European Joint Programme on Radioactive Waste Management

MOBILITY MISSION REPORT

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MISSION TITLE

Long-term corrosion monitoring of metals with coupled multi-electrode array (CMEA)

DESCRIPTION

Concerned organisations

Research entities

Concerned infrastructures or facilities

Not relevant

Concerned phases

Phase 5: Post-closure

Themes and topics

Theme 3: Engineered barrier system (EBS) properties, function and long-term performance

- Spent Fuel and high-level waste disposal canisters
- Clay-based backfills, plugs and seals

Keywords

Copper container, bentonite filling, anoxic condition, Canadian concept of DGR, coupled multi-electrode array

EXECUTIVE SUMMARY

ZAG participates in EURAD WP ACED Task 2 (Interface scale) for the Bacuce in situ experiments and investigates the corrosion behaviour of steel in bentonite-cement grouts (BCG) with low pH.

As a doctoral student at Slovenian National Building and Civil Engineering Institute, my PhD took a different path in research in nuclear enivronments. My research is based on long-term corrosion monitoring of copper and carbon steel in the environment of deep geological repositories. In the Canadian concept, the container will be made from carbon steel with a 3-mm copper coating. In case of damage to the coating on the copper container, the carbon steel will be exposed to both copper and surrounding environment, which can lead to galvanic corrosion of the steel container. The container will be exposed to an oxic environment and further to an anoxic environment for a longer period of time. The coupled multi-electrode array can enable long-term corrosion monitoring of metals in simulated groundwater and bentonite slurry in oxic and anoxic environment. The coupled multi-electrode array continuously monitors corrosion currents in space and time and enables simultaneous spatial and temporal insight into electrochemical processes on individual electrodes. In these experiements, the coupled multi-electrode array was introduced to the anoxic environment in the anaerobic chamber (glove-box) at room temperature. The experiements investigated the electrochemical processes in an anoxic environment in bentonite slurry and simulated groundwater only. This research was performed at Western University which, is founded or co-funded by the Nuclear Waste Management Organization (NWMO), which is part of EURAD as an international partner. The research at Western University focuses on the application of advanced electrochemical techniques and advanced surface anaylsis to enable research in various corrosion processes, especially those that may impact the integrity of the containers for storage of spent nuclear fuel.

1. MISSION BACKGROUND

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1.1. R&D background

In case of a defect in the Cu coating, surface damage may occur, potentially exposing carbon steel to the surrounding environment (e. g. groundwater, bentonite). This can lead to the formation of a copper-steel galvanic couple, which can cause intensive galvanic corrosion between the two metals. Therefore, it is also important to study the corrosion processes of galvanic corrosion in both oxic and anoxic environment.

1.2. Mission objectives

The main purpose of the research work is an in-dept understanding of the corrosion processes that take place in anoxic conditions on a copper container exposed to simulated groundwater using coupled multi-electrode array. The investigation can also be extended to systems where the mass flow of ions and oxidizing species is limited by a solid interface, such as bentonite saturated with simulated groundwater.

1.3. Mission request

The research activities within the planned 3-month research visit include the study of long-term corrosion montitoring of metals in simulated groundwater and in bentonite saturated with simulated groundwater in anoxic environment. Analysis of data obtained through monitoring and surface analysis of samples after exposure will also be included.

1.4. Mission composition

Host organisation

University of Western, London, Canada.

Host facility

University of Western, London, Canada

Surface Science Western, London, Canada

Mission dates

02nd March 2024 - 31th May 2024

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

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

Coupled multi-electrode array (CMEA)

Description

The coupled multi-electrode array is a method that enables simultaneous spatial and temporal measurements of electrochemical processes at different locations on the metal surface. This technique continuously measures corrosion curents in space and time on each electrode seperatly. It is a very valuble method for investigating localized corrosion and long-term corrosion monitoring in the laboratory and the field. The coupled multi-electrode array is designed to simulate the flat surface of the investigated material while simultaneously allowing monitoring of the corrosion currents. The samples usually consist of a larger number of electrodes of the same material to simulate larger surfaces. For measuring, the samples are connected to a zero resistance ampermeter. This method is widely used at home organization but not at host organization.

Usage

Long-term corrosion monitoring is still in progress for four coupled multi electrode arrays samples. The samples are combinations of copper and carbon steel to mimic galvanic corrosion that can occur in the Canadian concept for copper container for storage of spent nuclear fuel. The measurements take place in an anoxic environment in a bentonite slurry with simulated groundwater and in simulated groundwater only.

Benefits

With the CMEA method we can observe the development of corrosion currents on each of the electrodes. The method enables corrosion measurements in real time that take place on the surface of the electrodes. We can observed anodic and cathodic activities on electrodes.

Limitations

The CMEA samples are difficult to fabricate; the amount of data obtained by the method is large and it is therefore difficult to do the data processing.

Applicability

Development of the CMEA system and the manufacturing of samples were performed at ZAG. We often used CMEAs in research for corrosion monitoring (steel corrosion in concrete, void creation and study of possible crevice corrosion in porous media, drying of a droplet over a metal surface, scratching of metal over a surface).

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

RAMAN spectroscopy

Description

Raman spectroscopy is a technique for analysing the molecular structure of materials. It provides information of the chemical composition of materials by probing molecular vibrations. It is used in surface corrosion studies because it is a non-destructive technique. Raman spectroscopy operates through an inelastic scattering of light by molecules or cystal phases within the sample. The sample is illuminated with a high-intensity monochromatic laser, typically in the visible spectrum, with the exact wavelength depending on the specific exication surce. The laser's incoming light excites the molecules or crystal phases on the sample surface. As the system returns to a stable state, it realises photons in various energy transitions, creating the Raman signal.

Usage

The Raman spectroscopy was used to obtain information about the chemical composition of the surface of various samples. The Raman analysis was performed after the experiements were finished.

Benefits

Raman spectroscopy is non-destructive and requires minimal sample preparation It can be used for characterization of various materials.

Limitations

Raman spectroscopy is only applicable for Raman-active materials. Sometimes fluorescence and background noise make it unusable.

Applicability

I learned a lot about technique, which gives useful information about the sample's surface. I also learned important details about its use, which I will also take into account when using the analysis in our laboratory for further work.

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

Field Emission Scanning Electron Microscopes (FE-SEM)

Description

Field-emmision scanning electron microscopy (FE-SEM) is an advanced technique that provides a focused and stable electron source to obtain high-resolution images. The images offer detailed topographical, compositional or structural information about the sample. It is typically performed in a high vacuum because gas molecules tend to disturb the electron beam and the emitted secondary and backscattered electrons used for imaging. The FE-SEM provides high resolution, tipically in the range of a few nanometers, which helps examine fine detail in materials.

Usage

The FE-SEM was used to obtain information about the morphology of the sample's surface. Also, EDS (energy-dispersive X-ray spectroscopy) mapping was used to get the chemical composition of the surface.

Benefits

FE-SEM can examine minor area contamination spots at electron-accelerating voltages that are well-matched with EDS. With FE-SEM, we can observe high-quality and low-voltage images with slight electrical charging of the samples. FE-SEM also has a wide range of magnifications, from low to high, allowing one to observe small features. Because the electron gun provides high beam stability, the images are more precise and less noisy. FE-SEM can be used in many fileds, such as materials science, biology, electronics, nanotechnology, etc.

Limitations

The surface of samples for the FE-SEM method needs to be conductive; otherwise, it must be coated with a conductive material. Also, the electron source requires a high-vaccum environment to ensure electron stability and prevent cathode contamination. The FE-SEM electron sources suffer low beam current stability problems.

Applicability

The FE-SEM technique was never before been used to study surface morphology in my studies. With this technique, I gained new knowledge about its usefulness, operation, and how to better acquire images on samples with small features. I will use my FE-SEM knowledge in my further studies.

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

X-ray photoelectron spectroscopy (XPS)

Description

XPS (X-ray photoelectron spectroscopy) is an analyitical technique for studying the surface chemistry of materials. XPS offers detailed information about elemental composition, chemical states and electronic states with high surface sensitivity (1-10 nanometers of the material's surface). XPS spectra are collected by irradiating a material with a beam of X-rays while measuring the kinetic energy and number of photoelectrons emitted by the specimen. The electrons ejected within the sample have a low inelastic mean-free path and therefore escape from the surface only from the shallowest depths. XPS is based on the photoelectric effect and the conservation of energy, the binding energy of the electrons emitted from an atom of a specific element can be determined from their kinetic energy. XPS analysis is performed under ultra-high vacuum conditions.

Usage

XPS analysis, a technique that can identify and quantify the elements on the material's surface (depth 1-10 nm), provides valuable information about the oxidation states and chemical environments of surface species. It is used in the analysis of thin films and coatings, semiconducting materials, in nanotechnology applications, catalysis research, corrosion studies, and the study of polymers, organic materials, and geological sciences.

Benefits

The XPS technigue was used to obtain sensitive surface information of thin corrosion films, especially the oxidation states of copper and sulfur species on the surface.

Limitations

XPS uses a high vacuum, and some samples are not stable under those conditions. Some samples may produce severe charging problems that can compromise the quality of the analysis. Because it is surface-sensitive method (depth of analysis 1-10 nm), XPS is not an appropriate method for identifying bulk materials substrates.

Applicability

I learned a lot about XPS, how to analyse the collected data and how to interpret it. I will try to use this technique in my research. It is very useful for analyzing thin corrosion surface films.

3. MISSION FINDINGS AND CONCLUSIONS

3.1. Lessons learned and conclusions

A three-month visit to the Department of Chemistry at Western Univerity was very productive and instructive. The department is engaged in research of long-term storage of spent nuclear fuel in Canada. I met many new people, students and scientists at different stage in their development career. I also gained experience working in another laboratory. I noticed many little things that I didn't pay attention to before. I wasn't aware of their importance, but now I will include them in my research process and share it with my community at my home insitution. I also realized that things sometimes go differently than planed. Due to the difficulties in connecting the coupled multi-electrode arrays and zero resistance ammeters (ZRA) to the university grid, I learned very much about the network connections and how to solve them. I am very exited that we managed to set up coupled multi-electrode arrays and ZRA's in an anoxic chamber and that we set up the experiments. However, since the measurements began with delay, they will continue for another 2-3 months to obtain long-term measurements as planned in the research program. Also, during this process, I learned how to use and operate an anoxic chamber and also how to prepare solution and set up the experiements in the anoxic chamber.

Since some time passed before the implementation of coupled multi-electrode array samples and ZRA in the anoxic chamber, I started to perform other experiments. I worked with different potenciostats for electrochemical measurements, learned how to prepare reference electrodes, samples etc. For surface analysis, I used FE-SEM and XPS techniques, which I used for the first time. I gained much new knowledge about their usefulness, analysis and obtained data. I also became more familiar with spectroscopic Raman technique, in which I upgrade my knowledge and learned many details I was unaware of previoulsy. In my further research, I will include my newly gained knowledge about spectroscopic techniques for surface analysis.

3.2. Relevant findings and conclusions for home organisation

It is essential for ZAG that we introduce a coupled multi-electrode array into the anoxic chamber. That confirmed that the system can be introduce to an anoxic environment. The results will enable a deeper understanding of the corrosion processes on copper containers and the impact of galvanic corrosion under an anoxic environment. It was also beneficial to the study that we collaborated with Western University and had access to different surface analysis techniques. Our future paper will be higher quality and reach a broader scientific community.

3.3. Relevant findings and conclusions for host organisation

We still await the completion of the experiments, which were delayed significantly by unforeseen technical problems, so final conclusions cannot be drawn at this time. However, we at Western benefitted from Klara's visit by learning about the CMEA technique that she introduced, as well as the technical aspects of the instrumentation that she brought for her experiments, that initially caused so many difficulties because their underlying approach was very different from our previous experiences. For some years we have been seeking an opportunity to collaborate with the corrosion and materials research group at ZAG, so Klara's visit was an effective means of beginning to open that door. Klara's research work parallels and complements several lines of our own investigations and we expect it to help broaden our understanding and extend the context and applicability of both our work and hers/ZAG's. We look forward to the analysis and interpretation of the experimental data upon completion of the ongoing set of experiments, and anticipate preparing joint publications combining Klara's data and other relevant work from both groups.

3.4. Relevant findings and conclusions for other organisations

This work will benefit the mission of the Nuclear Waste Management Organization (NWMO, Toronto), the main industry partner of the researchers at Western University and the organization charged by the Government of Canada with responsibility for the safe, permanent management of Canada's spent nuclear fuel. The results of Klara's experiments will add to the scientific case underlying the deep geological repository approach to nuclear fuel waste management being investigated in Canada and other countries.

4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

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4.1. Generic potentials

Experiments with coupled multi-electrode array samples in an anoxic environment (glovebox) took some time to implement, and implementations of this system would be more manageable with a different data collection method than is currently the case. In the future, if the primary collection method does not allow us to do so, it would be necessary to consider collecting data in different way.

4.2. Potentials for home organisation

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4.3. Potentials for host organisation

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APPENDICES

Mission journal

From March 2nd to 3rd 2024: Travel from Slovenia to London, Canada. The main equipment was sent two weeks before, and other experimental setup was brought in-person.

From March 4th to 13th 2024: Settling down in the office, beginning of the administration process for obtaining permits and conducting online trainings to obtain access to the laboratory.

From March 14th to 31th 2024: Preparing four new coupled multi-electrode arrays samples for experiments in the anoxic chamber. The process of preparation of samples included cutting the wire, straightening and curving the wire, soldering, assembling, epoxy mounting, and sample cutting, grinding and polishing. In the meantime, despite our best efforts, we were unable to connect zero resistance ammeters to the university grid. On March 19th, attendance in lectures by students who presented to the commission from NWMO.

From April 1st to 21st 2024: Identifying errors with the connection of the devices to the university mean grid and cooperation with the I.T. department of the university. Preparation of copper samples (O.F.H.C. Cu and Cu-wire) for electrochemical experiments for electrochemical characterization. Conducting acid wash of glassware and started performing electrochemical measurements. An analysis of the obtained data followed the experiments. Also, in the meantime, I visited the Surface Science Western, where we performed surface analysis.

From April 22nd to 30th 2024: Preparing samples for new experiments with cyclic voltammetry, characterization of materials and conducting first experiments.

From May 1st to 12th 2024: Finding out what was wrong with the network connection with the devices. This was followed by solving the problem, coming up with a solution and proceeding with the solution. After checking the network connections with devices, the devices were placed in the anoxic chamber. In the meantime, electrochemical experiments were conducted.

May 13th: Setting up the experiments, preparation of samples, solution, bentonite slurry in anoxic chambers.

From May 14th: Starting the measuerement of four coupled multi-electrode array in anoxic chambers (final polishing of the samples, preparation of solution and bentonite slurry under anoxic conditions, set up the experiments).

May 15th to 21st 2024: Conducting electrochemical experiments and preparation of copper samples for surface analysis. Checking on the coupled multi-electrode experiments.

May 22nd 2024: The repetition of two experiments with coupled multi-electrode array samples, due to data collection issues. Identifying problems, reparing the samples and re-preforming experiments (preparation of sample surface, solution and bentonite slurry in anoxic environment).

May 23rd 2024: Performing XPS analysis of copper samples.

May 24th 2024: Performing FIB-cut analysis and Raman analysis on copper samples.

May 27th 2024: Performing FE-SEM analysis on copper samples.

May 28th and 29th 2024: Preparing and conducting new experiments on copper samples, to prepare the samples for XPS analysis.

May 30th 2024: Performing XPS analysis of copper samples.

May 31st 2024: The final checkup of the experiments in the anoxic chamber marked the end of this phase of the research visit.

Mission bibliography

MISSION BENEFICIARY

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REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
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