minerals

MDPI

Supplementary Materials for: Mechanisms Governing ^{90}Sr Removal and Remobilisation in a VLLW Surface Disposal Concept

1. Conceptual Design for Finnish Near Surface Repository

The current conceptual design for a Finnish near surface repository resembles the hazardous waste landfills defined by the Finnish Environment Institute [74,75] where the repository is designed to contain the retained radionuclides until their radiation risk has diminished to acceptable levels (a few hundred years) [76]. Figure S1 shows the main barriers in a landfill-type repository as described in the main text.

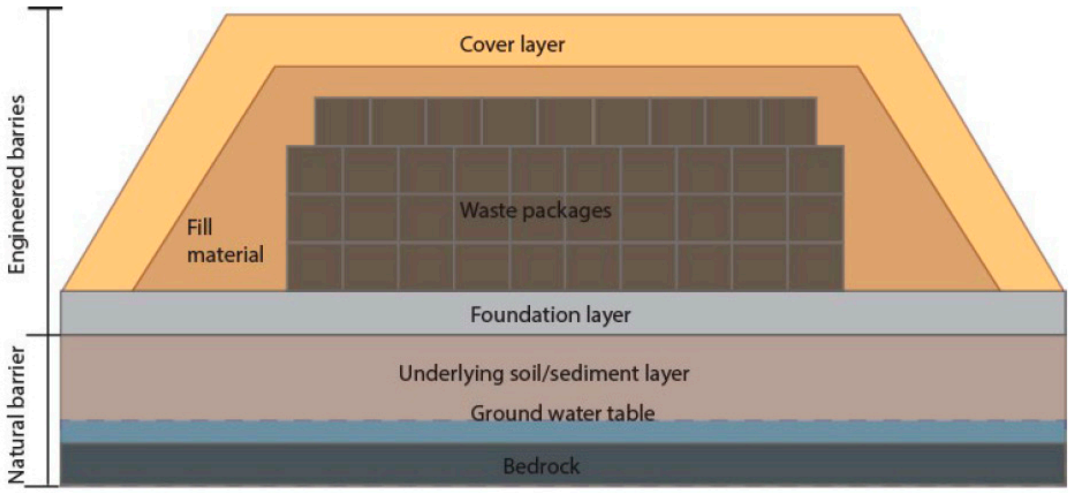

Figure S1. Main barriers in a landfill-type repository [10].

2. Column Design

A polypropylene column (10 cm vertical, 1cm inner diameter) was packed with layers of glass wool (1 cm vertical) and quartz sand (1 cm vertical) on both ends, while the remaining space in the column (6 cm vertical) was packed tightly with starting material (**Error! Reference source not found.**). A 3-way valve was attached at the outlet of the column with one valve for sample collection (with a syringe) and another for effluent / waste collection when not sampling. Columns were stored in the dark, at 21 ± 2 °C for the duration of the experiment.

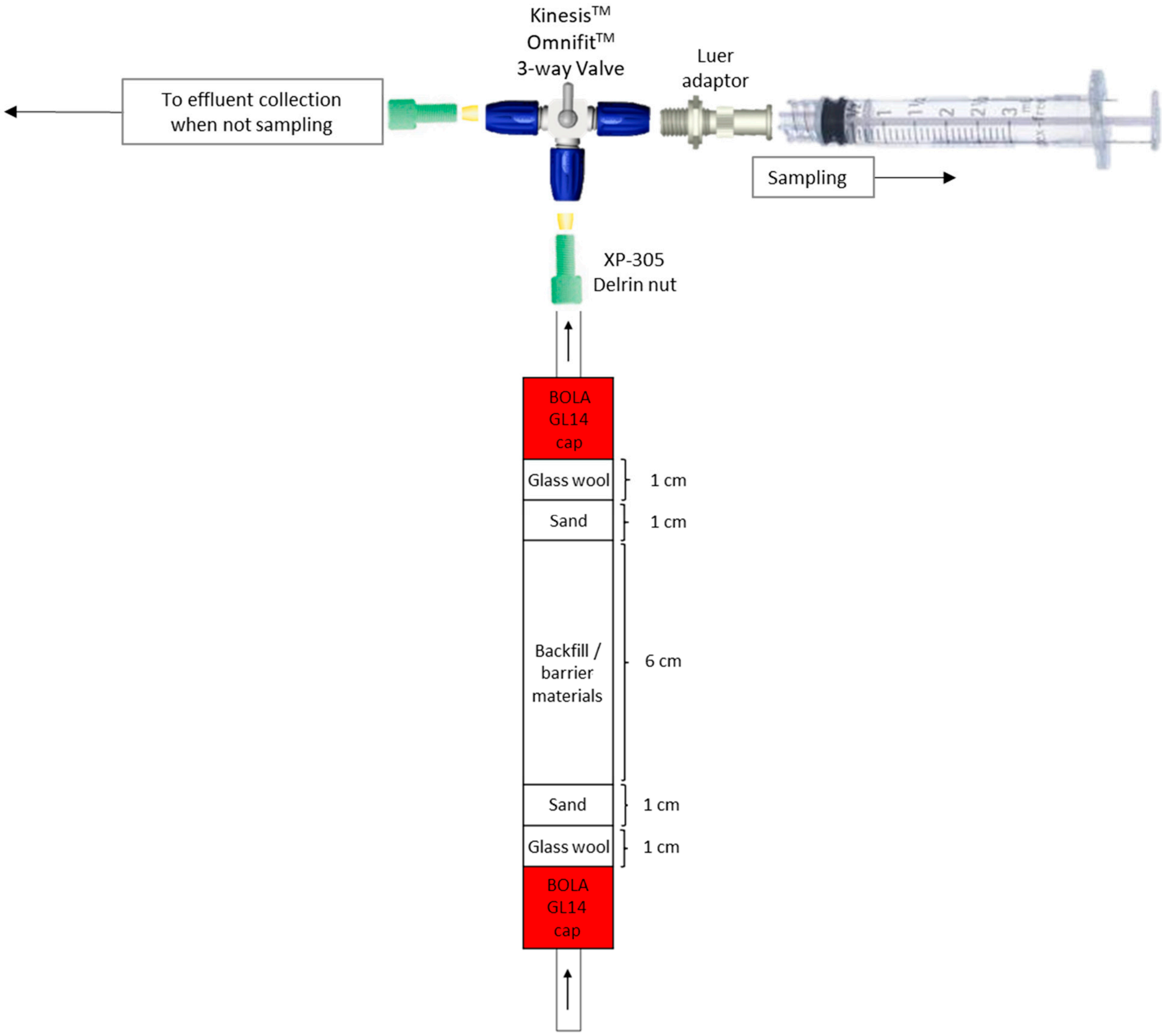

Figure S2. Schematic of columns.

3. Material Characteristics

Rock flour was sourced from within ~50 km distance of Olkiluoto, and was produced by Fescon/Maanrakennus Jouko Kärkkäinen Oy, Nakkilan murskaus. It was classified as diabase mafic rock type and is composed of quartz (SiO_2), crystabollite (SiO_2), albite ($NaAlSiO_3$), and dorrite ($Ca_2Mg_2Fe_4^{3+}(Al_4Si_2)O_{22}$). The bentonite used was LUXGEL EG 28, classified as aluminium hydro silicate (CAS 1302-78-9). It is composed mostly of smectite and quartz. Cation Exchange Capacities (CEC, $[Cu(trien)]^{2+}$) were determined for: i) rock flour (0.07-0.08 meq/g), and (ii) rock flour + bentonite (6%wt) (0.10 meq/g) [77].

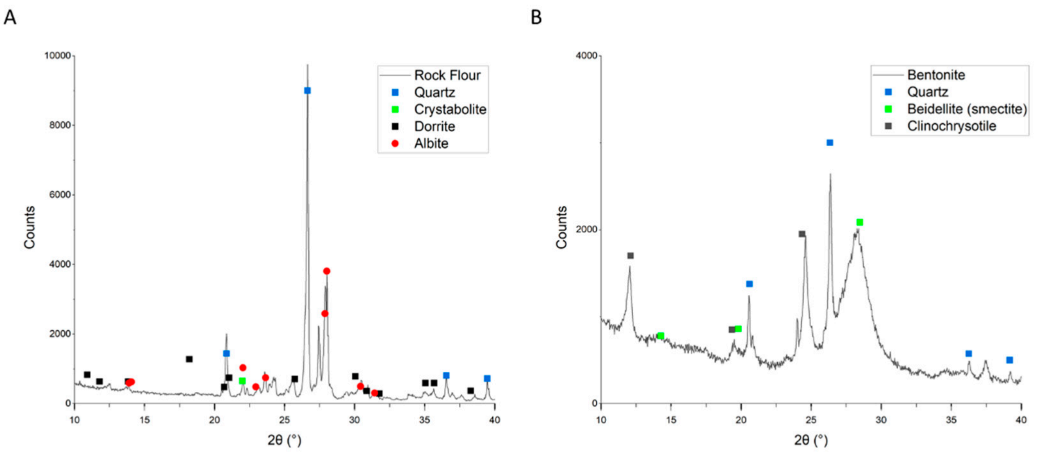

Figure S3. XRD patterns for the rock flour (**A**), and bentonite (**B**). Peaks: quartz (PDF 00-046-1045), crystabollite (PDF 00-039-1425), dorrite (PDF 00-045-1408), albite (PDF 00-041-1480), beidelite (smectite) (00-043-0688), and clinochrysotile (00-043-0662).

Table S1. Composition of starting materials rock flour, bentonite, and steel coupons determined by XRF.

Element	Rock Flour (mg/kg)	Bentonite (mg/kg)	Steel Coupons (mg/kg)
Si	445400	482900	
Al	154400	155600	
Fe	134000	69000	To balance
Mg	80800	24500	
Ca	75400	9700	
Na	25700	33200	
Ti	18000	11700	
K	9700	9400	
P	3000	1300	70
Mn	1900	200	1900
Ba	492	205	
Sr	369	145	
V	182	117	20
Zr	107	206	
Zn	104	74	
Ni	103	39	200
Cr	82	103	300
Cu	55	38	
Ce	49	45	
Y	21	33	
Rb	18	41	
La	17	43	
Nb	4	30	
U	2	4	
V			20
C			250
S			70
N			20

4. Additional Geochemical and Spectroscopy Data

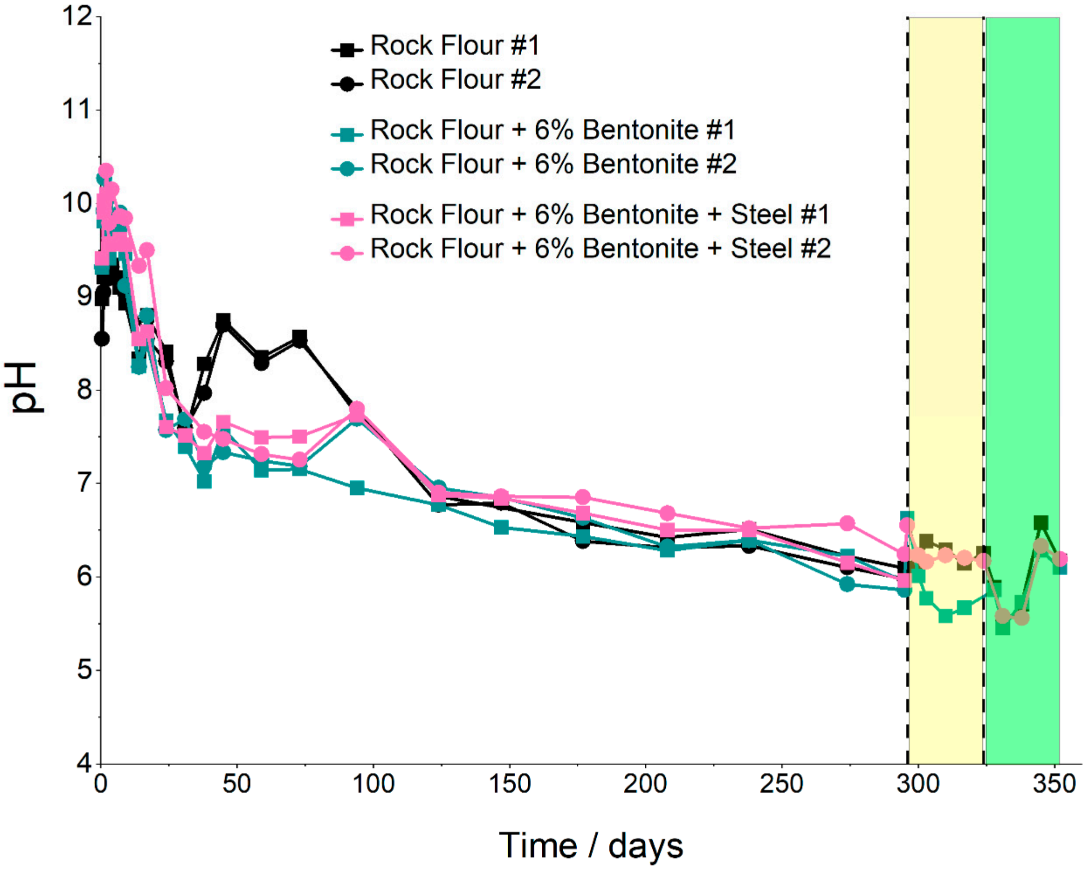

Figure S4. pH values across all experiments during 352 days of experimentation. **(Black)** rock flour, **(green)** rock flour + bentonite (6 wt.%), and **(pink)** rock flour + bentonite (6 wt.%) + steel coupons. During initial experiments (first 295 days), each column system was run in duplicate, and individual columns (per system) are represented by squares and circles. For remobilisation experiments, one column from each system was continued for 28 days with rainwater (yellow) and a further 28 days with seawater (green).

Table S2. Concentration of Sr extracted per lixiviant from column starting materials.

System	Exchangeable (mg/kg sediment)	Carbonate (mg/kg sediment)	Reducible (mg/kg sediment)	Oxidisable (mg/kg sediment)	Residual (mg/kg sediment)	Total (mg/kg sediment)
Rock flour	35.6 ± 6.0	7.9 ± 2.3	2.1 ± 0.8	0.8 ± 0.2	25.1 ± 7.5	71.5 ± 16.8
Bentonite	130.1 ± 5.7	32.0 ± 0.8	5.1 ± 0.4	1.0 ± 0.1	31.2 ± 9.4	199.4 ± 16.3
Rock flour + Bentonite (6 wt.%) [(A)]	41.3 ± 6.0	9.3 ± 2.2	2.0 ± 0.8	0.8 ± 0.2	25.5 ± 7.6	78.9 ± 16.7

Data reported as an average of quintuplicate measurements. Error reported as standard deviation. (A) was calculated as a weighted average between rock flour (94 wt.%) and bentonite (6 wt.%).

Table S3. Mass balance of Sr in effluents and Sr associated with column solids in each system.

System	Total Sr added (mg) (A)	Added Sr retained in the column (mg) (B)	Added Sr retained in the column (%)	Sr remobilised to rainwater (mg)	Sr remobilised to seawater (mg)	Total Sr remobilised from columns (mg)
Rock flour	7.1	3.95	56	0.9	0.4	1.3
Rock flour + Bentonite (6 wt.%)	7.1	4.42	62	0.5	1.9	2.4
Rock flour + Bentonite (6 wt.%) + Steel coupons	7.1	4.73	67	0.2	3.1	3.3

(A) was calculated with total volume of water pumped into each column (3.5 L ± 0.3 L) × concentration of Sr in the influent (2 mg/L). (B) was calculated as the difference between the total added Sr and the Sr in the effluent (Figure 1). Error in concentrations is ± 1.2 mg and ± 25%.

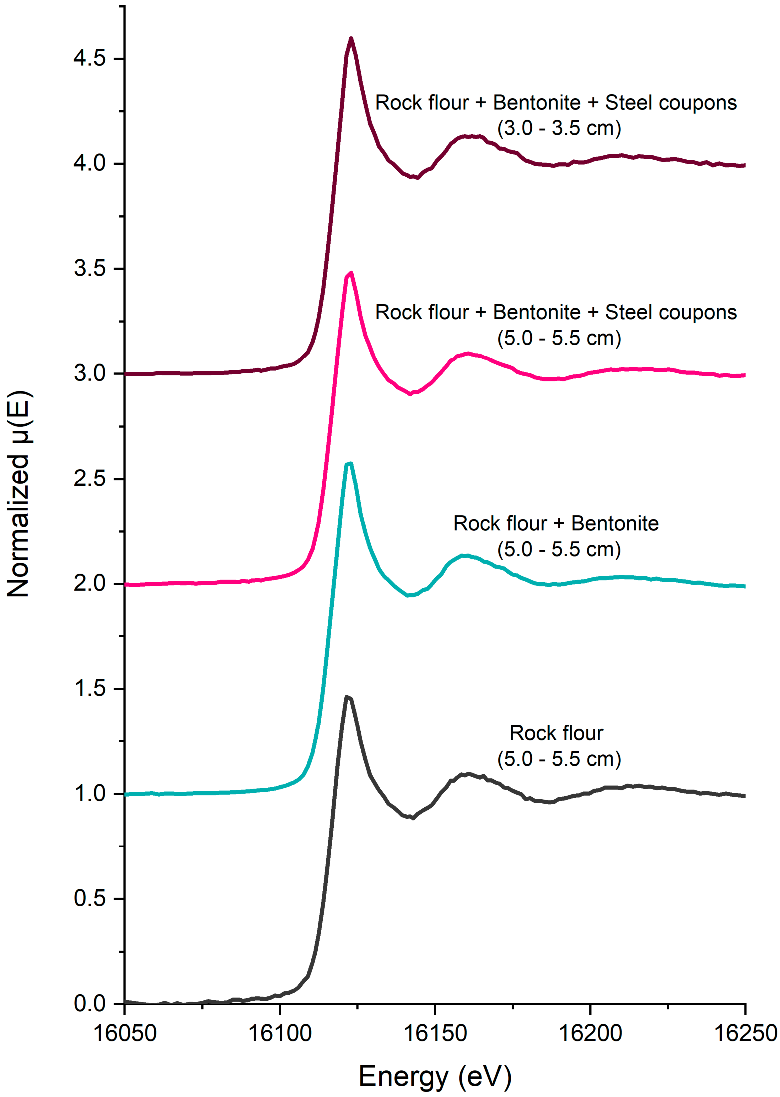

Figure S5. Normalized Sr K-edge XANES spectra (bulk) for all samples.

5. EXAFS Fit Parameters

Table S4. Fit results for EXAFS data fitting for rock flour (5.0 cm – 5.5 cm), rock flour + bentonite (5.0 cm – 5.5 cm), rock flour + bentonite + steel coupons (5.0 cm – 5.5 cm and 3.0 cm – 3.5 cm). Uncertainty in interatomic distances (Å) is stated in brackets for the last decimal place. Uncertainty in Debye-Waller factors is quoted in brackets for the last decimal place. [(a)]F-test results; $\alpha > 0.95$ statistically improves the fit with 2 σ confidence. $S0^2$ was fixed to 1 for all samples.

Sample	Scattering path	N	R (Å)	σ^2 (Å^2)	E_0 (eV)	R-factor	Confidence of adding shell (%)[a]
Rock flour 5.0 cm – 5.5 cm	Sr-O	9	2.55 (3)	0.010 (1)	-2.2	0.020	
Rock flour + bentonite (6 wt.%) 5.0 cm – 5.5 cm	Sr-O	9	2.54 (2)	0.014 (1)	-2.5	0.009	
	Sr-Si/Al	1.4	3.35 (2)	0.006 (3)			99%
Rock flour + bentonite (6 wt.%) + steel coupons 5.0 cm – 5.5 cm	Sr-O	9	2.54 (1)	0.013 (1)	-2.0	0.008	
	Sr-Si/Al	1.4	3.35 (2)	0.011 (4)			100%
Rock flour + bentonite (6 wt.%) + steel coupons 3.0 cm – 3.5 cm	Sr-O	9	2.56 (1)	0.012 (1)	-1.0	0.005	
	Sr-Si/Al	1.4	3.33 (3)	0.009 (4)			98%

6. PHREEQC Modelling

Thermodynamic modelling of the starting rainwater influent was completed using PHREEQC (version 3.6.2) coupled to the phreeqc.dat database (Table S5). All predicted species had a negative saturation index (Table S6).

Table S5. Input for PHREEQC calculations.

SOLUTION 1	
temp	25
pH	9
pe	4.5
redox	pe
units	ppm
density	1.02
Sr	2
K	0.45
S(+6)	2.53
N(-3)	1.88
Mg	0.1
Ca	0.67
Na	1.15
P	0.22

Table S6. Output of PHREEQC calculations, saturation indices.

Phase	Saturation Index[A]	Chemical Formula
Anhydrite	-5.15	$CaSO_4$
Celestite	-2.63	$SrSO_4$
Gypsum	-4.84	$CaSO_4{:}2H_2O$
$H_{2(g)}$	-27.05	H_2
$H_2O_{(g)}$	-1.5	H_2O
Hydroxyapatite	-0.25	$Ca_5(PO_4)_3OH$
$NH_{3(g)}$	-6.11	NH_3
$O_{2(g)}$	-29.19	O_2

[A]For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm. For ideal gases, phi = 1.