MOBILITY MISSION REPORT

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MISSION TITLE

Multiple monitoring techniques for carbon steel corrosion in bentonite-cement grout

DESCRIPTION

Concerned organisations

Research entities

Concerned infrastructures or facilities

High performance computer micro tomography instruments

Concerned phases

Phase 4: Facility operation and 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
- Cementitious-based backfills, plugs and seals
- EBS system understanding

Keywords

Low pH bentonite-cement grout; oxic phase; carbon steel liner corrosion; French concept of DGR; corrosion monitoring

EXECUTIVE SUMMARY

ZAG participates in EURAD WP ACED Task 2 (Interface scale) for the Bacuce in-situ experiments, and investigates the corrosion behavior of steel in bentonite-cement grouts (BCG) with low pH. In the Bacuce experiment, ZAG developed and manufactured electrical resistance (ER) corrosion sensors. These were installed into the Bacuce exposure experiment. In this experiment the corrosion of mock-up carbon steel liner in contact with BCG saturated with local groundwater is investigated at 80°C in anoxic environment. ER measurements were found to agree with post-mortem analysis of samples after removal from the Bacuce experiment (2+ years exposure).

Our preliminary investigations indicated possible corrosion in oxic conditions at room temperature. In the French concept of high-level waste (HLW) disposal, the carbon steel liner will be in contact with BCG. The BCG will (more or less) approach saturation with local groundwater, and this system will be under oxic conditions initially for a certain time period, since waste packages will not be inserted immediately. It is therefore of interest to study the interaction between carbon steel and saturated BCG at room temperature, under oxic conditions. These oxic conditions might lead to corrosion that needs to be characterized and quantified.

We decided to carry out dedicated laboratory experiments at room temperature and under oxic conditions with on-line and in-situ measurements of effective steel corrosion rates using ER sensors. Measurements from ER sensors were taken in parallel to electrochemical corrosion rate measurements (linear polarization technique – LPR), open circuit potential (OCP) measurements and also electrochemical impedance spectroscopy (EIS). In order to get a full insight into the actual morphology of these corroding steel electrodes, we performed these experiments at Manchester University (UK), allowing access to across length-scale micro computed tomography (CT) machines. Manchester University takes part in the Eurad Magic workstream, using their CT set-up for imaging cement and the effect of microbial activity.

We decided to perform two separate visits to Manchester for setting-up and concluding our planned work programme (two short 5-day visits). During the first visit, the experiment was set up and CT scans were performed after 2 days of exposure, augmented by electrochemical corrosion rate measurements. The 2nd stay was carried out 6 months later, with the corrosion damage then well evident in recorded CT images. Effective corrosion rates were automatically measured and logged throughout the whole exposure period for in excess of 6 months. In order to carry out this experimentally challenging task, me (Dr Miha Hren) and my coworker (Dr Bojan Zajec) applied for support from the Eurad mobility grant. The mission was successfully completed with the return of the experimental setup (exposure vessels & ER sensors) to our lab at ZAG in April 2024, where we will do the post-mortem destructive analyses of the exposed steel samples.

1. MISSION BACKGROUND

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1.1. R&D background

The idea here of the proposed mobility scheme is to capitalise on Manchester's expertise in 3D material characterisation using X-ay Computed Tomography (XCT) and apply this knowledge to one of the corrosion systems relevant to WP ACED. The expected results of the proposed experiments is directly relevant for the French HLW disposal concept (Cigeo project). In this project, HLW would be immobilized in a glass matrix and then quenched into a stainless steel container, with this package then encapsulated into a cylindrical carbon steel overpack and inserted in in a carbon steel casing tube forming a horizontal micro-tunnel drilled in the highly impermeable argillaceous host rock. The BCG would be injected between the carbon steel casing and the host rock, in the volume left by the coring operation. To study the effect of carbon steel in contact with BCG saturated with the local groundwater, the Bacuce in-situ experiment had started in 2020, taking place in the IRSN underground research laboratory (URL). One key task is to study the influence of non-continuous, non-perfect contacts or the presence of voids that are filled with grout porewater solution on (carbon) steel corrosion. The whole setup is sealed with resin from the surrounding air to preserve the anoxic conditions.

In WP ACED, ZAG developed, fabricated and installed electrical resistance (ER) corrosion sensor for in-situ corrosion rate monitoring within the Bacuce experiment. These are non-invasive sensors where corrosion rate is determined from the monitoring of the electrical resistance vs. time. The thickness change of exposed part of ER sensor is reflected in its change of resistance. The ER sensors were located very close to the carbon steel tube (mimicking the liner) and were (presumably) immersed in synthetic porewater and not in the cementitious material. Two such experiments were conducted with the French BCG concept and one with Belgian CEM I paste concept. The effective thickness change of the sensor was sampled every 8 hours for the duration of almost two years. The three boreholes were over-cored and extracted a few months ago, and are awaiting for detailed post-mortem analysis.

It should be noted that ER sensors cannot detect localized corrosion, so it could be that there was significant pitting or crevice corrosion present on the exposed samples. High corrosion rates with clear signatures of localized corrosion were found in our preliminary (laboratory) measurements when experiments were conducted in oxic BCG saturated with porewater (pH ≈ 11). These contradictory results and the shortcomings of the ER sensor prompted us to do more research on this topic.

1.2. Mission objectives

To carry out dedicated laboratory experiments with on-line and in-situ measurements of effective corrosion rate using ER sensor (corrosion of carbon steel) fully and partially embedded in the saturated BCG environment. Measurements from ER sensors will be compared to electrochemical corrosion rate measurements (linear polarization technique – LPR) and open circuit potential (OCP) measurements. These measurements would be complemented by high-resolution CT measuremtns (provided in-kind by the host organization that would reveal the actual morphology of the corroding sensor steel electrode, and thus indicate temporal and spatial evolution of localized corrosion (main reason for mission). Other in-situ monitoring techniques are also possible. The omission of anoxic & high-temperature requirement makes such an experiment feasible and easily transferable, particularly for micro-CT scanning.

1.3. Mission request

To approve the mission for me and my coworker to carry out the experimental set-up and data treatment/visualisation, to carry out the measurement campaign at University of Manchester where periodic (during both short stays) micro CT scanning will be performed. The mission ends with the return of the full experimental setup (vessels, exposed samples) to our lab at ZAG where we will do the post-mortem destructive analyses.

1.4. Mission composition

Host organisation

University of Manchester, UK

Host facility

Department of Materials | Metallurgy & Corrosion, National Facility for X-ray Computed Tomography (NXCT)

Mission dates

03rd September 2023 – 10th April 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

Electrical resistance (ER) corrosion sensors + comparison to 3D X-racy CT data

Description

ER sensor is a device made of thin metal of interest (in our case carbon steel) that forms conductor exposed to the environment, while part of it is protected from environment (reference resistor). With external electronic read-out unit the electrical resistance of the exposed conductor is accurately measured (temperature is compensated by the measurement of resistance of reference resistor) and converted to the average thickness of the exposed conductor. Thickness is decreasing with time due to the corrosion. This technique is not being used at host organization, it is widely used at home organization.

The ER sensors were here for the first time combined with 3D X-ray CT scanning to inform about the true extent of corrosion measured by the ER sensors.

Usage

Precise long-term (6+ months) corrosion monitoring was performed on 4 ER sensors that represented combinations of fully/partly embedded carbon steel sheet/wire in BCG saturated with synthetic ground water (SGW). These materials are prescribed in the French DGR CIGEO project and WP ACED Task 2 experiment “Bacuce”.

Benefits

Thanks to ER sensors & read-out units, the remaining thickness was measured every 30 minutes and temporal evolution of corrosion process was monitored for a duration in excess of 6 months. All experiments were conducteed without external interference in the observed system.

Limitations

ER sensors cannot distinguish between localized corrosion and general corrosion, we just get the effective steel sample (conductor) thickness. This is the reason why micro-XCT was used at the host facility.

Applicability

Used ER corrosion sensors have been developed and manufactured at ZAG and we use them often in our corrosion research and monitoring.

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

Computed Tomography (microCT)

Description

MicroCT uses the attenuation of x-rays to produce 3D volume representations of a scanned object. The CT scanning was done at UK's national research facility for lab-based X-ray Computed Tomography (NXCT), which is part of the host organization. They house multiple CT devices ranging from industrial CTs, micro CTs and nano CTs. They also employ experts who are trained in acquiring the CT images and analysing the results. During both our stays, we used two of their devices depending on the available beamtime: Nikon High Flux Bay and Zeiss Versa 520.

Usage

The microCT technique was used to scan and obtain a 3D model of the corrosion damage of the ER sensors. The exposed part of ER sensors was embedded in BCG, thus inaccessible for surface/visual inspection. The initial CT scan of all specimens was preformed at the start of the exposure (during our first stay), which was followed by a second CT scan after 6 months of exposure (during our second stay). This allowed us to do a comparison of corrosion damage before and after the exposure, without destroying the specimens. The data sets obtained here were then compared to recorded ER data of all samples.

Benefits

The main benefit of the technique is the ability to see actual corrosion damage over time in a non-destructive way. Data about the location and extent of corrosion damage is valuable in interpreting the ER sensor monitoring results and also electrochemical measurements (open circuit potential and linear polarization resistance) that were also carried out at the beginning of the exposure and after 6 months (parallel to the CT scans).

Limitations

The main limitations of the technique is its resolution, which requires sufficient corrosion damage to take place before the damage is visible, and the relatively long scanning times which usually span multiple hours for each specimen. This makes the technique relatively expensive, and you need to carefully plan and use the limited available beamtime. In our case the X-ray attenuation from the Pt wire electrode (used as pseudo-reference electrode) somewhat impaired the CT scans.

Applicability

The raw data that the technique produces needs to be analysed using advanced image segmentation software and powerful workstations. We already have such software and hardware available at the home institute, including employees capable of segmenting and analysing the 3D scans.

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

Electrochemical measurement methods relevant for corrosion

Description

The exposed part of the ER sensor can be used as an electrode (when ER sensor read-out unit is disconnected). In order to facilitate electrochemical measurements, the exposure vessel was equipped with Pt wire (as pseudo-reference electrode) and graphite counter electrode, together forming the three-electrode system. Various electrochemical measurement techniques are extensively used in the corrosion lab. of the host organization and they are very well equipped with all necessary experimental setup (potentiostats, reference electrodes, glassware and other laboratory consumables).

Usage

During both stays, the extensive electrochemical characterization of the exposed part of the ER sensor was performed in-situ. For this purpose the following electrochemical techniques were applied: open circuit potential (OCP) measurement, linear polarization resistance (LPR) measurements and during 2nd stay also electrochemical impedance spectroscopy (EIS).

Benefits

Application of above named electrochemical techniques offers complementary information on the average corrosion rate and general state of the corrosion process of the exposed part of the ER sensor.

Limitations

All electrochemical methods require certain assumptions and prior knowledge about the possible chemical processes of the system under investigation in order to correctly interpret the results in terms of corrosion rate. Additionally, similarly to ER sensor measurement, one cannot distinguish for sure between localized and uniform corrosion since the response is obtained from the whole surface of the electrode.

Applicability

Several relevant details about the application and interpretation of used electrochemical techniques have been learned, that will be implemented in our laboratory.

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

None.

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

The mission proved very successful: we managed to ship our small experimental setup to the host organization, assemble it there and perform all analysis and characterizations at the beginning of the exposure at host organization. During the entire exposure (6 months) the corrosion rate was uninterruptedly monitored by our ER sensors. During 2nd stay (after 6 months) at the host organization the final characterization with microCT and electrochemical methods was carried out. It was found that in 6 months the localized form of general corrosion (not pitting or similar) has developed in all 4 specimens, in all cases only in the region that is embedded in the CBG.

As someone who has been working with the microCT technique for over 8 years, I have gained additional experience working with new microCT machines and learning new procedures from experienced operators. I learned additional techniques to select appropriate filters for CT scanning, and gained knowledge about the relationship between spatioal resolution and Z-ray source power that certain X-ray tubes have. It was also my first time experiencing a microCT machine with a walk-in type of construction, which has certain benefits when positioning the specimen and searching for the optimal source-to-object distance.

In the field of electrochemical techniques, I learned how to work with smaller and more portable devices that have enough accuracy for basic electrochemical measurements, such as OCP and linear polarization. These devices are much faster and easier to use compared to larger, complex potentiostats, which increases productivity and optimizes experimental workflow.

I also had the opportunity to present my work to the team working at the host organization. This was followed by a great discussion, so it not only allowed me to improve my public speaking skills, but also critically think about how I can improve my work in the future.

3.2. Relevant findings and conclusions for home organisation

For ZAG it is relevant that we proved our ER corrosion sensor reliable and trustworthy measuring devices. Although the oxic phase of interaction between carbon steel and BCG & SGW is not directly addressed in EURAD WP ACED Task 2, where ZAG participates, the current results definitely contribute to relevant findings of corrosion behaviour of this system. For ZAG it is highly important that its employees participated in the collaboration with Univ. of Manchester, jointly participated in the experimental campaign and had access to its micro-CT facilities.

3.3. Relevant findings and conclusions for host organisation

The application of multi-modal experimental set-ups, using ER sensors in combination with electrochemistry and X-ray CT scanning proved to be successful. The combination of all techniques allowed a comprehensive picture of the corrosion rate, type and changes in reaction kinetics to be identified for the investigasted scorrosion system. The work will be published in a peer reviewed journal.

3.4. Relevant findings and conclusions for other organisations

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4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

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4.1. Generic potentials

The exposure vessel was equipped with Pt wire (as pseudo-reference electrode) and graphite counter electrode as planned. The Pt wire was parallel to the exposed part of ER sensor and this Pt wire turned out to be source of minor beam hardening and scatter on CT scans. If I had known this effect beforehand, I would have introduced Pt wire for Pt pseudoreference electrode from the bottom, so it would not obstruct the imaging of ER sensor.

4.2. Potentials for home organisation

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4.3. Potentials for host organisation

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APPENDICES

Mission journal

Sunday, September 3rd 2023: Travel from Slovenia to Manchester, UK. All parts of experimental setup were brought in-person.

Monday, September 4th 2023: Settling down in the lab, necessary administration (card for entrance to lab), discussion on the actual schedule of activities. Attendance of inauguration lecture. Quick visit of NXCT facility. Start of preparation and assembling the actual experimental setup: 4 exposure vessels with ER sensor and both electrodes.

Tuesday, September 5th 2023: Finalization of exposure vessels, testing of ER sensors' read-out units (data loggers), first round of electrochemical measurements. Start of measurement & logging with ER sensors.

Wednesday, September 6th 2023: Transfer of first two exposure vessels (specimens) to NXCT facility for micro CT scanning, instalment of each ER sensor on in microCT machine. Installation and then scanning of two exposure vessel. Meanwhile electrochemical measurements on the other two exposure vessels.

Thursday, September 7th 2023: Transfer of the remaining two exposure vessels to NXCT for microCT scanning, quick review of scans obtained in previous days. Electrochemical measurements on the two exposure vessels, that have been already scanned. Verification measured data from ER sensors.

Friday, September 8th 2023: Quick review of obtained CT scans, transfer of remaining two exposure vessels from NXCT back to laboratory, further electrochemical measurements. Data processing of raw data from electrochem. measurements, preparation of the 4 exposure vessels & data-loggers for automatic measurement until next visit.

Saturday, September 9th 2023: Travel home to Slovenia.

Sunday, March 3rd 2024: Travel from Slovenia to Manchester, UK.

Monday, March 4th 2024: Settling down in the lab, necessary administration (card for entrance to lab), discussion on the actual schedule of activities. Visual analysis of the exposure vessels with ER sensors. Electrochemical measurements on all 4 exposure vessels.

Tuesday, March 5th 2024: Transfer of first exposure vessel (specimens) to NXCT facility for micro CT scanning, instalment of each ER sensor on in microCT machine. Installation and then scanning of two exposure vessel. Meanwhile electrochemical measurements on the other three exposure vessels.

Wednesday, March 6th 2024: Further microCT scanning of exposure vessels, during this stay a better CT machine was available and each ER sensor had a small section scanned also in high resolution. Meanwhile electrochemical measurements on the other exposure vessels that were not being scanned.

Thursday, March 7th 2024: Further microCT scanning of exposure vessels, quick review of CT scans. Meanwhile electrochemical measurements on the other exposure vessels that were not being scanned.

Friday, March 8th 2024: Transfer of exposure vessels from NXCT back to laboratory, further electrochemical measurements. Quick analysis of all electrochemical results, summary of ER sensor results and CT scans and their comparison. Discussion and planning for what next and how to ship the experiment (4 exposure vessels) back to our lab at ZAG. Invited talk (in front of mostly lab members) about the current study.

Saturday, March 9th 2024: Travel home to Slovenia.

April 10th 2024: The parcel with the experiment (4 exposure vessels) has been shipped to our lab at ZAG for end of experiment and destructive analysis to be performed at ZAG. End of mission.

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MISSION BENEFICIARY

Miha HREN
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Department of Materials, Laboratory for Metals, Corrosion and Anticorrosion protection
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PARTNER EXPERTS CONTRIBUTING TO THE MISSION

Host organisation experts

Dr Dirk L Engelberg | Professor in Materials Performance & Corrosion | School of Natural Sciences | Department of Materials | Metallurgy & Corrosion | The University of Manchester

Dr Jiaqi Xu | Techinical Specialist | In-situ rigs experiment | National Research Facility for X-ray CT | Herny Moseley X-ray Imaging Facility (HMXIF) | Manchester

Home organisation experts

Dr Tadeje Kosec | Research councillor, Head of the Laboratory | Laboratory for Metals, Corrosion and Anticorrosion protection | ZAG

Dr Andraž Legat | Research councillor | Laboratory for Metals, Corrosion and Anticorrosion protection | ZAG

Other organisations experts

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REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
May 3rd 2024	Dr. Miha Hren	Dr. Tadeja Kosec	Prof. Dr. Dirk L Engelberg