

Inhibiting radionuclide migration using colloidal silica grout

Arianna Gea Pagano, University of Strathclyde TRANSCEND/NDA/NWDRF Virtual Conference







What is colloidal silica?







What is colloidal silica?



What triggers gelling?

- Electrolyte accelerator
- Change in pH
- Temperature



Colloidal silica treatment for repair of degraded cementitious waste packages

Cement encapsulation of ILW:

- Favoured waste disposal method for ILW in the UK
- Cement provides good shielding against radionuclide migration



 Radioactive waste embedded into a <u>cementitious matrix</u> by pouring grout into 500 L stainless steel drums



Colloidal silica treatment for repair of degraded cementitious waste packages

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Colloidal Silica treatment for waste packages repair

Colloidal silica reactivity with cement

Colloidal silica injection through cement cracks



Abundance of calcium ions within the cracks deriving from cement hydration (portlandite, Ca(OH₂))





Colloidal Silica treatment for waste packages repair

Experimental programme: fractured cement cores for CS treatment

1. Natural fracture network (1 core)



2. Single vertical fracture (multiple cores)

Brazilian tensile splitting test (BTS)







Colloidal Silica treatment for waste packages repair

Experimental equipment for CS treatment

Core-holder setup, used to:

- measure core's permeability ٠
- treat core with colloidal silica •





Colloidal Silica treatment for waste packages repair

Experimental equipment for CS treatment (2)





Colloidal Silica treatment for waste packages repair

Experimental equipment for CS treatment (3)





Colloidal Silica treatment for waste packages repair

Experiment 1: natural fracture network Fracture network creation



The intact core was placed in a loading frame and cracked by performing a UCS test. The applied force was continuously measured during the test to derive the compressive strength of the intact core.





Colloidal Silica treatment for waste packages repair

Experiment 1: natural fracture network

Colloidal silica treatment

1. Colloidal silica grout injection



- 2. Curing stage (72 hours, 20°C)
 - 72 hours, 20°C within core-holder



• \geq 1 month, 20°C submerged in water



Colloidal Silica treatment for waste packages repair

Experiment 1: natural fracture network

Results (1): Microstructural analysis



X-CT 3D phase reconstruction



Cross-sections before and after



Colloidal Silica treatment for waste packages repair

Experiment 1: natural fracture network

Results (2): Permeability reduction



Treatment with colloidal silica resulted in a permeability reduction of two orders of magnitude compared to the permeability of the fractured core before treatment.



Colloidal Silica treatment for waste packages repair

Experiment 1: natural fracture network

Results (3): Strength recovery



The treated core was placed in a loading frame and cracked by performing a UCS test. The core recovered about 40% of its initial strength (UCS of intact core) after treatment with colloidal silica grout.





Colloidal Silica treatment for waste packages repair

Experiment 2: single vertical fracture





Colloidal Silica treatment for waste packages repair

Experiment 2: single vertical fracture

Brazilian tests results before and after treatment with colloidal silica



→ Strength recovery between 20% and 93% of average tensile splitting strength of intact cores!



Colloidal Silica treatment for waste packages repair

Experiment 2: single vertical fracture

Brazilian tests results before and after treatment with colloidal silica





Colloidal Silica treatment for waste packages repair

Experiment 2: single vertical fracture

Brazilian tests results before and after treatment with colloidal silica





Colloidal Silica treatment for waste packages repair

Next steps

- 1. Secondary-Ion Mass Spectrometry (SIMS) for C-S-H detection
- 1. Spike colloidal silica grout with D_2O



2. SIMS for C-S-H detection





Colloidal Silica treatment for waste packages repair

Next steps

2. Cement mix for ILW cement encapsulation

Current cement mix

 Ordinary Portland Cement (CEM II/A-L, class 42.5N), w:s = 0.375 by weight Cement mix for future experiments

Blast furnace slag (BFS) + Ordinary Portland Cement mix:

- SL 3:1 BFS:PC mix, w:s = 0.35
- BEP formulation of 5:1 GGBS:CEM I at a w/s ratio of 0.5



Thank you

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Electrokinetic Remediation and Combination with Colloidal Silica Grouting

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Transformative Science and Engineering for Nuclear Decommissioning

Electrokinetic Remediation, EKR



 $H_2O \rightarrow 2 H^+ + \frac{1}{2}O_2(\uparrow) + 2 e^-$ E⁰ = - 1.229 ∨

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



Advantages of EKR

• In-situ (or ex-situ)

Worker safety



• Cheap



Adaptable

Electrode material Electrode placement Electrolyte Voltage Additives Duration (In-)organic + radionuclide Combination (EKR-Bio...)



EKR for Nuclear Decommissioning



57 La Lanthanum 138.90547	58 Cerium 140,756	59 Praseodymium 140.90765	60 Nd Neodymium 144.242	Promethium	62 Sm Samarium 150.36	63 Europium 151,964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162,500	67 Ho Holmium 164.93033	68 Erbium 197259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
Actinium (227)	90 Th Thorium 232.0377	Protactinium 231.03588	92 Uranium 238.02891	93 Np Neptunium (237)	94 Plutonium (244)	95 Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	Fermium (257)	101 Md Mendelevium (258)	Nobelium (259)	Lawrencium

Red further testing; Yellow demonstrated, not widespread; Diagonal yellow demonstrated, not on radionuclide; Green multiple studies. (t_{1/2} < 1 y excluded)



EKR for Nuclear Decommissioning

		TRL for nuclear	Duration?	Cost?	Comments	How can EKR help?
EKR	4	4 - 6	Variable	Low	✓ Flexible✗ Unproven	
Bio-						Factor
and		5 - 7	High	Low	✓ Sustainable✓ Slow	nutrient
Phyto-						movement
ISCO		4 - 6	Low	Variable	✓ Quick✗ Permeability	<i>In-situ</i> barrier generation (FIRS)
Colloids	Turk	5 +	Variable	High	✓ Immobilisation✗ Unproven	Colloidal Silica?



Ferric Iron Remediation and Stabilisation



Purkis et al., manuscript in prep.; Cundy et al., Appl. Geochem., 2005, 20, 841



Case Study – FIRS

- Metre scale in simulated materials
- In-situ barrier growth in real materials?
- Sellafield sand + simulant groundwater
- Steel electrodes
- Vary:
 - Electrode placement
 - Voltage
 - Duration
- Monitor:
 - Barrier over time
 - pH
 - Sorptive properties, etc...





Case Study – FIRS

- *In-situ* barrier growth in soil subsurface?
- Sellafield sand + simulant groundwater
- Steel electrodes
- Vary:
 - Electrode placement
 - Voltage
 - Duration
- Monitor:
 - Barrier over time
 - pH
 - Sorptive properties, etc...





Colloidal Silica Grouting

• (Nano)-Particulate SiO₂



• Gelate with accelerant (NaCl)



Dallari et al., Sci. Adv., 2020, 6, eaaz2982; Wong et al., Eng. Geol., 2018, 243, 84



Colloidal Silica Grouting + EKR

• Inject into contaminated soil

• Impermeable (10⁻¹⁰ – 10⁻⁸ m.s⁻¹)



Sand before (L) and after (R) grouting

• Trap radionuclides – combined approach?





"Valley of Death"

- EKR limited at scale
- Stakeholder engagement?
 - Decision support tools







EKR Decision Support Tools



Purkis, Hemming, Warwick, Graham, Cundy, submitted to J. Haz. Mater.



Conclusions and Acknowledgements

- EKR: *in-situ*, cheap, flexible ۲
- Limited at scale
- **Combined** approaches ullet
 - FIRS: iron barriering
 - Electro-grouting: colloidal Si
- Both impermeable (10⁻⁹ m.s⁻¹), sorptive •
- DSTs to avoid "valley of death"? ۲



















Case Study 2 – Fukushima Simulant

<u>Fukushima, 2011</u>

~ 3 PBq ¹³⁷Cs & ⁹⁰Sr in soil (30 km) 160,000 t soil at > 8 KBq/kg (2014) \$50 – 150 billion (2016)





[¹³⁷Cs], Japan, 19/04/2011 Fukushima: 11/03/2011

PNAS, 2011, 108, 19530; Environ. Sci. Technol., 2014, 48, 13053; J. Environ. Radioactiv., 2016, 151, 512


Case Study 2 – Fukushima Simulant

- 6:1 clay-peat soil (TOC = 11.6 %, pH 5.4)
- 15 or 20 V (0.5 V/cm) \rightarrow low energy EKR
- Monitor: pH
 [Cs] and others by XRF







Case Study 2 – Fukushima Simulant

- 6:1 clay-peat soil (TOC = 11.6 %, pH 5.4)
- 15 or 20 V (0.5 V/cm) \rightarrow low energy EKR







220 330 440 550 660 770

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Predicting Gamma Dose Rates from Underground Contaminated Structures with Limited Information

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University of Surrey Transcend Virtual Conference







Project Overview

- Develop a non-intrusive method to analyse gamma signals from underground contaminated pipes to TRL: Level 6
- Identify radioisotopes present within gamma signals
- Determine dose rate at a given depth for a given structure



https://en.wikipedia.org/wiki/Technology_readiness_level



Project Overview

- Develop a non-intrusive method to analyse gamma signals from underground contaminated pipes to TRL: Level 6
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Key Challenges

- Large, unknown distances between the contaminated structure and detector
- Multiple, unknown numbers of isotopes present within the contaminated structure
- This results in low signal to noise ratio gamma spectra with overlapping photopeaks





Wavelet Analysis: Theory

- Wavelet analysis offers a method of identifying the location of low SNR signals in photopeaks
- A wavelet is a short wave-like oscillation with an amplitude that begins and ends at 0
- Transforms a signal into the energy scale domain
- Scale is a "pseudo wavelength" for a wavelet, small scales respond strongly to high frequency events such as noise. Large scales respond to lower frequency events such as photopeaks.
- Performing multiple wavelet transforms over a range of scales creates a scaleogram which is used for analysis

https://en.wikipedia.org/wiki/Continuous_wavelet_transform

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



Wavelet Analysis: Results



Maxima Lines

White lines on the scaleogram are the local maxima of each transform

Interpreting the Scaleogram

- Shorter lines at low scales represent noise
- Larger lines correspond to larger features e.g. photopeaks and the Compton continuum



Wavelet Analysis: Results



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, any line wholly above the red line corresponds to a feature too thin to be a photopeak



Analysis





Identifying Isotopes

- A machine learning algorithm is in development to convert the output from the wavelet program into a prediction of isotopes present in a spectrum
- Supervised ANN's require a large training set. Collecting these spectra experimentally would be impractical
- To address this, a GEANT4 simulation has been used to create this training set





Creating the Training Set

- A training set of 5000 spectra was created
- The training set was comprised of ¹³⁷Cs, ⁶⁰Co and ⁴⁰K
- Equal numbers of each of the 8 possible combinations of isotope were created
- This training set was used to train a neural network by inputting the normalised counts for each channel
- The set was then wavelet analysed and used to train a second neural network for comparison





Results: Neural Networks

 Normalised Counts Network
 Simulated Data Accuracy: 85%
 Experimental Accuracy: 0%

 Wavelet Analysed Network
 Simulated Data Accuracy: 75%
 Experimental Accuracy: 100%





Conclusions

- The wavelet analysed training set created an algorithm capable of identifying spectra collected experimentally
- By removing information such as noise and the Compton continuum from a training set it might be possible to create a neural network capable of identifying isotopes in spectra collected from various environments
- The testing set used was very small. This was because they were the only available spectra during lockdown when access to the lab was restricted



Future Work

- Quantify the effectiveness of these programs with larger experimentally generated testing sets
- Compare different types of neural network and different levels of "filtering" unhelpful information (noise etc.) from gamma spectra before training a network on the data
- Use these methods on data from an underground contaminated pipe at Winfrith and quantify the effectiveness of these methods against more intrusive sampling methods



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Application of low-energy electrokinetic clean-up techniques to problem nuclear contaminants and sites

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JointNuclear (TRANSCEND/NDA/NWDRF) Virtual Conference 2-3 December 2020





MSci Geology University of Southampton 2016-2020

PhD University of Southampton 2020-2024





 $H_2O \rightarrow 2 H^+ + \frac{1}{2} O_2 (\uparrow) + 2 e^-$ E⁰ = - 1.229 V

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



Difficult to Measure Radionuclides:

•	lodine-129	•	Chlorine-36
•	Technetium-99	•	Carbon-14

Strontium-90
 Tritium



Project Aims

• Apply electrokinetic remediation to:

- Radionuclides with no/few remediation options
 DTMs
- Different materials found at nuclear sites
 - \circ soils, concrete, sludges and other materials



Any questions?

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TRANSCEND/NDA/NWDRF Virtual Conference

2-3 December 2020

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







PhD student: Soraia S C Elisio Academic supervisor: Malcolm J Joyce

Industrial supervisors: James Graham Central Laboratory, National Nuclear Laboratory Ltd. Barrie Greenhalgh Radiometric Systems Group, Sellafield Ltd.







Outline of Presentation

- Context to the problem: why is this important?
- Case study: Magnox Swarf Storage Silo (MSSS)
- Subsurface contamination: current practice
- Challenges and aims
- Possible Solution
 - Radiometric logging detector
 - Concept and components
- Validate and calibrate the system
 - Concept and components
- Future work





CASE STUDY

Magnox Swarf Storage Silo (MSSS) at Sellafield Nuclear Reprocessing Plant

Lancaster Star University





Taken from Priority programmes and major projects performance report (Data as at end September 2015)



Taken from Sellafield Ltd, "The Magnox Swarf Storage Silo: Making our most hazardous facility a safer place," Youtube, 2017

Active ground leaks Maximum anticipated dose rate 1 Gy/h

Rock core samples

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Taken from The Sellafield Contaminated Land and Groundwater Management Project

Water samples



Schematic of a typical groundwater monitoring well



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





Geiger counter

Nal:Tl

CdZnTe

e.g. Preamplifier

e.g. Analog and Digital

Pulse height analysis

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Radiometric logging probes

Borehole geophysical logging



Gamma Radiation Detection System



Gamma log at Maxey Flats site (Keys, 1997)

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CASE

STUDY

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Challenges/aims:

Characterisation of sub-surface contamination within MSSS

Lancaster Star University

- To be deployed in a real environment
- Continuous monitoring system
- Existing in-ground assets:
 - Steel tubes
 - Ø 75 mm
- Sub-surface high radiation levels: 1 Gy/h
- Discrimination of key radionuclides (Gamma-ray photons + Bremsstrahlung photons)



Possible Solution: Gamma Radiation Detection System

Sensing element ----- Sig

NATIONAL NUCLEAR Sellafield Ltd





Scintillation detector Ø10 x 10 mm CeBr₃ (Scionix) Good energy resolution: 4 % @ 662 keV Fast decay 17 ns Radiation hardness up to 100 kGy

Residual intrinsic activity



Quarati, F. G. A. *et all* (2013), Scintillation and detection characteristics of high-sensitivity CeBr₃ gamma-ray spectrometers

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Challenges/aims:

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65 mm

Depth profiles: counts vs depth





Validate the concept and calibrate the system

• Construction of test pipe



- 1. Blind tube (steel)
- 2. Sand retaining tube (plastic) 5. Bas



- 3. 'Void' tubes (plastic)
- 4. Source holders (plastic)
- 5. Base support



Non-toxic pit sand







Validate the concept and calibrate the system

- A. Radiological testing
- A. Temperature dependence, waterproofing, vibration tests, etc
- B. Extension of a single detector to a blind tube string network -> 3D underground mapping
- C. Create a 3D picture of sub-surface heterogeneity within MSSS at the Sellafield site



1 m³ Tank soil



What's next?



GAME CHANGERS



Characterisation and monitoring using in-ground assets Thank you

Hybrid

Soraia Elisio s.elisio@lancaster.ac.uk







Assessing the strength of biomineral strategies for

concrete repairs

Thanos Karampourniotis, University of Strathclyde

Theme 2: Site Decommissioning and Remediation





WHAT IS THE PROBLEM WE ARE ADDRESSING?

- The UK's nuclear infrastructure is ageing and many structures are past their original design life.
- Concrete assets in nuclear sites are exposed to harsh environmental conditions.
- The degradation and cracking of concrete in these sites.
 - We have to guarantee the safety of the structures, until the decommissioning process is completed.

ounces in New Protection, educed the Status

SILE, SOURCE, I NE GUARDA



WHAT THE SOLUTION WE ARE PROPOSING IS

Limitations of the traditional concrete-repair techniques:

Cement: Big particle size, which makes it difficult and not efficient to treat micro cracking.

Resins: A short-term solution in concrete-repair that does not provide any mechanical strength.

Microbially Induced Carbonate Precipitation:

At the University of Strathclyde we are working on a novel concrete-repair strategy which focuses on bringing concrete to its original condition.

A long-term repair technique that can:

- Decrease concrete's permeability
- Increase its mechanical strength.



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THE AIMS OF THIS PHD ARE

- To help repair concrete structures in nuclear sites so that they are fully functional and safe for the duration of the decommissioning process.
 - To help with the research the University of Strathclyde is conducting on bio-mediated repair techniques.
 - To contribute to the field trials that will take place at docks located in Devonport, Plymouth
- To develop a modelling strategy, validate it and show it can predict the mechanical behavior of MICP-treated concrete.
 - To optimize the repair strategy which is investigated.



| cavendish | nuclear



Degraded concrete in Devonport

3 December 2020



MICP VIA UREA HYDROLYSIS




FINITE ELEMENTS MODEL

During the first year of this PhD research:

A Finite Elements Model using the meso-scale approach has been developed and calibrated against experimental results.

The experimental results are extracted from Dominique Tobler's (2018) research and used to calibrate the Finite Elements Model.

This model has been used to explore the importance of the calcite (calcium carbonate) geometry on the final shear strength of the repair.



GRANITE CORES AND BSE IMAGING





Calcite crystals bridged the fracture after the MICP treatment was implemented



BSE imaging of the 4th granite core that was treated with the MICP repair technique



DIRECT SHEAR TESTING



Shear Load System 5 mm Minimum Shear Load System 5 mm Minimum Fincopsulating Material Rock Specimen Test Harizon Horizontal displacement Specimen Holding Ring Rollers



Direct shear box

Schematic test setup

After the direct shear test



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

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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





CALIBRATION OF THE MODEL - MESH DEPENDENCY

FG2 Core







CALCITE DISTRIBUTION STRATEGIES

DIFFERENT CALCITE



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Yellow elements: Cohesive behavior assigned

Purple elements: Frictional behavior assigned



DIFFERENT AMOUNT OF CALCITE CONNECTING THE TWO REGIONS



"Random distribution" of calcite

"Pillars distribution" of calcite models





CONCLUSIONS

- A Finite Elements Model has been developed and calibrated against experimental data, showing that it can predict the behavior of the experimental cores.
 - 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.



FUTURE WORK

Design and conduct our own experiments using the MICP repair strategy using concrete specimen in:

- Tensile testing
- Compressive testing
 - Shear testing

And compare the obtained results with the ones that the Finite Elements Model provides us with.



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Thank you

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