Diffusion of ions through colloidal silica gel

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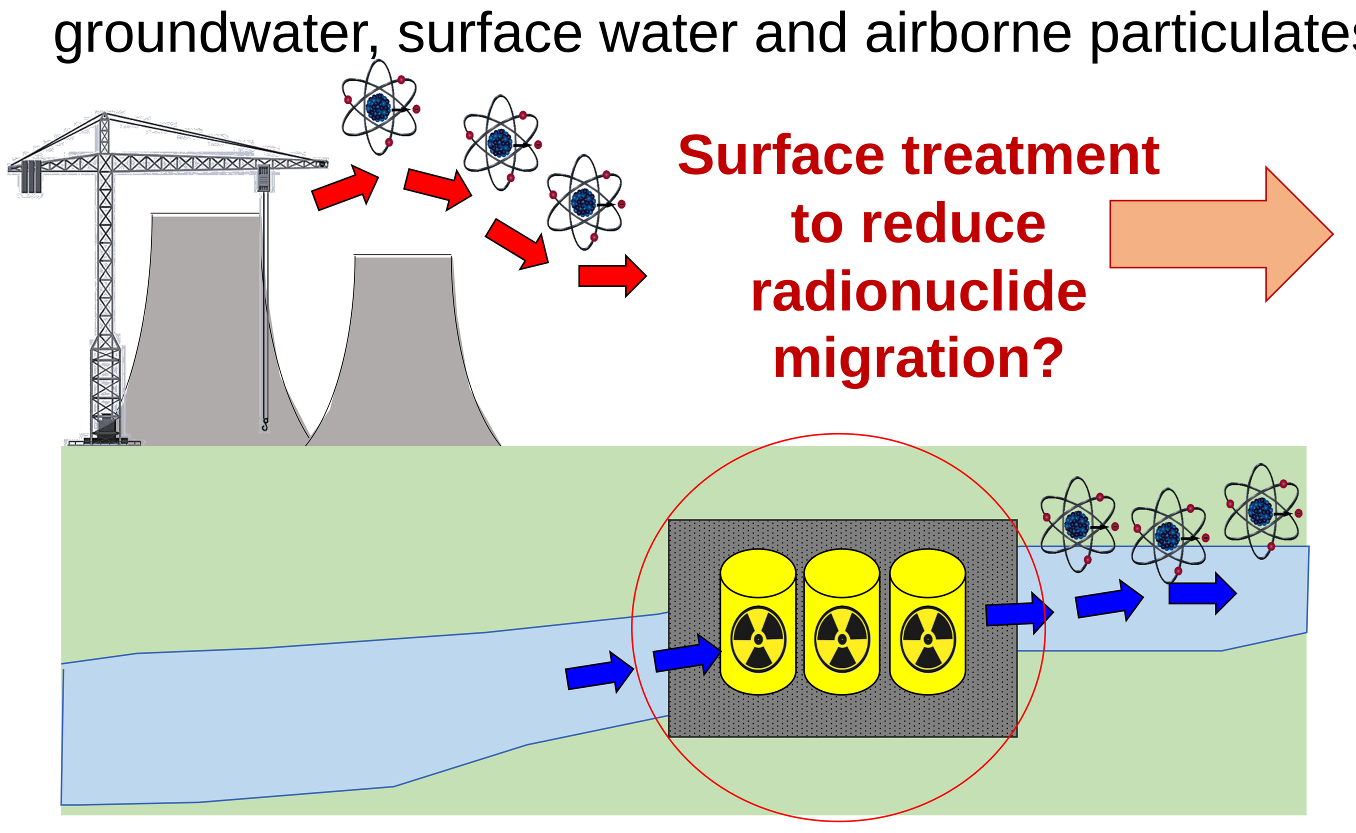
The Problem: Radionuclide migration in nuclear site decommissioning

Nuclear site decommissioning involves several stages, including **waste retrieval**, **decontamination**, **deconstruction** and **remediation** of the surrounding land. As decommissioning proceeds, there is a severe **risk of radiation exposure due to the spread of radionuclides** in groundwater, surface water and airborne particulates.



COLLOIDAL SILICA GROUT TREATMENT:

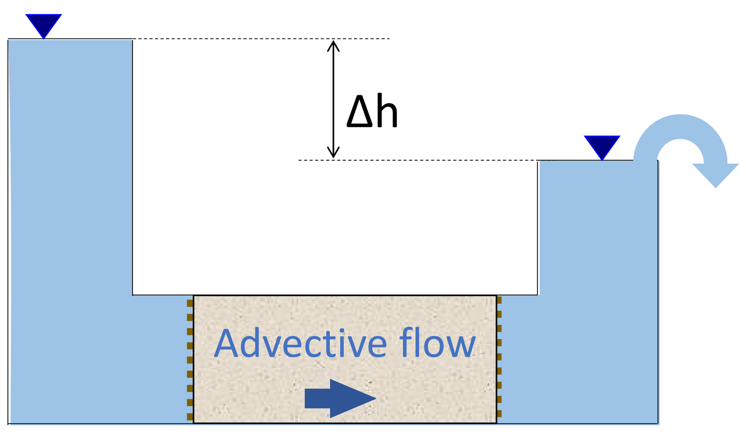
Use of **colloidal silica to treat surface soils** as a risk mitigation measure for inhibiting radionuclide migration. Research will focus on:

- optimisation of sorption/desorption grout properties by addition of other materials (e.g. clay minerals);
- feasibility of in- and ex-situ vitrification/cementation of grouted soils, minimising waste volumes via redeployment of the silica as an integral component of the wasteform;
- repair of existing degraded cementitious waste packages;
- combining colloidal silica grout containment and in-situ vitrification with the electro-kinetic technique.

Contaminant transport through silica gel

Colloidal silica (CS) is an aqueous dispersion of silica particles (SiO_2). Upon destabilization, siloxane bonds are formed and the colloids form a continuous gel. Mechanisms of contaminant transport through silica gel include:

- **Advection**: groundwater flow

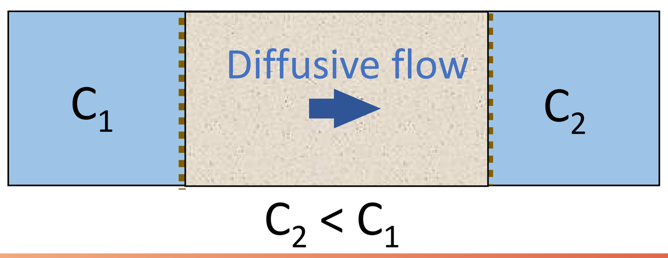


Advective mechanisms through gelled silica are controlled by the gel's hydraulic conductivity. Previous experimental investigations (Wong et al. 2018*) showed an extremely low hydraulic conductivity of silica gel:

1D advective flux in porous media:

$$J = Ck\frac{\partial h}{\partial x} \qquad k = 10^{-9} m/s$$

- **Diffusion and retardation**: molecular diffusion and adsorption/desorption



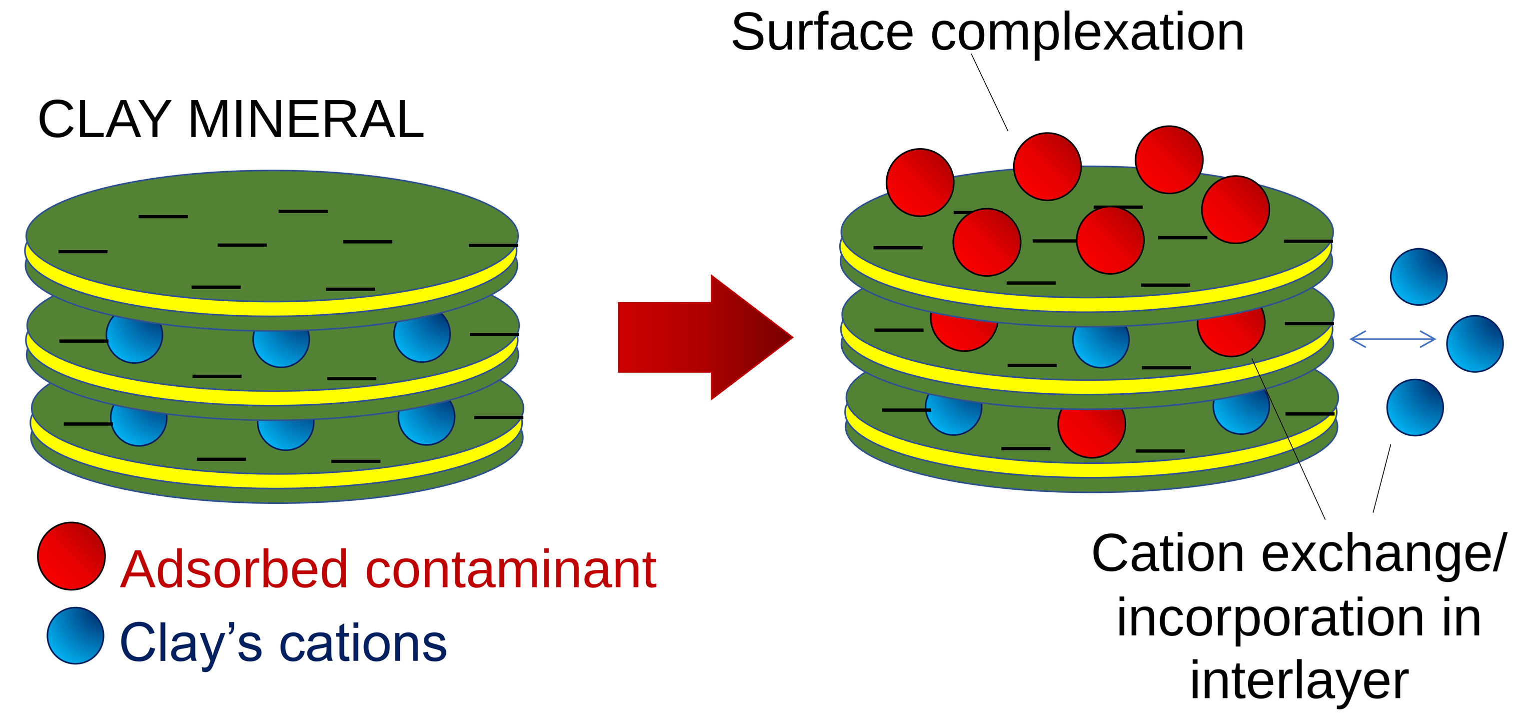
Diffusive rates across gelled silica may be significant, and **have not yet been characterised**.

1D diffusion equation in porous media:

$$\frac{\partial C}{\partial t} = \frac{D_m}{R}\frac{\partial^2 C}{\partial x^2} \qquad D_m/R = ?$$

ADDITION OF CLAY MINERALS to silica gel:

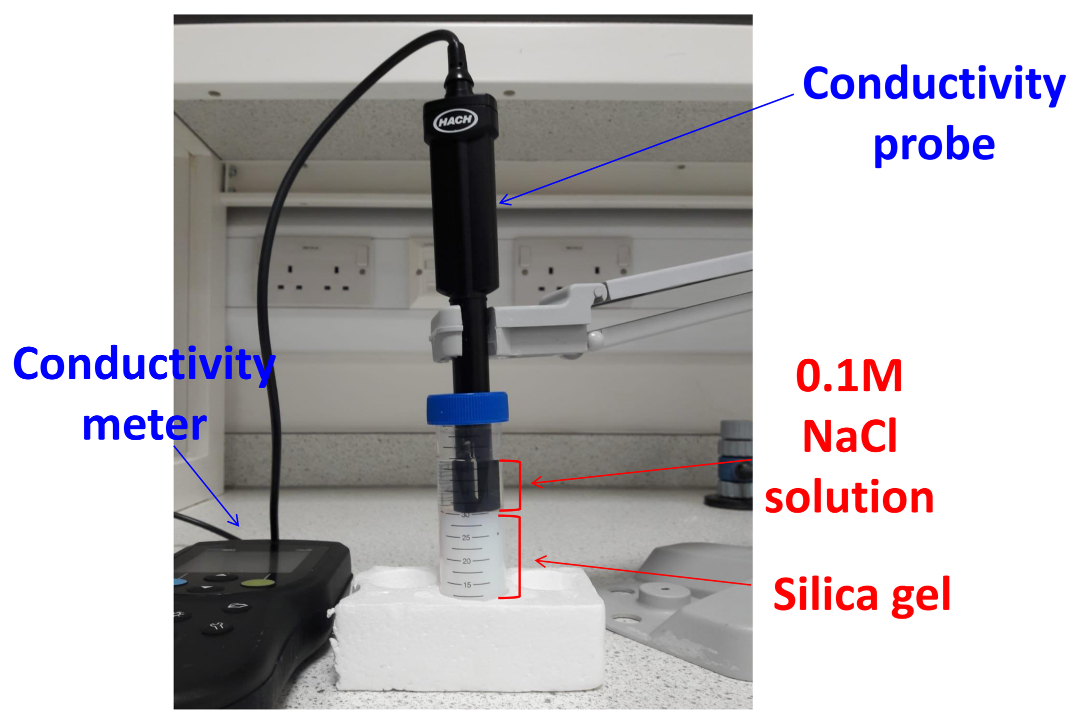
The migration of ions through silica gel by diffusion and retardation may be reduced by the addition of clay minerals to the silica matrix, due to surface complexation and incorporation of contaminants in clay minerals interlayers:

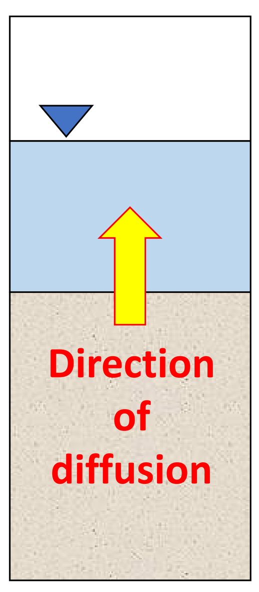


→ *Effect of addition of clay minerals to silica gel on diffusion properties has to be investigated.*

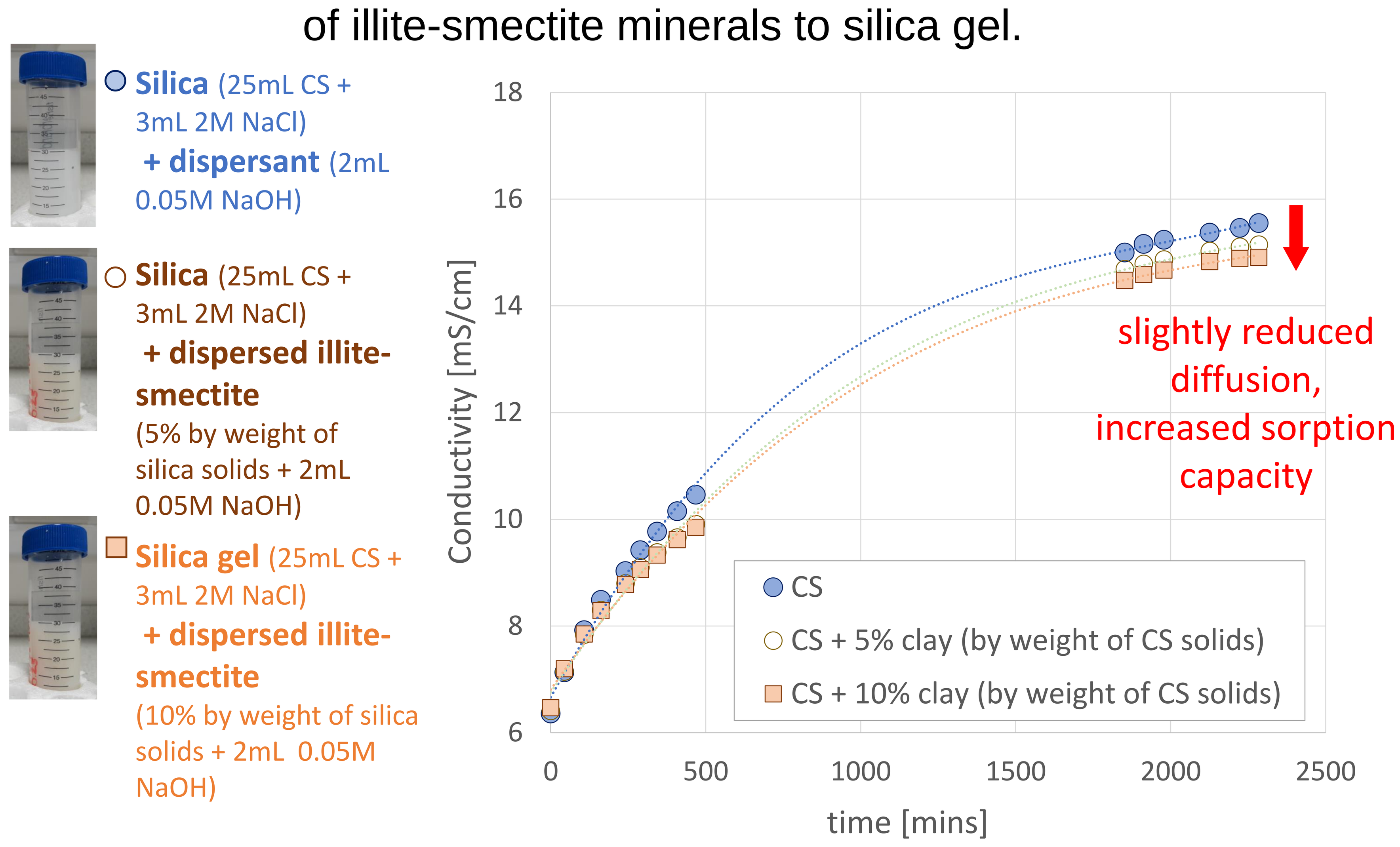
Diffusion experiments: reservoir method

- One-dimensional diffusion of NaCl from a gelled silica sample into a reservoir solution (thoroughly mixed) was investigated.
- Na^+ cations migration was monitored by measuring the change in electrical conductivity in the reservoir solution overtime.
- The effect of small fractions of dispersed illite-smectite clay minerals added to the silica gel was investigated.





RESULTS: Slightly reduced diffusion of Na^+ ions after addition of illite-smectite minerals to silica gel.



WORK IN PROGRESS: diffusion of radionuclides through pure silica gel, and silica gel + dispersed illite-smectite.

*References: Wong, C., Pedrotti, M., El Mountassir, G. & Lunn, R. J. 2018. A study on the mechanical interaction between soil and colloidal silica gel for ground improvement. Engineering Geology.

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Energy For a Low Carbon Future

Electrokinetic Remediation

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What is Electrokinetic Remediation (EKR)?

- Clean-up of UK's nuclear legacy estimated at ~ £200 billion over 100 years,
- Urgent need to reduce decommissioning cost – new approaches to remediation?
- Must work in soils, sands, concretes, cements, groundwater, *etc.*, AND be site-scalable, cheap, energy efficient and sustainable,
- Many methods available:

Options?

	Bio- and Phyto-	Redox	'Dig and Dump'	Thermal	EKR
✓	Renewable, 'green'	Quick	Simple, convenient		**Adaptable**
✗	Slow nutrient delivery	Expensive (nano-ZVI £££)	Just 'moving' contamination	High energy cost	**Unproven**

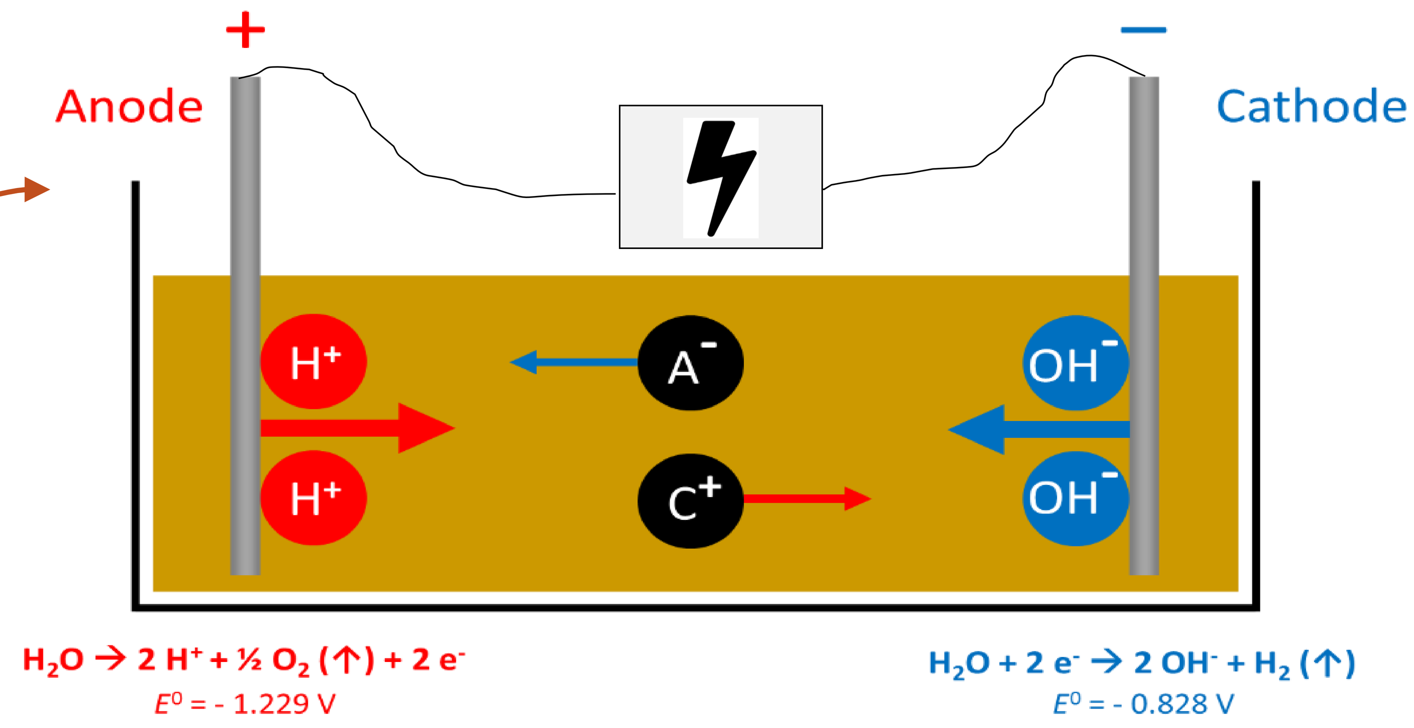


Figure 1: A typical electrokinetic cell. C^+ are cations and A^- are anions.

Decontaminate by electrocution, concentrating pollutants within cell or electrodes. Adaptable and low-energy waste minimisation technique.

Case Study 1 – Fukushima Simulant[1]

- Fukushima-Daiichi, Japan, 2011
- INES level 7 disaster, 50,000+ evacuated
- > $150 billion in damage
- **3 PBq ^{137}Cs + ^{90}Sr in soil**
- 'Dig and dump'
- 160,000+ t at > 8 KBq/kg (2014)

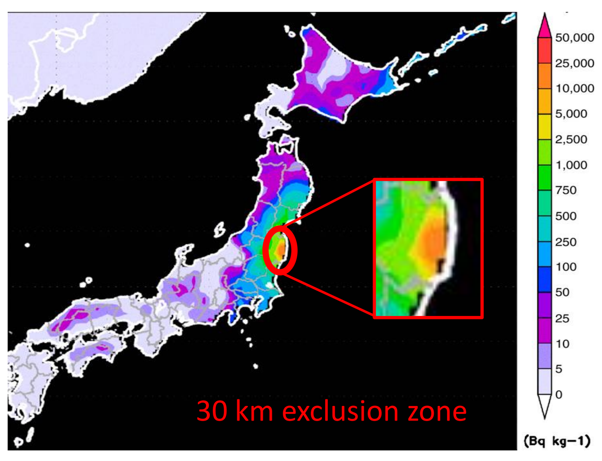
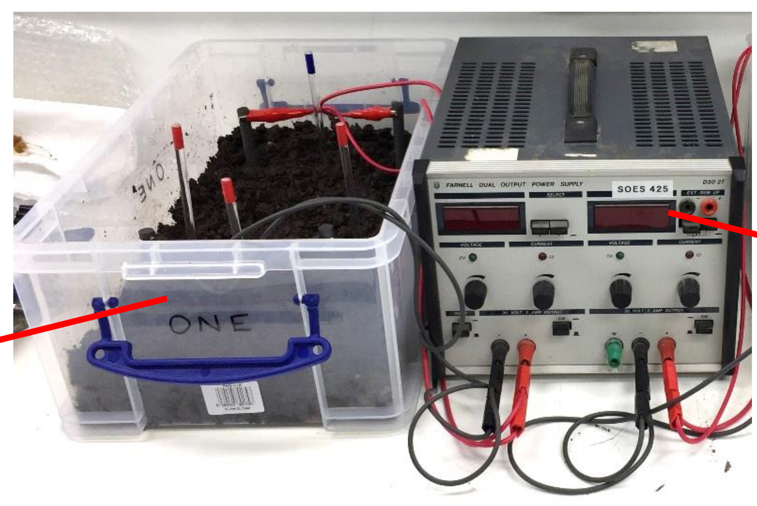


Figure 2: [Cs] in Japanese soil following Fukushima (11-04-2011)

How is EKR useful?

Fukushima soil simulant, **6:1 clay-peat**. Doped with radiostable **Cs^+**. **Sr^{2+}, KCl** and **citric acid** also added to look at how naturally occurring species affect EKR.



Low energy (15 or 20 V) power supply with **graphite electrodes** embedded in soil simulant over **20 days.**

Figure 3: Cell set-up used in our labs. Only one of the 4 cells we used is shown here.

We then monitored movement of Cs^+ (and other ions) across cell by X-ray fluorescence; $[Cs^+]_0$ = 133 ppm. The Ca^{2+}, Sr^{2+}, La^{3+}, S (as $[SO_4]^{2-}$) and Cl^- shown in Figure 5 were all intrinsic to the soil:

EKR has drastic effect on Cs^+ distribution across cell. 20 V over 20 days leaves some soil **observably free of contamination.** Sr^{2+}, KCl and citric acid have no effect on Cs^+ movement. **Further work needed.**

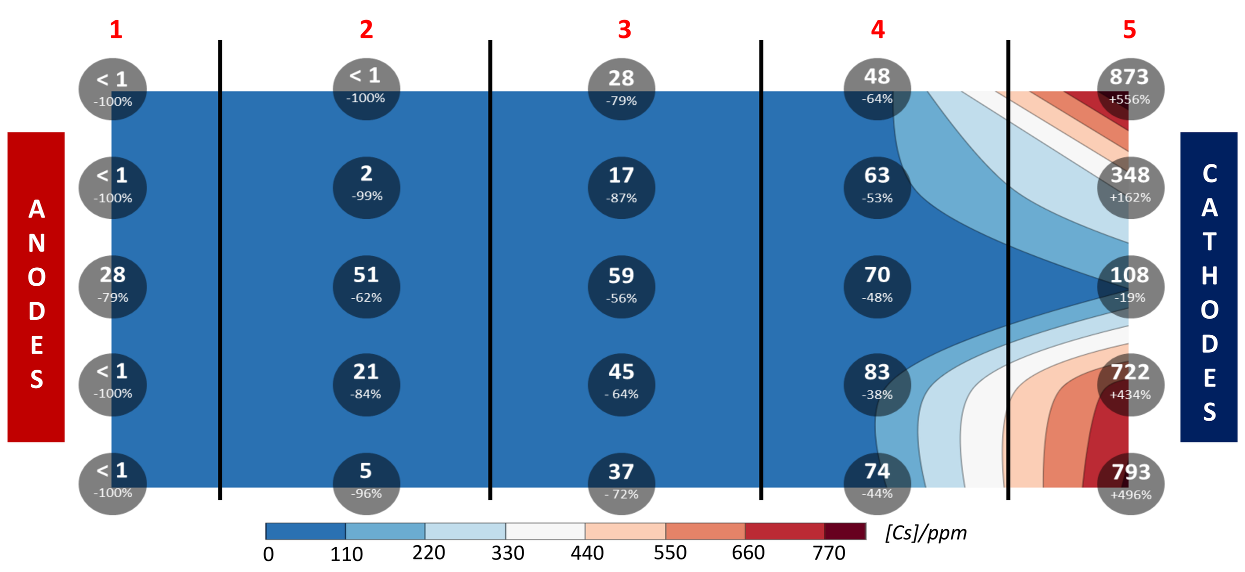
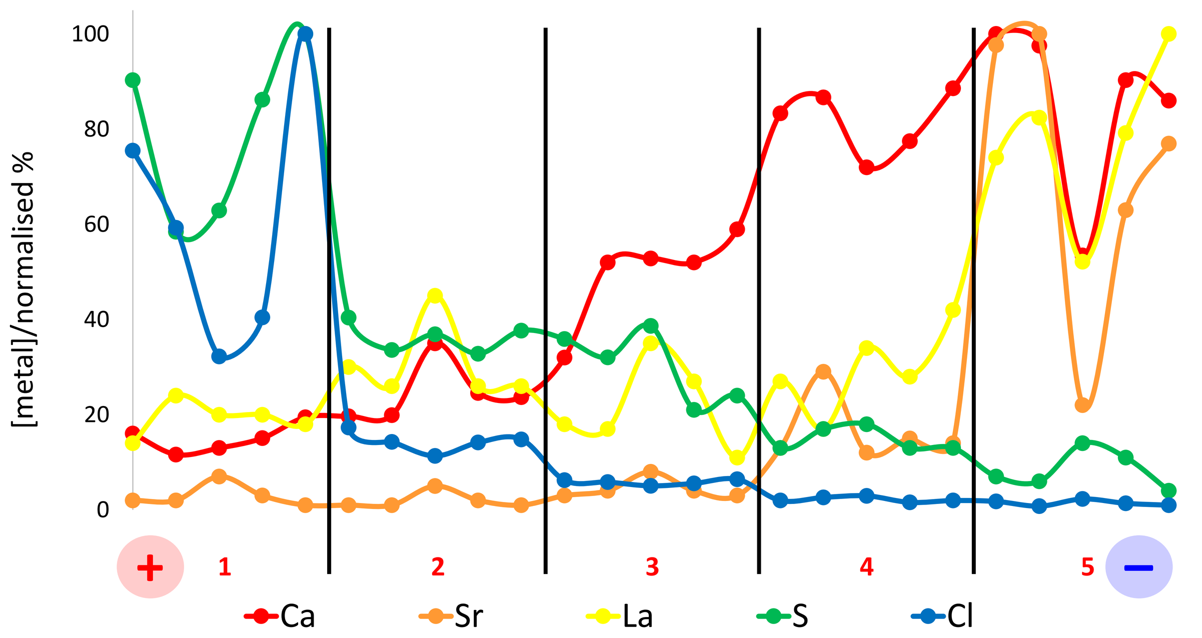


Figure 4: [Cs] in the cell following EKR. Numbers in circles are absolute values of [Cs], above percentage change from the initial Cs^+ concentration of 133 ppm.



Other ions are **also mobilised from soil matrices by EKR.** Cations migrate towards the cathode (column 5), and anions towards the anode (column 1).

Is EKR also effective on ^{90}Sr and lanthanides?

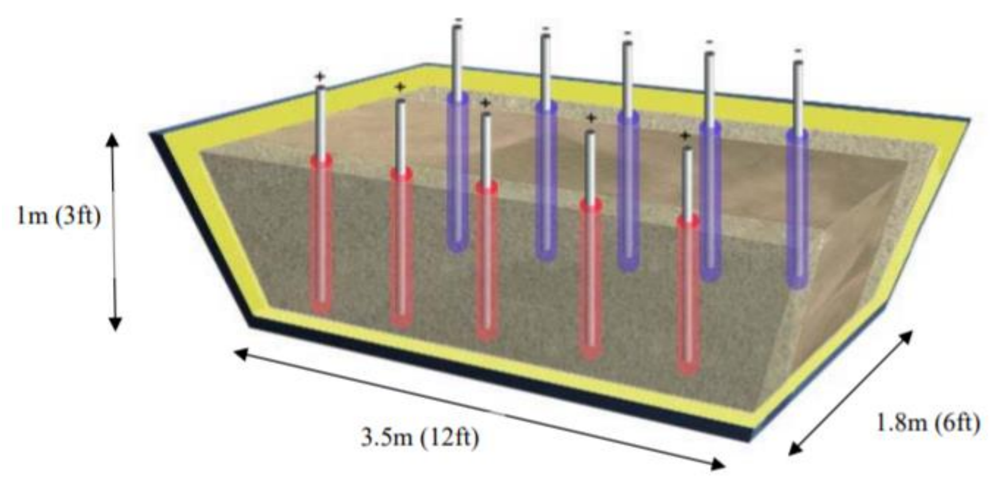
Figure 5: Normalised concentrations of selected ions across the cell after EKR. Columns 1 – 5 correspond to the sampling columns shown in Fig. 4.

Case Study 2 – Plutonium at AWE[2]

- Atomic Weapons Establishment (1950 –)
- Nuclear weapons manufacture
- Plutonium contamination
- Soil stored *ex*-situ, pending treatment
- Pilot study, 2011

Figure 6: Example of Pu-contaminated soil stored at Aldermaston site.

How was EKR useful?



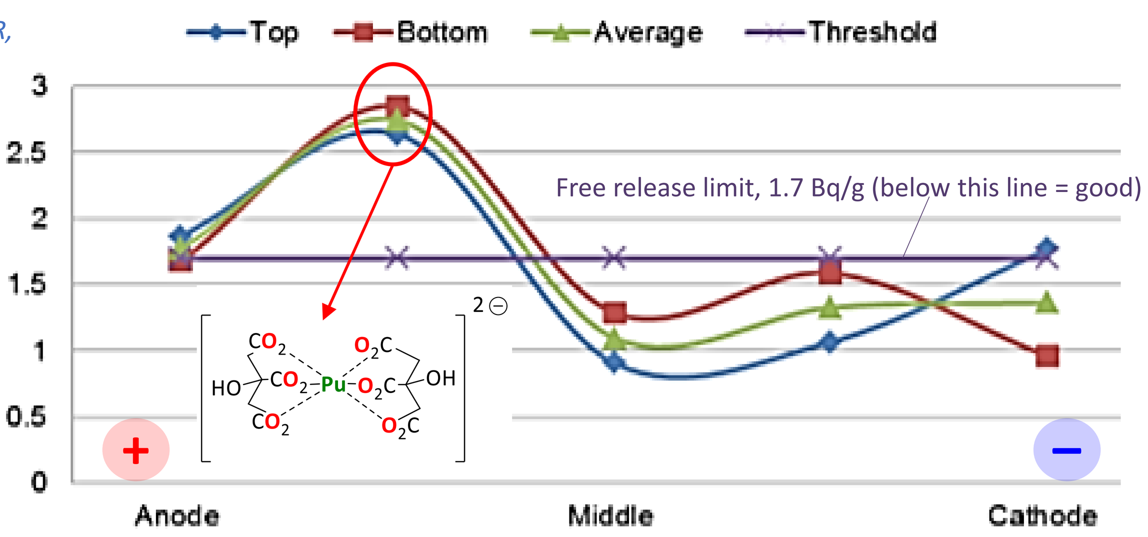
- 10 steel electrodes, in AWE soil and groundwater
- 12 V battery, 60 days
- Aim for **'free release' soil, 1.7 Bq/g** (can be landfilled)
- Citric acid added to mobilise plutonium (as the citrate)

Figure 7: The EK cell used for AWE remediation work. The scale, metres, is much larger than our previous work examining Fukushima simulants.

After EKR we then examined the distribution of Pu in soil by α-spectroscopy:

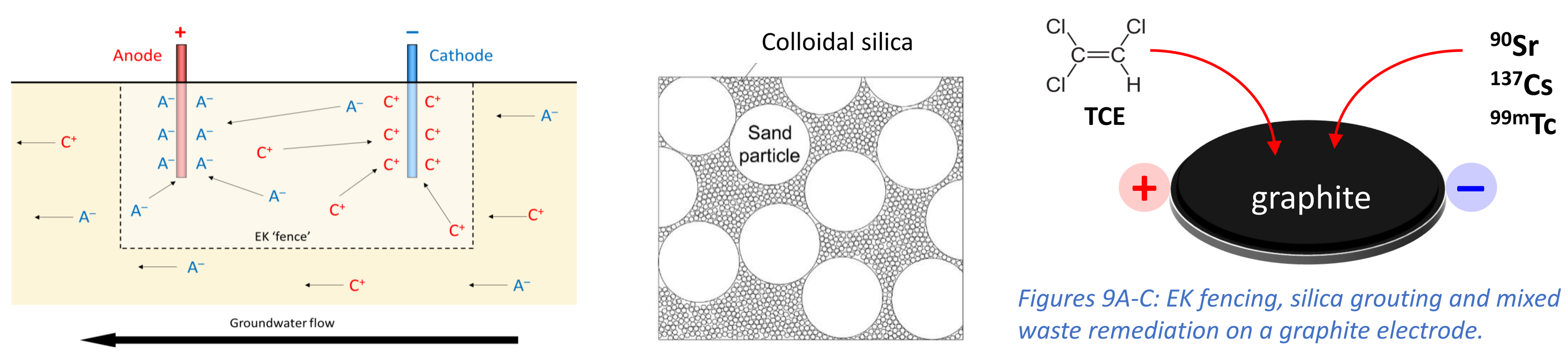
Figure 8: Pu distribution in the soil after EKR, and structure of negatively charged Pu citrate, inset

60% of soil below 'free release' limit, so can be landfilled. Movement of Pu towards anode. First example of EKR on Pu-contaminated soil but not tested widely.



EKR for TRANSCEND[3]

- EKR lacking scalable or combined uses for industrial sites, so:
- Study on **nuclear site materials** and simulants
- **With other techniques**; EK fencing, silica grouting, on mixed wastes?



Figures 9A-C: EK fencing, silica grouting and mixed waste remediation on a graphite electrode.

References

1: PNAS, 2011, 108, 19530; Environ. Sci. Technol., 2014, 48, 13053; J. Environ. Radioactiv., 2016, 151, 512; Environ. Sci. Technol., 2018, 52, 6390. 2: J. Haz. Mater., 2011, 186, 1405. 3: Chemosphere, 2017, 166, 549; Engin. Geol., 2018, 243, 84; J. Haz. Mater, 1995, 40, 117.

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An advanced blind-tube monitoring instrument to improve the characterization of subsurface radioactive plumes

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Background

Nuclear legacy facilities containing radioactive waste, such as storage ponds, tanks and silos, can be damaged by aging, adverse environmental conditions and retrieval activities on site. When the integrity of such a structure is compromised, the hazardous, anthropogenic, radioactive substances contained within them can leak into the subsurface (i.e., the earth material near to but not exposed at the surface of the ground). If methods of mitigation are not applied, these contaminants can disperse in the soil, potentially contaminating groundwater, presenting an elevated risk to health and the environment. Thus, it is important to assess the ground associated nuclear facilities, principally to detect whether these potentially hazardous materials have been released to the environment and also to determine if known areas of contamination are changing with time [1,2].

Assessing subsurface ground contamination

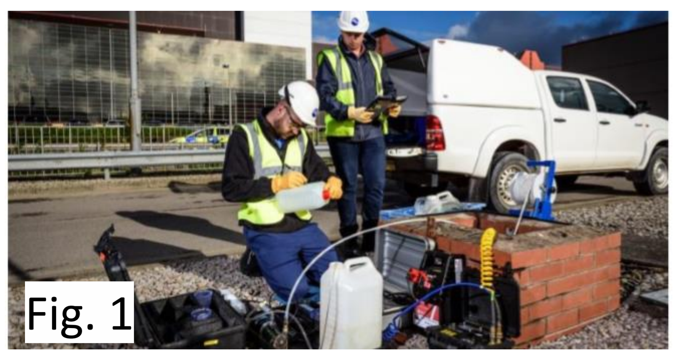


Fig. 1

Standard techniques to site characterization involve sampling from boreholes and subsequent laboratory analysis [1,2].

X Time consuming X Produce secondary waste

X Higher dose to workers X Expensive

Less-intrusive, in-situ measurements can be done with portable logging devices deployed in boreholes/blind-tubes [3].

Sensing Probe + Electronic Modules + Push-rod cable Power/USB cables + Laptop/Software

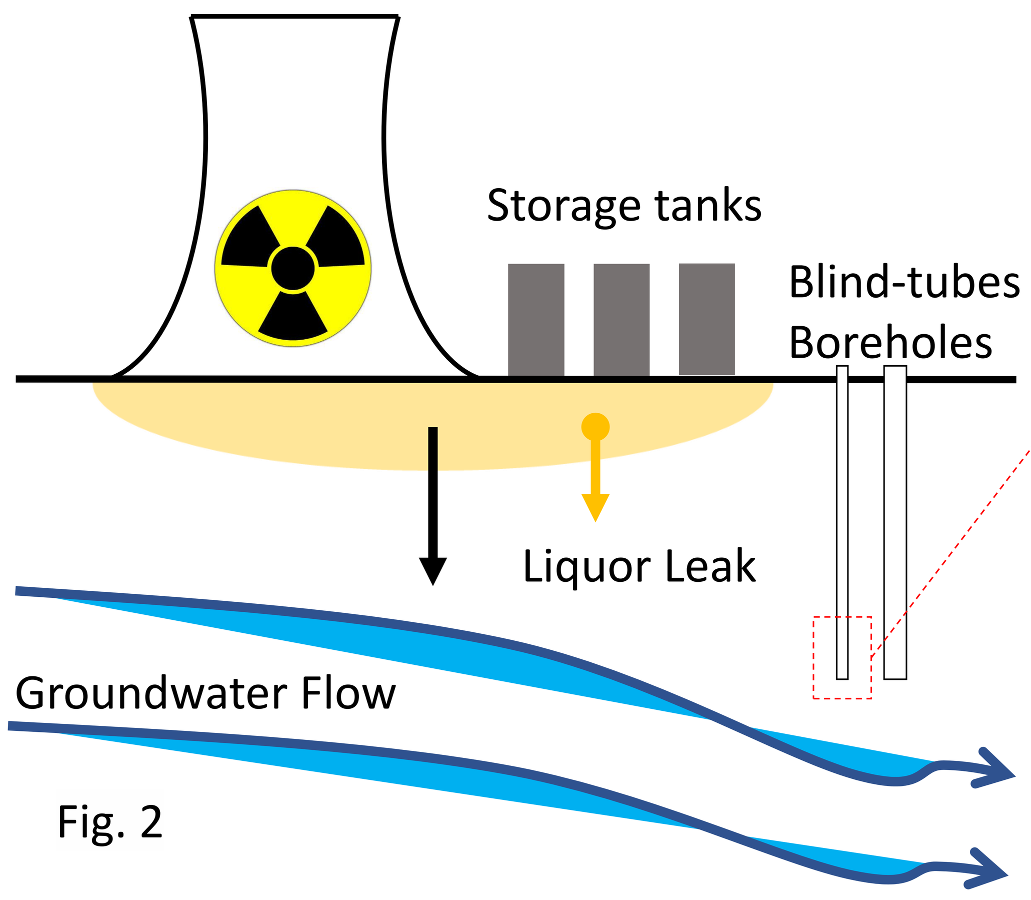
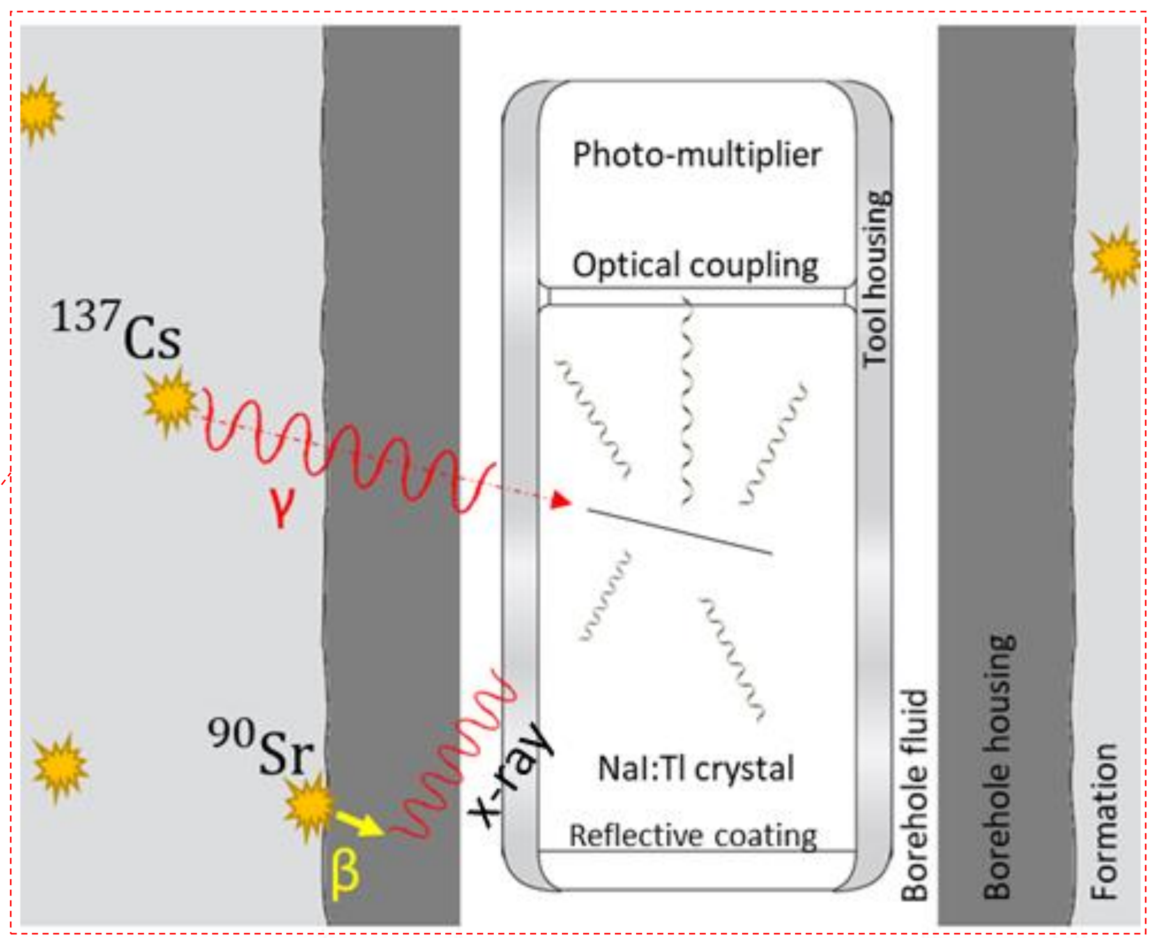


Fig. 2



Aim of this project

Research, design and test an in-situ leak detection system:

1. To use as a portable depth characterization tool.
2. For long-term monitoring of ground contamination.
3. To yield a degree of spectroscopy to identify **Cs-137** and potential **Sr-90**.

Current technology

Sensing Probe	Observations [4]
GM Tube	✓ Identifies trends in activity over the time X Has no ability to speciate signal
NaI:Tl	✓ Identifies trends in activity over the time ✓ Speciate dominant radionuclides ✓ Cheap and well characterised technology X Has low energy resolution X Saturates in high dose rates
HPGe	✓ Has high energy resolution ✓ Cleary speciate radionuclides X Operate at low temperature X Operate for short periods of time X Does not fit in blind-tubes
CdZnTe	✓ Has moderate energy resolution ✓ Speciate radionuclides X Limited life in high dose environments

Performance criteria

- → Robust to the effects of high-dose environments (1Gy/h).
- → Compatible with the size of existing blind-tubes (min Ø 75 mm).
- → High levels of energy resolution.
- → Resilient to harsh environmental conditions.

Potential solution

SCINTILLATOR CRYSTAL DETECTORS [5-11]

KEY PARAMETERS	NaI:Tl	LaBr3:Ce	**CeBr3**	CLYC:Ce (Cs2LiYCl6:Ce)	CLLB:Ce (Cs2LiLaBr6:Ce)	GAGG:Ce $Gd_2Al_2Ga_3O_{12}$:Ce
Detection efficiency Zeff; ρ [g/cm3]	51; 3.7	47; 5.1	46; 5.2	54; 3.3	47; 4.1	54; 6.7
Energy resolution FWHM @ 662-keV	6.5 – 10 %	2.5 – 3 %	3.2 – 4 %	4.5 – 5 %	2.9 – 3.5 %	4.5 – 4.8 %
Radiation hardness Dose [Gy] @ Gamma-ray	10^1	10^5	10^5	?	?	10^3
High count-rate capability Decay time [ns]	230	16	17	1 50 1000	120 500	88
Hygroscopic	Yes	Yes	Yes	Yes	Yes	No

Laboratory experiments/simulation

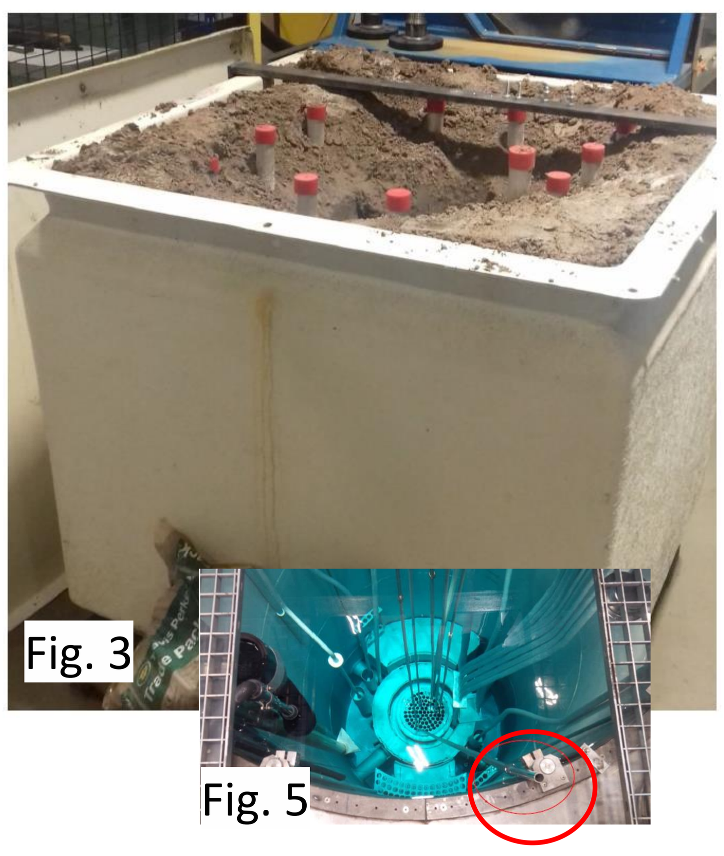


Fig. 3

Fig. 5

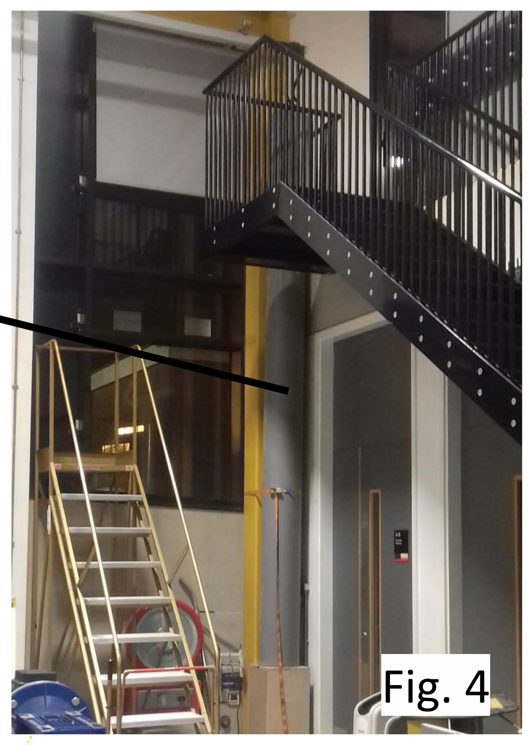


Fig. 4

GEANT4 A SIMULATION TOOLKIT

Research plan

Develop statement of requirements

Set up laboratory based tests (Fig. 3, 4)

Set up outdoor field tests (Sellafield site)

Look for the ideal sensing probe

Test its resilience (Fig. 5)

References

[1] Groundwater monitoring at Sellafield: Annual data review 2016. Sellafield Ltd
[2] Savana River Site Environmental Report for 2017, Chapter 7
[3] Guidelines for radioelement mapping using gamma ray spectrometry data 2003. IAEA
[4] Official documents given by Sellafield Ltd
[5] https://www.crystals.saint-gobain.com/
[6] https://www.x-zlab.com/product/
[7] https://johncaunt.com/materials/
[8] https://scionix.nl/scintillation-crystals/#tab-id-8
[9] S. Ihantola *et al* (2018), doi: 10.2760/703301
[10] M. Yoneyama *et al* (2018), doi: 10.1088/1748-0221/13/02/P02023
[11] W. Drozdowski *et al* (2008), doi: 10.1109/NSSMIC.2008.4774965

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Predicting Gamma Dose Rates with Limited Information

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Project Overview

It is essential that buried and potentially contaminated structures can be quantitatively assessed to facilitate future decommissioning of nuclear sites. This PhD, funded by the Nuclear Decommissioning Authority, will seek to develop a robust methodology to predict gamma dose rates in contaminated pipes based on limited direct information.

The project objective is to minimise and, where possible, avoid intrusive sampling and analysis whilst still acquiring sufficient information to justify management options for radioactively contaminated underground pipes and other structures at UK nuclear sites.

Use of a waste pipe due for decommissioning at Winfrith nuclear power station has already been agreed. Data will be collected from both representative laboratory tests and field trials completed at Winfrith. Spectral analysis will draw on a range of signal processing techniques to improve dose rate confidence.

This PhD consists of 4 primary interconnected avenues of research.

- Lab-based experiments will be used to explore and later verify the attenuating effects of soil when detecting gamma rays.
- Simulations of pipes at Winfrith will be created using data from the lab-based experiments.
- Field-based experiments will gather data with unknown sources of radiation to identify and make dose rate calculations.
- Signal analysis techniques will be used to identify radioisotopes present in the data collected from the field. It is also expected that these photopeaks will have low signal to noise ratios so identifying these peaks will be a non-trivial process.

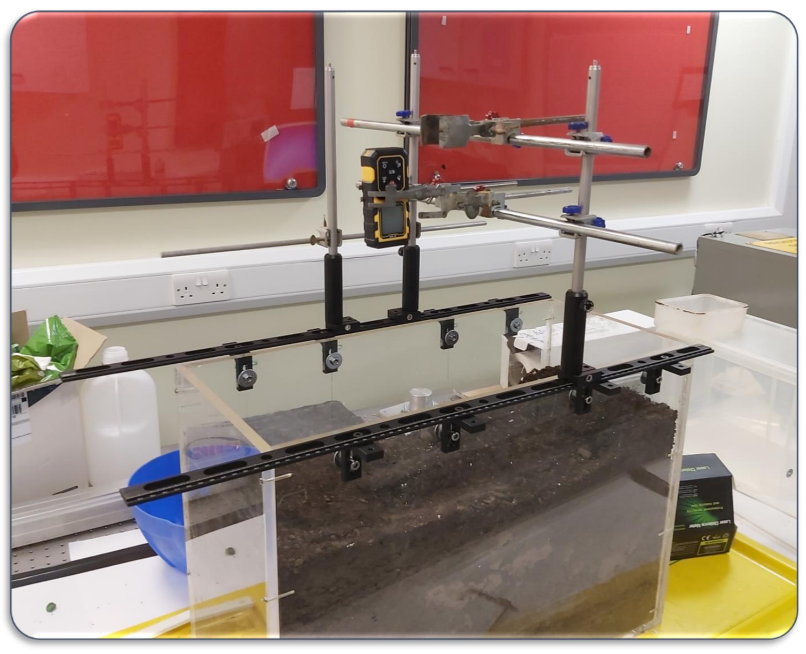

Figure 1: University of Surrey soil tank used for preliminary experiments exploring measurable gamma signals from buried sources.

Depth Study Experiment

Initial data has been taken to explore the attenuating properties of soil in gamma spectroscopy. To conduct this experiment a scintillator with a 2" diameter NaI crystal was mounted above a tank of soil. A ^{137}Cs source was buried at various depths and a spectrum was built up over 1 hour at each depth. The experiment was also repeated in air and 3 background spectra were taken, averaged and subtracted from both the soil and the air results. The 662 keV peak for these results can be seen to the right.

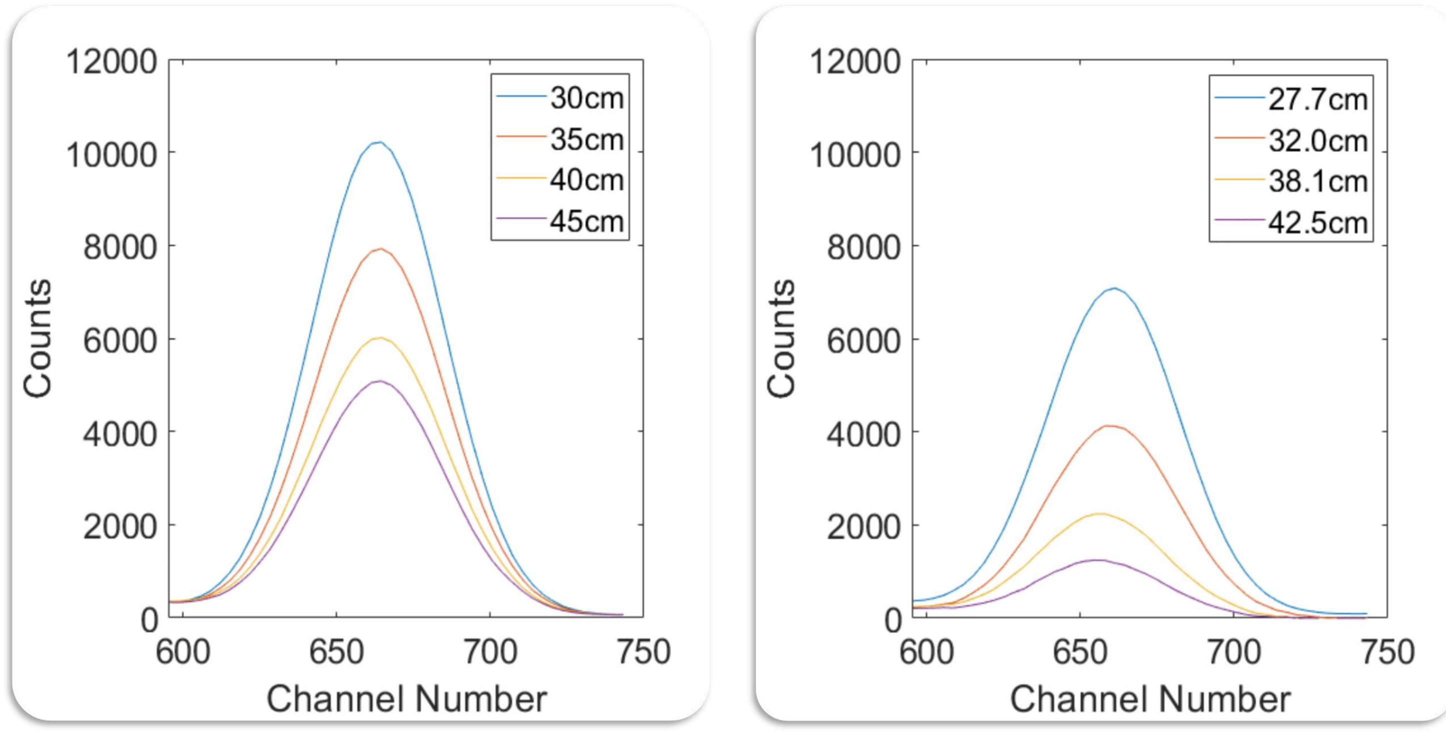

Figure 2: Left: ^{137}Cs, 662 keV peak at increasing detector to source distance in air. Right: the same experiment and photopeak repeated in soil.

The results of this experiment show a significant decrease in the number of counts detected at each depth. This data will be used to validate simulations of the pipe created in GEANT4. GEANT4 uses Monte Carlo methods to simulate the passage of high energy particles through matter. By validating future models with lab-measured data, the model can then be adapted to simulate realistic structures such as the pipe at Winfrith power plant. Finally, the spectra measured from this experiment can also be used to begin development of a program to identify weak photopeaks with low signal to noise ratio.

Wavelet Analysis

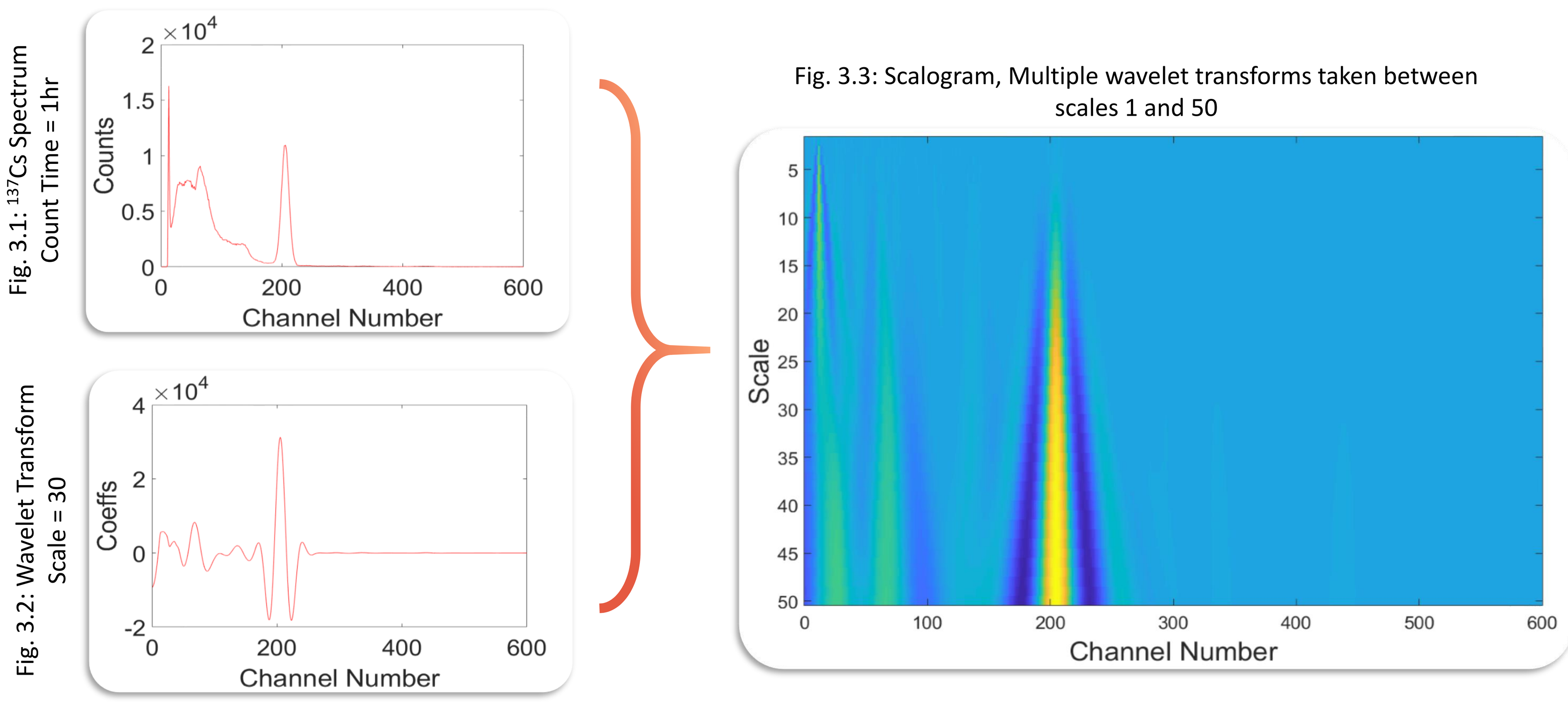

Figure 3: A diagram showing the creation of a scalogram through multiple wavelet transforms "stacked" on top of each other.

It is expected that spectra collected from the pipe at Winfrith will have a low signal to noise ratio and therefore signal processing techniques may add value in peak identification and dose rate calculations. Wavelet transforms show potential in creating a solution to this problem being capable of identifying events within a spectrum with a given full-width half-maximum by tailoring the range of scales selected for the transform. The equation for a wavelet transform is below where *T(E,s)* is the coefficient value, *f* is the function and *Ψ* is a wavelet. A wavelet is a finite wave starting from an amplitude of 0, increasing, then returning to 0. There are many types of wavelet each with difference use cases, *Sullivan et.al.* have determined that a biorthogonal wavelet (Bior2.6) is the most suited to determining the location of gamma peaks [1].

$$T(E,s) = \int f(t)\Psi^{*}_{E,s}(t)dt$$

Scales can be thought of as a pseudo frequency for the wavelet. By selecting a range of scales to wavelet transform it is possible to greatly reduce unwanted features from a gamma spectrum. Noise, for example can be thought of as a very high frequency feature. By avoiding scales better at picking up these features these unwanted events can be minimised in the scalogram. This can be seen in figure 3.2 where the 662 keV peak at channel 210 (seen in figure 3.1) produces significantly larger coefficient values than the x-ray at channel 10 even though more x-rays have been detected.

[1] Clair Sullivan, M.E. Martinez, and S.E. Garner. "Wavelet Analysis of Sodium Iodide Spectra". J NUCL SCI TECHNOL, (Nov. 2006), 2916–2922

Initial Results

A program has been developed to identify low signal to noise ratio peaks using a biorthogonal wavelet approach. In order to detect these peaks wavelet transform modulus maxima lines (WTMM lines) are identified by taking the local maxima of the modulus of each wavelet transform. Gaussian like distributions like associated photopeaks produce straight WTMM lines and a least squares regression can then be used to create a lines of best fit for these. The highest r^2 values should be for WTMM lines created as a result of a gaussian like features. Lines with an r^2 value lower than a user defined threshold can be deemed a product of noise and removed.

Figure 4 shows the first results of this program. A NaI scintillator was suspended over the soil tank for 1 hour with the only sources in the room being ^{137}Cs and ^{152}Eu kept in lead-lined containers in a safe approximately 1 meter from the detector. The r^2 filter managed to eliminate all the unwanted WTMM lines and, by taking the x-value of the intersection of these WTMM lines the peak locations of ^{137}Cs and naturally occurring ^{40}K (with a peak height of only ~60 counts) were able to be detected, the detected peaks locations are shown in figure by the vertical lines.

This result shows the potential of wavelet analysis in determining low signal to noise ratio peaks. However, it should be noted this result required the manual adjustment of the threshold r^2 value used to filter the results and the manual selection of scales. Improvements will be made to make the program more "robust", capable of automatically detecting the optimal scale range to use as well as applying additional filters

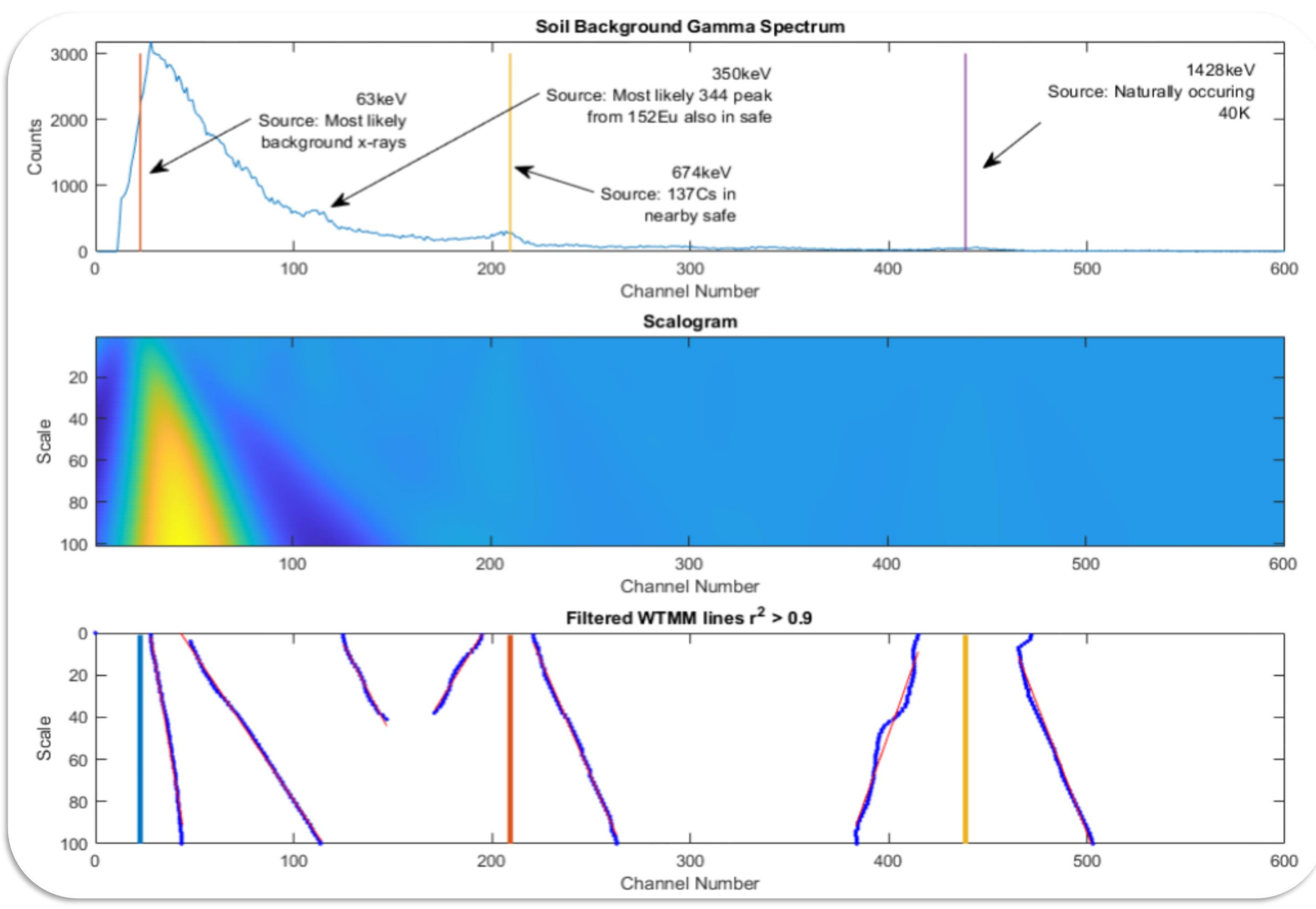

Figure 4: Initial results of the peak detection program where the blue lines are WTMM lines and the vertical lines show detected peaks

Assessing the strength of biomineral strategies for concrete repairs

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Problem Introduction

- It is a challenge for modern Civil Engineers to monitor and repair deteriorating concrete infrastructure.
- Many concrete assets in the UK are past their original design life and have an increased risk of failure.
- The rate of concrete degradation on individual structures is highly variable.
- Concrete structures (ports, roads, bridges, buildings) have been exposed to a unique combination of environmental conditions resulting in the degradation and cracking of the concrete.

Project aims

Aim: To model and evaluate the strength of the biomineral concrete repair strategy, Microbially Induced Calcite Precipitation (MICP) being developed at the University of Strathclyde.

Objective 1: To repair degraded concrete cores in the laboratory and compare their strength against more traditional repair techniques.
Objective 2: To develop a numerical model to simulate the mechanical behavior of the MICP-repaired concrete.
Objective 3: To improve the design of the repair strategy and provide information for field trials conducted in year-3 of the PhD.

Microbially Induced Calcite Precipitation

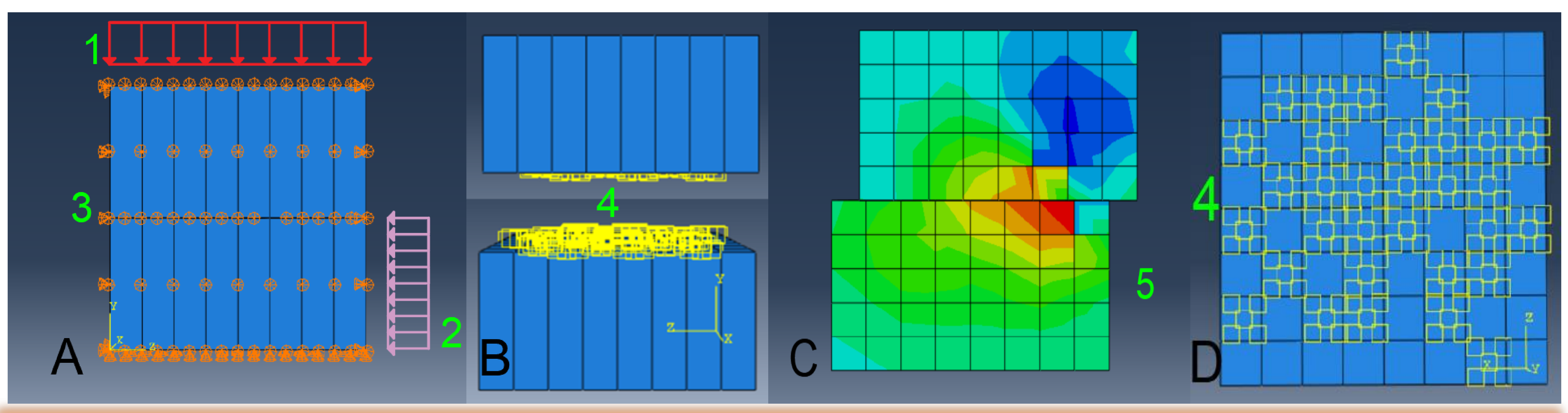
- The biomineralization process used in this research is Microbially Induced Calcite Precipitation (MICP) via urea hydrolysis.
- Firstly, this process depends on a ureolytic bacterium (like sporosarcina pasteurii) that hydreolyzes urea into ammonia and carbonic acid.
- Secondly, what follows is the production of ammonium ions and an increase in the pH around the bacterial cell.
- Then as the pH rises, bicarbonate ions (formed by carbonic acid) create carbonate ions, which in the presence of calcium ions lead to the precipitation of calcite.[1]
- No research has yet modelled the mechanical performance of MICP-repaired concrete. Such a model could be used to inform treatment strategies.

Mesoscale modelling - FEM

- Mesoscale modelling of concrete is being performed by conceptualizing a fractured core as a composite material under various loading conditions.
- A Finite-Element model has been constructed, which gives a good representation of the MICP-repair under shear failure.

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.*

1: Vertical Load
2: Boundary Condition: Velocity
3: Horizontal fracture
4: Calcite distribution on rock's surface
5: Displacement



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References

1. El Mountassir et al., 2013, *Water Resources Research*, https://doi.org/10.1002/2013WR013578
2. Whiffin et al., 2007, *Geomicrobiology Journal*, http://dx.doi.org/10.1080/01490450701436505
3. Chu et al., 2013, *Geotechnique*, *http://dx.doi.org/10.1680/geot.SIP13.P.007*
4. Minto et al., 2016, *Water Resources Research*, https://doi.org/10.1002/2016WR018884

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