European Joint Programme on Radioactive Waste Management

MOBILITY MISSION REPORT

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MISSION TITLE

Trip to the ESRF

DESCRIPTION

Concerned organisations

The University of Helsinki, The European Synchrotron Radiation Facility (ESRF)

Concerned infrastructures or facilities

Experimental infrastructure (synchrotron)

Concerned phases

Phase 3: Facility construction

Phase 4: Facility operation and closure

Phase 5: Post-closure

Themes and topics

Remove this entire field as well as every below theme and topic that do not apply

- Theme 3: Engineered barrier system (EBS) properties, function and long-term performance
    - Clay-based backfills, plugs and seals
- Theme 4: Geoscience to understand rock properties, radionuclide transport and long-term geological evolution
    - Long-term stability (uplift, erosion and tectonics)
    - Perturbations (gas, temperature and chemistry)
    - Aqueous pathways and radionuclide migration
- Theme 5: Geological disposal facility design and the practicalities of construction, operations and closure
    - Facility and disposal system design
- Theme 7: Performance assessment, safety case development, and safety analyses
    - Integration of safety-related information
    -

Keywords

Radionuclide release mechanisms; radionuclide transport; Bentonite barrier, effect of temperature .

EXECUTIVE SUMMARY

The aim of this mobility event was to study the coordination environment of Sr sorbed to altered bentonite materials for potential use as a buffer material in high activity nuclear waste disposal scenarios using Sr K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Here, we measured 6 samples where Sr has been sorbed to untreated and heat-treated (150 °C, for up to 36 months) bentonites at two pH regimes (8 and 13). The project is part of the EURAD-funded HITEC work package which seeks to improve Thermal, Hydrological and Mechanical (THM) understanding of clay-based materials exposed to elevated temperatures (>100 °C) for extended timescales. As well as studying the physicochemical changes to the material, we wish to provide a quantitative and mechanistic description of the effects of elevated temperature on bentonite / radionuclide interactions via the use of combined Sr sorption isotherm experiments and EXAFS analyses.

The analysis of results is still ongoing

1. MISSION BACKGROUND

International radioactive waste disposal plans employ a multi-layered natural and engineered barrier system to limit radionuclide mobility towards the surrounding biosphere. One of the engineered barriers is a “swelling buffer material” such as bentonite which provides mechanical and chemical stability and protection to the waste-containing canisters The bentonite barriers, which are kept near the waste canister, will be exposed to heat generated by the adjacent spent nuclear fuel, and this heat exposure may exceed 100 °C for extended timescales [1]. Given the importance of the bentonite barrier to the safety case it is imperative that we understand its THM and chemical (THMC) behavior and how they could be affected by heating processes. If we can show that the buffer properties are not significantly compromised by the heating process, thereby allowing for a higher temperature-limit on the canister this could: (1) reduce the cooling time of spent nuclear fuel and, (2) store spent nuclear fuel closer together in the repository. Thus causing significant savings in both space and money.

1.1. R&D background

In this project, we examined the physicochemical changes of Na-Wyoming bentonite following heat treatment (150 ^{o}C) over a 3 year period. Thus far, our study shows visible bentonite alterations in the x-ray diffractograms with increasing heat treatment time (Figure 1), and we also observe a significant change in the cation exchange capacity after 36 months of heat treatment. Further, we assess how these physicochemical changes to the bentonite structure affect its interactions with radionuclides (e.g., Sr-90) at circumneutral (pH 8) and alkaline (pH 13) conditions. In Sr sorption isotherm experiments (Figure 2), we find a large difference in Sr uptake in neutral (approx. 40%) vs. alkaline (approx. 90%) regimes, with slightly lower uptake on heat-treated bentonite than fresh. EXAFS analyses are key to understanding Sr sorption mechanisms and can clearly resolve the difference between inner- and outer-sphere sorption mechanisms (e.g., [2], [3]). We would like to assess the differences in the Sr speciation in the two pH regimes, and shed light on any detectable differences in the complex structure on the bentonite material following heat treatment.

References

[1] Ewing, R. C. (2015) ‘Long-term storage of spent nuclear fuel’, Nature Materials, 14(3), pp. 252–257. [2] Fuller, A. J. et al. (2014) ‘Ionic strength and pH dependent multi-site sorption of Cs onto a micaceous aquifer sediment’, Applied Geochemistry, 40, pp. 32–42 [3] Ho, M. S. et al. (2023) ‘Mechanisms Governing 90Sr Removal and Remobilisation in a VLLW Surface Disposal Concept’, Minerals, 13(3), p. 436.

Please help – I would like to add a figure?

1.2. Mission objectives

The aim of this mobility event was to study the coordination environment of Sr sorbed to altered bentonite materials for potential use as a buffer material in high activity nuclear waste disposal scenarios using Sr K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

1.3. Mission request

To the Mobility Evaluation Committee,

I am an early career researcher, working in the EURAD-HITEC work package based at the University of Helsinki. I am seeking mobility funding to fund my travel, accommodation, and subsistence during an HITEC experiment at the European Synchrotron Radiation Facility (ESRF). The scientific proposal was recently accepted for award of beam-time and the experiment has been scheduled for November 2023.

Briefly, the HITEC work package seeks to improve thermal, hydrological and mechanical (THM) understanding of clay-based materials exposed to elevated temperatures (>100 °C) for extended timescales [1]. As well as studying the physicochemical changes to the material, my work seeks to provide a quantitative and mechanistic description of the effects of elevated temperatures on bentonite – radionuclide interactions via use of combined Sr sorption isotherm experiments and EXAFS analyses. My research in the HITEC project therefore has two tasks: task 1: characterisation of Na-Wyoming Bentonite exposed to high temperature (150 °C) over extended timescales (36 months); and task 2: to understand the consequences of potential changes to the material following of heat treatment, and implications therein for radionuclide retention.

Thus far, XRD analysis has shown extensive bentonite alteration with increasing heat treatment time, and we observe a significant reduction of the cation exchange capacity after heat treatment (-30%). Further, we assess how these physicochemical changes to the bentonite structure affect its interactions with radionuclides in early release scenarios (e.g., Sr-90) under circumneutral (pH 8) and alkaline (pH 13) conditions. In Sr sorption isotherm experiments, we find a large difference in Sr uptake in neutral (approx. 40%) vs. alkaline (approx. 90%) regimes, with slightly lower Sr uptake onto heat-treated bentonite compared to fresh bentonite. EXAFS analyses ESRF will be key to understanding changes in the Sr sorption mechanisms. Critically, EXAFS can clearly resolve the difference between inner- and outer-sphere sorption mechanisms in environmental systems (e.g., [2], [3]). The results of my ESRF experiment will reveal the sorption mechanism and Sr local coordination environment.

The experiment at ESRF was recently selected for funding. In writing the proposal I have built collaborations with Prof. Nina Huittinen (Freie Universität Berlin / Helmholtz-Zentrum Dresden-Rossendorf) and Prof. Kristina Kvashnina (ESRF/ Helmholtz-Zentrum Dresden-Rossendorf). This experiment is crucial to complete my HITEC study and EXAFS is the only suitable method to elucidate subtle changes in the Sr sorption mechanisms, the results will significantly increase the scientific quality of the work. This opportunity will also allow me to:

- Network with other researchers and practitioners, potentially leading to future collaborations or job opportunities.
- Gain inspiration and new perspectives that will help me advance my own work and contribute to the broader scientific community.
- Establish myself as a young researcher.

Unfortunately, as a ECR, my funding is currently limited and I am unable to attend the experiment without financial assistance. I am therefore applying for a EURAD mobility grant, and I would be extremely grateful for any support that can be provided. If awarded funding, I will use it to cover my flights, accommodation, and subsistence during the beam-time.

Thank you for considering my request for funding. I believe that this experiment is vital to my current HITEC work and its contributions will be relevant to not only the HITEC community but to all researchers interested in bentonite as a barrier in waste geological disposal scenarios. Moreover, this will be an excellent opportunity for me to further my professional development, network, and contribute to the advancement of my work in HITEC. If you require any additional information or have any questions, please do not hesitate to contact me.

Faithfully,

Dr. Gianni F. Vettese

Radiochemistry A217b, Radiochemistry Unit,

Department of Chemistry, University of Helsinki,

A.I. Virtasen Aukio 1, Helsinki, 00560

+35829503360927

1.4. Mission composition

Host organisation

The European Synchrotron Radiation Facility

Host facility

BM 20 ROBL

Mission dates

The Experiment took place between 07/11 – 09/11. Travel was one day either side.

2. MAJOR PRACTICES, TECHNIQUES, METHODS, TOOLS OR SYSTEMS OPERATED OR STUDIED

X-ray Absorption Spectroscopy (XAS) is a synchrotron based technique that fires high energy X-rays onto a sample of interest. In a similar fashion to XRF some X-rays are absorbed by atoms within the sample causing excitation and/or ejection of a core electron. Upon electron ejection or excitation an electron of higher energy moves from a higher shell to the now-vacant core hole, to balance the energy excess energy is lost as a secondary fluorescent X-ray (Auger electron). We can measure either the transmission of the incoming X-ray as a function of energy or measure the fluorescence at right angles to yield information on samples. X-ray Absorption Near Edge Structure (XANES) describes oxidation state and bond angles for local geometry and, Extended X-ray Absorption Fine Structure (EXAFS), by comparison, can describe interatomic distances and local coordination number.

2.1. Practice, technique, method, tool or system operated or studied during the mission

XANES and EXAFS

Description

Radionuclide dedicated synchrotron beamline.

Usage

We measured six powder samples comprised of stable Sr sorbed to bentonite at two pH regimes (8 and 13) for untreated and heat-treated (150 °C) bentonites at two different aging time points (22 and 36 months) (Table 1). Samples were prepared under anaerobic conditions (to exclude CO_2) as wet pastes in SH-XAFS-1 sample holders, sealed with 12 micron Kapton foil windows and glued round the edges only (to prevent contact of the sample with organics) for Sr EXAFS measurement (*K* ~16). Samples will be shipped in an inert gas container at room temperature but the EXAFS measurements at the strontium K-edge (16105 eV) were collected in fluorescence mode under cryogenic conditions. The three samples at pH 13 have higher sorption compared to the three samples at pH 8, their concentration is expected to be approximately 1500 ppm and 800 ppm Sr respectively (Table 1).

Table 1*: EXAFS Sample list and concentrations*

	Approximate Sr concentration (ppm)		
Sample pH	Unaltered	Heat-treated (22 month)	Heat-treated (36 month)
8	700	600	600
13	1700	1600	1600

Benefits

XAS is highly sensitive to first coordination shell of elements and is element specific.

Limitations

Access to synchrotrons is generally the limiting factor, the application process is very tough and has a low success rate. Moreover data analysis is complex, requiring experienced analysts.

Applicability

Molecular scale analysis of radionuclides in samples allows us to understand the mechanisms governing interactions e.g. Sr sorption to bentonite.

2.2. Practice, technique, method, tool or system operated or studied during the mission

Not applicable.

Description

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Usage

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Benefits

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Limitations

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Applicability

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2.3. Practice, technique, method, tool or system operated or studied during the mission

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Description

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Usage

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Benefits

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Limitations

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Applicability

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2.4. Practice, technique, method, tool or system operated or studied during the mission

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Description

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Usage

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Benefits

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Limitations

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Applicability

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3. MISSION FINDINGS AND CONCLUSIONS

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3.1. Lessons learned and conclusions

Thus far we have identified clear differences in the Sr sorption mechanisms to bentonite at pH 8 and pH 13. There are no significant difference in bonding mechanisms before and after heat treatment suggesting that the effect of heating bentonite at 150 degrees for up to 36 months has little effect on the radionuclide retention capabilities of the bentonite. Although, because data analysis is complex it is still ongoing.

3.2. Relevant findings and conclusions for home organisation

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3.3. Relevant findings and conclusions for host organisation

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3.4. Relevant findings and conclusions for other organisations

See above

4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

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4.1. Generic potentials

Provide mechanistic understanding of radionuclide retention mechanisms to compliment quantitative data

4.2. Potentials for home organisation

This has built a strong network for Young Researcher Gianni Vettese with a world leading synchrotron facility. From this networking opportunity he will be able to win more synchrotron access.

The data are also highly relevant to the work and will provide invaluable contributions to the scientific findings. This will significantly increase the impact factor of the publication (expected 2024).

4.3. Potentials for host organisation

Build networks with users at the University of Helsinki

APPENDICES

Mission journal

Travel to and from synchrotron day before and after experiment. During experiment we work up, ate breakfast and continued to work straight for the 2 days. Samples were set in an autosampler and we carried out the measurements.

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MISSION BENEFICIARY

Gianni F. Vettese
Post-doctoral Researcher
Radiochemistry Unit, Chemistry department
The university of Helsinki, Finlan

PARTNER EXPERTS CONTRIBUTING TO THE MISSION

Host organisation experts

- Damien Prieur, Andrea Scheinhost, Kristina Kvashnina

Home organisation experts

- Gianni Vettese

Other organisations experts

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REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
Date of last signee	Gianni Vettese	N/A	Damien Prieur
	Visa	Visa	Visa