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# Radionuclide transport in barrier materials

Gianni F. Vettese<sup>1\*</sup>, Mallory Ho<sup>1</sup>, Paula Keto<sup>2</sup>, Suvi Lamminmäki<sup>2</sup>, Emmi Myllykylä<sup>2</sup>, Minna Vikman<sup>2</sup> & Gareth T. W. Law<sup>1</sup>

<sup>1</sup>The University of Helsinki, Radiochemistry Unit, Helsinki, Finland

<sup>2</sup>VTT Technical Research Centre of Finland, Helsinki, Finland



# VLLW Disposal Concept

- VLLW - LILW currently disposed of in VLLJ caves 60-100 m underground (Olkiluoto).
- VLLW includes **operational & decommissioning waste / radionuclides with short half lives** ( $\sim 30$  y *i.e.*  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ) that will decay to stability in a few hundred years.
- **Finnish Nuclear Energy Act (990/1987) permits storage of VLLW in Near-surface repositories.**
- Significant **cost savings** vs. geological disposal.
- Demanding near-surface conditions affected by seasons and climate change.

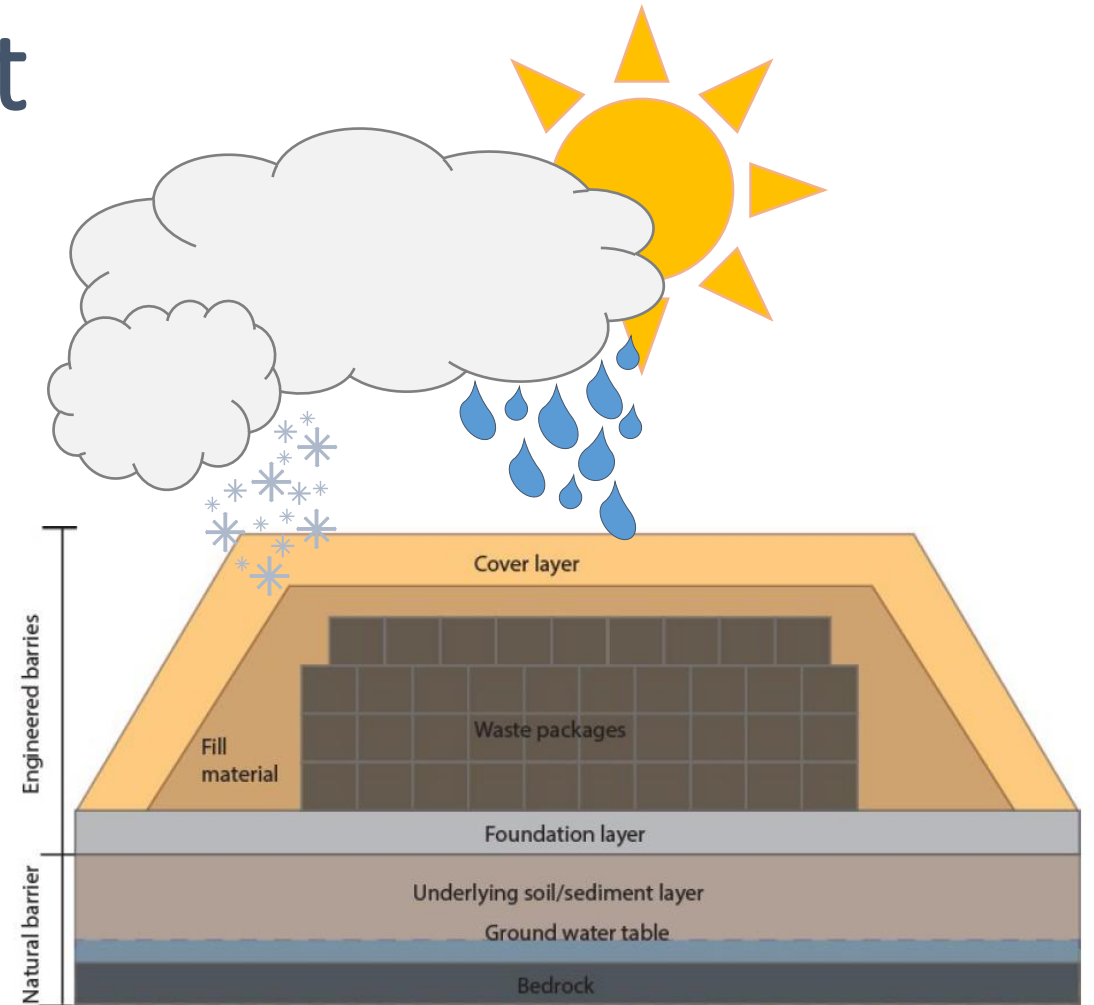


Illustration of a landfill-type near-surface repository.



# Aims and Objectives

## Develop a robust and repeatable experimental system which enables:

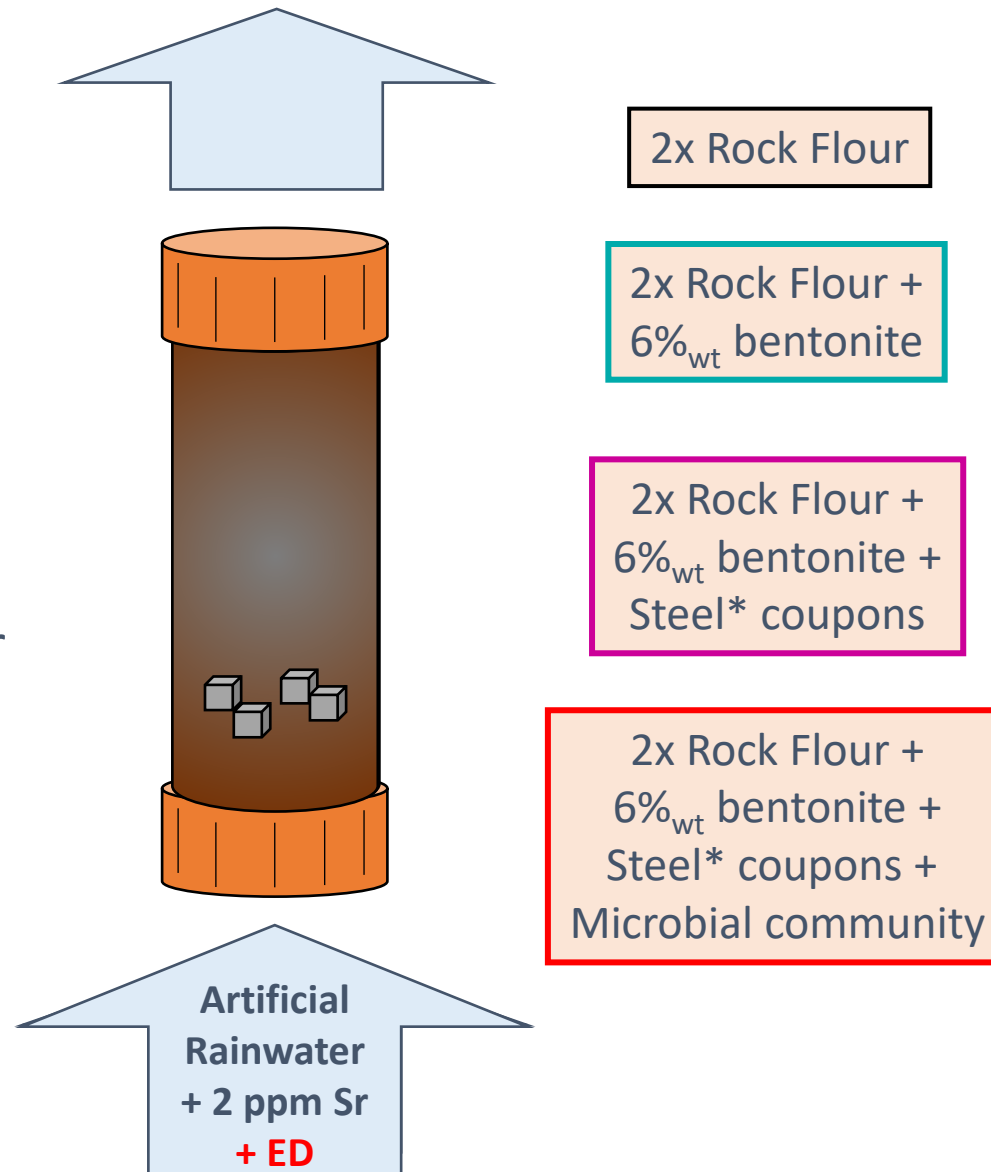
- **Task 1:** Study the **transport** and /or potential **retention mechanisms**, and speciation of key, risk-driving radionuclide(s) ( $^{90}\text{Sr}$ ) in selected barrier materials, considering the conditions prevailing in a Finnish near-surface repository.
- **Task 2:** Study the **evolution of the engineered barrier(s)** (corrosion, microbial activity, organic matter degradation) under the conditions that would be expected in a Finnish near surface repository.
- **Task 3:** Provide results on the performance of the selected near-surface disposal concept and engineered barriers that **can be applied in the safety case** and optimisation of the Finnish near-surface repositories.





# Methodology

- 4 progressive experimental systems representative of barrier materials.
- Established column experiments set up [1,2].
- Columns (vs batch microcosms) better environmental representations:
  - Open flowing systems
  - More realistic solid : solution ratios
  - More appropriately packed materials
- Significant timescales (~300 day)

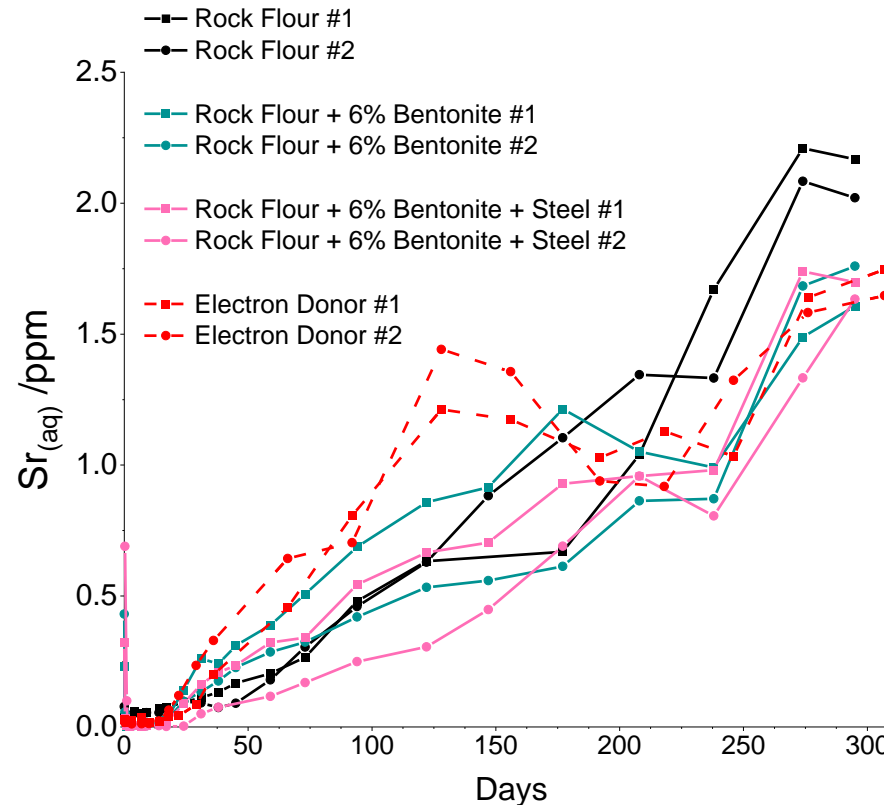


Rainwater Recipe	
Species	mg/L
K <sup>+</sup>	0.76
Ca <sup>2+</sup>	0.67
Sr <sup>2+</sup>	1.80
Na <sup>+</sup>	1.15
Br <sup>-</sup>	4.00
Mg <sup>2+</sup>	0.30
SO <sub>4</sub> <sup>2-</sup>	3.84
pH	5



# Aqueous Analyses

- **Sr well retained across all systems.**
- **Bentonite addition increases Sr sorption capacity ~20%.**
- Microbial activity has little effect on Sr retention.
- **pH equilibrates to ~6.5 in abiotic experiments.**
- **Microbial activity causes increase to ~7.5.**
- **No evidence for colloid formation.**



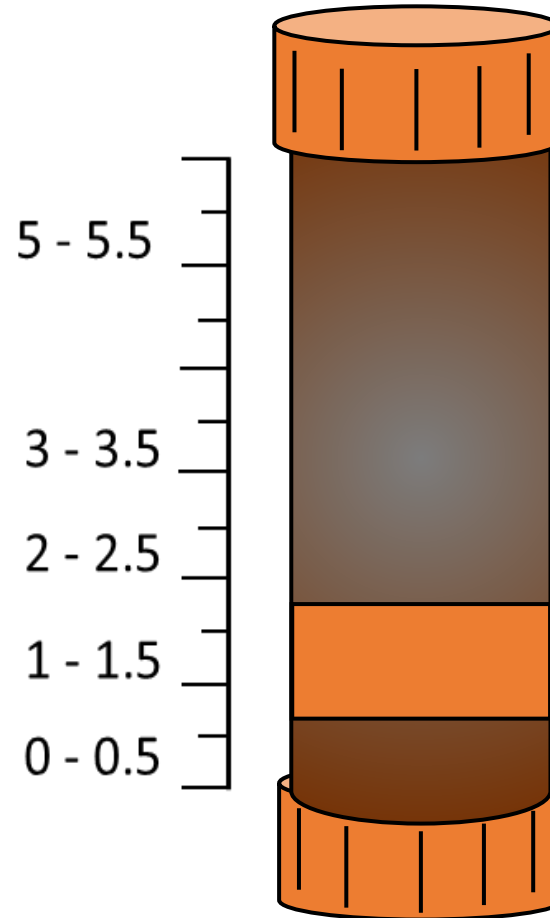
Sr in effluent: **(black)** rock flour, **(green)** rock flour + bentonite, **(pink)** rock flour + bentonite + steel coupons and **(red)** rock flour + bentonite + steel coupons + electron donor amended.

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# Experimental End-Point

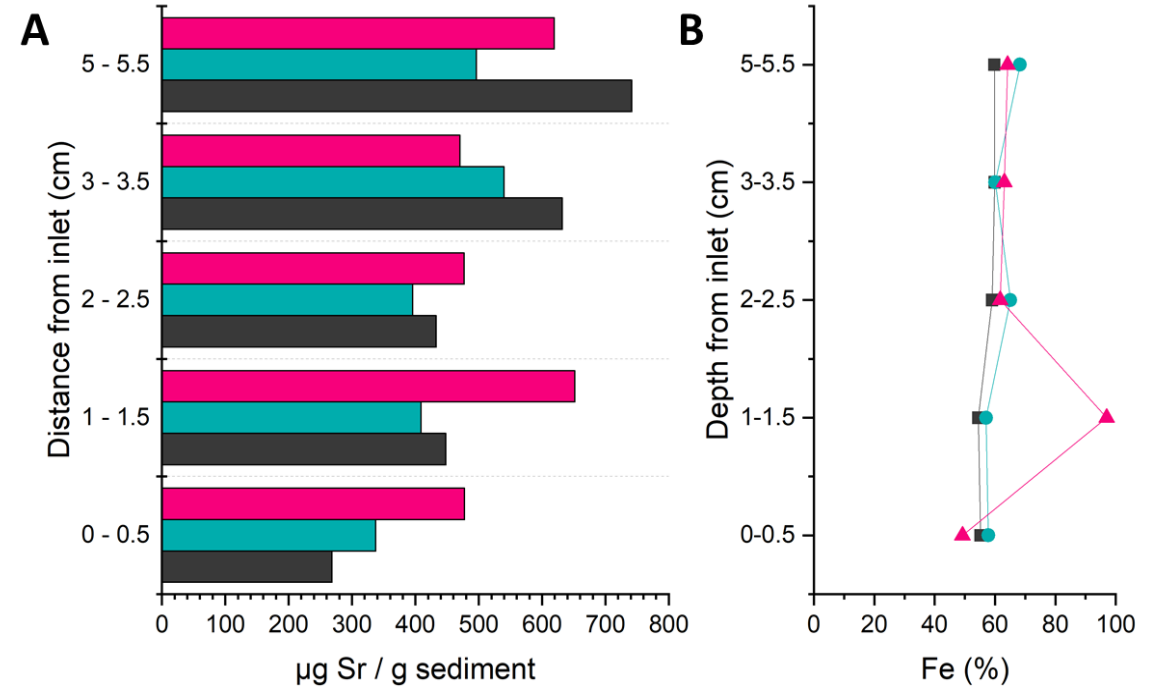
- After ~300 days, **1** of each column is section and preserved for **analysis**.
- **1** column used for **remobilisation** studies.
- Steel corrosion observed (mild steel: EN 10130/AISI 1008).





# Experimental End-Point

- *Aqua-regia* digests show **Sr was evenly distributed throughout each column\***.
- [Sr] 250-750  $\mu\text{g Sr / g}$  solids.
- Fe(II) content increased where steel coupons were.



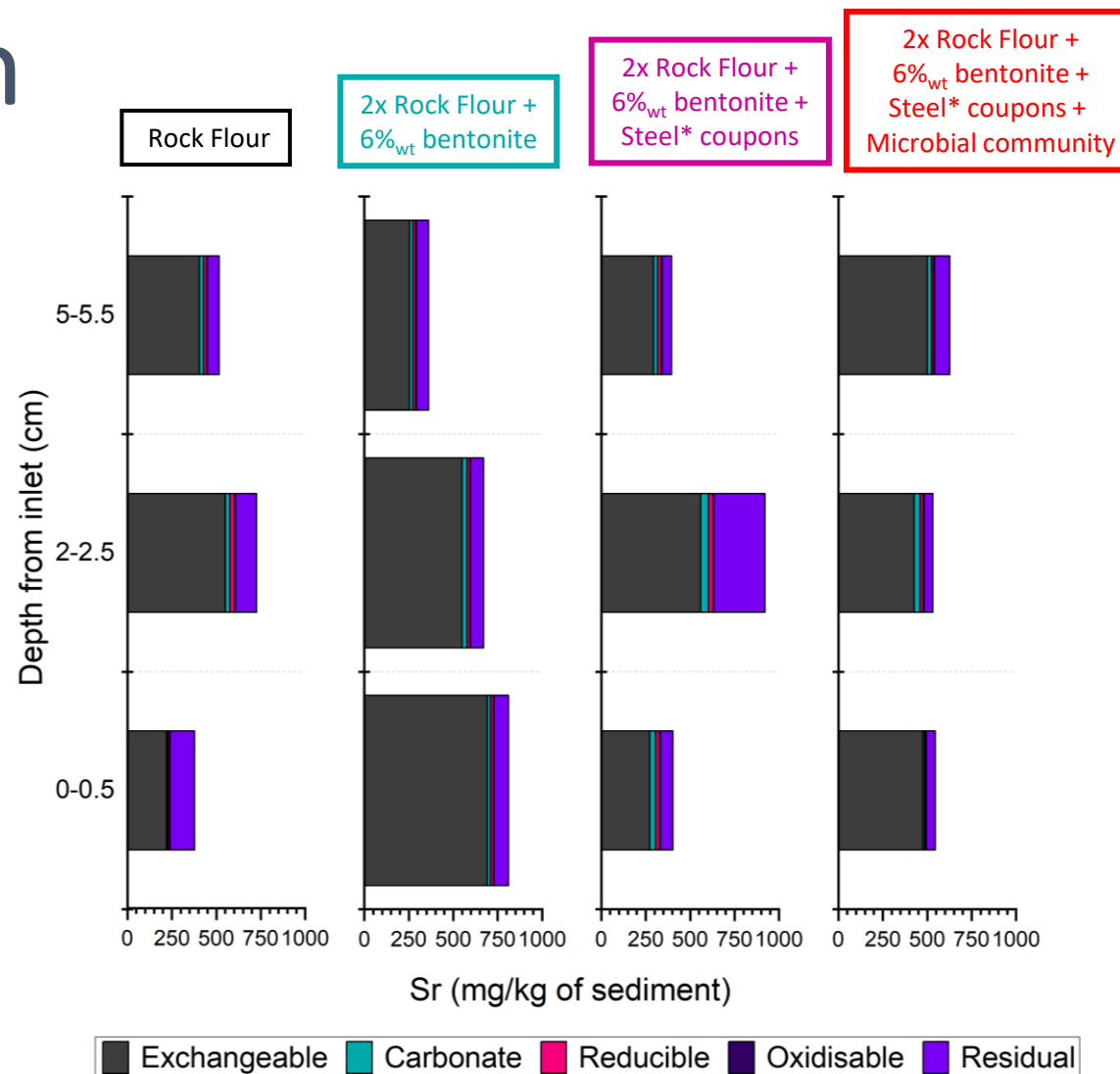
(A) Concentration of Sr and (B) % bioavailable Fe(II) in column systems: **(black)** rock flour, **(green)** rock flour + bentonite, and **(pink)** rock flour + bentonite + steel coupons and **(red)** rock flour + bentonite + steel coupons + electron donor amended.



# Sequential Extraction

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- **Exchangeable:**  
MgCl<sub>2</sub> (1 M) pH7
- **Carbonates:**  
Na-Acetate (1 M) pH 5
- **Reducible Fe/Mn Oxides:**  
NH<sub>2</sub>OH.HCl (0.5 M) pH 1.5
- **Oxidisable:**  
H<sub>2</sub>O<sub>2</sub> (8.8 M) + NH<sub>4</sub><sup>-</sup>  
Acetate (1 M) pH 5
- **Residual:**  
*Aqua Regia*



Concentration of Sr extracted per lixiviant.

\*Error for triplicate conducted for 0–0.5 cm section from the rock flour system was 2.00%, 0.50%, 0.30%, 0.01%, 0.03% and 6.00% for the respective fractions.

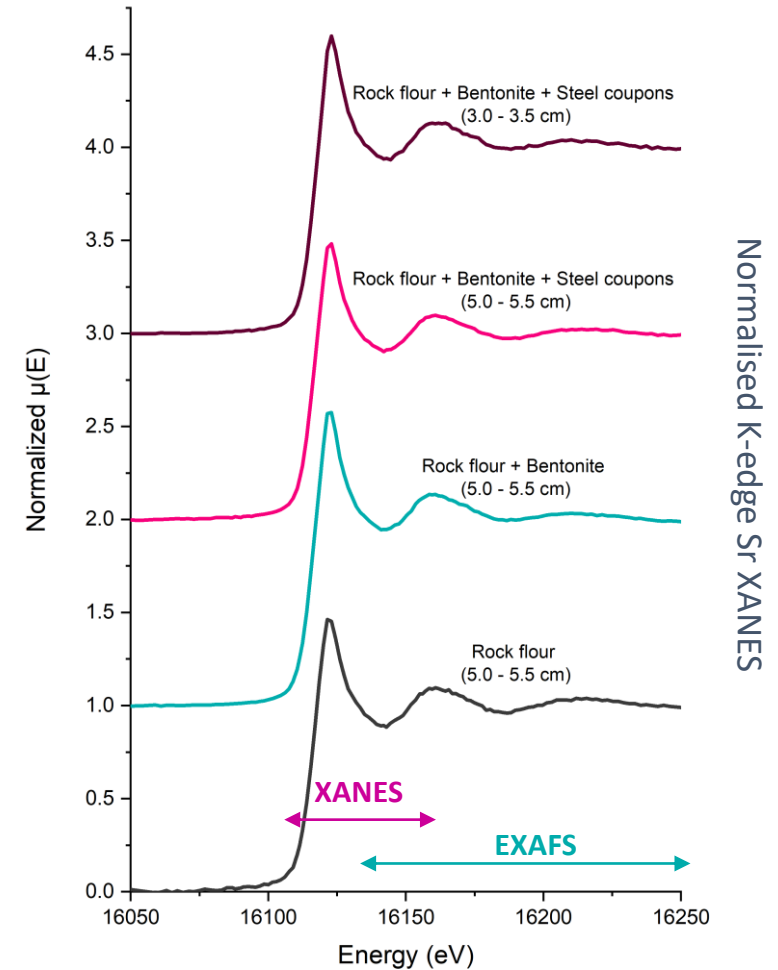
[1] Tessier, A.; Campbell, P. G. C.; Bisson, M. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal. Chem.* **1979**, *51* (7), 844–851. [2] Cleary, A.; Lloyd, J. R.; Newsome, L.; Shaw, S.; Boothman, C.; Boshoff, G.; Atherton, N.; Morris, K. Bioremediation of Strontium and Technetium Contaminated Groundwater Using Glycerol Phosphate. *Chem. Geol.* **2019**, *509* (September), 213–222.





# Molecular Scale Sr Analysis: XAS

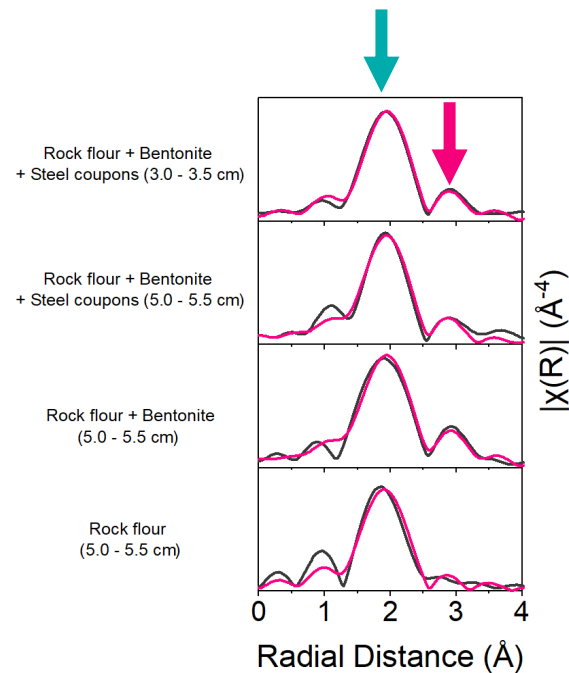
- Synchrotron analysis at INE Beamline (KIT) allows bulk Sr analysis:
- **XANES**: valence determination & limited info on coordination environment
- **EXAFS**: Detailed analysis of coordination environment and geometry (bond lengths, coordination number & species of atoms)





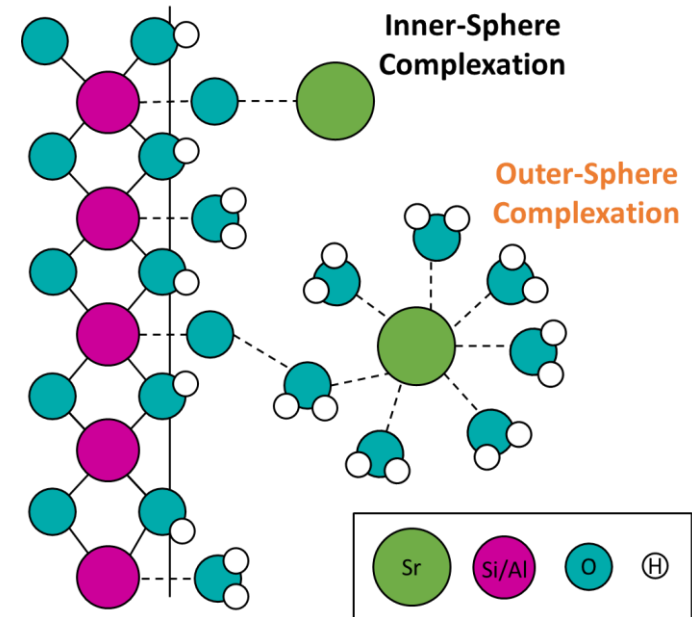
# Molecular Scale Sr Analysis: EXAFS

- EXAFS confirms **weak outer-sphere sorption** as dominant mechanism for Sr removal.
- Different binding** for systems w/o bentonite.



Sr-O ( $\sim 9$ , 2.55  $\text{\AA}$ )

Sr-Si/Al ( $< 1$ , 3.34  $\text{\AA}$ )

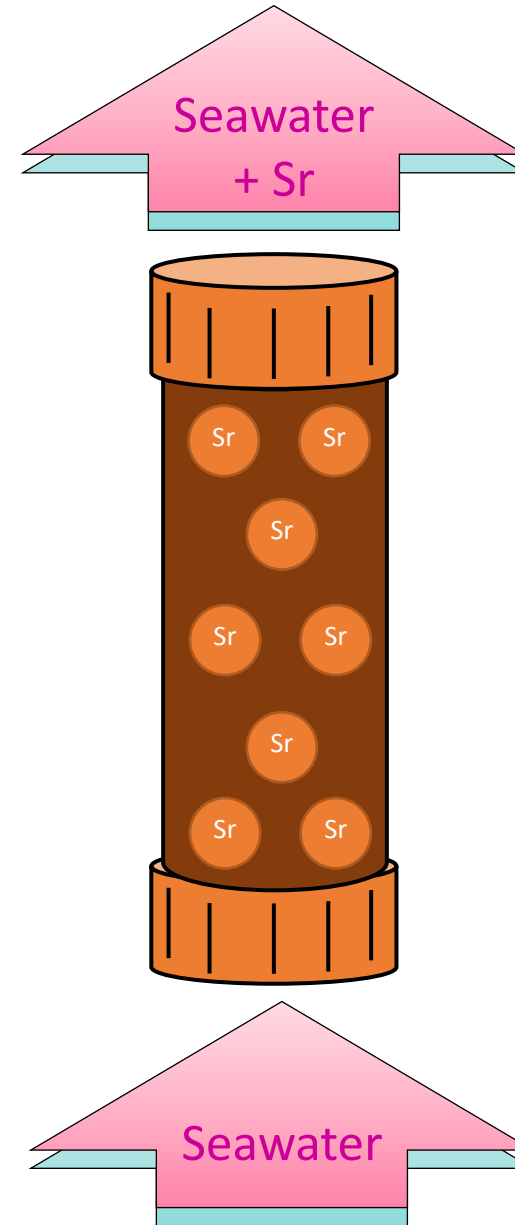




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# Remobilisation Experiments

- Short-term **remobilisation** experiments assessed the stability of the barrier material following influx of **rainwater** (1 month) and **seawater** (1 month).

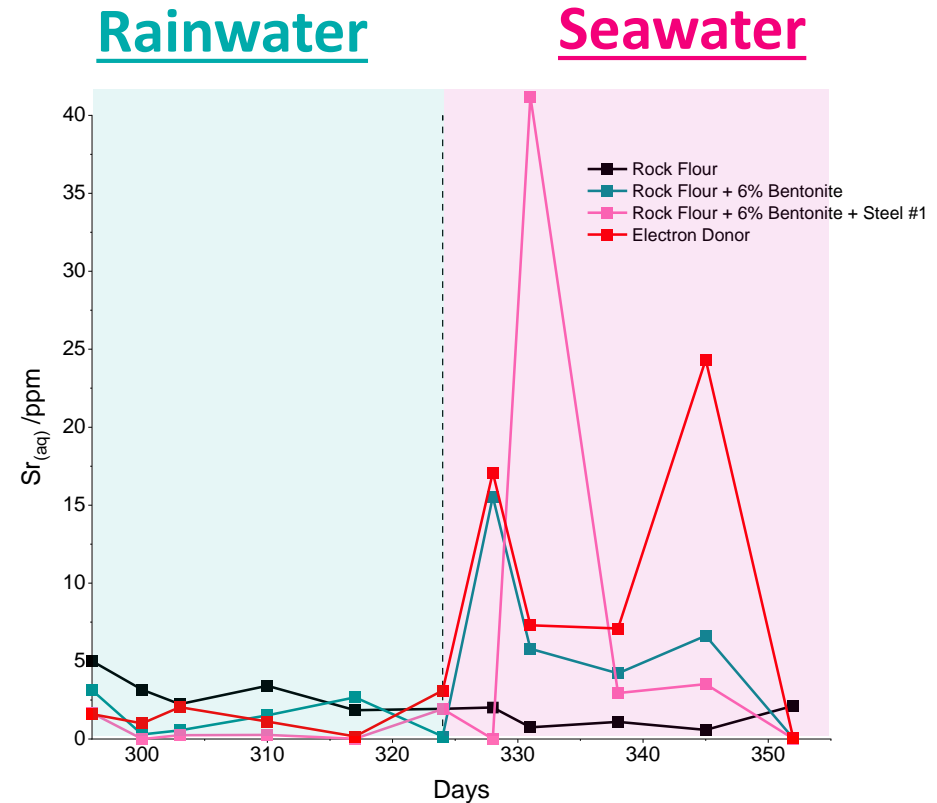




# Remobilisation Experiments

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- pH slowly decreases ~0.5 pH units with pH 5 **rainwater**.
- pH slowly increases ~ 1 pH unit with pH 8 **seawater**.
- Low IS **rainwater** remobilises Sr slowly.
- High IS **seawater** remobilises Sr bound to bentonite strongly. RF systems most stable.



Sr in effluent for remobilisation experiments: **(black)** rock flour, **(green)** rock flour + bentonite, and **(pink)** rock flour + bentonite + steel coupons and **(red)** rock flour + bentonite + steel coupons + electron donor amended.



# Conclusions

- Flowing column experimental system developed to **mimic VLLW disposal** relevant to Finland.
- **Sr retained** with just rock flour but **addition of bentonite improves capacity**.
- **Microbial activities** may increase pH but ultimately **do not have significant effect on Sr mobility**.
- Colloid formation not expected.
- **Remobilisation greater in seawater**.
- Sequential extractions and XAS suggest Sr mobility is governed by **weak outer-sphere sorption mechanisms** at pH 6.5-7.5.
- **Suggests that barrier + backfill materials proposed for VLLW disposal are suitable for Sr retention**.
- Sr binding dominated by weak interactions, **susceptible to remobilisation by high IS water**.
- **Experimental methodology is robust and adaptable suitable for a range of other experiments in future**.
- **Dissemination: Publication** submitted. GV presented multiple **talks** across Europe. MH **PhD thesis defended**.



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# Thank you!



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## With thanks to:

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