

RESEARCH REPORT

VTT-R-00942-22

KYT SURFACE: Status Report on radionuclide transport

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beyond the obvious




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Summary <p>The work presented in this report belongs to the second phase of the KYT SURFACE project concerning near surface repositories in Finland. In the second phase, the work in the KYT SURFACE project was divided into three tasks: 1) Radionuclide Transport, 2) Biodegradation of Waste and Steel Corrosion and 3) Performance of Engineered Barriers. This report was written as a part of task 1 with focus on studying the radionuclide transportation in critical barrier materials. Performance of the barrier materials was examined in flow through column experiments. New column setup was tested but proved problematic for controlling the experimental conditions and for the further processing of the column materials. Analysed data for the effluent concentrations show good retention of strontium in the column materials. Results presented in this status report should not be used for risk assessment or as a basis for planning as such.</p>	
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Name: Heidi Krohns-Välimäki

Title: Research Manager



Preface

This report was compiled in 2021 as part of the KYT 2022 Programme (Finnish Research Programme on Nuclear Waste Management 2019-2022). The KYT 2022 programme focuses on nationally important research topics with the aim to maintain and enhance national know-how in nuclear waste management and to promote collaboration between authorities, the nuclear industry and scientists.

The experiments and a preliminary version of this report were made by senior scientists Emmi Myllykylä and Mélanie Gouëlle. Results were checked and this report edited by Suvi Lamminmäki.

“Dei quali accidenti di gravità, di velocità, ed anco di figura, come variabili in modi infiniti, non si può dar ferma scienza. e però per poter scientificamente trattar cotal material, bisogna astrar da essi, e ritrovate e dimostrate le conclusioni astratte dagli impedimenti, servircene nel praticarle con quelle limitazioni, che esperienza ci verrà insegnando.” -Galileo Galilei, 1638, Discorsi e dimostrazioni matematiche intorno a due nuove scienze.

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1. Introduction

KYT SURFACE project examined near surface repositories (specifically the landfill type), for waste deposition of short-lived very low level waste (VLLW). Water intrusion into the deposited waste packages may induce release of radionuclides into the surrounding geo/biosphere. Radionuclide transport within and in the vicinity of the repository will be controlled by reactive transport processes and chemical reactions. Chemical reactions include precipitation, dissolution and adsorption or desorption.

In phase 2 of the KYT Surface project, UH (University of Helsinki) and VTT started to examine the transport of select risk-driving radionuclides (^{90}Sr , ^{36}Cl) from the Very Low Level Waste (VLLW) inventory, through the different barrier materials. Column flow-through rigs were constructed based on an existing HY design (Bower et al., 2019) and these columns were filled with materials representative of a near surface repository (rock flour, bentonite, and steel were used). VTT's column setup differed from the one used at the university of Helsinki: Aim of the different setup was to achieve higher compaction of the fill materials. Water simulant, representative of intruding rainwater was then pumped through the columns along with low concentrations of elements representing the radionuclides of interest. Effluents from the columns were continually monitored to examine radionuclide transport and speciation or alternatively the ability of the barrier materials to retain these radionuclides should they be released from the waste forms. Phase 2 of the project primarily focussed on constructing the columns, preparing the materials, and starting the experiments. All phase 2 tasks were achieved. Phase 3 consisted of continuing the column experiments until 1 year of flow had been achieved.

The objective of the present work was to study the transport and /or potential retention mechanisms, and speciation of key risk-driving radionuclides in selected barrier materials, considering the conditions prevailing in a Finnish near surface repository. First part of this report describes the two facilities used to perform the experiments under oxic and anoxic conditions. Then, the analyses of the effluents during the one-year sampling are discussed.

2. Experimental setups used in the project

2.1 Setup for the experiments made in oxic conditions

The system consisted of a peristaltic pump, 3 steel columns and sampling tubes: Accu-rated PVC Manifold pump tubing Kendall Elkay, size inner diameter = 0.6, maximum operating temperature: 94°C. (Figure 1). Columns #1 and column #2 were filled with crushed rock with 6% Luxgel EG28¹ which is representative of “barrier / sealing material” (Keto et al., 2021) and 3 pieces of steel. The third column was filled only with a mixture of crushed rock with 6% Luxgel EG28. The masses of mixture and steel used are presented in Table 1. The pumping speed is fixed to “-7.00” according to previous measurements to target a pumping rate of 1 ml/h.

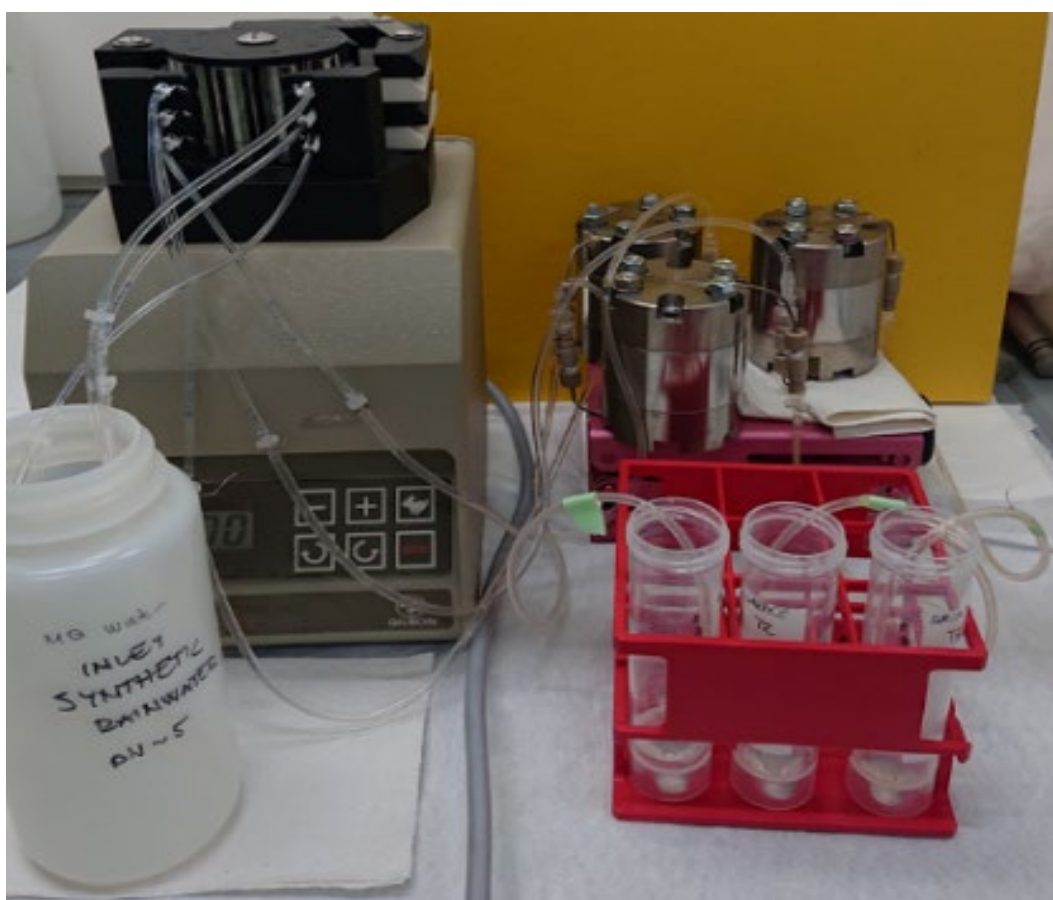


Figure 1. Setup for the experiments made in oxic conditions.

Table 1. Column filling.

	Column #1	Column #2	Column #3
Mass of mixture filled in column [g]	16.0739	16.1587	16.8942
Mass of 3 pieces of steel [g]	0.3159	0.3007	0

¹ Mineralogical composition: Mafic rock type, diabase. Plagioclase (47%), clinopyroxene (33%), olivine (17%), opac (2%), accessory minerals (<1%).

At the inlet and outlet of each column, a sintered plate was used. The plates were made of titanium. Thickness of the plates was 1.3448 m and the diameter 23 mm. Columns were packed with the mixture of crushed rock with 6% Luxgel EG28. Steel chips were added after about 8.73 g of mixture was packed into the column.



Figure 2. Example of column filling.

2.2 Setup for the experiments performed in anoxic conditions

The experimental setup for the anoxic tests was similar to the one used in the oxic tests but for the used pump and inlet tubing leading to the columns. Capillary pump from Agilent 1100 Series (Figure 3) was used for the pumping. The capillaries leading to the columns were made of steel in comparison to the tubings used in the oxic test setup made of PVC. The objective of this change was to avoid the leakages observed in the oxic test setup and to ensure a constant flow rate.

The first plunger has a stroke volume in the range of 20–100 μl depending on the flow rate. The microprocessor controls all flow rates in a range of 1 μl –10 ml/min. The system is pressure tight up to 300 bar. During the tests, the stroke was fixed to 100 μl ; small flow rates use a small stroke volume while higher flow rates use a higher stroke volume. At the beginning of the test, the pressure was measured to be 4 bars. The pressure increased as the test was running.

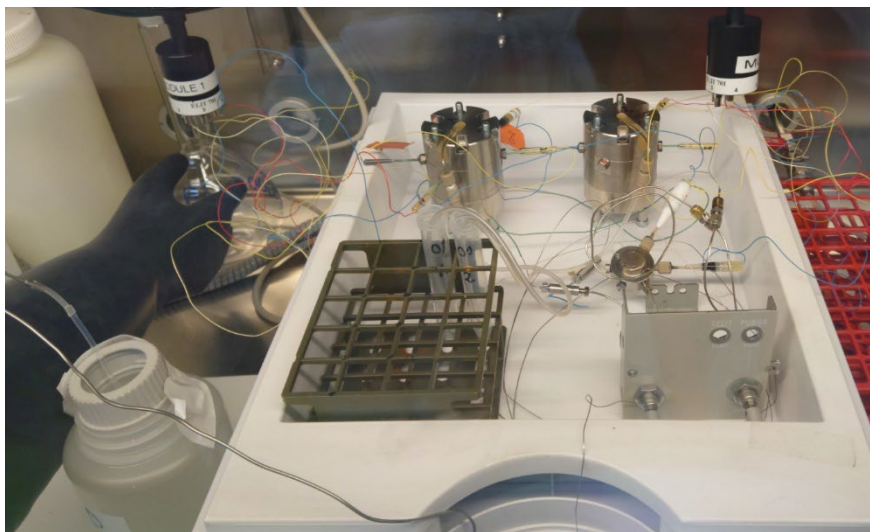


Figure 3. Setup for the experiments made in anoxic conditions.

The columns were filled in the same way as the columns for the oxic tests (Table 2).

Table 2. Column filling for the preliminary test.

	Column #1	Column #2
Mass of mixture filled in column [g]	15.96	16.6

First, preliminary tests were run to optimize the pumping parameters. It was observed from these first tests, when the columns were unpacked, that the finest material (for example the bentonite clay) was moved towards the outlet. Difference between the inlet and outlet of the column can be seen in Figure 4.



Figure 4. Columns after few days of use. Difference in the dispersion of the filling materials was observed.

After this the columns were packed using bentonite-rock mixtures and steel pieces. Table 3 presents the mass of mixtures and steel pieces used for packing the columns.

Table 3. Column filling for the experiment.

	Column #1	Column #2
Mass of mixture filled in column [g]	16.14	15.61
Mass of 3 pieces of steel [g]	0.3118	0.3033

The columns were equipped with electrodes to measure on-line the oxidation/reduction potential (Eh), the potential of hydrogen (pH) and concentration of chlorine (chloride ion-selective electrode) (see Figure 5).

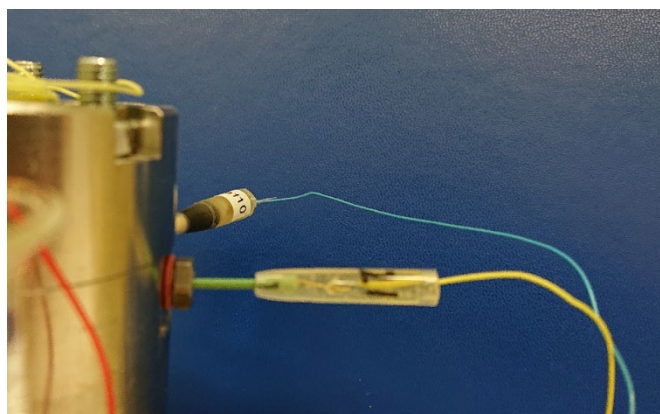


Figure 5. On-line monitoring electrode.

2.3 Composition of the synthetic rainwater used for the tests

2.3.1 Experiments made in oxic conditions

The composition of the synthetic rainwater used for the experiments is presented in Table 4. Before being used for the tests, the pH (originally measured at 4.05) is adjusted to pH = 5±0.1 with a solution of NaOH (0.2 M) and NaOH (0.02M).

Table 4. Composition of the synthetic rainwater.

Representative rainwater	ppm
K ₂ SO ₄	1.69
CaSO ₄	2.26
SrCl ₂ ·6H ₂ O	6.07
NaBr	5.15
Mg ₃ (PO ₄) ₂ ·4H ₂ O	1.24
H ₂ SO ₄	1.34
NaNO ₃	5.6
NH ₄ OH	3.65



2.3.2 Experiments made in anoxic conditions

For the anoxic tests, microbial inoculum was prepared by the Metals and materials recovery (BA3607) laboratory. Lactate and acetate (Table 5) were added to the rainwater. As the pH (initially of rainwater 4.08) reached 5.72 after addition of lactate and acetate, hydrochloric acid (HCl) was added to decrease pH to 5.

The solution was degassed overnight with argon prior placing in the glovebox. Inside the glovebox, microbial inoculum was added to the inlet rainwater solution.

Table 5. Amount of lactate and acetate added to 2 l of rainwater.

	Mass for 2l of rainwater solution [g]
Acetate	0.1635
Lactate	0.2288

2.4 Schedule description of the samplings

The schedule for sampling the solutions passing through the columns is settled as followed: during the first 24h (1h, 2h, 3h, 6h, 10h and 24h), then every 3 days till 18 days and every 30 days between 30 days and 300 days.

3. Analysis of the experiment conditions and effluent concentrations

3.1 Experiments performed in oxic conditions

3.1.1 Evolution of the volumetric flow rate through the columns

Figure 6 presents the evolution of the volumetric flow rate going through the columns in the experiment. During the first 12 days, the volumetric flow rate decreased drastically from about 4 ml/h to 0.1 ml/h. Difference between columns having in steel chips (columns #1 and 2) and column without steel chips (column #3) is noticeable. After 12 days, the volumetric flow rate passing through columns #1 and 2 became constant around 0.1 ml/h, the volumetric flow rate in column #3 reached steadiness around 0.01 ml/h.

After 150 days, a significant increase in the flow rates of the two columns #1 and #2 was observed, while in the third column the flow rate decreased. It was originally deduced that this could have been due to a new pathway forming in the column materials. This however does not seem probable as the changes in the two columns are very simultaneous and similar. Changes in the third column flow rate seem to also correlate to the changes in the other two. This suggests that there has been a change in the functioning of the peristaltic pump or in the measurement of the flow rate.

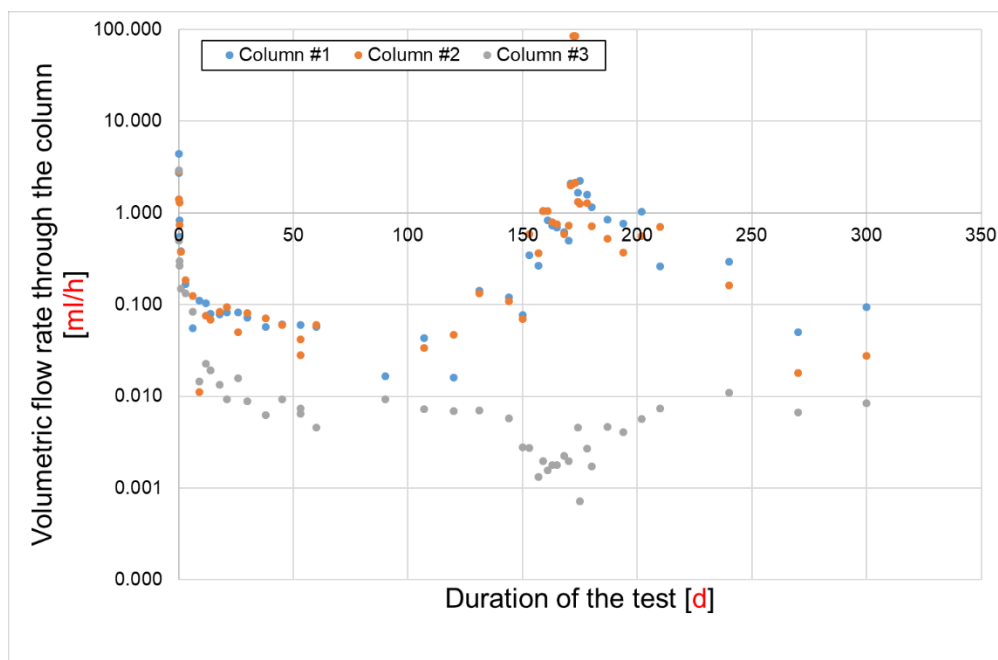


Figure 6. Evolution of the volumetric flow rate going through the columns during the experiment.

3.1.2 Evolution of the pH of the sampling

Figure 7 presents the evolution of the pH of solution going through the columns during the experiment. The inlet synthetic rainwater has a pH of about 5. The effluents after the columns present a pH of about 9 during the first 18 days, and then a pH close to 8. A slight change in the pH of the solution can be observed at the time of the changes happening in the flow rate.

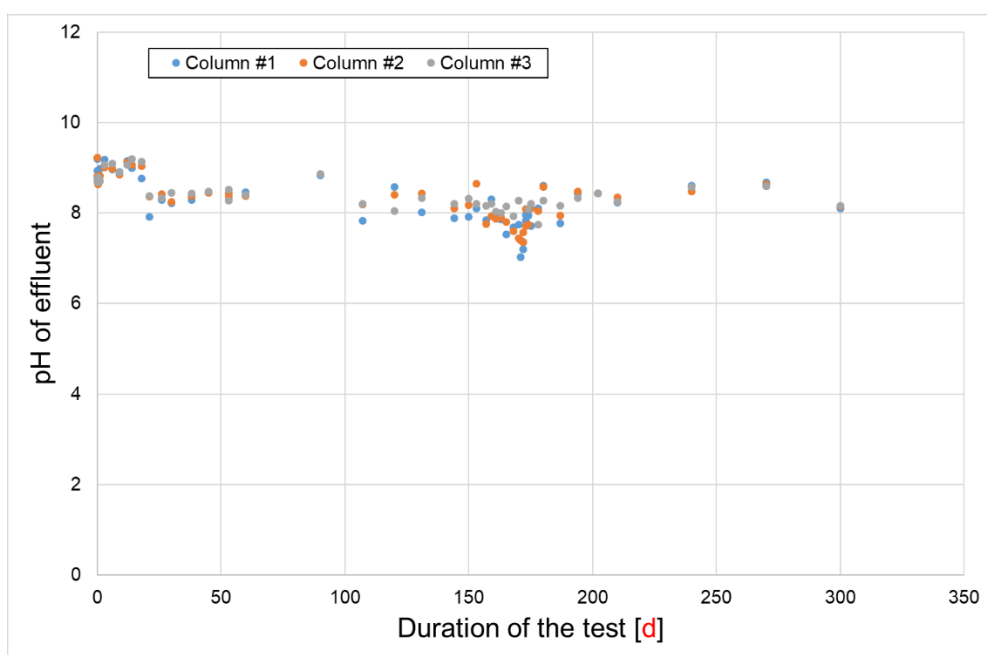


Figure 7. Evolution of the pH of solution going through the columns during the experiment.

3.1.3 Evolution of the composition of the effluent

Concentrations of elements in the effluent solution were analysed with ICP-OES (5110 SVDV, Agilent Technologies) and with ICP-MS (Element2, ThermoScientific). The ICP-OES measurements made had unfortunately been under the detection limits of the spectrometer, so information of the effluents was mainly gained through ICP-MS analysis. Analytes of special interest in these experiments were Sr and Cl. The results for Cl and Br were analysed with ICP-MS, but the measurements did not produce reliable results, concentrations of Br could indicate a possible problem with the rainwater simulant. However, analysis of halogens such as Cl and Br is a challenge even in best possible conditions, so no direct conclusions can be drawn.

Analysis of the effluent samples indicate that Sr is well retained in the column systems. After approximately 50 days of the experiments the Sr concentrations in the effluent begin to increase, most likely due to the sorption sites becoming increasingly occupied (Figure 8). Main competing cations include Ca and Mg (Figure 9). Other trace elements were also analysed, but no real conclusions can be made from the effluent concentrations because of the complex nature of the trace elements and their affinity to different possible sorption sites in the fill materials.

Figure 8 shows for column #3 lower concentrations of Sr and a less drastic change in the increase happening after the 150-day mark. Column #3 had no steel inserts (However the column rigs were made of stainless steel.), but the difference is most likely due to the different flow rates of the solution through the column.

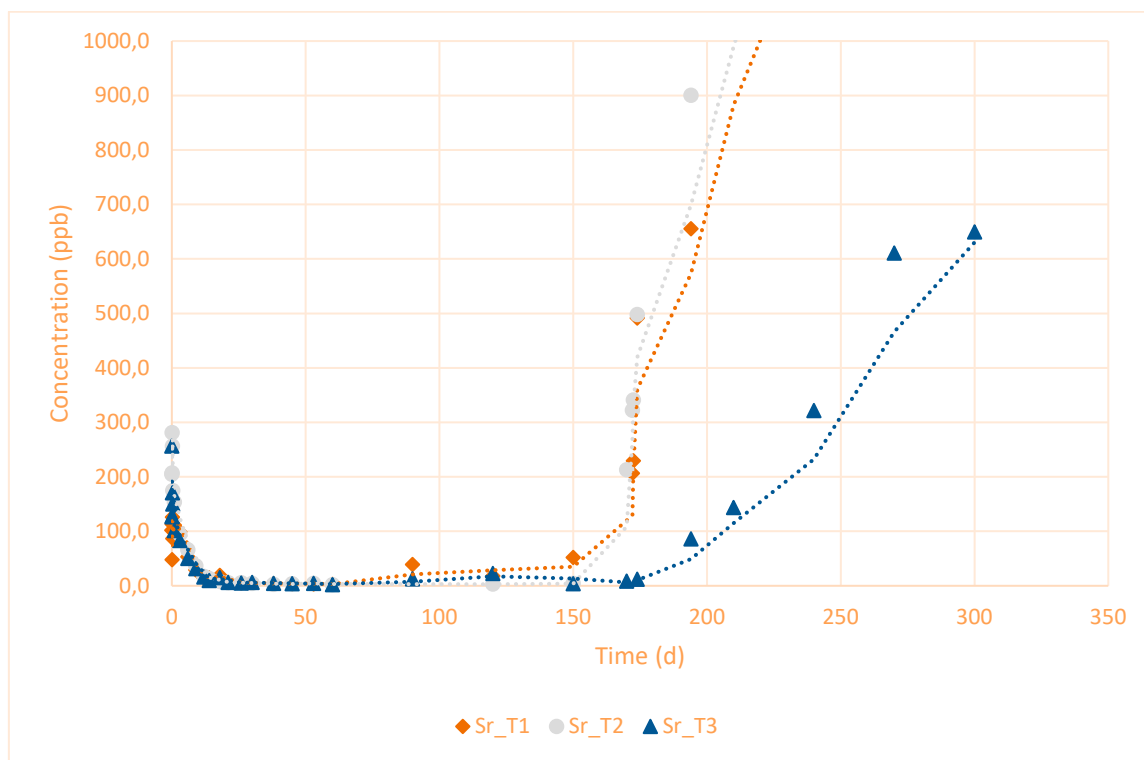


Figure 8. ICP-MS data for Sr concentrations in the effluents of the three different columns (T1: column #1, T2: column #2 and T3: column #3) of the experiment made in oxic conditions.

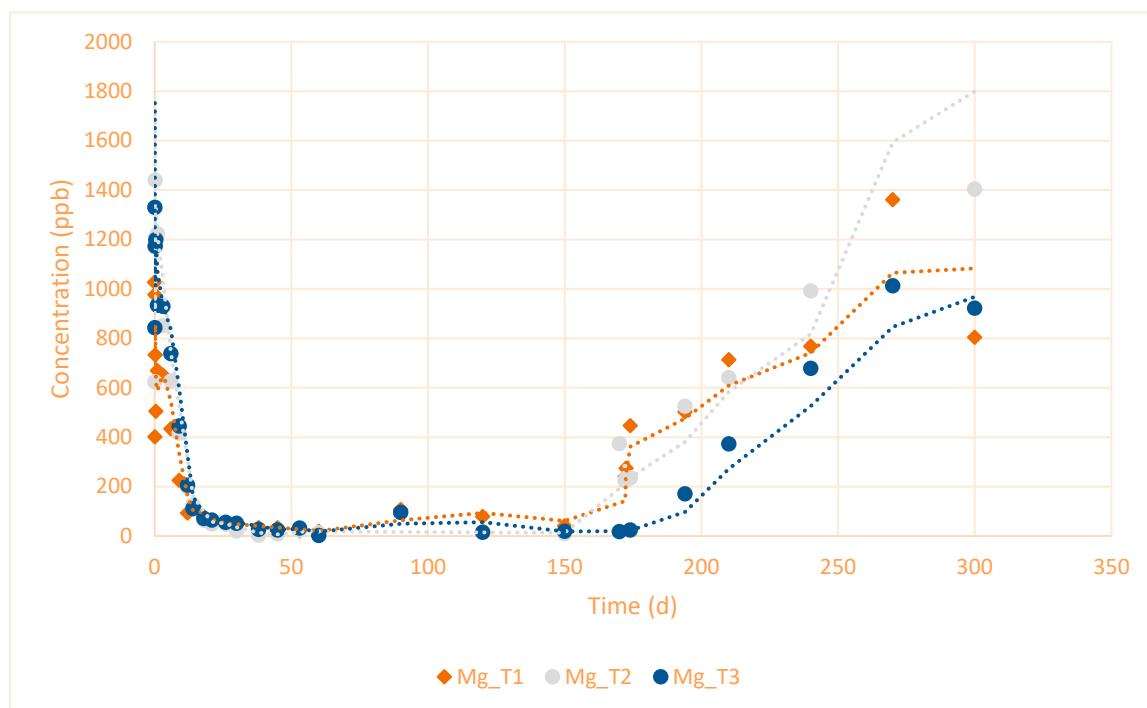


Figure 9. ICP-MS data for Mg concentrations in the effluents of the three different columns (T1: column #1, T2: column #2 and T3: column #3) of the experiment made in oxic conditions.

3.2 Experiments performed in anoxic conditions

3.2.1 Evolution of the volumetric flow rate through the columns

The experiments made did not fill the requirements set for anoxic conditions, due to the malfunction of used glovebox. Because of this, parameters like the redox-potential could not be successfully measured. Figure 10 presents the evolution of the volumetric flow rate going through the columns during the experiment. The flow rate varies significantly.

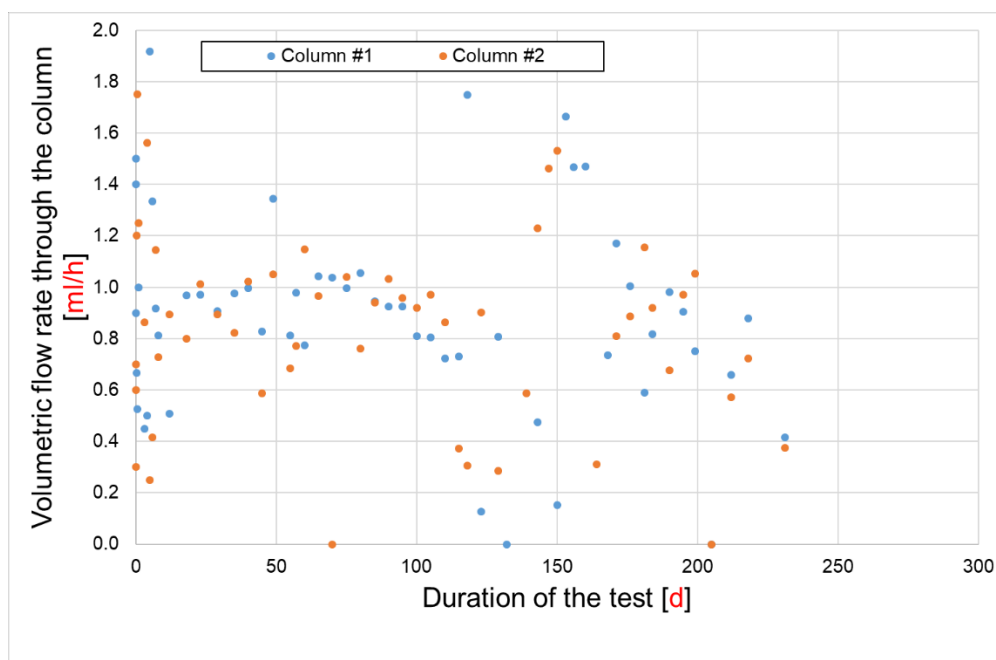


Figure 10. Evolution of the volumetric flow rate going through the columns during the experiment.

3.2.2 Evolution of the composition of the effluent

Concentrations of elements in the effluent solution were again analysed with ICP-OES (5110 SVDV, Agilent Technologies) and with ICP-MS (Element2, ThermoScientific). As for the oxic experiments also similarly for the anoxic ones the ICP-OES measurements made had unfortunately been under the detection limits of the spectrometer, so information of the effluents was gained solely through ICP-MS analysis. The results for Cl and Br had been analysed with ICP-MS, but the results could not be evaluated because an addition of HCl acid had been made in the experiment to adjust the water simulant pH. More specific information on the addition (i.e., the amount and timing) was not recorded accurately enough. Sample markings after 150 days were incongruent, and the results had to be omitted from this report.

Analysis of the effluent samples indicate that Sr is again well retained in the column systems. The rise in concentrations is somewhat quicker than in the previous experiments, the results cannot be directly compared reliably because of the difference in the measurement setup (Figure 11). Magnesium concentrations are presented figure 12.

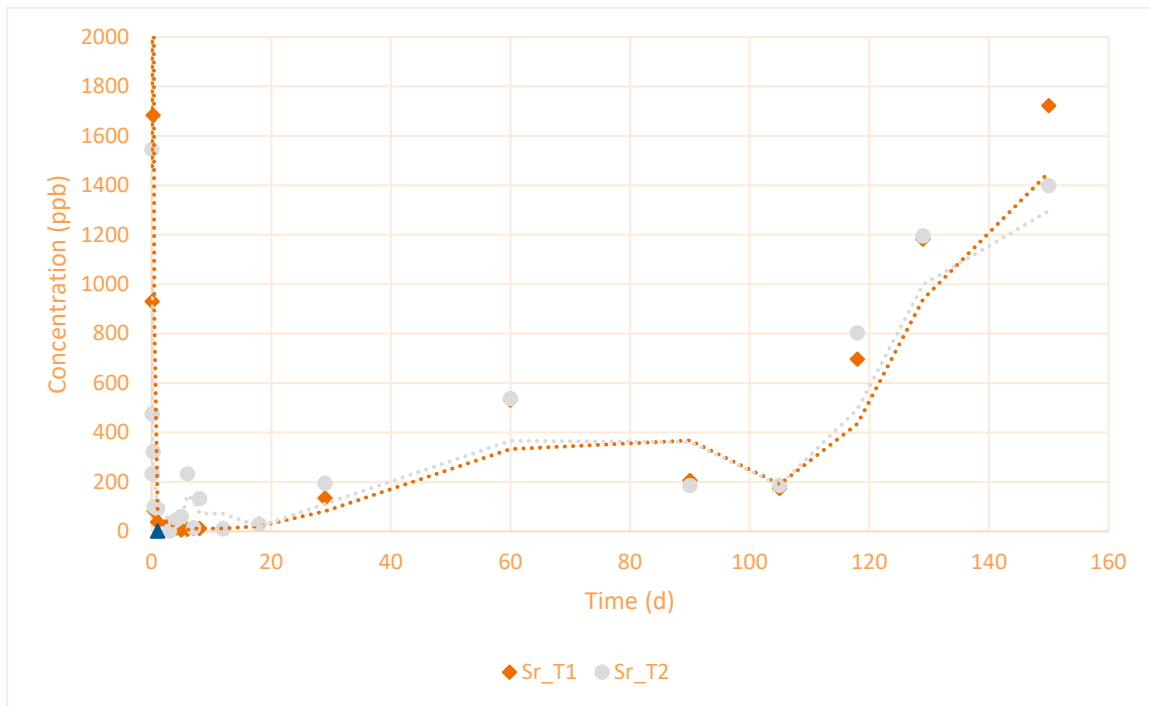


Figure 11. ICP-MS data for Sr concentrations in the effluents of the two different columns (T1: column #1, T2: column #2) of the second experiment made.

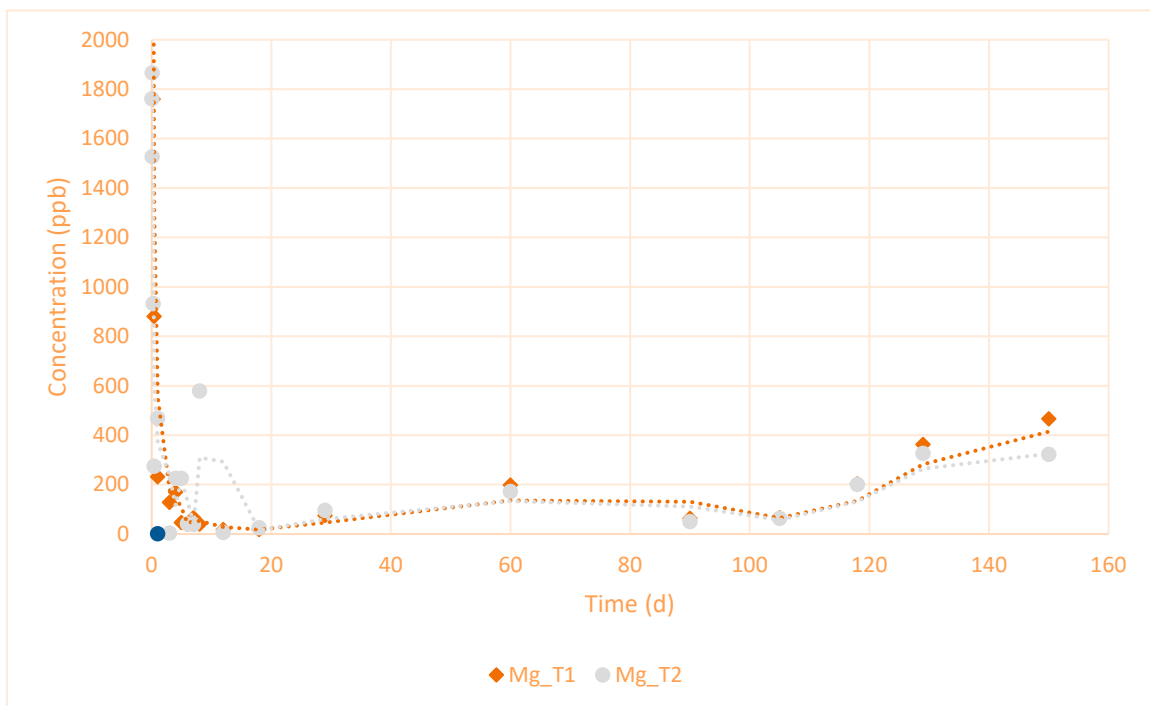


Figure 12. ICP-MS data for Mg concentrations in the effluents of the two different columns (T1: column #1, T2: column #2) of the second experiment made.



4. Conclusions

Radionuclide transport experiments performed at VTT for the KYT Surface -project faced several difficulties. The anaerobic experiments did not fill the requirements set, due to the malfunction of used glovebox. The experimental setup used in experiments, both oxic and anoxic conditions, was something not previously tested at VTT. It was designed to better represent the conditions, like density of the material, present at the VLLW- repository. This resulted in difficulties with adjusting the flow rate in the experiments etc. Ensuring constant flow rate is important for the assessment of concentration levels in the effluent. More careful consideration into the feasibility of experimental design needs to be done in the future if new setups are to be used. Optimization of the design needs to be done before any long-term experiments are begun, at least in the level of estimating possible sources of uncertainty. Monitoring of the different parameters affecting the experimental setup (e.g., the static pressure level at the inlet side of the columns, pump rpm etc.) is important for the validation of the results.

During the project it was concluded that the setup used at University of Helsinki was better suited to studying the retention capability of the repository materials through column experiments. VTT's analysis of the effluents from the column experiments show similar behaviour of analytes to the experiments made at the University of Helsinki. Analysis of the effluent samples indicate that Sr is well retained in the column systems, after approximately 50 days of the experiments (oxic conditions) the Sr concentrations in the effluent begin to increase, most likely due to the sorption sites becoming increasingly occupied.

The results analysed with ICP-OES were later re-examined and some of those were found to be under the detection limits of the ICP-OES equipment. This means that reliable data from the effluent analysis was mainly gained through ICP-MS measurements. Measurements of the chlorine concentrations were re-examined and did not give reliable results in either of the experiments: These results have been omitted from the ICP-MS measurement data.

Post-mortem analysis for the columns could not be reliably performed partly due to information lost in the personnel changes that occurred during this project. Additionally, the removal of the column materials from the steel columns had not been as successful as was required for further analysis. Information loss during changes in personnel is a significant problem and good processes for such occurrences need to be established to minimize the negative impacts.

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