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Sr behaviour in Flow-Through Columns Representative of Near-Surface Disposal of Very Low Level Radioactive Wastes

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VLLW Disposal Concept

- VLLW - LILW currently disposed of in VLJ caves 60-100 m underground (Olkiluoto).
- VLLW includes **operational & decommissioning waste / radionuclides with short half lives** (~30 y *i.e.* ^{90}Sr, ^{137}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.

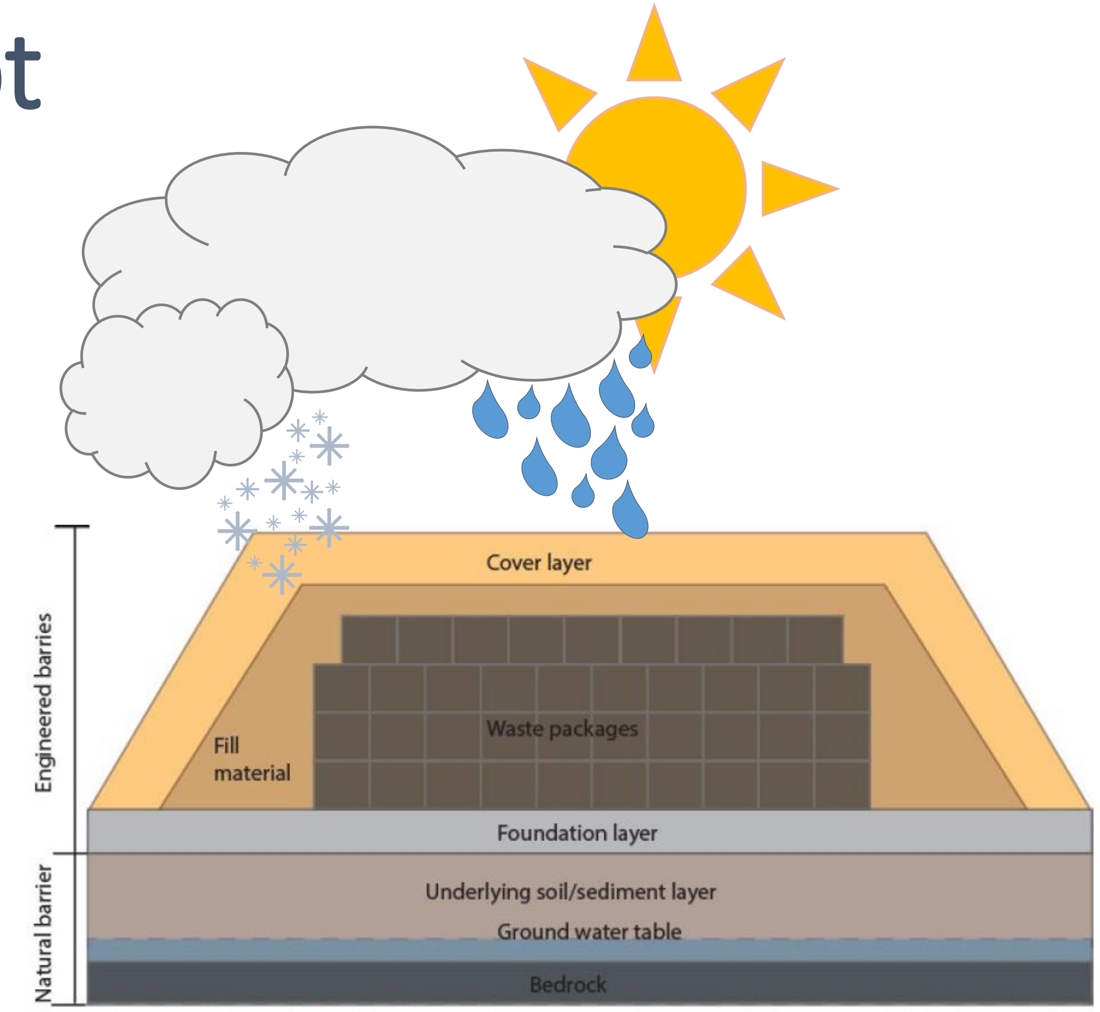

Illustration of a landfill-type near-surface repository.

Keto, P. et al. (**2020**) KYT SURFACE Near Surface Repositories in Finland. Available at: http://kyt2022.vtt.fi/kyt2022_seminar_sept_2019.htm. (Accessed: 23 August 2021).

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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}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.

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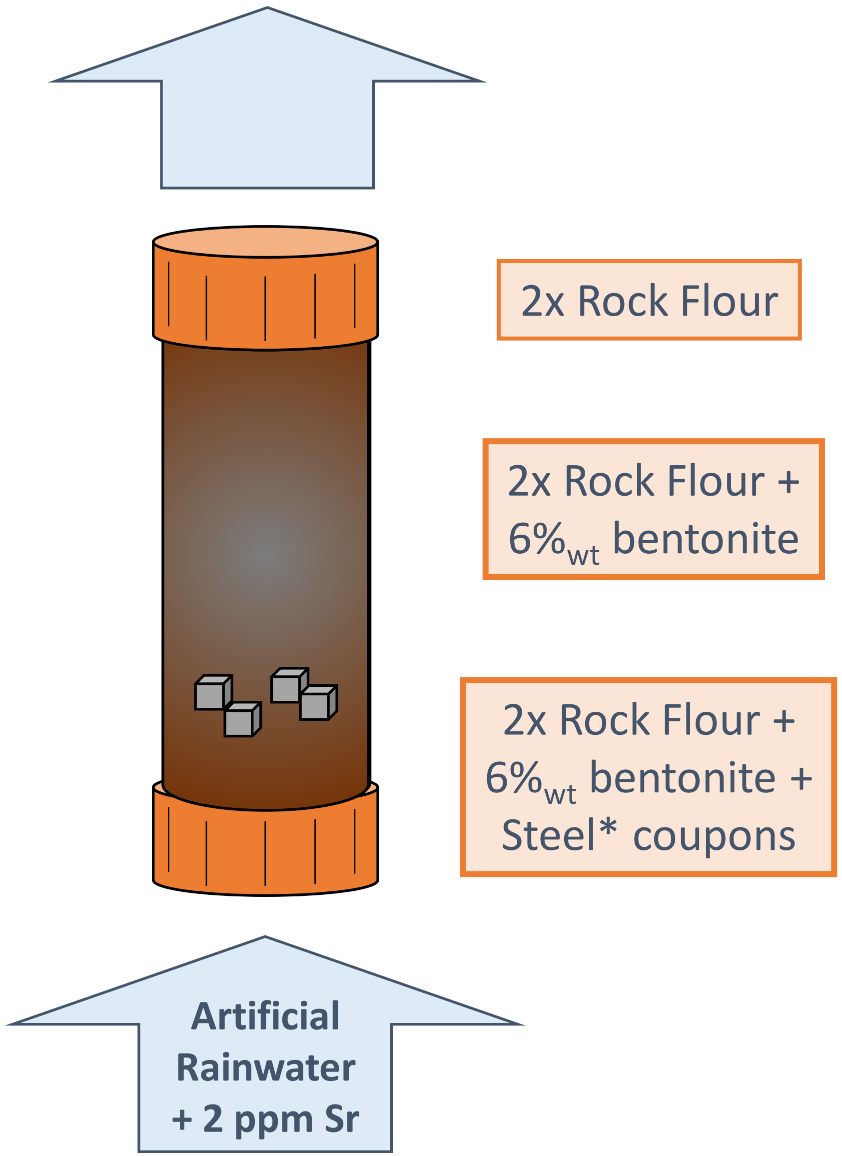
Methodology

- **3** 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^+	0.76
Ca^{2+}	0.67
Sr^{2+}	1.80
Na^+	1.15
Br^-	4.00
Mg^{2+}	0.30
SO_4^{2-}	3.84
pH	5

[1] Bower, W. R. et al. (**2019**) 'Metaschoepite Dissolution in Sediment Column Systems - Implications for Uranium Speciation and Transport', Environmental Science and Technology, 53(16), pp. 9915–9925. [2] Ho, M. S. et al. (**2022**) 'Retention of immobile Se(0) in flow-through aquifer column systems during bioreduction and oxic-remobilization', Science of The Total Environment, 834, p. 155332.
*Mild steel EN 10130/AISI 1008.

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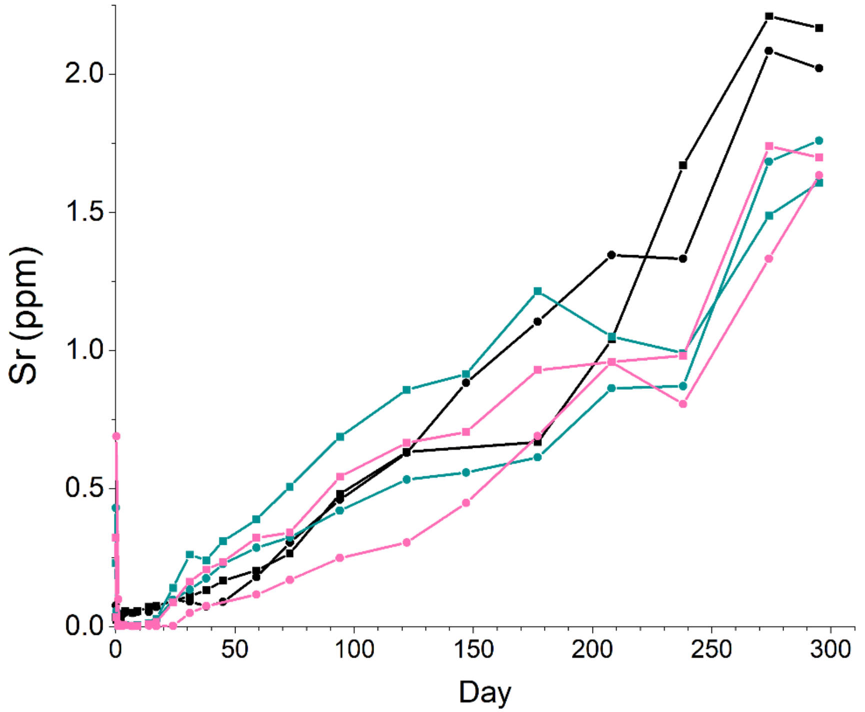
Aqueous Analyses

- **Sr well retained across all systems.**
- **Bentonite** addition **increases Sr sorption capacity** ~20%.
- **pH** equilibrates to **~6.5** in **abiotic experiments**.
- **No** evidence for **colloid** formation.



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

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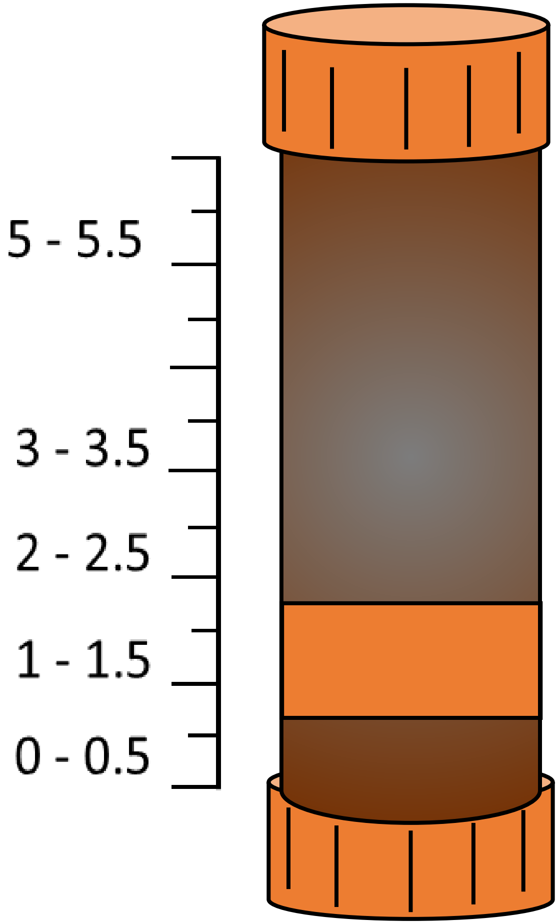
Experimental End-Point

- 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).



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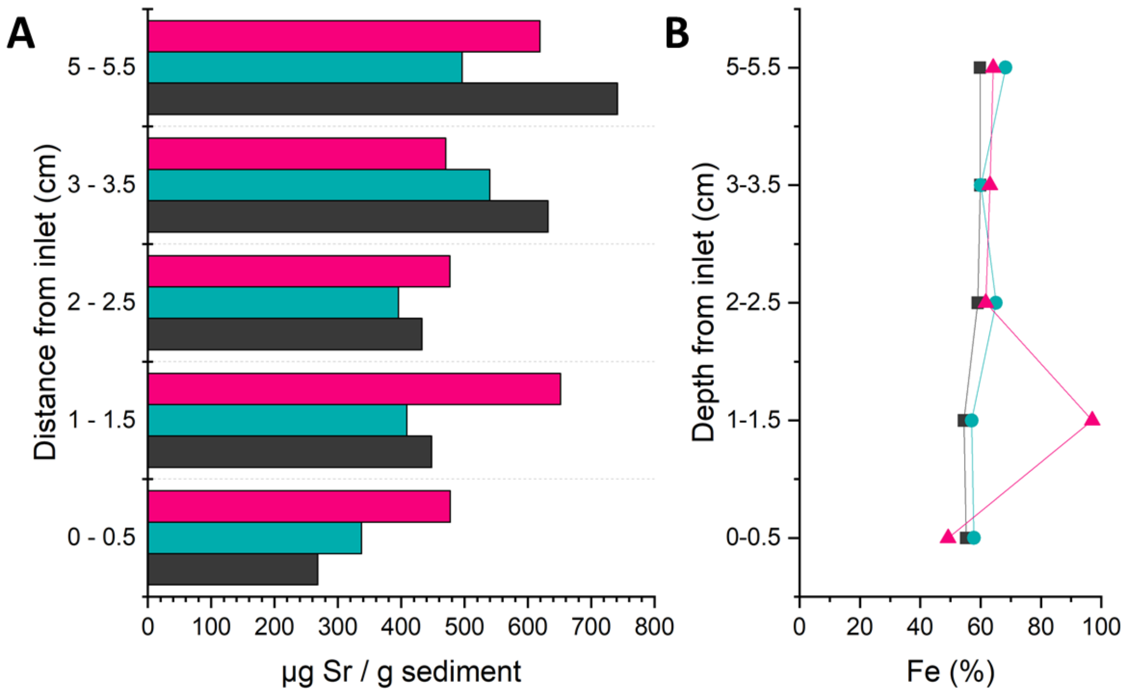
Experimental End-Point

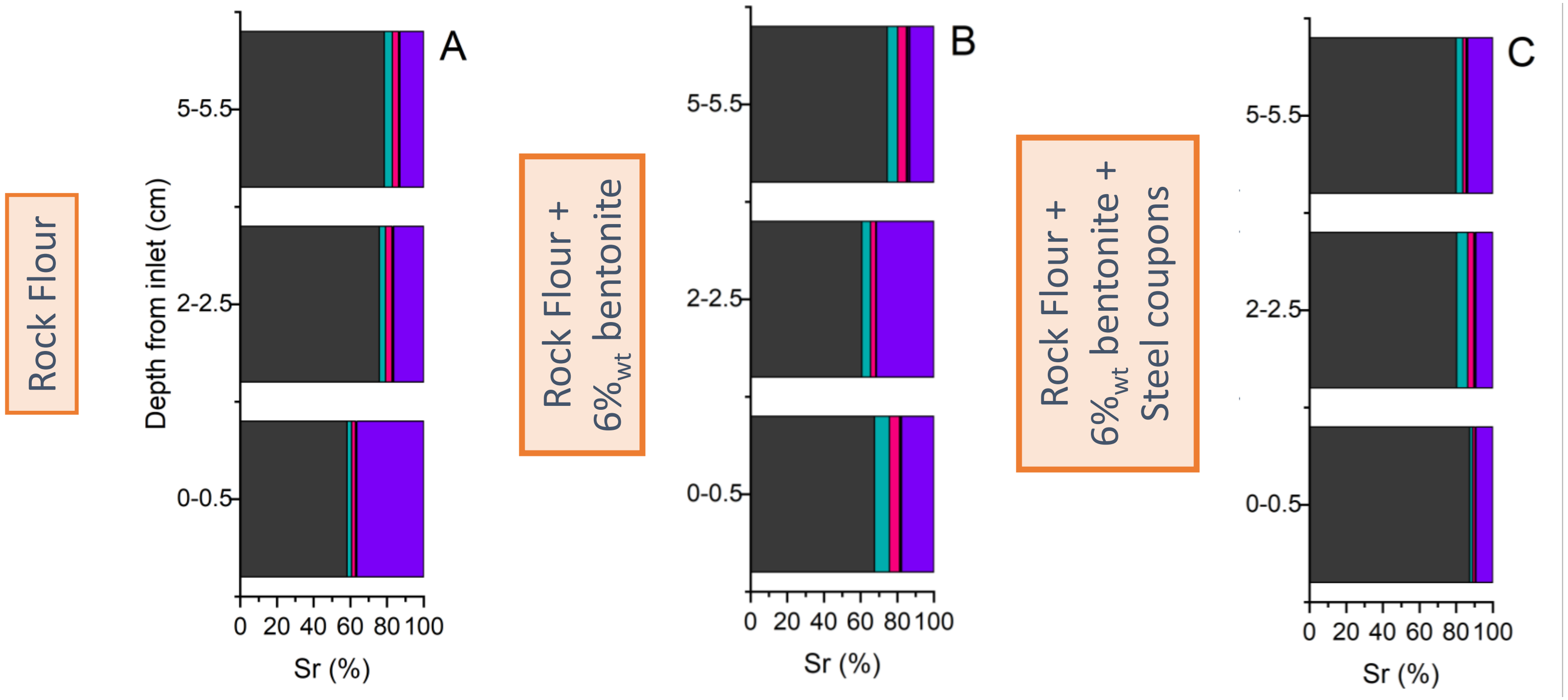
- *Aqua-regia* digests show **Sr was evenly distributed throughout each column.**
- [Sr] 250-750 µg Sr / g solids.
- Fe(II) content increased where steel coupons were.



(**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.

Bulk Sr distribution & Speciation: Sequential Extraction

- **Exchangeable**:
  $MgCl_2$ (1 M) pH7
- **Carbonates**:
  Na-Acetate (1 M) pH 5
- **Reducible Fe/Mn Oxides**:
  $NH_2OH.HCl$ (0.5 M) pH 1.5
- **Oxidisable**:
  H_2O_2 (8.8 M) + NH_4-Acetate (1 M) pH 5
- **Residual:**
  Aqua Regia



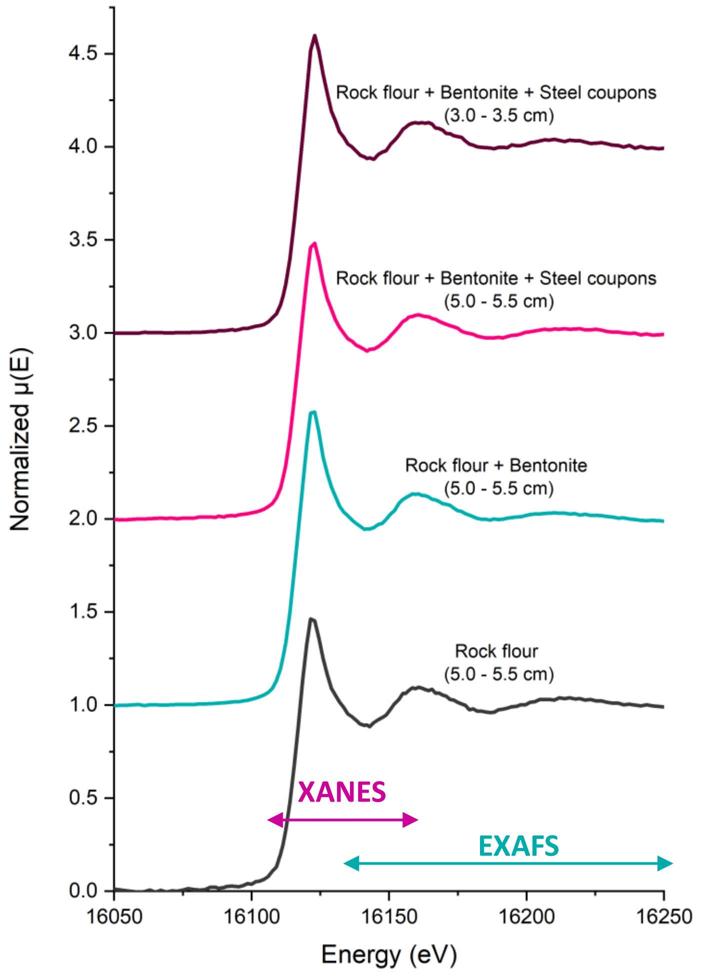
Concentration of Sr extracted per lixiviant.

*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)

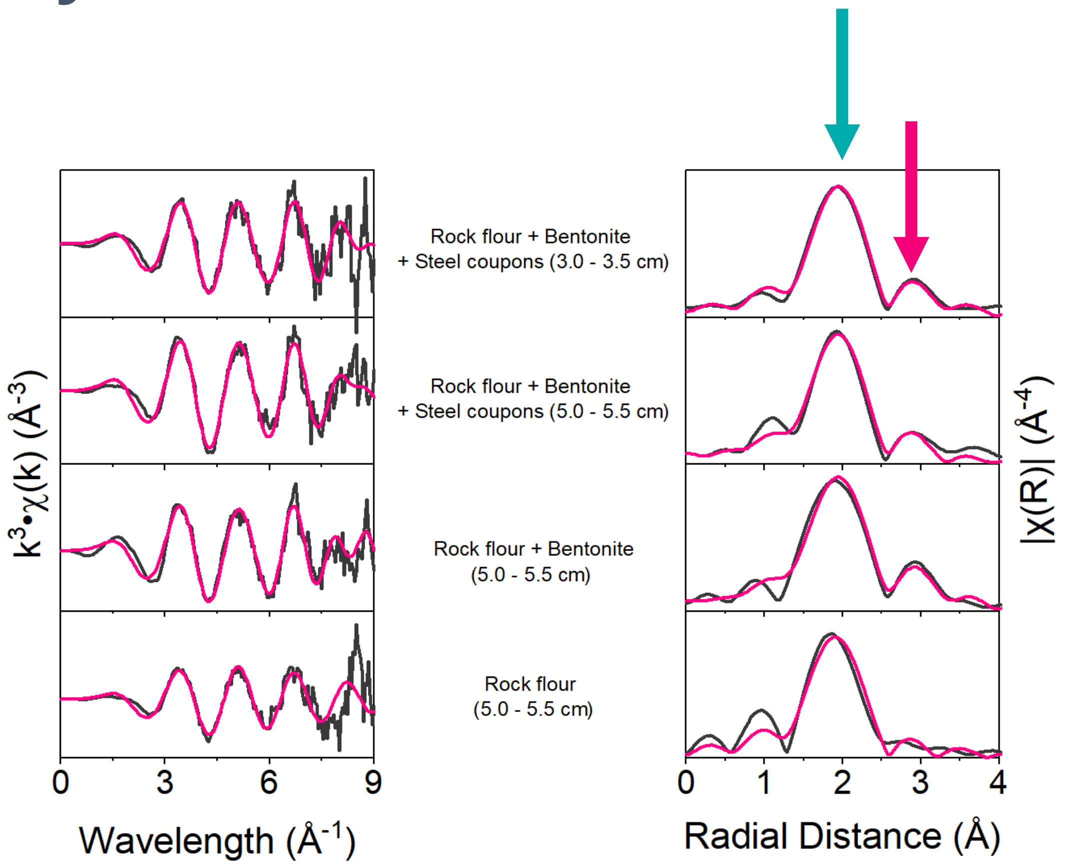


Normalised K-edge Sr XANES

Molecular Scale Sr Analysis: EXAFS

EXAFS confirms **weak outer sphere sorption** as dominant mechanism for Sr removal.

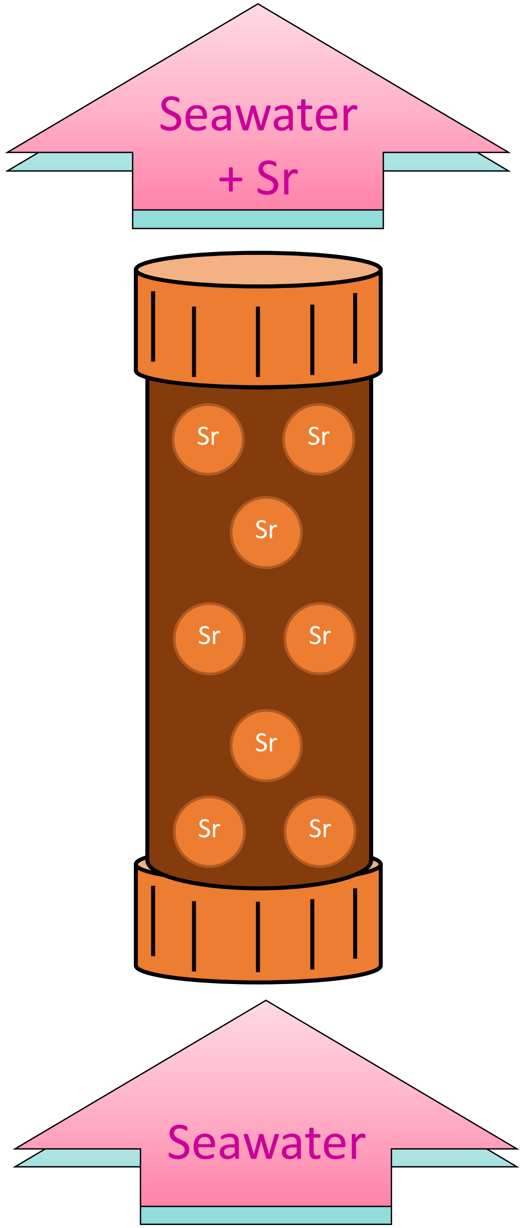
Rock flour	**Sr-O** (9, 2.55 Å)
+ Bentonite	**Sr-O** (8.5 2.55 Å)
	Sr-Si/Al (0.7, 3.34 Å)



Sr K-edge EXAFS spectra Experimental data (black), best fits (red): (left) k^3 weighted data; and (right) Fourier transforms.

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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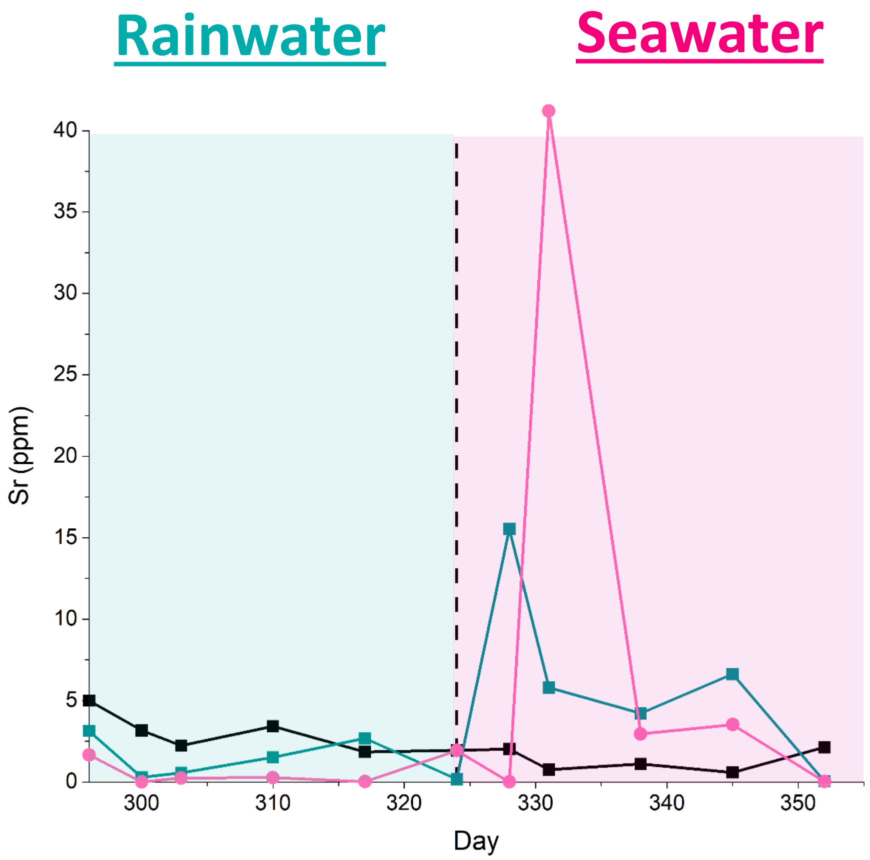
- pH remained stable.
- Low IS **rainwater** remobilises Sr slowly.
- High IS **seawater** remobilises Sr bound to bentonite strongly. RF systems most stable.



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

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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**.
- 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.**
- To be published shortly.

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