

# MOBILITY MISSION REPORT

*This work has been partially supported by the EURAD project that has received funding from H2020-EURATOM 1.2 under grant agreement ID 847593.*

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## MISSION TITLE

Role of organics in radionuclide retention on cement materials

## DESCRIPTION

### Concerned organisations

Research entities

- Karlsruhe Institute of Technology (KIT) – Institute for Nuclear Waste Disposal (INE).
- Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT)

### Concerned infrastructures or facilities


Laboratories from INE , located at KIT Campus North.

### Concerned phases

Does not apply

### Themes and topics

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)
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- Aqueous pathways and radionuclide migration

Theme 7: Performance assessment, safety case development, and safety analyses

- Integration of safety-related information
- Performance assessment and system models
- Treatment of uncertainties

### Keywords

Low level radioactive waste, cementitious materials, Timed-Resolved Laser Fluorescence Spectroscopy (TRLFS), actinides, nickel, citric acid (CA), Isosacharinnic acid (ISA), portlandite, sorption, solubility

## EXECUTIVE SUMMARY

Radionuclide (RN) interaction with cementitious materials and its hyperalkaline environment must be studied for a correct prediction of radionuclide migration in the long term. One of the important points to predict RN migration is to know their solubility and speciation. Solubility of RN and their interactions with organic compounds present in the repositories are reported in Nuclear Energy Agency (NEA) reports like its chemical thermodynamics volume 9, which was published in 2005 [1].

In particular, studies related to Ni-citrate systems in alkaline and hyperalkaline systems are quite limited. Also, some inconsistencies related with the values facilitated are discussed. Similarly, the mechanistic understanding of the uptake of An(III) by cementitious materials in the presence of organic ligands is very limited, particularly due to the low concentrations in the aqueous phase and thus the limitations with regard to the use of spectroscopic methods.

In this context, the research stay of Oscar Almendros at KIT-INE focused on two objectives using different experimental techniques: (i) the study of Portlandite-Cm(III)-CA/ISA systems with TRLFS, and (ii) the solubility of the binary system Ni-citrate. The latter is expected to provide a sound understanding of the aqueous speciation in the presence of this organic ligands, which is considered as a key input for the for the interpretation and modelling of the ternary system with cement phases.

TRLFS measurements allowed the identification of both aqueous complexes and sorbed species in the system Portlandite-Cm(III)-CA/ISA, as well as their corresponding evolution with increasing ligand concentrations. In combination with the wet-chemistry data obtained at CIEMAT for analogous system, these results will contribute to unravel the complex mechanisms driving the retention of An(III) under these conditions.

Solubility studies have allowed to gain a sound understanding of complexation phenomena for the Ni(II)-CIT system, both in the absence and presence of Ca. In contrast to initial expectations, Ca does not outcompete Ni(II) for CIT complexation, but instead participates in the formation of ternary complexes of the type Ca-Ni(II)-CIT. Thermodynamic models are currently being derived, and these will be a key input for the the modelling of sorption data obtained in the wet-chemistry experiments at CIEMAT.

## 1. MISSION BACKGROUND

### 1.1. R&D background

Radionuclide retention on natural and engineered barriers is a relevant topic of study in the context of underground repositories for nuclear waste disposal. In the event of formation water interacting with the waste, aqueous systems may form eventually promoting the migration of radionuclides into the biosphere. Thus, all the processes that can affect radionuclide retention / mobilization must be analysed in detail. In this context, sorption is considered as one of the main processes limiting the release of radionuclides from the repository.

Large inventories of organic materials (paper, tissues, plastics...) are expected in repositories for low and intermediate level waste (L/ILW). The degradation of these materials may result in the formation of organic ligands capable to form stable complexes with radionuclides, which may enhance their solubility, hinder sorption, and thus potentially promoting their mobilization from the repository.

A mechanistic understanding of radionuclide retention and behaviour in complex environments and their interactions with barrier materials is fundamental to optimize the safety of radioactive waste repositories.

Theme 4 of the European Joint Programme on Radioactive Waste Management (EURAD) roadmap: "Geoscience to understand rock properties, radionuclide transport and long-term geological evolution", includes as main objective radionuclide migration studies in complex materials.

The Cement-Organic-Radionuclide Interactions (CORI) work-package within EURAD has the objective to study and develop knowledge about the interaction of radionuclides in cementitious systems with organic compounds expected in radioactive waste.

### 1.2. Mission objectives

The title of my thesis is "Analysis of the interactions between organics and radionuclides for the performance assessment of the barriers of radionuclide waste repositories", being directly integrated in CORI, as stated in IPR3 (Formal 3d Interim Progress Report). The work plan of my thesis includes the study of U(VI), Ni(II), An(III) and An(IV) (as well as their analogues) sorption on cementitious minerals (ettringite, portlandite) and on cement at different degradation stages, in the presence of organics. Within this framework, the main proposed activity during my visit at KIT-INE, will be related to the study of the ternary system cement phases-An(III)/Ln(III)-citrate. The main cement phase considered for this research stay is portlandite, which is also one of the phases considered within my PhD thesis. For specific systems, the effect of ISA will be also considered. Special emphasis will be given to the spectroscopic characterization of these systems by Time Resolved Laser Fluorescence Spectroscopy (TRLFS) with Cm(III). Note that, based on the similar ionic radii, curium is often used as analogue of other trivalent actinides and lanthanides ( $r_{\text{Cm}^{3+}} = 1.09 \text{ \AA}$ ,  $r_{\text{Am}^{3+}} = 1.10 \text{ \AA}$ ,  $r_{\text{Pu}^{3+}} = 1.12 \text{ \AA}$ ,  $r_{\text{Eu}^{3+}} = 1.07 \text{ \AA}$ ). TRLFS is a very sensitive technique not available at CIEMAT that allows the accurate speciation of the Cm(III)

probe both in the aqueous and solid phases. It is thus expected to provide key insights for the mechanistic interpretation of the uptake process by the investigated cement materials. Systematic sorption experiments with these systems have been done at CIEMAT using a Eu(III) tracer.

The second objective deals with the system Ni(II)-citrate, for which comprehensive solubility experiments will be performed using a well-defined solid phase. A remarkable effect of citrate was observed for the sorption experiments at CIEMAT with citrate, and the solubility study at KIT-INE will provide key inputs on the thermodynamic description of this system. The next step in my PhD thesis aims at the surface complexation modelling of this system, which requires an accurate knowledge of the speciation of Ni-Cit in the aqueous phase. Considering the expertise and excellent analytical techniques available at KIT-INE, the outcome of the research done at KIT-INE will provide key inputs for the surface complexation modelling to be completed afterwards at CIEMAT.

### 1.3. Mission request

To analyse the adsorption behaviour of Cm in portlandite in the presence of organics using TRLFS, a technique not available at CIEMAT.

To improve thermodynamic data of the Citrate-Nickel under alkaline-hyperalkaline conditions.

To learn different experimental methodologies from specialists in thermodynamic and spectroscopic techniques.

### 1.4. Mission composition

#### Host organisation

KIT

#### Host facility

INE

#### Mission dates

From 1<sup>st</sup> September 2022 to 28<sup>th</sup> February 2023

## 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

Timed-Resolved Laser Fluorescence Spectroscopy

#### Description

The TRLFS is a spectroscopic technique used as a sensitive and selective method for chemical speciation.

#### Usage

TRLFS has been used to investigate the speciation of Cm(III) in the ternary system portlandite-An(III)-ISA/CA system. Because of its sensitivity, the method provides information on the speciation both in the aqueous and solid phases.

#### Benefits

TRLFS technique allows the study of the speciation at ultratrace concentration, thus avoiding the need of concentrated solutions as required for other spectroscopic techniques, which can easily result in the formation of solid phases.

#### Limitations

The main limitation is the availability of the method, which is only accessible in a few laboratories worldwide. The technique is also limited to a number of radionuclides (Cm(III), Am(III), U(VI), Eu(III), etc., being Cm(III) the one showing the most sensitive spectroscopic properties

#### Applicability

The data gained with this technique has direct application for the understanding of the sorption mechanisms, and thus for the development of surface complexation models for these systems.

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

Undersaturation solubility experiments.

#### Description

This method relies on the equilibration of a well-defined solid phase with an aqueous solution with controlled ionic strength, pH and ligand concentration. Obtained solubility

data allow to derive thermodynamic models, that afterwards can be applied in geochemical calculations or, for instance, in the derivation of surface complexation modelling. The method is particularly useful when dealing with elements / conditions characterized by low / very low solubilities.

## Usage

This method is very simple and robust, but requires the use of gloveboxes with a controlled atmosphere (Ar), as well a analytical methods for the quantification of the metal concentration in solution (ICP-MS in the case of nickel) and solid phase characterization (XRD).

## Benefits

The main benefit refers to the possibility of gaining sound thermodynamic models for systems forming sparingly soluble phases. The solubility of nickel in alkaline conditions is in the range of  $1 \text{ E-7 M}$ , and thus the applicability of spectroscopic techniques is not feasible.

## Limitations

The main limitation of this technique is relatively long equilibration times that are required for some systems. For this reason, my research stay was initiated with the preparation of the solubility experiments with nickel, and was continued with the Cm(III)-TRFLS studies, for which very fast equilibration times are foreseen.

## Applicability

The results obtained with this method can be directly applied (and are fully complementary) to my work at CIEMAT with the sorption experiments on the ternary system cement phases-Ni(II)-organics. The information gained during my stay at KIT-INE will represent a key contribution for deriving the surface complexation models using the sorption data obtained at CIEMAT.

### 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

#### 3.1. Lessons learned and conclusions

This stay end up being quite productive. With the solubility study I have learned about Ni properties and behavior under alkaline to hyperalkaline environment with different conditions and, most important, how to conduct them. These proved being quite interesting at the end. Learning how to prepare and conduct them, the interpretation of solubility plots and understanding the mathematical meaning of the slope has been remarkable towards the work of my thesis.

The data obtained for this type of experiments may be later introduced in thermodynamic databases which, in the end, are used for the modelling of safety condition for repositories. This topic alone shows the relevance of this type of studies and the importance of understanding how they work for future development of thermodynamic databases.

Learning how TRLFS works as a technique and its applications has proven to be quite interesting. The instrument itself is made up from many parts and different electronics, being its manipulation quite delicate. Security measures have been taught to ensure no potential injury happens when manipulating the instrument. Using the TRLFS proved to be challenging at the beginning but with the good guidance that I had, both instrument handling and mathematical treatment of the obtained data end up being feasible, nonetheless. The TRLFS analysis showed me the relevance of this technique to evaluate Cm(III) speciation and its potential use for other radionuclide speciation studies.

Both technics showed their remarkable importance for the study of the topics within my thesis. Learning the procedure to use them has been a pleasant experience and I would like to stress how helpful the data obtained from the experimentation will help towards the development of my thesis.

The main findings and conclusions can be defined as follows:

##### Portlandite-An(III)-ISA/CIT

- Citrate and ISA form stable complexes with Cm(III) in hyperalkaline conditions in the presence of Ca. These complexes could be observed by TRLFS.
- In the presence of portlandite, Cm(III) forms stable surface complexes. Although data evaluation is still on-going, experimental observations hint towards the possible incorporation of Cm(III) in the portlandite structure.
- At intermediate ligand concentrations, the formation of both aqueous complexes and surface / incorporated species is confirmed by TRLFS.

##### Ca-Ni(II)-CIT

- Solubility data confirms the formation of stable complexes Ni(II)-CIT in alkaline to hyperalkaline conditions.
- The current thermodynamic data selected in the NEA-TDB (exclusively binary Ni(II)-CIT complexes) are insufficient to properly explain the experimental observations obtained in this work. Strong evidence has been obtained pointing towards the formation of ternary complexes Ni(II)-OH-CIT.



- In the presence of Ca and hyperalkaline conditions, evidence has been obtained on the formation of ternary / quaternary complexes Ca-Ni(II)-OH-CIT. Such complexes have not been described before, and can represent a significant change in the prediction of Ni(II) retention in cementitious systems relevant for L/ILW.
- Thermodynamic models derived in this work will be further used at CIEMAT for the derivation of surface complexation models on the system cement phases-Ni(II)-CIT.

### **3.2. Relevant findings and conclusions for home organisation**

The stage has been very useful to enrich the Thesis work of the student who learned a lot about solubility studies and spectroscopic techniques that are not available at the home organisation. The systems he studied are very relevant in the frame of radioactive waste disposal in cement and the results are of interest for the participation of CIEMAT in EURAD (CORI WP).

### **3.3. Relevant findings and conclusions for host organisation**

The host organization has many on-going and past activities dedicated to the interaction of radionuclides with organic ligands. Citrate and ISA have been the target of previous studies, but to date the systems investigated by Oscar Almendros had not been studied at KIT-INE. The results obtained during this research stay help to understand the trends in the complexation of organic ligands with different radionuclides, and further on their impact on the retention by cement phases

### **3.4. Relevant findings and conclusions for other organisations**

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## 4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

### 4.1. Generic potentials

Does not apply

### 4.2. Potentials for home organisation

The work carried out by Oscar in KIT-INE is very relevant for future studies that will be carried out at CIEMAT in the frame of RN migration in cementitious environment and also for all the future studies of RN transport in the presence of organics. The experience gained by Oscar in the stage will be very fruitful for these future studies.

### 4.3. Potentials for host organisation

The research stay of Oscar Almendros at KIT-INE has contributed to strengthen the connection with CIEMAT, also improving the interlink between different partners of the CORI WP.

## APPENDICES

### Mission journal

This Journal is organized following the activities done for each different month of the stay. The experimentation adapted depending on the availability of the instruments and equipment.

September: Sample preparation for Ni-citrate systems with pH ranging from 9 to 13.5 at different ionic strengths (0.1 and 1 M NaCl) and citrate concentration (from  $1e-4$  to  $5e-2$  M). Also preparation of Ca-Ni-citrate systems with 20mM calcium at ionic strength 0.1M NaCl and citrate concentration of  $1e-3$ M, pH ranging from 9 to 12.4. Previous modelling for the samples system was done before starting the laboratory work to decide the best approach towards the experimentation. pH evaluation has been done constantly for all the samples through the stay.

October: Preparation of Ni-citrate serie at ionic strength 3 M NaCl, pH ranging from 9 to 13.5. First ICP-MS results for the Ni-citrate systems and evaluation. Decision to proceed with more ICP-MS analysis in the future and to prepare new series for Ni-citrate system at different conditions.

November: Preparation of Ni-citrate serie at ionic strength 0.5M NaCl, pH ranging from 9 to 13.5. Preparation of two new series with calcium, at ionic strength 1 and 3 M NaCl with 20mM calcium and  $1e-3$ M of citrate, pH ranging from 11 to 12.4. ICP-MS analysis for all the series.

December: More data evaluation and ICP-MS analysis. Preparation of the last batch of samples, at ionic strength 0.1, 1 and 3 M NaCl at pH 10, 11 and 13; respectively. Citrate concentration for these samples varied from  $5e-5$  to 0.1M. Sample preparation for TRLFS,  $[Cm] = 1e-7$ M in portlandite systems with ISA and CA at concentrations  $1e-5$ ,  $1e-3.5$  and  $1e-2$ M.

January: TRLFS measurements. Data discussion and agreement on how to proceed with the technique. ICP-MS analysis for the Ni-citrate systems and discussion of the results. Modelling and approach to the equilibrium constant calculation for the systems.

February: Last TRLFS measurement and ICP-MS analysis. Discussion on the mechanisms driving the uptake of Cm(III) by portlandite in the presence of ISA and CIT. Progress in the thermodynamic modelling of the solubility measurements. Definition of the structure and basis for a joint manuscript.

### Mission bibliography

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## MISSION BENEFICIARY

Oscar Almendros Ginestà  
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## PARTNER EXPERTS CONTRIBUTING TO THE MISSION

### Host organisation experts

- Dr. Xavier Gaona. Aquatic Chemistry Group Leader (INE).
- Dr. Marcus Altmaier. Deputy Director of INE.
- Dra. Sarah Duckworth (INE), post-doc.
- Dra. Chenming Shang (INE), post-doc.

### Home organisation experts

- Dra. Tiziana Missana. FAPF-CIEMAT Unit Director

### Other organisations experts

- Klikněte nebo klepněte sem a zadejte text.

## REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
Date of last signee	Oscar Almendros-Ginestà	Tiziana Missana	Xavier Gaona
	Visa	Visa <i>Digitally signed by Tiziana Missana - Madrid, 30/3/2022</i>	Visa 