MOBILITY MISSION REPORT

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MISSION TITLE

Low-level Uranium Analysis

DESCRIPTION

Concerned organisations

- Research entities

CEA Paris-Saclay, France
Amphos 21, Spain

Concerned infrastructures or facilities

Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR), CEA

Concerned phases

Phase 5: Post-closure

Themes and topics

- Theme 3: Engineered barrier system (EBS) properties, function and long-term performance
    - Cementitious-based backfills, plugs and seals
- Theme 7: Performance assessment, safety case development, and safety analyses

- Treatment of uncertainties

Keywords

Radionuclide transport; adsorption; uranium; CASH; cements

EXECUTIVE SUMMARY

Cements feature prominently in most radioactive waste repository scenarios and will likely affect the behavior of dissolved radionuclides. Organic compounds are found in some radioactive waste matrices with a variety of sources and also have the potential to control radionuclide mobility. Despite this, the interactions of cements, radionuclides and organic molecules have received relatively little attention.

Amphos 21 has been investigating the sorption of uranium to hydrated cement phases in the presence and absence of organic molecules (isosaccharinic acid, ISA; adipate; phthalate). Due to the U detection limits of the ICP-MS instrument used (ca. 2×10^{-9} M) there have been difficulties obtaining reliable measurements of uranium solution concentrations.

The purpose of the internship was to facilitate the analysis of uranium in solution in samples using the instruments and measurement expertise developed by the research group of Dr Nathalie Macé at CEA. Dr Macé runs a dedicated trace level laboratory for measurement of radionuclides at the Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR), CEA Paris-Saclay. Here, U detection limits for the ICP-MS are ca. 1.5×10^{-11} M. The research internship was a 5-day visit to CEA in which he observed, and aided in taking samples and preparing them for analysis via ICP-MS.

As a result of the visit, important results were obtained showing that the effect of organic molecules on uranium sorption to cementitious phases is dependent both on the organic molecule and the solid phase.

1. MISSION BACKGROUND

1.1. R&D background

Within the CORI WP, Amphos 21 has been investigating the sorption of uranium to hydrated cement phases in the presence and absence of organic molecules. Cements feature prominently in most radioactive waste repository scenarios and will likely affect the behavior of dissolved radionuclides. Organic compounds are found in some radioactive waste matrices with a variety of sources and they, and their degradation products also have the potential to control radionuclide mobility. Despite the implications of the presence of these materials for the fate of radionuclides, and the associated impacts on the Safety Case for low and intermediate level (L/IL) waste disposal, the interactions of cements, radionuclides and organic molecules have received relatively little attention.

As part of our work, we have studied the sorption of three organic molecules (adipate, phthalate and ISA) and uranium on to calcium aluminum silicate hydrates (CASH). Given the solution conditions of our experiments, the solubility of uranium is relatively low (around 10^{-7} M). This limits our starting uranium concentration. In contrast, the sorption affinity of uranium for the cementitious phases is extremely high. In combination, this has resulted in very low concentrations of uranium in our samples. Due to the U detection limits of the ICP-MS we are using (c. 2×10^{-9} M) we are having difficulties obtaining reliable measurements of the uranium solution concentrations in our experiments. Although we have altered some of our experimental parameters (e.g., reducing the solid to liquid ratio) to maximize U solution concentrations, and although we already have sorption results for the CASH-U system, we are still unable to produce the reliable and consistent measurements that this work requires. In turn, this limits the data we can provide to the CORI WP concerning the behavior of uranium in organic-rich, cementitious environments.

The L3MR laboratory, where Dr Nathalie Macé has been a researcher since 2009, is dedicated to measuring and modeling radionuclide migration through different porous matrices, including cementitious phases. For this purpose, an experimental platform of radiolabeled tracer analysis and counting has been developed in the department since 2002. The L3MR is divided into four different working-areas: one for sample preparation and conditioning, one for non-active physico-chemicals analysis, one for trace-level element analysis, and a radiochemistry lab, where a large radioisotope library can be handled, including ^{238}U.

Using classical analytical procedures, L3MR can achieve c.a. 1.5×10^{-10} mol/L with 5% uncertainty as the lowest measurable U concentration. However, under the optimized conditions established at L3MR (i.e., using ^{204}Tl as an internal standard, ultrapure HNO3 solution, ultrapure water (Milli-Q, Millipore) and working in a trace area laboratory where solutions are exclusively prepared in dedicated fume hoods) has decreased the quantification limit by a factor of 10 to reach ca. 1.5×10^{-11} mol/L with a precision close to 5%. Such a quantification limit is necessary to measure with accuracy the low U values in solution in sorption/desorption experiments with cementitious matrices and especially when U(VI) solubility is low (around 10^{-7} M) as is the case with CASH phases.

1.2. Mission objectives

This research internship entails a suite of experiments to both validate our existing U measurements and to expand on them in order to provide comprehensive insight into uranium behavior. It will involve performing U sorption isotherms with initial concentrations ranging from 4×10^{-7} M to 1×10^{-9} M in both the presence and absence of ISA at concentrations of 10^{-3} M and greater. ISA has been chosen as the candidate organic due to our existing data that shows a greater sorption affinity for CASH solids compared to adipate and phthalate species. In addition, ISA has also demonstrated an impact on the sorption behavior and solubility of U in our systems. These are sorption experiments of the kind that Amphos 21 has performed previously in the CORI WP.

To improve efficiency, the relevant solid, solution, and organic materials to be used in the experiments will be prepared by Amphos 21 and sent to CEA ahead of the research internship. Amphos 21 has experience of successfully sending samples under a controlled atmosphere to collaborators. Upon receipt, ^{238}U and ISA will be spiked into samples by colleagues at L3MR. Samples will be equilibrated under a controlled atmosphere for 14 days. To optimize resources, the research internship will be limited to 1 week, coinciding with the sampling of the experiments. The applicant will be present to prepare the samples in the dedicated trace-level laboratory as well as to learn how to run the sample solutions on the ICP-MS. There will be a maximum of 100 samples for processing and analysis including standard calibration. The work commitment is expected to be a total of 5 working days.

Training benefits to the applicant

It is expected that the applicant will gain invaluable technical knowledge of the measurement of trace level uranium concentrations. They will also gain experience working in a European research institute and will have the opportunity to learn first-hand about European approaches to radioactive waste management. It will also provide them with the platform to expand their European scientific network.

Benefits to the Partner organizations

For CEA and Amphos 21, the internship heralds the start of a more intense collaboration between the two partners. This has promising implications for future knowledge development (for example in a collaboration within the next Joint European Program) and transfer for the science of radioactive waste disposal. CEA has excellent laboratory and instrument capabilities whilst Amphos 21 possesses extensive expertise in modeling the behavior of radionuclides in waste disposal scenarios.

Benefits to EURAD and CORI

For EURAD and the CORI WP, the internship will result in important data pertaining to the improved scientific basis for the Safety Case for L/IL waste repositories featuring high organic content. This internship would strengthen the research outcomes of the CORI WP by capitalizing on the advances made at both Amphos 21 and CEA to produce high quality scientific data.

1.3. Mission request

The Mobility Grant Application is for a proposed research internship of Dr James Begg (Amphos 21, Spain), to CEA Paris-Saclay, France. This is an internal EURAD WP (CORI) mobility action.

The purpose of the internship is to facilitate the analysis of U in solution in samples generated by Amphos as part of the CORI WP using the instruments and measurement expertise developed by the research group of Dr Nathalie Macé at CEA. This cooperative research plan, which leverages the expertise available at both the sending and receiving partners, will result in the generation of cutting-edge scientific data pertaining to the safe management of radioactive waste.

1.4. Mission composition

Host organisation

CEA Paris-Saclay

Host facility

Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR)

Mission dates

5/12/2022 – 9/5/2022

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

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

Anoxic sampling of sorption experiments.

Description

An approach to sampling of sorption experiments that sees samples being ultracentrifuged and then transferred to a controlled atmosphere. An aliquot of supernatant is taken for meaurment of U concentration via ICP-MS.

Usage

Demonstration of entry and exit procedures for both personnel and samples for a controlled access radiochemistry laboratory.

Use of ultracentrifuge for solid/liquid phase separation.

Transfer of samples into a controlled-atmosphere glovebox.

Gravimetric sampling of supernatants.

Benefits

The centrifugation provides excellent particle size discrimination. Working in a controlled atmosphere glovebox ensures that the experiments mimic redox conditions expected in a waste repository. Gravimetric sampling contributes to the accuracy of the measurements.

Limitations

This approach to sampling is time intensive. The transfer of samples after centrifugation can lead to particle re-suspension.

Applicability

A gravimetric approach to sampling could be employed in the home laboratory to improve accuracy of sample measurements. This is a simple change that could be easily adopted. In addition, a switch to a centrifugation-only approach for solid/liquid phase separation may allow a smaller particle size discrimination than the approach taken currently (centrifugation followed by 0.22 µm filtration).

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

Measurement of U via ICP-MS in a trace-level laboratory

Description

Preparation and measurement of samples with low solution concentrations of U in a dedicated low level facility.

Usage

Samples are transferred from the sampling laboratory to the clean ICP-MS laboratory. Personnel follow clean lab protocols to enter the laboratory. Samples are acidified with ultrapure HNO_3 (either added as concentrated HNO_3 or diluted in 2% HNO_3) and spiked with ^{204}Tl as an internal standard. Samples are then added to the autosampler with calibration standards and blanks.

Benefits

The use of ^{204}Tl as an internal standard, ultrapure HNO_3 solution, ultrapure water and working in a trace area laboratory where solutions are exclusively prepared in dedicated fume hoods allows for low detection limits with the ICP-MS. This allows improved accuracy of measurement for the low U values in solution in sorption/desorption experiments with cementitious matrices where U sorption is high.

Limitations

Samples may fall outside the concentration range covered by the calibration standards, especially if they have been diluted based on expected concentrations. This may necessitate re-sampling of the experiments which may be an issue if the experiments have limited volume.

The method requires a dedicated work area which may not be structurally achievable.

Applicability

In principal, the creation of a dedicated area for trace level analysis at the home institution is not practicable. However, some aspects of the method, such as use of ultrapure HNO_3 may reduce background noise and improve detection limits.

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

Replace this entire field with the name of the practice, technique, method, tool or system that is the object of this mission.

Description

Replace this entire field with a description of the implementation of this practice, technique, method, tool or system at the host organisation.

Usage

Replace this entire field with a description of your operation or study of this practice, technique, method, tool or system during the mission.

Benefits

Replace this entire field with a description of the benefits for implementing this practice, technique, method, tool or system.

Limitations

Replace this entire field with a description the limitations of this practice, technique, method, tool or system.

Applicability

Replace this entire field with a description of how this practice, technique, method, tool or system could be implemented in or adjusted to your home context.

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

Replace this entire field with the name of the practice, technique, method, tool or system that is the object of this mission.

Description

Replace this entire field with a description of the implementation of this practice, technique, method, tool or system at the host organisation.

Usage

Replace this entire field with a description of your operation or study of this practice, technique, method, tool or system during the mission.

Benefits

Replace this entire field with a description of the benefits for implementing this practice, technique, method, tool or system.

Limitations

Replace this entire field with a description the limitations of this practice, technique, method, tool or system.

Applicability

Replace this entire field with a description of how this practice, technique, method, tool or system could be implemented in or adjusted to your home context.

3. MISSION FINDINGS AND CONCLUSIONS

3.1. Lessons learned and conclusions

The research visit demonstrated that CEA and Amphos 21 can undertake successful collaborative research. Importantly, the process showed that experiments can be sent between laboratories meaning that each can focus on their own area of expertise, allowing for greater efficiency. One important lesson was the need for very clear and unambiguous experimental protocols to accompany any samples that are transferred to avoid later uncertainty. That this kind of approach can be successful has promising implications for future knowledge development.

The visit also provided Amphos 21 with an appreciation of the instrumental capabilities available at CEA Paris-Saclay as well as a more detailed knowledge of the procedures for trace level measurements. Understanding the length of time taken for sample processing as well as the types of concentrations that can be reasonably measured is invaluable for future experiment planning

Finally, the internship has produced good data pertaining to the improved scientific basis for the Safety Case for L/IL waste repositories featuring high organic content. This is particularly important in the context of the CORI WP.

3.2. Relevant findings and conclusions for home organisation

The L3MR at CEA Paris-Saclay can comfortably measure uranium concentrations as low as 1×10^{-11} M. They are well set up to receive, process, and analyze samples. In addition, they have excellent radiochemical facilities as well as instruments that would be useful for materials analysis, such as surface area and crystallographic structure.

As a result of the uranium measurement capabilities at CEA, it was possible to calculate U sorption K_d values for to calcium aluminium silica hydrate (CASH) phases with the same Ca:Si ratio but different Al:Si ratios phases as well as a crushed cement phase. The calculated values were of the order of 10^5 L/kg for the CASH with the higher Al:Si ratio and the cement. For the CASH with the lower Al:Si ratio, the K_d was on the order of 10^7 L/kg. The presence of ISA at a concentration of 10^{-2} M decreased uranium sorption for all solids, reducing the calculated K_d values by up to an order of magnitude.

3.3. Relevant findings and conclusions for host organisation

This section is not mandatory but can be prepared with the mission supervisor or mentor from the host organisation. If applicable, replace this entire field with a description of about 200 words of findings and conclusions that are specifically relevant to the host organisation. If not applicable, remove the entire section.

3.4. Relevant findings and conclusions for other organisations

4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

This entire section shall be maximum one page (remove this entire sentence).

4.1. Generic potentials

This section is not mandatory. If applicable, replace this entire field with a description of about 150 words of generic potential improvements or developments you can suggest for the practices, techniques, methods, tools or systems operated or studied during the mission. If not applicable, remove the entire section.

4.2. Potentials for home organisation

This section is not mandatory but can be prepared with the mission supervisor or mentor from your home organisation. If applicable, replace this entire field with a description of about 150 words of specific potential improvements and developments you can suggest for your home organisation. If not applicable, remove the entire section.

4.3. Potentials for host organisation

This section is not mandatory but can be prepared with the mission supervisor or mentor from the host organisation. If applicable, replace this entire field with a description of about 150 words of specific potential improvements and developments you can suggest for the host organisation. If not applicable, remove the entire section.

APPENDICES

Mission journal

Monday, December 5th. Arrival at CEA. Badging at North Gate. Welcome from Dr Macé. Introduction to other researchers, technicians and administrative staff in the facility. Tour of the offices. Safety briefing. Lab tour. Meeting with Dr Bruneel about the experiments and sampling program including discussion of some issues in experiment preparation. Overview from Dr Bruneel about ICP-MS approach including calibrations with Tl spike, volume of sample, run times and sensitivity. Review of data generated in initial experiments. Discussion of sampling plan. Tour of controlled laboratory.

Tuesday, 6th December. With Dr. Macé: sampling of sorption experiments (U-pthalate). Introduction to approach to sampling for ICP-MS analysis (gravimetric preparation of samples). Ultra-centrifugation of samples. Entry of samples into controlled atmosphere glovebox and sampling of supernatant. Transfer of samples to clean laboratory for ICP-MS analysis. With Dr. Bruneel: introduction to clean lab protocols. Preparation of samples for measurement (acidification, Tl spiking). Start of analysis run.

Wednesday, 7th December. With Dr. Bruneel: sampling of sorption experiments (U-ISA). Ultracentrifugation, sampling inside glovebox, transfer to clean lab. Preparation of samples for ICP-MS measurement. Set up of instrument run. In office: initial analysis of results from 6/12/22.

Thursday, 8th December. With Dr. Bruneel: sampling of sorption experiments (U-isotherm). Ultracentrifugation, sampling inside glovebox, transfer to clean lab. Preparation of samples for ICP-MS measurement. Analysis of data.

Friday, 9th December. Analysis of data with Dr. Macé and Dr. Bruneel. Identification of samples below detection limit. With Dr. Macé: re-sampling of identified experiments. Ultracentrifugation, sampling inside glovebox, transfer to clean lab. Preparation of samples for ICP-MS measurement. Discussion of next steps and treatment of data. Departure from CEA.

MISSION BENEFICIARY

James BEGG
Consultant
Nuclear Services
Amphos 21, Spain

PARTNER EXPERTS CONTRIBUTING TO THE MISSION

Host organisation experts

- Dr. Nathalie Macé; Ingénieur Chercheur, Laboratoire de Mesure et Modélisation de la Migration des Radionucléides (L3MR), CEA
- Dr. Yaana Bruneel; Postdoctoral Researcher, L3MR, CEA

Home organisation experts

- Dr. David García; Group Manager, Nuclear Services, Amphos 21

Other organisations experts

REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
8/1/2023	James Begg	David García Cobos	Nathalie Macé