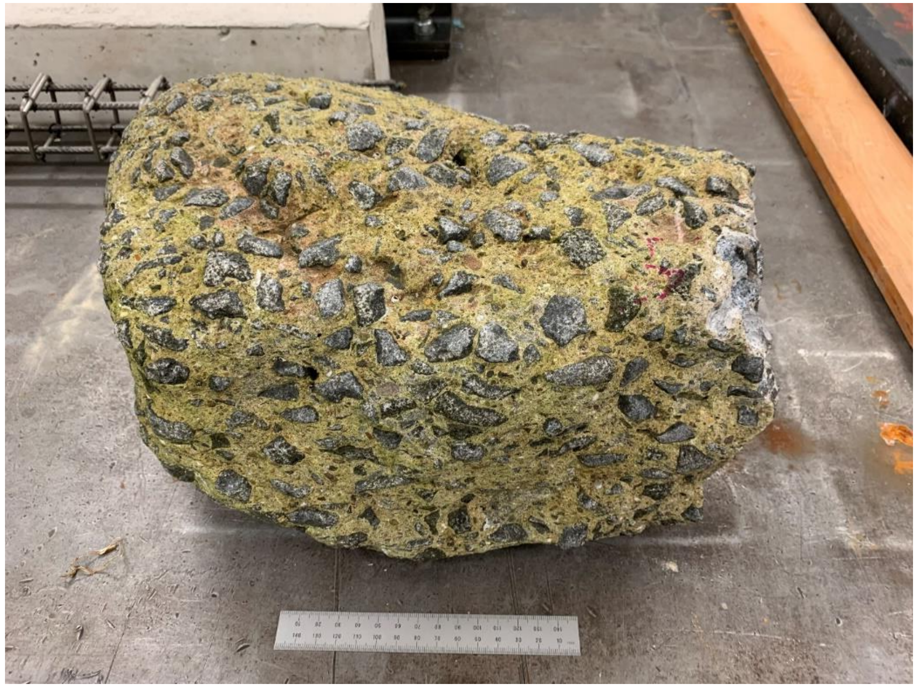
Concrete Samples

~60 year old concrete blocks collected from Hunterston foreshore, intertidal zone

Civil & Environmental Engineering
Centre for Ground Engineering & Energy Geosciences

Concrete Samples

Large blocks cut down to produce 36x72mm concrete cores



Concrete Samples

Visual Examination and X-CT analysis revealed a natural fracture network in the concrete samples

Concrete Samples

Initial testing revealed that some cores could be treated as-is, while others had too low a permeability to be treated effectively

5 cores selected for testing, 2 with natural fracture networks, and 3 with induced fracture networks

A core-holder setup was used to treat the samples, through injection of treatment solutions through the core

Next Step: Concrete Block-scale Testing

Bench-scale induced cracks in cores

- Optimisation of fluids & delivery methods
- Suitable filler materials

Block-scale testing

- Treatment of a wide range of crack sizes & orientations

Field implementation

Summary and Conclusions

- We have tested biomineralisation of calcite as a method to repair fractures in degraded concrete through injection of treatment solutions through concrete cores

- Significant permeability reductions were observed

- Treated cores were found to gain mass, based on dry weight measurements

X THE PLACE OF USEFUL LEARNING

University of Strathclyde Glasgow

Transformative Science and Engineering for Nuclear Decommissioning

Reducing hazard in spent fuel removal at high temperature using colloidal silica gel

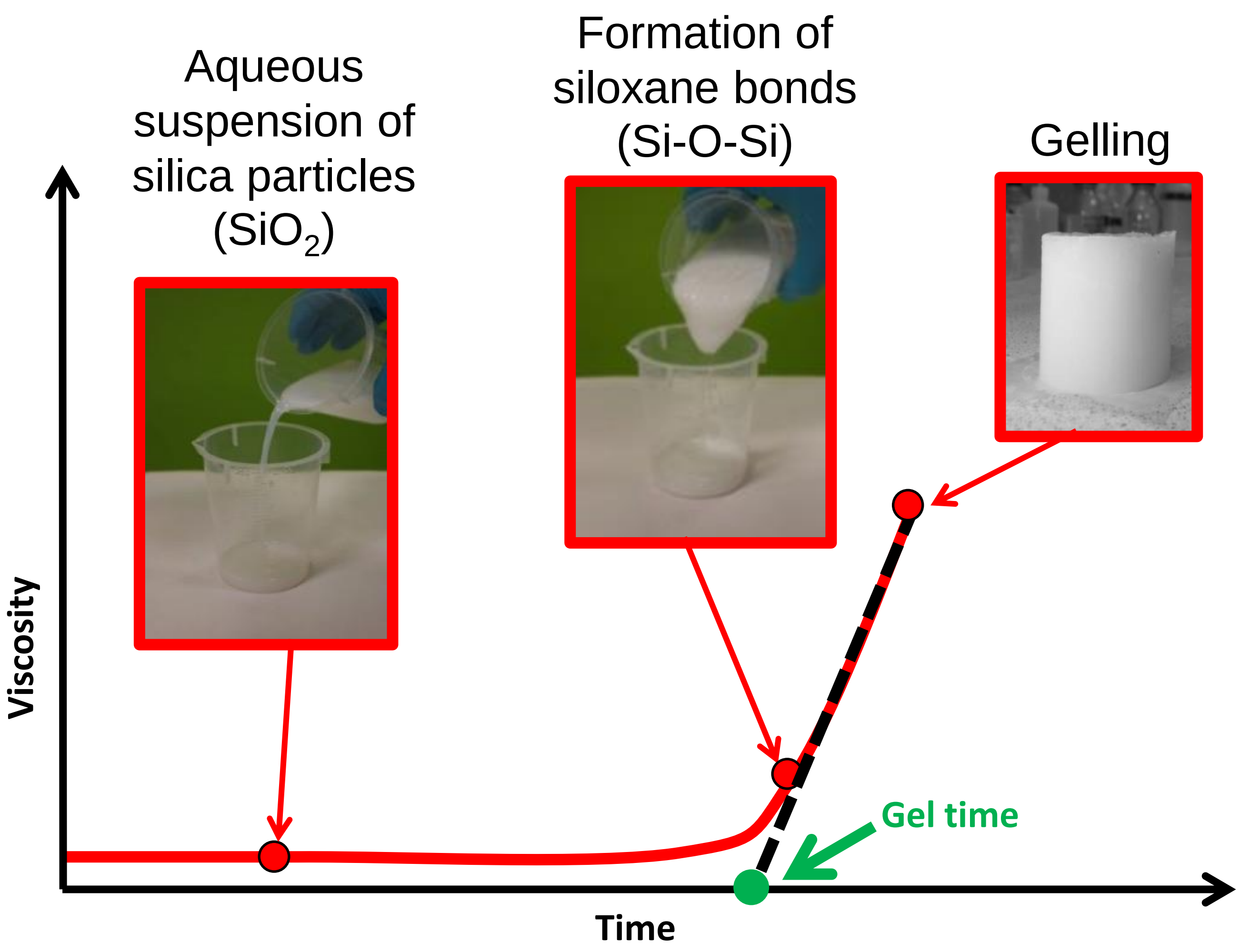
Arianna Gea Pagano, University of Strathclyde

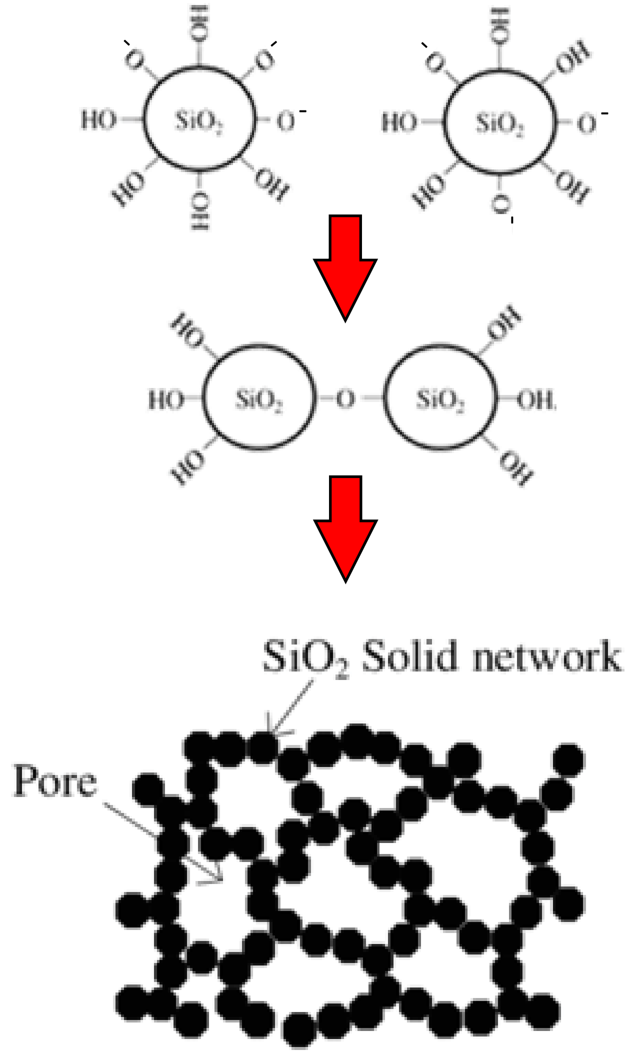
TRANSCEND Theme 2 meeting

14/05/2021

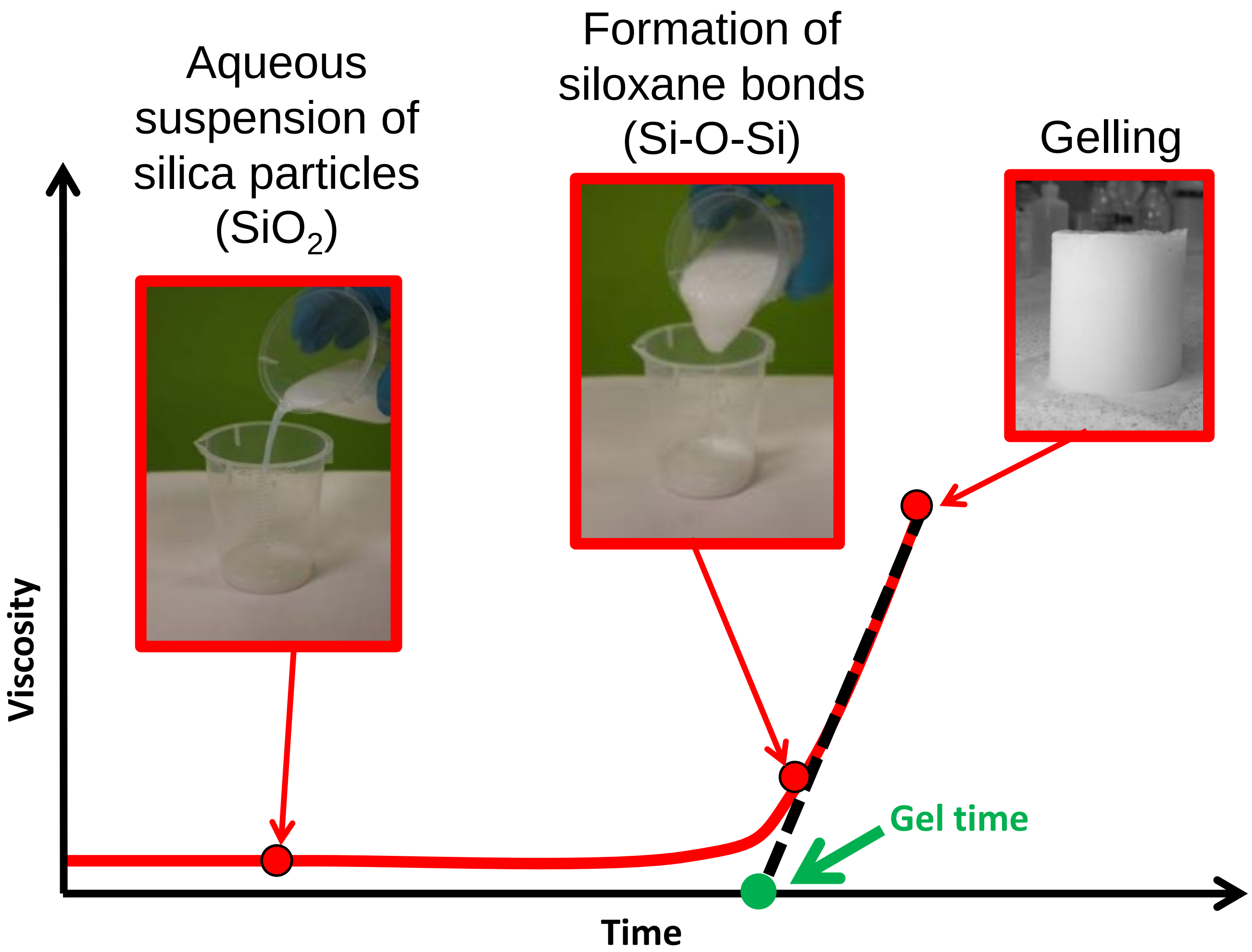
For a Low Carbon Future

What is colloidal silica?





What is colloidal silica?

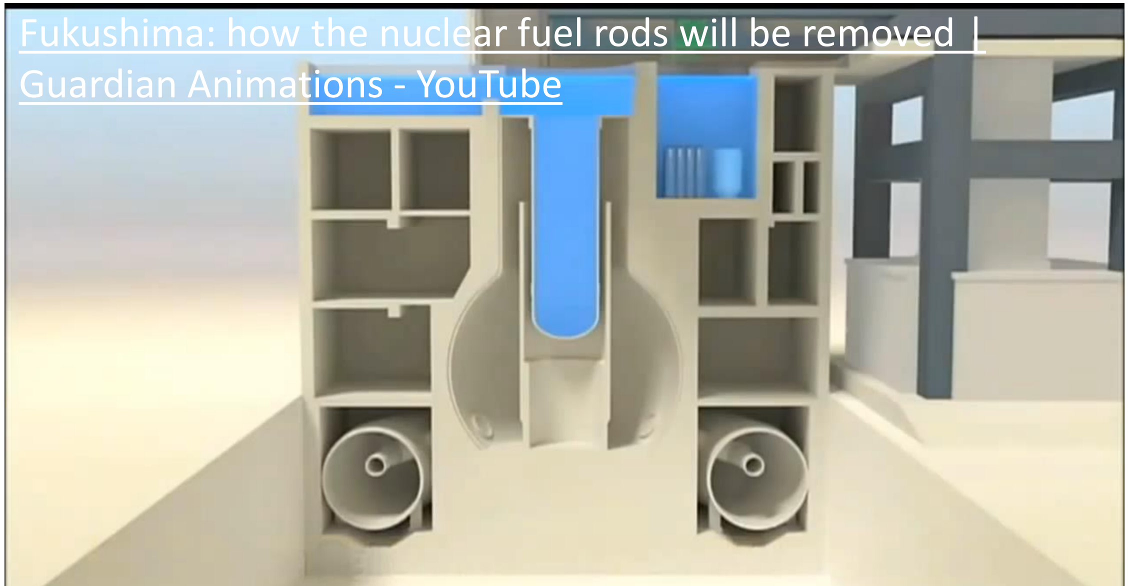


What triggers gelling?

- Electrolyte accelerator
- Change in pH
- Temperature

Site decommissioning: removal of spent fuel and radioactive waste

Fukushima: how the nuclear fuel rods will be removed | Guardian Animations - YouTube



The Magnox Swarf Storage Silo: Making our most hazardous facility safer - YouTube

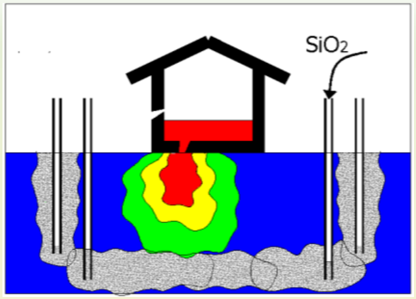
Hazard:

- Release of airborne radioactive particulate during transport
- Loss of radioactive debris in the rack during fuel retrieval
- Waste corrosion may make the material not strong enough to be lifted up
- …

OBJECTIVE: Reduce hazard in spent fuel removal at medium and high temperature by grouting the radioactive waste prior to retrieval

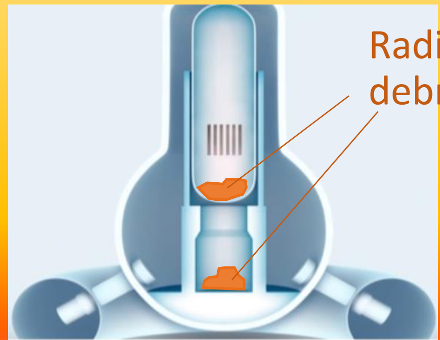
Site decommissioning: range of operating temperatures

- Remediation of heavily contaminated soils



- Removal of spent fuel rods from SFP
- Removal of radioactive waste from storage silos

- Removal of radioactive debris following nuclear accidents

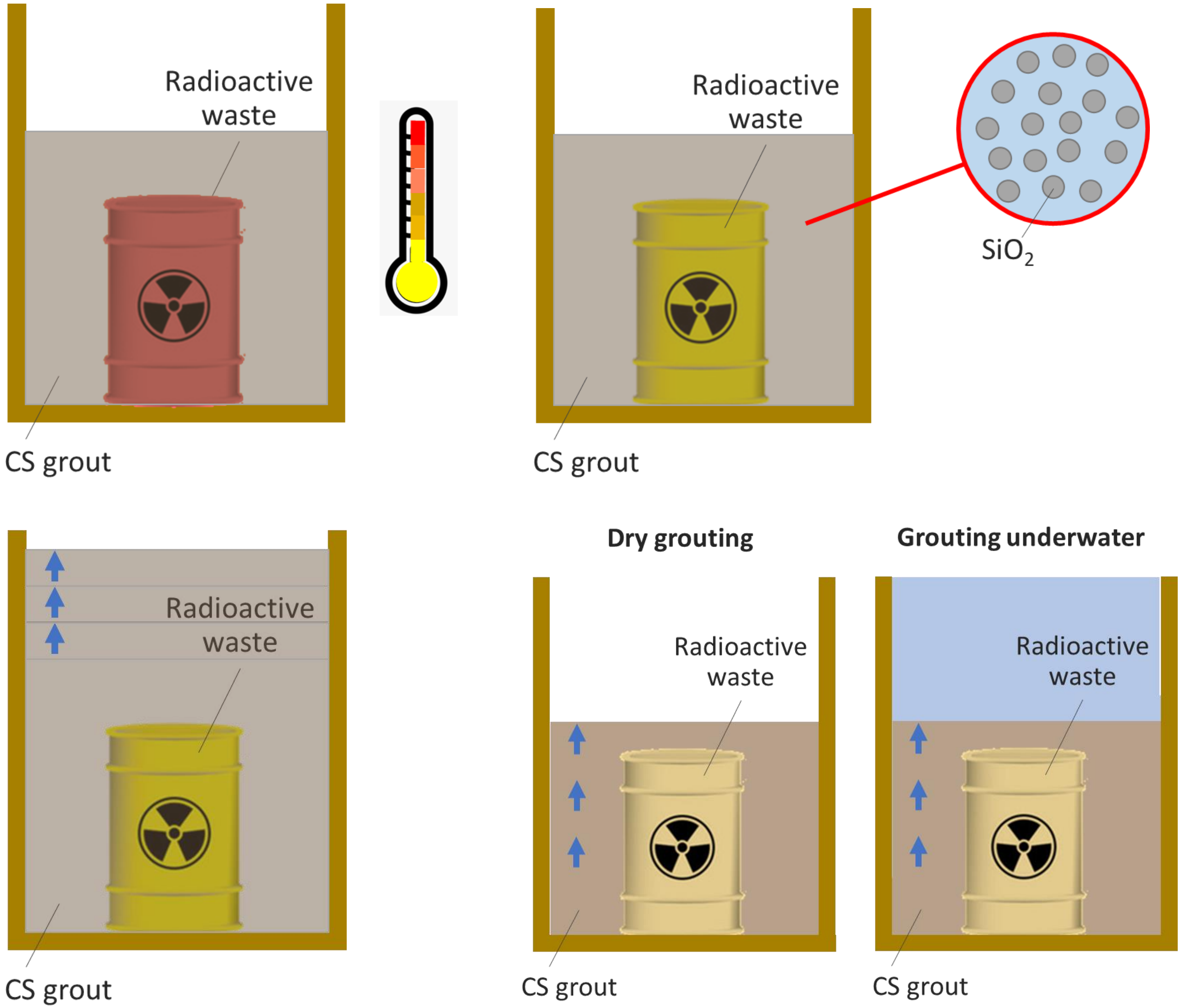


Ambient temperature

40 - 60°C

> 100°C

CS grouting around radioactive waste at high temperature

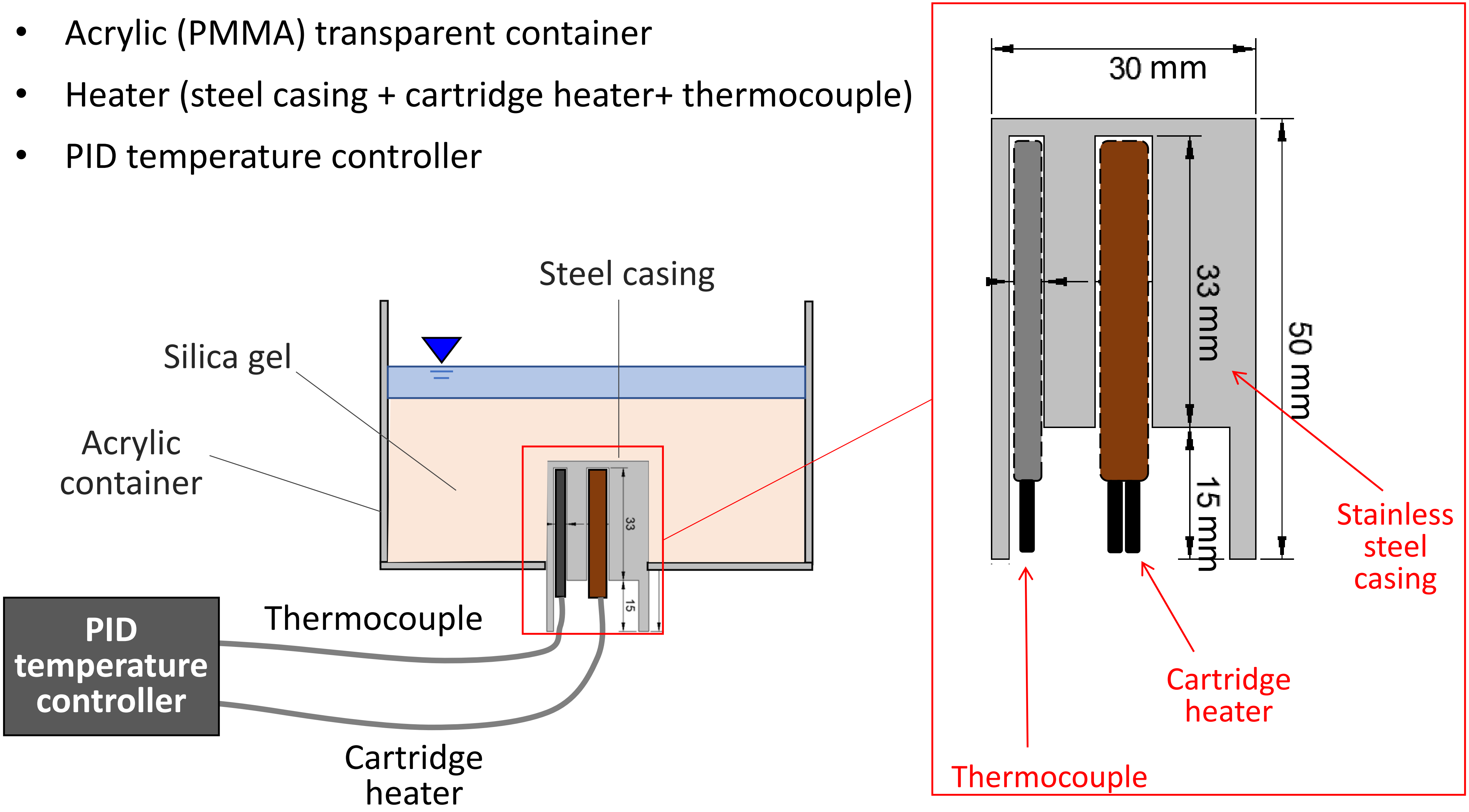


POSSIBLE VARIABLES:

- Temperature of the radioactive waste (from ambient to > 100°C)
- Grout volume
- Grout properties (e.g. silica concentration)
- Gelling conditions (dry, underwater)

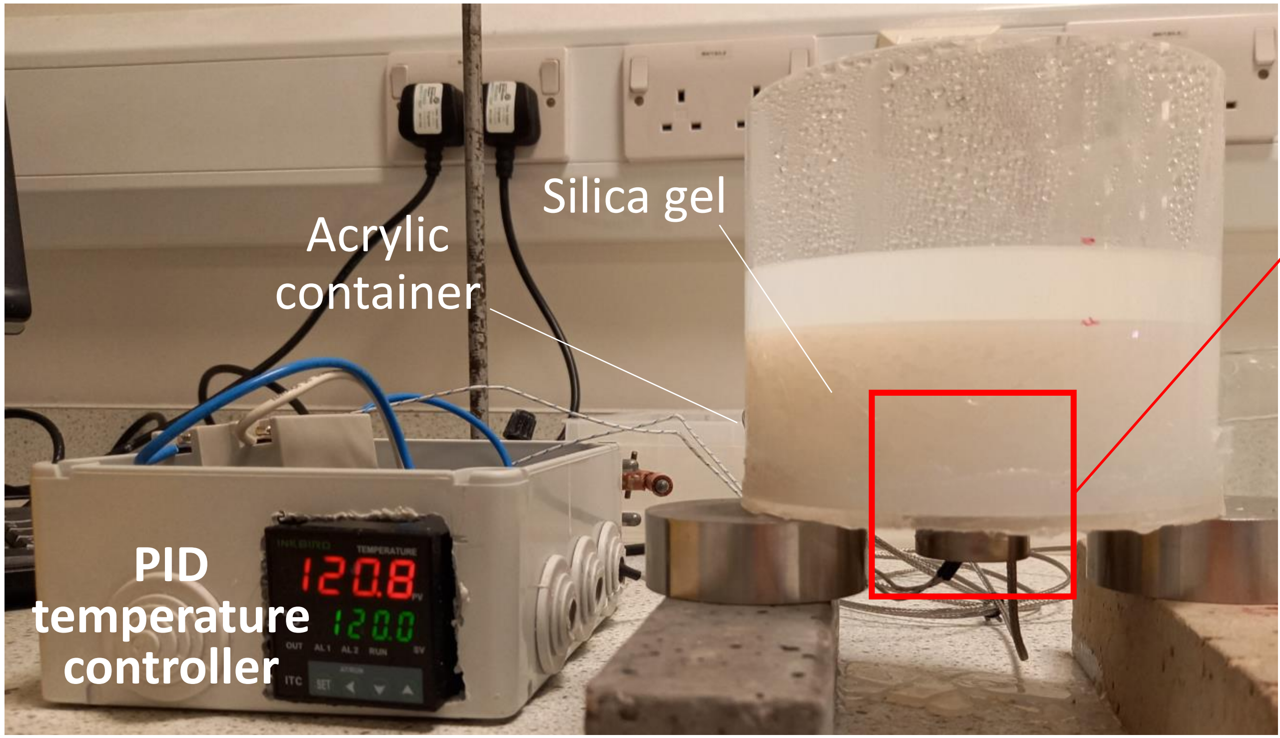
Experimental setup: schematic view

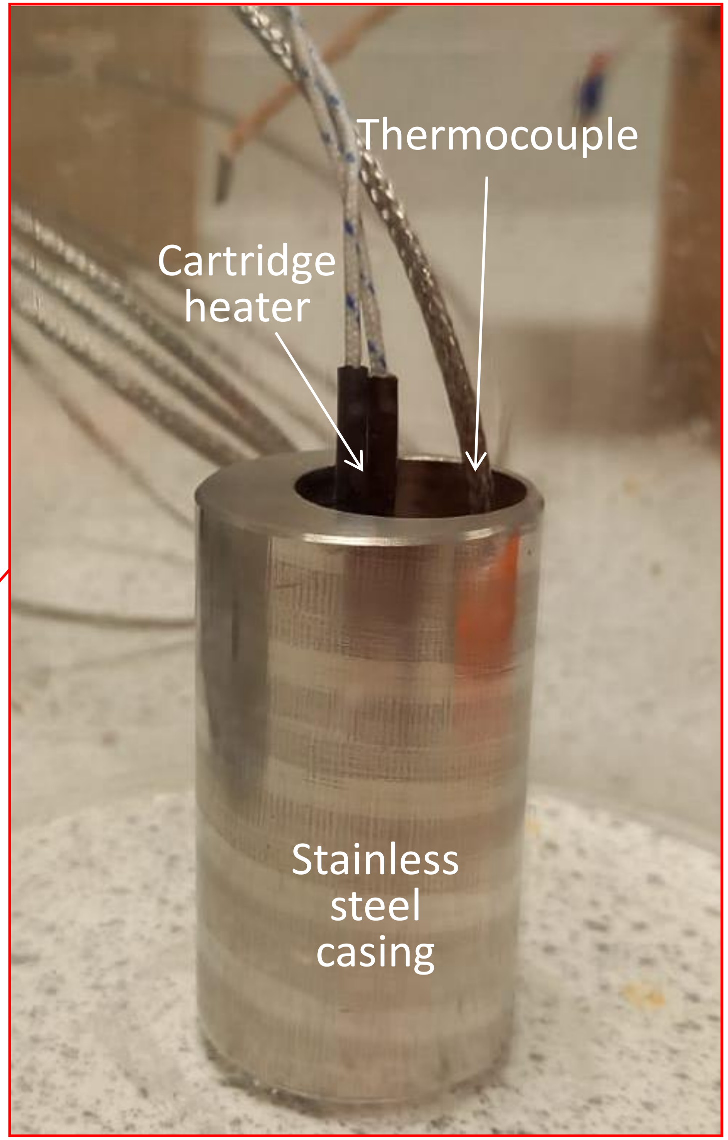
- Acrylic (PMMA) transparent container
- Heater (steel casing + cartridge heater+ thermocouple)
- PID temperature controller



Experimental setup

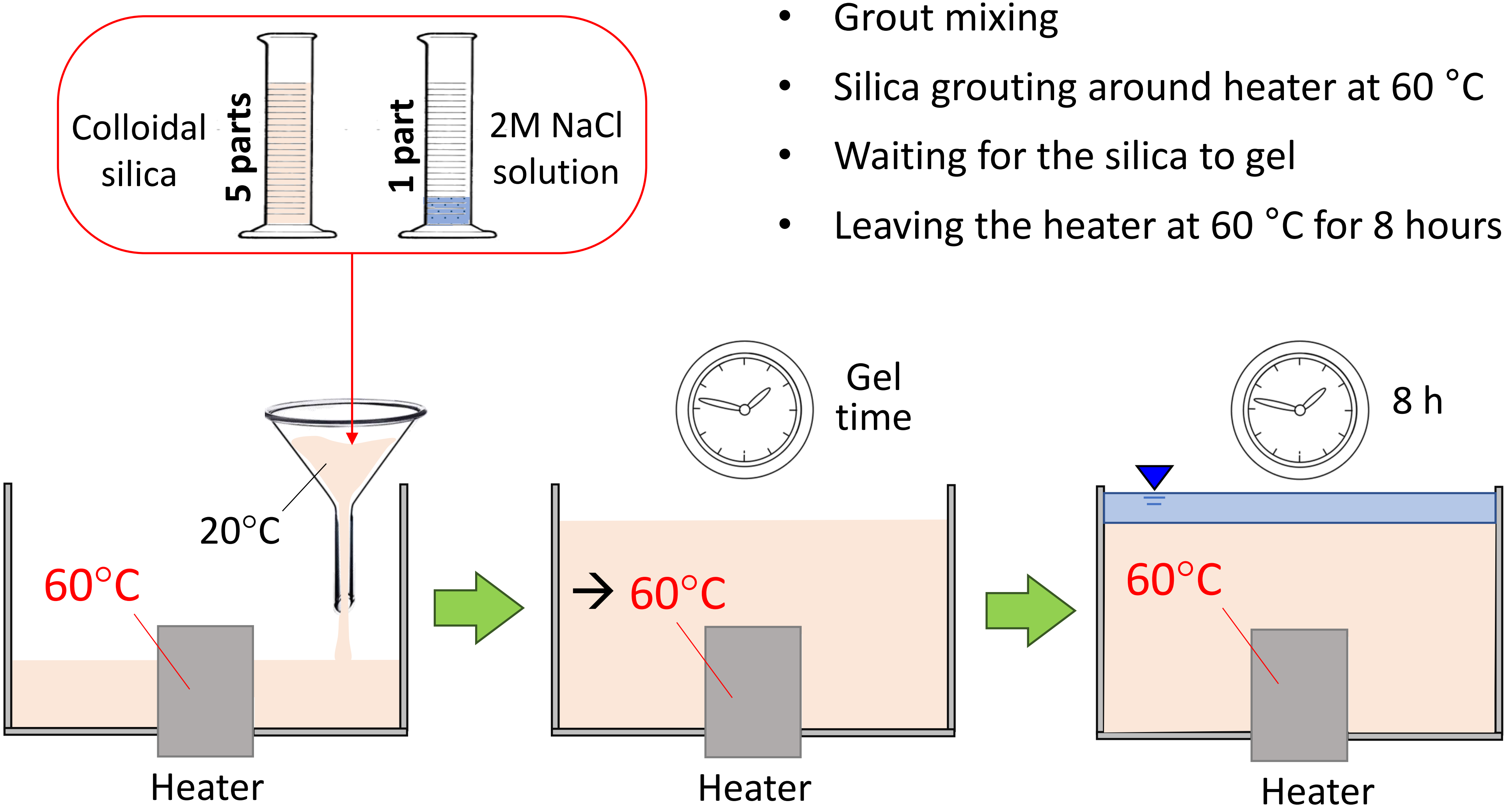
- Acrylic (PMMA) transparent container
- Heater (steel casing + cartridge heater+ thermocouple)
- PID temperature controller



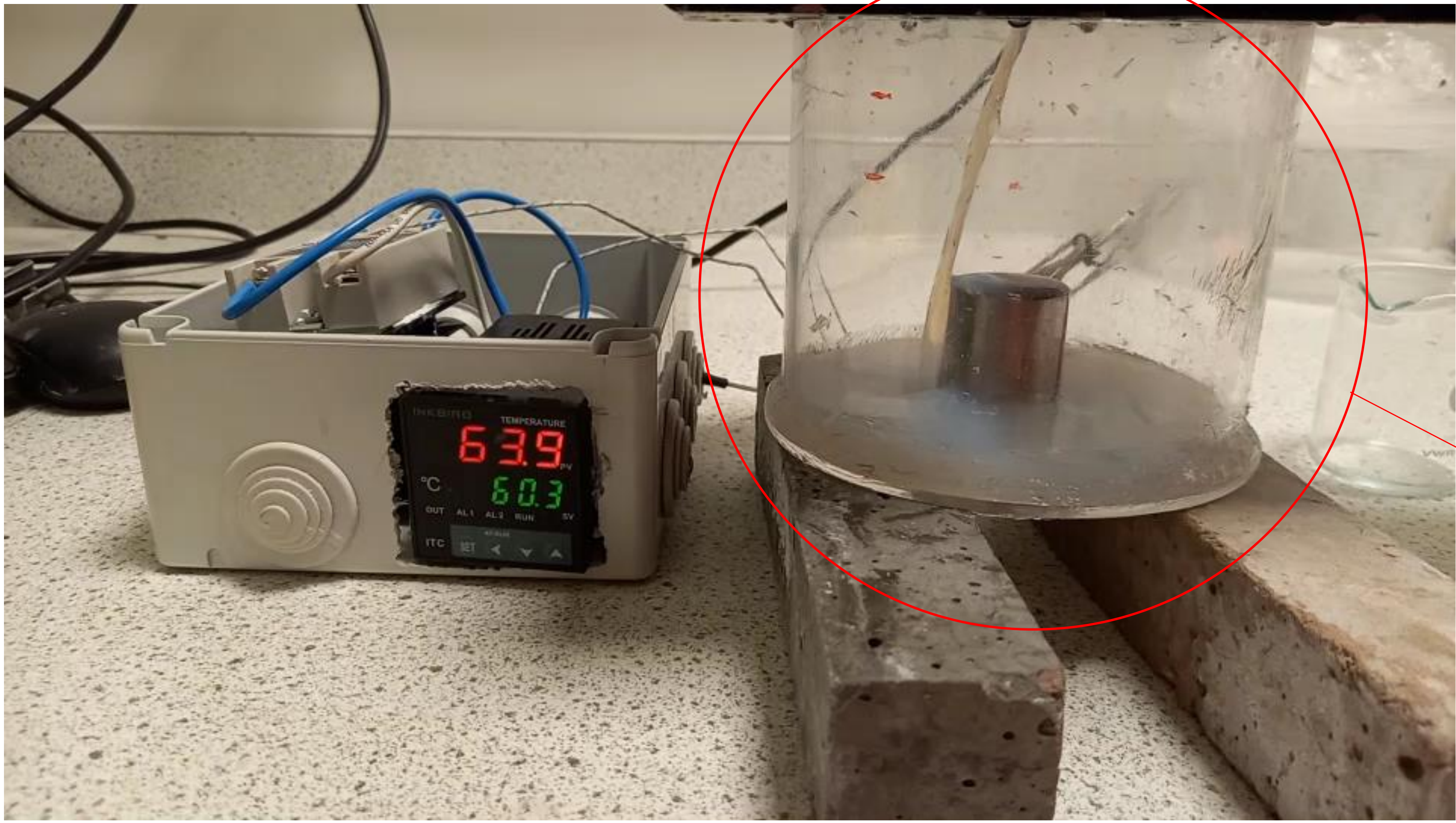


Experiment 1: grouting around an object at 60°C

- Grout mixing
- Silica grouting around heater at 60 °C
- Waiting for the silica to gel
- Leaving the heater at 60 °C for 8 hours



Experiment 1: grouting around an object at 60°C



Setup transferred to XCT after 8 hours

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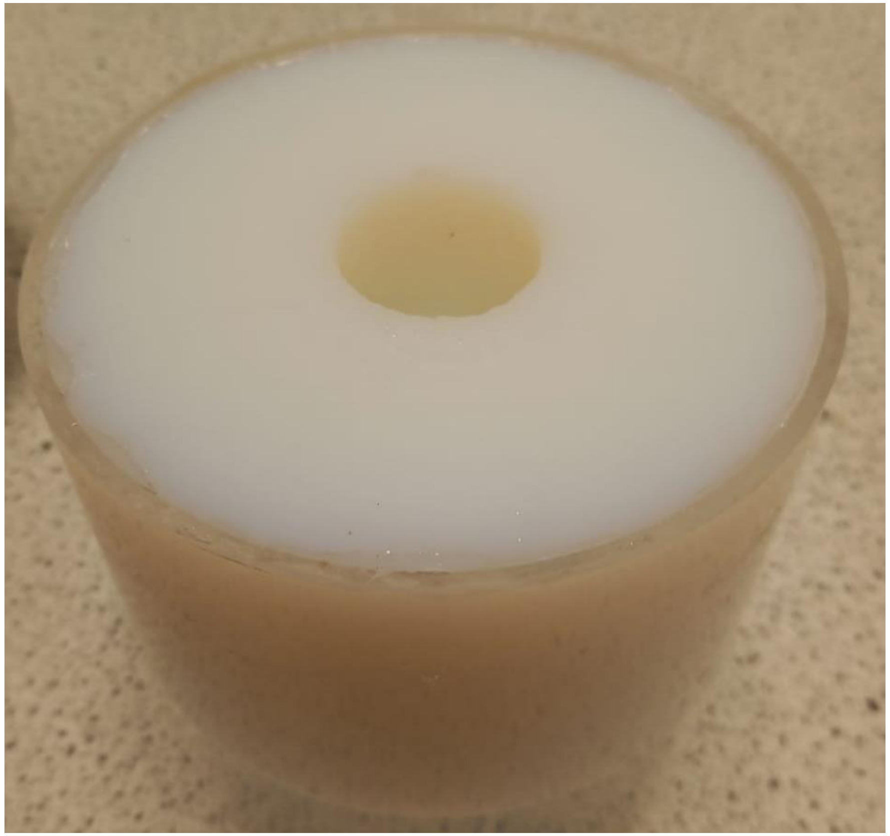
Transformative Science and Engineering for Nuclear Decommissioning

Experiment 1: grouting around an object at 60°C

Sample extrusion

Bottom – after heater removal



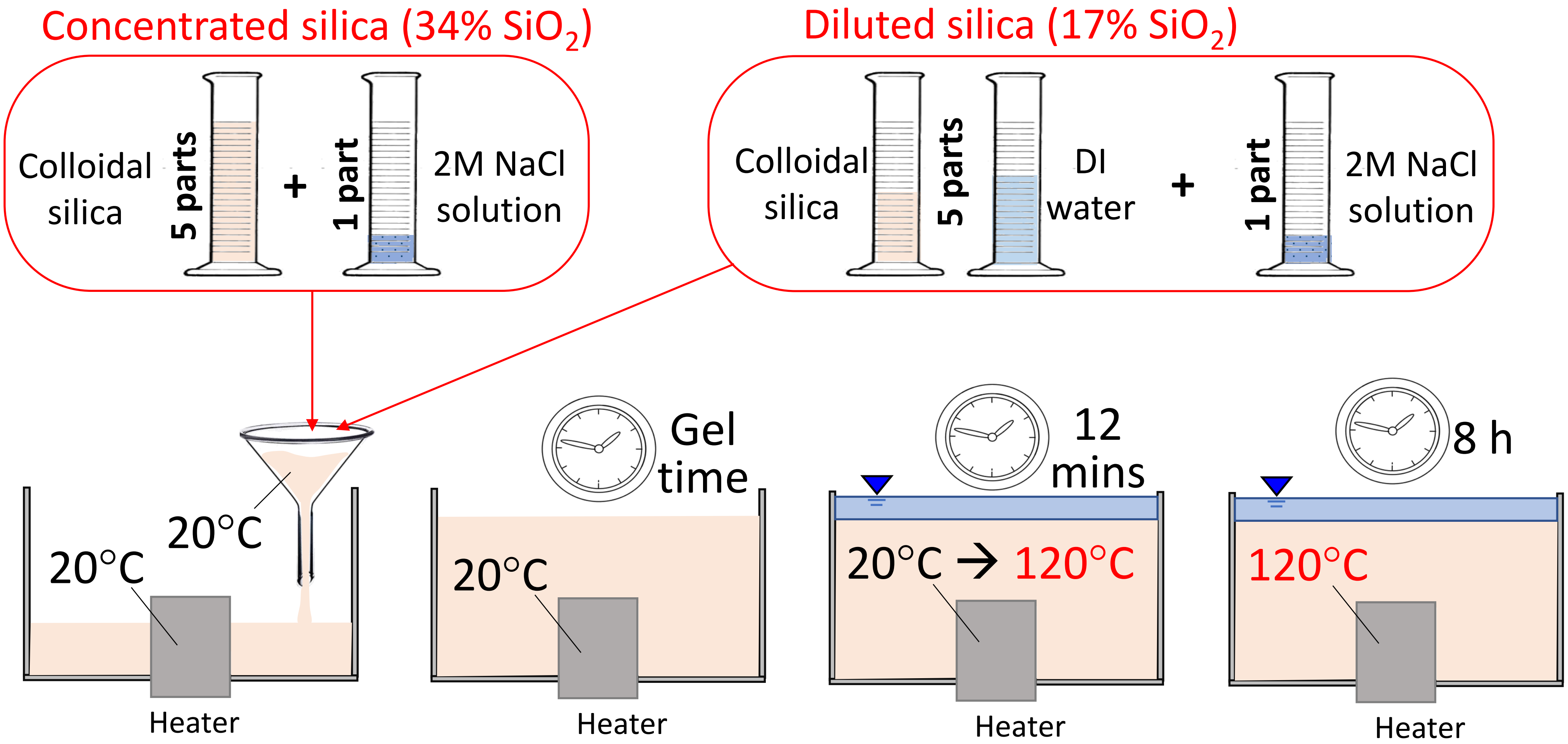
Top – after extrusion

From visual inspection + XCT data:

- No connected cracks
- Small, isolated cracks due to decreased gas solubility with increasing temperature

Grouting at higher temperature: 120°C

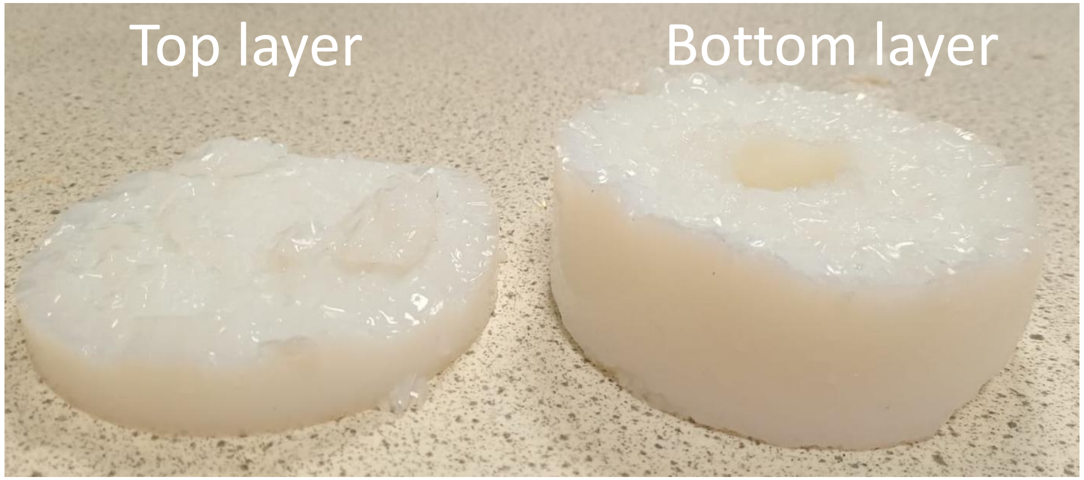
1. Effect of silica concentration



Grouting at higher temperature: 120°C

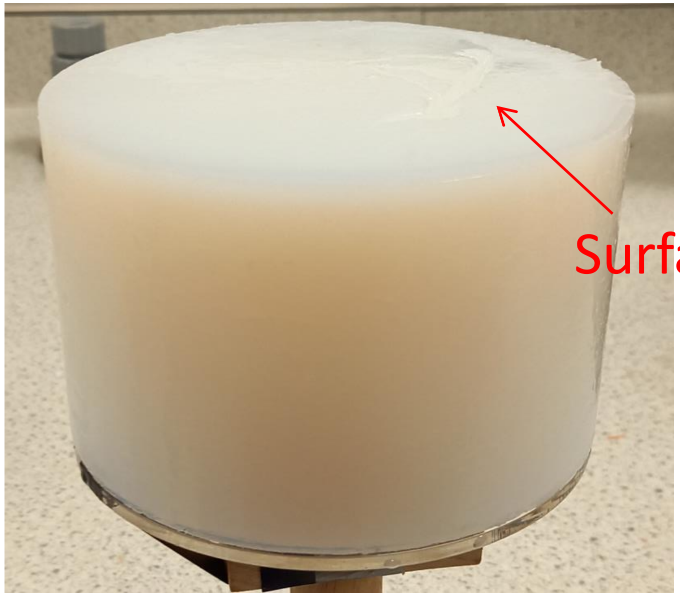
1. Effect of silica concentration

- Silica concentration: 34%



'Hard' extruded gel

- Silica concentration: 17%



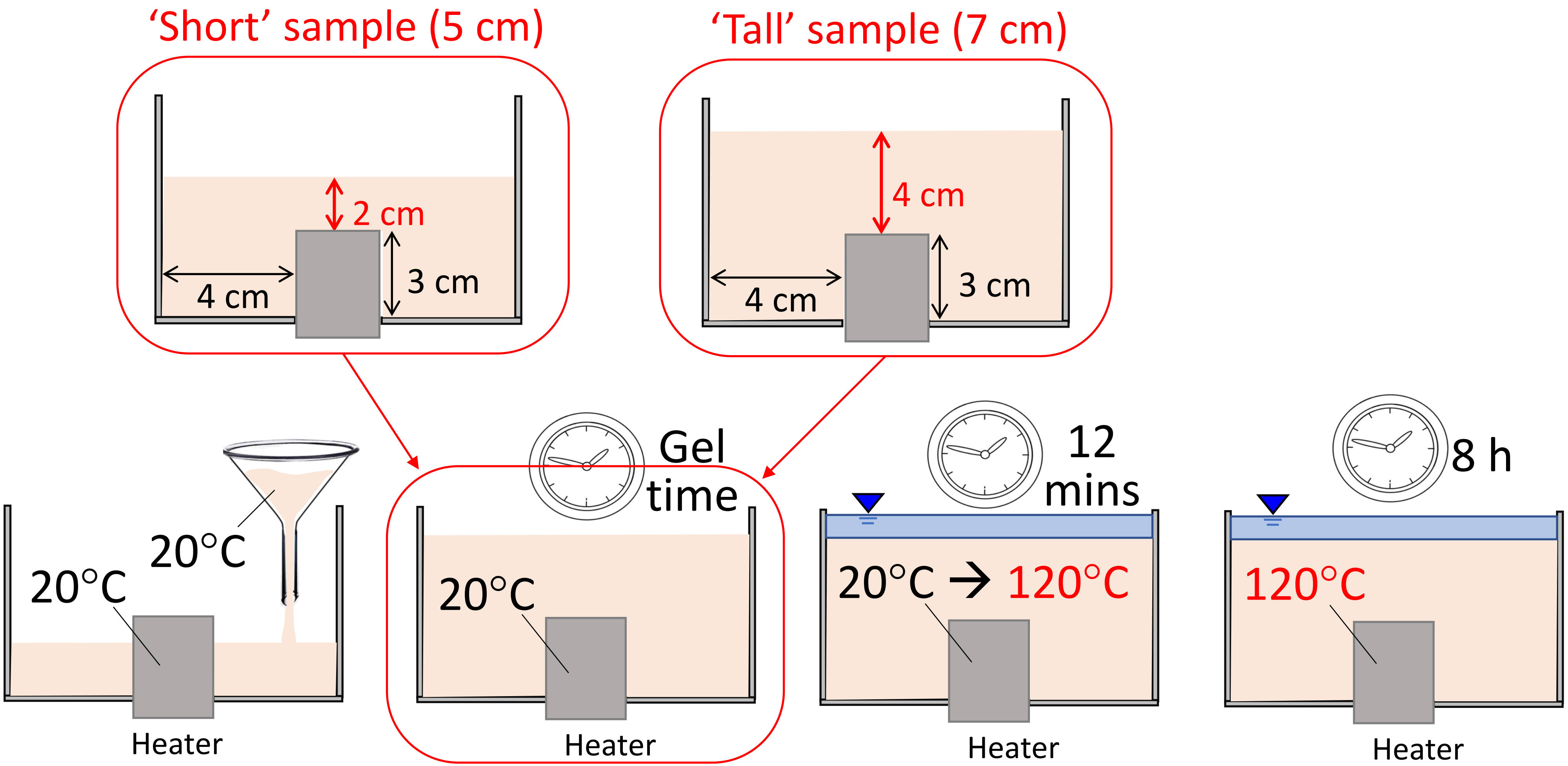
'Soft' extruded gel

From visual inspection + XCT data:

- Surface and radial cracks, resulting in gel breakage upon extrusion
- Reduced cracking, intact gel upon extrusion

Grouting at higher temperature: 120°C

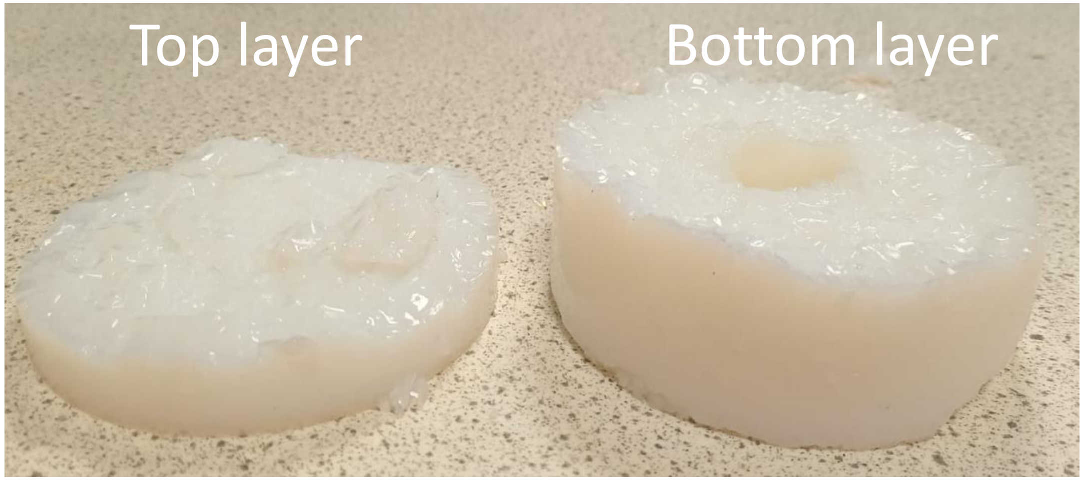
2. Effect of sample height



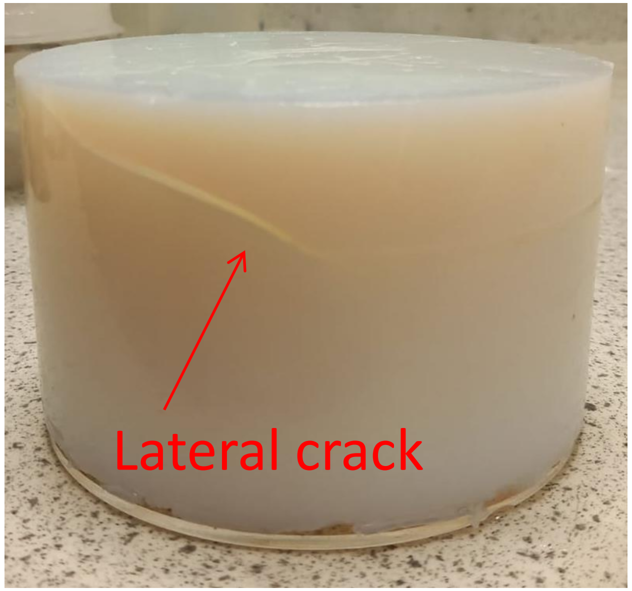
Grouting at higher temperature: 120°C

2. Effect of sample height

- Sample height: 5 cm



- Sample height: 7 cm

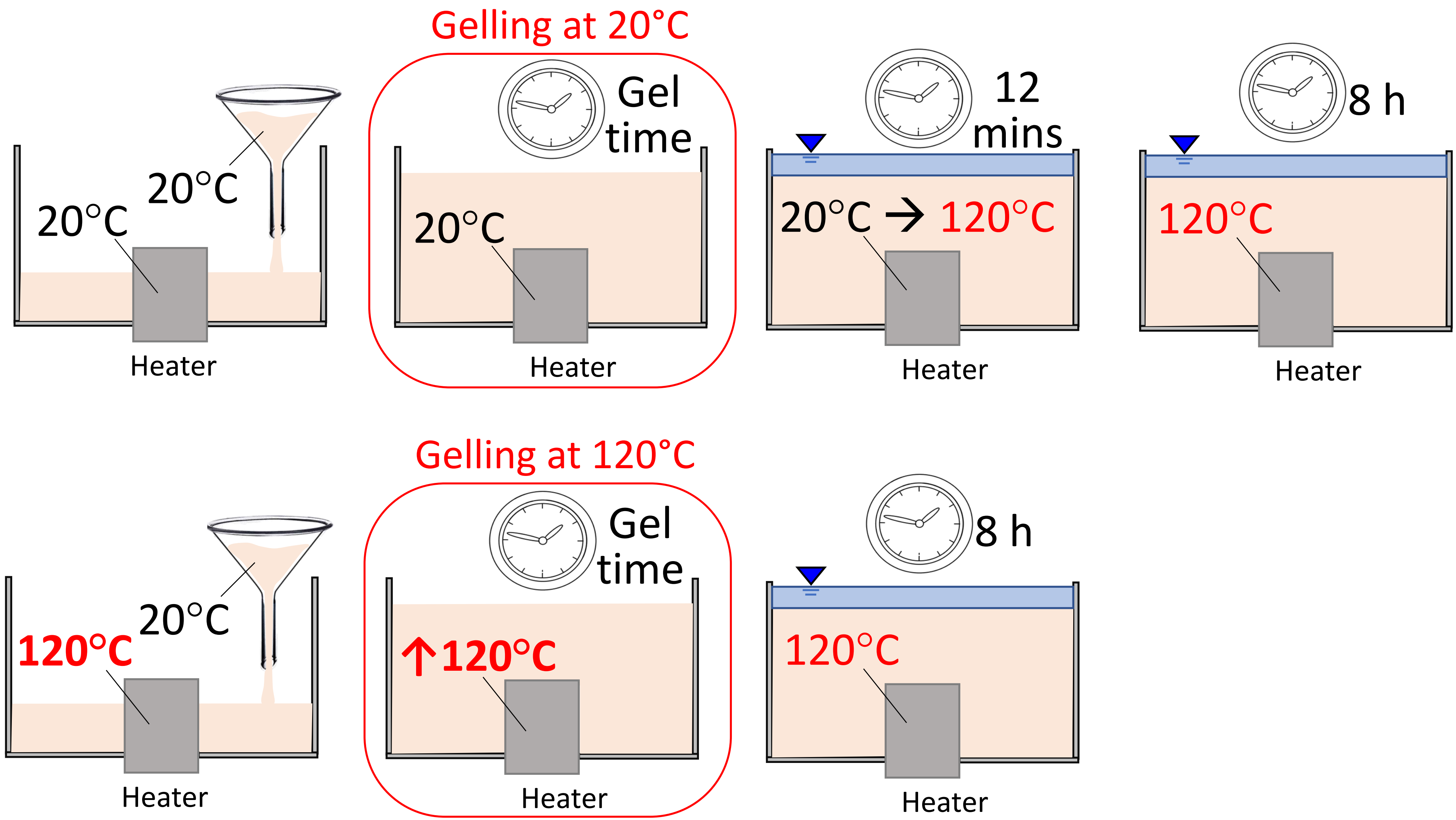


From visual inspection + XCT data:

- Surface and radial cracks, resulting in gel breakage upon extrusion
- Reduced cracking, intact gel upon extrusion

Grouting at higher temperature: 120°C

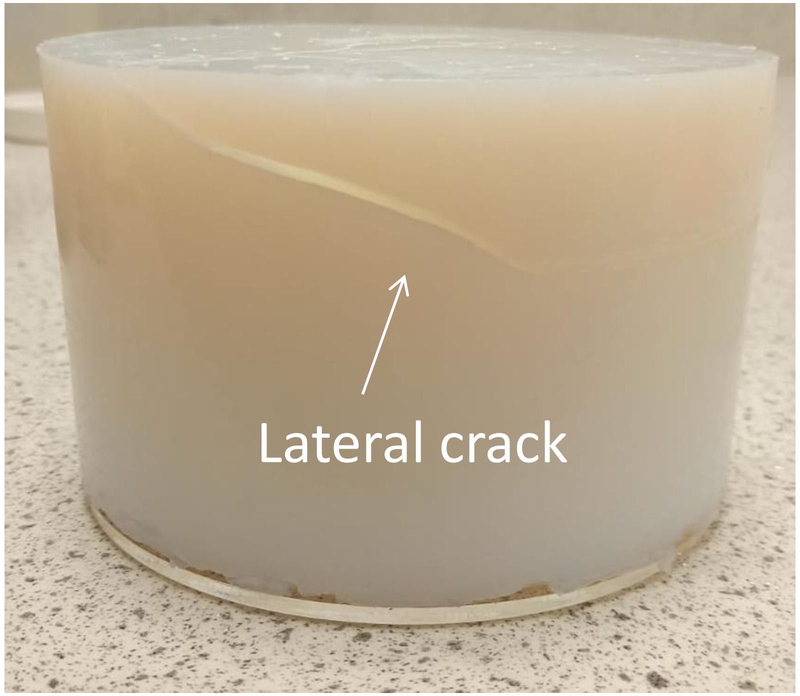
3. Effect of heating condition at gelling



Grouting at higher temperature: 120°C

3. Effect of heating condition at gelling

- Gelling at 20°C



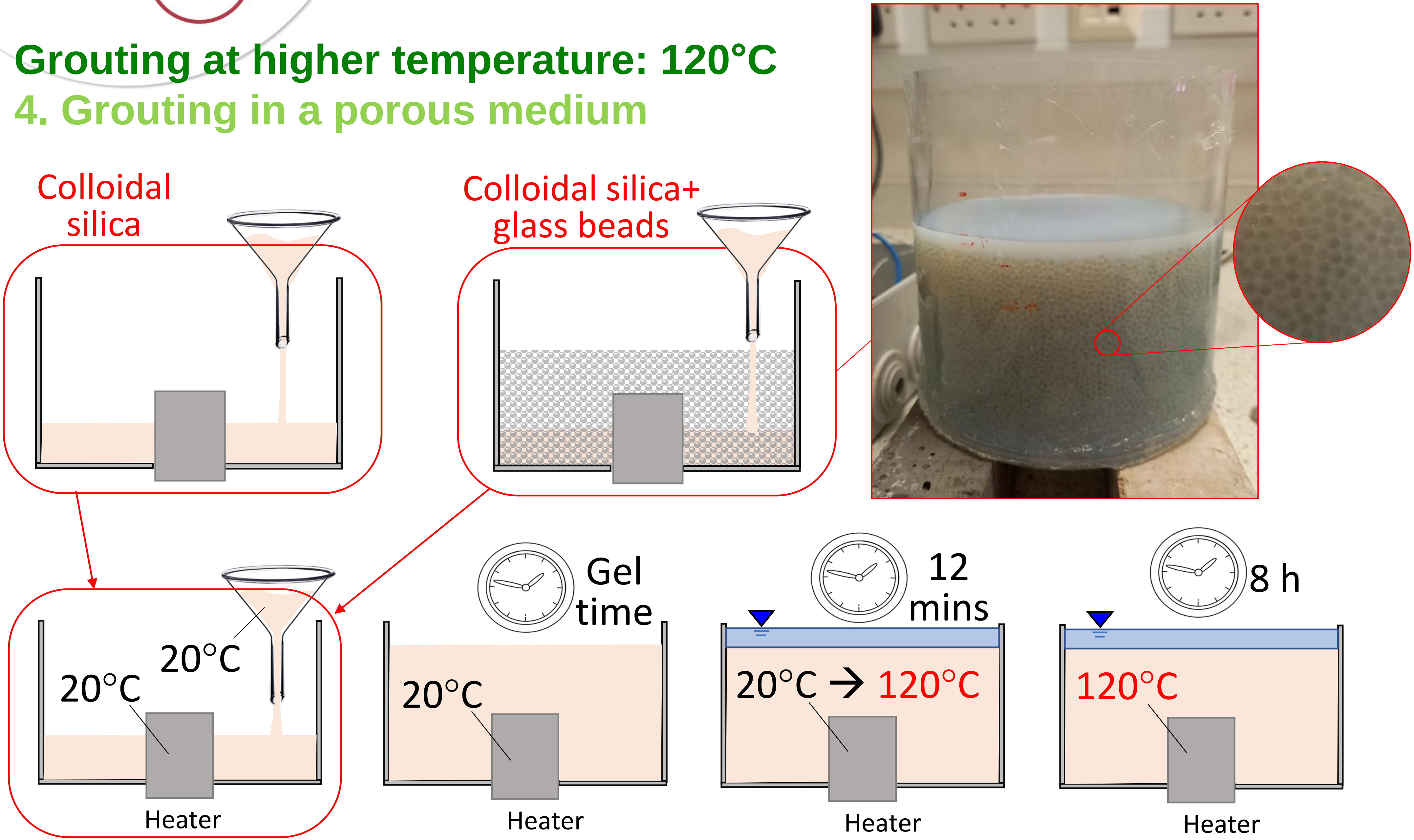
- Gelling at 120°C

From visual inspection + XCT data:

- Reduced radial cracking when gelling at 120 degrees
- 'Looser' silica gel above the heater when gelling at 120 degrees

Grouting at higher temperature: 120°C

4. Grouting in a porous medium

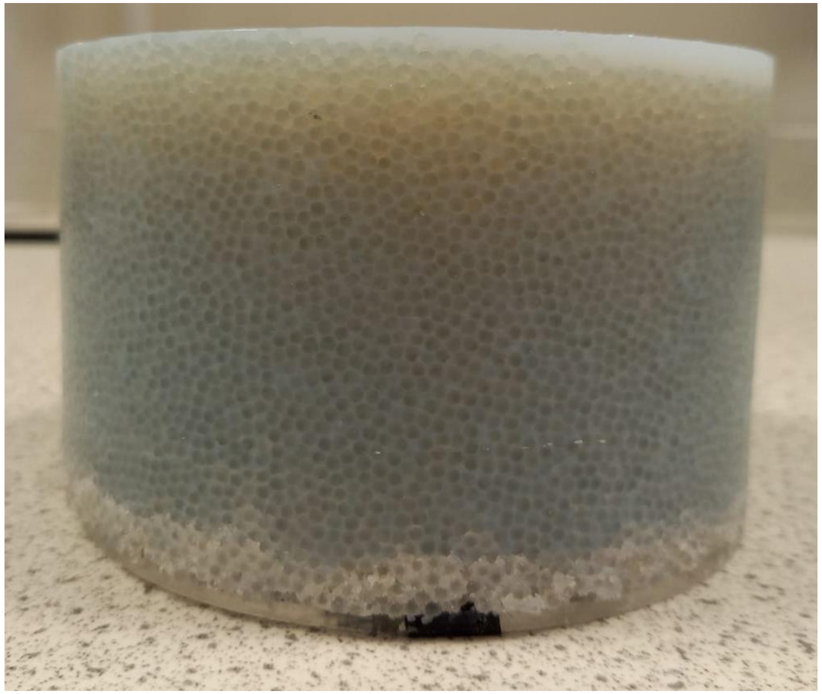


Grouting at higher temperature: 120°C

4. Grouting in a porous medium

- Silica gel

- Grouted glass beads



From visual inspection + XCT data:

- Grouted glass beads sample is fully intact (no surface or radial cracking)

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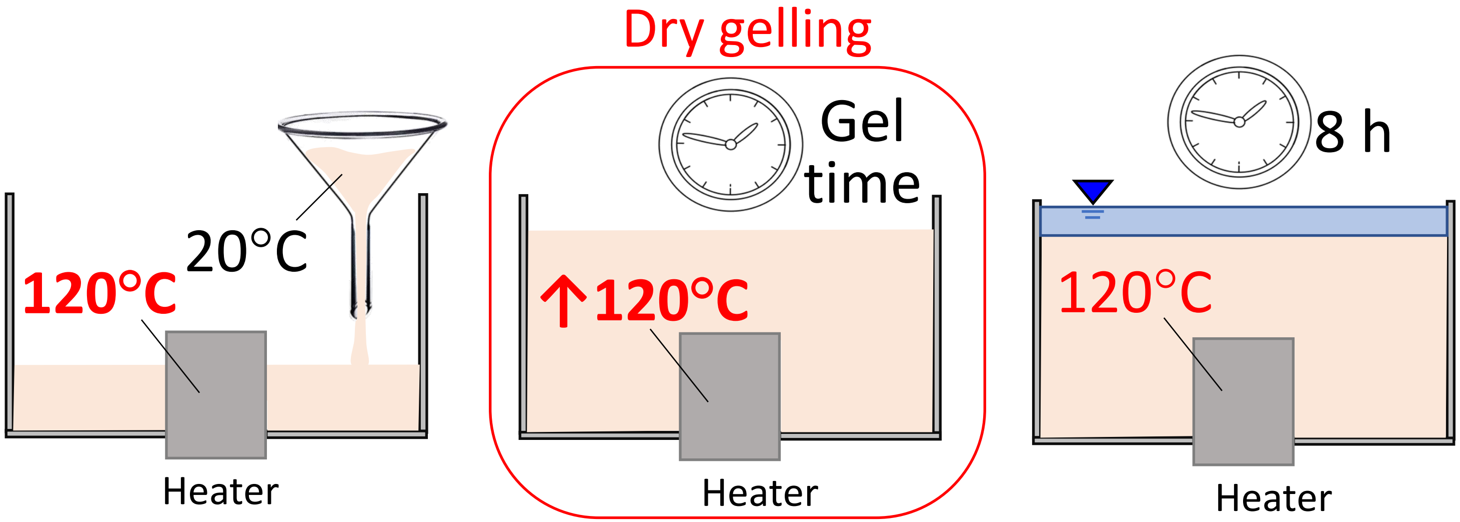
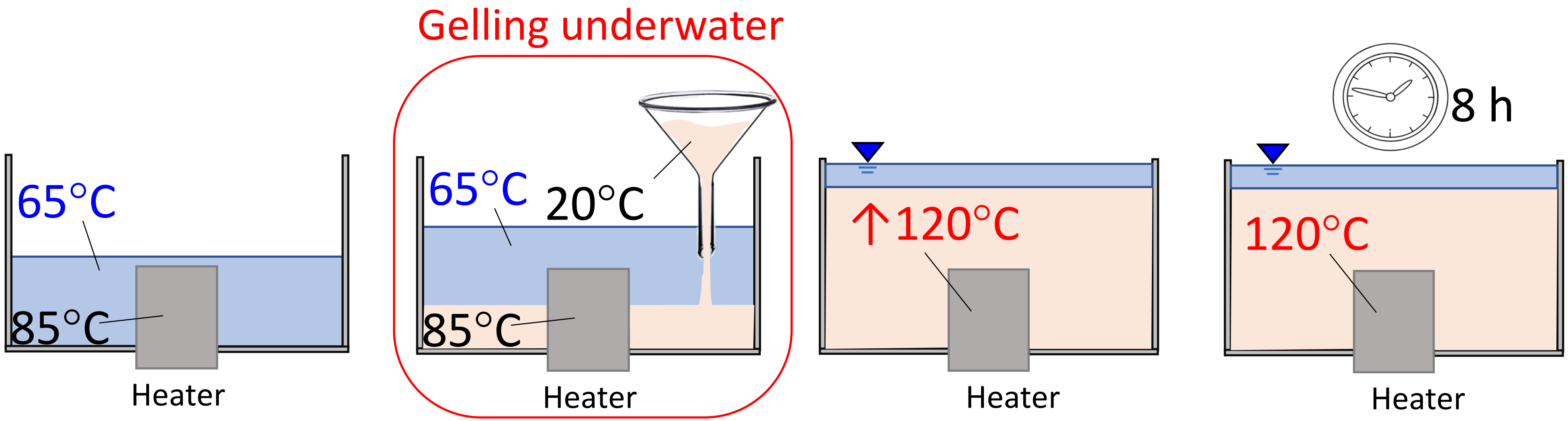
Grouting at higher temperature: 120°C

5. Dry gelling and gelling underwater





Grouting at higher temperature: 120°C

5. Dry gelling and gelling underwater

Grouting at higher temperature: 120°C
5. Dry gelling and gelling underwater

- Dry gelling
- Gelling underwater

From visual inspection + XCT data:

- Reduced surface/radial cracking (intact gel upon extrusion) when gelling underwater

Conclusions

- Colloidal silica grouting is suitable for grouting around medium-temperature (40-60°C) waste

- At higher temperature (>100 °C):
  - Lowering the silica concentration has a beneficial effect on crack formation
  - The formation of surface cracks may be inhibited or reduced by increasing the volume of grout above the waste
  - Grouting porous media improves the performance of the grout against crack formation
  - Gelling underwater reduces radial and surface cracking

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Thank you

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