MOBILITY MISSION REPORT

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MISSION TITLE

A visit to TNO laboratory to learn electrochemistry technique

DESCRIPTION

Concerned organisations

- Research entities
- Technical support organisations

Concerned infrastructures or facilities

- High-performance computing
- Research laboratory
- Environmental monitoring facilities

Concerned phases

- Phase 2: Site characterisation

Themes and topics

- Theme 4: Geoscience to understand rock properties, radionuclide transport and long-term geological evolution
    - Radionuclide migration

Keywords

Redox properties; mediated electrochemical reduction (MER) and oxidation (MEO); electron accepting and electron donating capacities; reduction degree.

EXECUTIVE SUMMARY

The redox potential is an important property of redox-active clay minerals that are involved significantly in radionuclides retention. The redox potential controls the possibility of the occurance of redox reactions between redox sensitive radionuclides (e.g. Tc, Se, or U) and Fe(II)/Fe(III) bearing clay minerals. Therefore, it is necessary to have accurate measurements of the redox potential of clay minerals in order to understand the redox mechanism. However, due to the extremely slow electron transfer between clay minerals and working electrode, redox potentials of clay minerals are hard to measure by conventional potential measurement techniques, such as an Eh meter. Mediated electrochemical reduction (MER) and oxidation (MEO) are newly developed techniques introducing mediators into the system, which are redox-active organic molecules that facilitate electron transfer between clays minerals and working electrode, so that equilibrium between the clay mineral and working electrode can be obtained. This visit to TNO is to learn how to implenment MER and MEO, analyse data, and relate the property to the understanding of my research project. Reduced clay mineral samples (e.g. montmorillonite SWy, nontrinite NAu, and Texas montmorillonite STx) were sent to TNO. Different reduction degrees of clay minerals contain different Fe(II)/Fe(III) ratios, which cause different redox potentials of the clay minerals. By applying an external potential to the specific electrochemical cell setup, the clay minerals can be either reduced (Fe(III) to Fe(II)) or oxidized (Fe(II) to Fe(III)), and the current induced by mediated electron transfer between clay mineral and working electrode can be measured. By applying different external potentials with corresponding mediators, I am able to obtain a profile of Fe(II) fraction in the clay minerals and applied potential Eh, from which the standard reduction potential of the clay minerals can be determined and with that the relation between the redox potential and the Fe(II) content of clay minerals.

1. MISSION BACKGROUND

1.1. R&D background

The PhD project is dedicated to improve the understanding of the coupled adsorption and electron transfer reactions governing the retention of redox-sensitive radionuclides on Fe(II)/Fe(III) bearing clay minerals. One of the focal points of this project is the mediated electrochemical reduction (MER) and oxidation (MEO). MEO/MER method is a powerful approach to directly measure the redox properties of structural Fe in the clay minerals. Dr. Alwina Hoving from the Netherlands organization for applied scientific research (TNO), project partner within task "redox reactivity of radionuclides on mineral surfaces" from the WP Future is a recognized expert in the application of MEO/MER technique to introduce the applicant into this quantification technique. The obtained complementary data will help to correlate mineral properties with respect to its redox reactive iron content to the degree of radionuclides retention.

1.2. Mission objectives

The objectives are that the applicant can learn how to use the experimental set-up and how to perform and interpret the measurements. Afterwards, she will be able to use the technique in her own laboratory and characterize her own samples.

1.3. Mission request

Visit TNO and learn MER/MEO technique from Dr. Alwina Howing.

1.4. Mission composition

Host organisation

Netherlands Organisation for Applied Scientific Research (TNO)

Host facility

Falcuty Geoscience Laboratory

Mission dates

9 August 2021 – 13 August 2021

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

The mediated electrochemical reduction (MER) and oxidation (MEO)

Description

MER and MEO rely on the use of one-electron-transfer mediating compounds, such as mediators, to facilitate electron transfer between the sample of interest and a working electrode. The whole setup consists of electrochemical cell, potentiostat, and computer. In the experiment, an electrochemical cell containing a pH-buffered solution is set to a constant Eh value while the current is measured over time. In the presence of a mediator in the redox equilibrium with the working electrode, known amounts of a sample are added to the electrochemical cell, resulting in current responses that can be integrated to directly determine the number of electrons transferred to or from the working electrode.

Usage

The whole operation is in the glove box, which is to prevent oxidation of my reduced samples. Hence, everything is brought into the glove box before start. Then, first, turn on potentiostat, and then connect all the cables of working electrode, counter electrode, and reference electrode between potentiostat and electrochemical cell. Second, add buffer electrolyte into the cell. Third, open software in the computer, set parameters, and run the program. Fourth, add mediator into the cell; let it run until the background is stable and low. Fifth, add clay suspension into the cell and continue to let it run for about an hour until the current is stable. Repeat this action for about three times. Once it is finished, disconnect, clean, and close everything. Finally, collect the data and process them correctly.

Benefits

The number of electrons transferred to and from the clay mineral can be directly quantified; the experiments can be conducted under well-controlled solution and Eh conditions; the analysis can be performed on the time scale of minutes to hours.

Limitations

This method requires the complete experiment setup in order to carry out this experiment.

Applicability

I have all the equipment for the setup in my own lab. Therefore, now that I have experience with the procedure, I can start testing the set-up and afterwards can measure EDC and EAC and potentially Eh of my clay minerals in my lab.

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

N/A

Description

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Usage

Klikněte nebo klepněte sem a zadejte text.

Benefits

Klikněte nebo klepněte sem a zadejte text.

Limitations

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Applicability

Klikněte nebo klepněte sem a zadejte text.

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

N/A

Description

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Usage

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Benefits

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Limitations

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Applicability

Klikněte nebo klepněte sem a zadejte text.

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

N/A

Description

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Usage

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Benefits

Klikněte nebo klepněte sem a zadejte text.

Limitations

Klikněte nebo klepněte sem a zadejte text.

Applicability

3. MISSION FINDINGS AND CONCLUSIONS

3.1. Lessons learned and conclusions

After this mission, I now know the theories and principles behind this technique, each component of the whole setup, sample preparation, the procedures of assembling the setup, the steps of carrying out the whole experiment, data process and analysis, etc. The whole process gives me a clearer view and better understanding of MEO and MER, which is an extremely important technique in my PhD project. The obtained redox properties of clay minerals, including redox potential Eh, Fe(II) content, etc, plays an important role during radionuclides retention on clay minerals. With the help of these obtained data, I can have more direct perspectives on understanding and explaining the results of my experments, so that I can proceed to accurately design upcoming experiments. To a certain extent, it is a crucial step and fosters the pace of my PhD project. Overall, MEO and MER is a really useful technique in directly measuring the redox properties and reactivities of particular minerals phases. It breaks the barriers of having difficulties in establishing redox equilibria between the clay minerals and working electrodes in electrochemical measurements. It will be more frequently used in characterizing redox properties of not only well-structured minerals but also poorly defined natural samples that contain mixtures of redox-active minerals and organic constituents, and will further contribute to advance an improved understanding of electron transfer to and from minerals in environmentally relevant redox processes. Moreover, it is a successful collaboration between these two institutes in the frame of EURAD Future. I had the chance to talk to different researchers in that lab. Knowing different projects broadens my view in geoscience and waste treatment field. Talking to people who have similar projects gives me more idea on experiment planning and project management. I am very thankful for this mission. I hope this mission can be a good example for the subsequent collaborations.

3.2. Relevant findings and conclusions for home organisation

N/A

3.3. Relevant findings and conclusions for host organisation

N/A

3.4. Relevant findings and conclusions for other organisations

N/A

4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

4.1. Generic potentials

N/A

4.2. Potentials for home organisation

N/A

4.3. Potentials for host organisation

N/A

APPENDICES

Mission journal

Day 1: lab tour, lab safety orientation and exam. Knowing experiment setup and trying to assemble by myself under supervision.

Day 2: Start experiments with two clay mineral samples – Chlorite and Montmorillonite llite. Two different external potentials were applied, one strongly reducing and one strongly oxidizing with corresponding mediators. I added the samples in triplicate. After measurements, learn to read and understand the graph.

Day 3: Prepare electrolyte buffer at a different pH. Repeat the same procedure with same samples and parameters as day 2. Compare the results with day 2.

Day 4: Learn to export data, process data, and calculate to the information I need. Results discussion.

Day 5: Results discussion. Clear up everything, return everything, and finish.

Mission bibliography

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MISSION BENEFICIARY

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PARTNER EXPERTS CONTRIBUTING TO THE MISSION

Host organisation experts

- A.L. (Alwina) Hoving, Geological Survey of the Netherlands, Netherlands Organisation for Applied Scientific Research (TNO)
- Thom Claessen, faculty Geoscience laboratory, Utrecht University

Home organisation experts

- Maria Marques Fernandes, Laboratory for Waste Management, Paul Scherrer Institut

Other organisations experts

N/A

REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
18/10/2021	Yanting Qian	Maria Marques Fernandes	Alwina Hoving
	Yanting Qian	Maria Marques Fernandes	Alwina Hoving