LONG-TERM MONITORING OF GALVANIC CURRENTS OF COPPER-STEEL COUPLING IN AN ANOXIC ENVIRONMENT

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INTRODUCTION

The internationally accepted solution for the long-term storage of high-level radioactive waste and spent nuclear fuel is a **deep geological repository (DGR).** The main component is a closed metal container surrounded by an additional barrier, such as a bentonite or cement mixture. In many countries (Sweden, Canada, Finland…), the inner steel container has an additional outer barrier of **copper**. If a copper coating (Canadian concept of the container with a **3 mm thick copper coating**) has an undetected defect, the steel container may be exposed to the environment, and galvanic corrosion may occur.

The **focus** of the present work is the **long-term monitoring** of copper and steel corrosion currents when steel is galvanically coupled with copper in anoxic environment. The study was performed in a bentonite mixture, saturated with a saline solution containing sulphide ions and in a solution only in an anoxic environment.

METHODOLOGY

MATERIALS

1 carbon steel (CS) electrode

24 copper (Cu) electrode

CS/Cu ratio: 1/24 = 0.042

Surface electrode area: 0.00196 cm^2

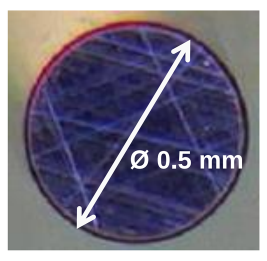

Figure 1: Cu electrode.

- **Coupled multi-electrode array – CMEA coupled with zero resistance ammeter (ZRA)** → allows continuous monitoring of currents in space and time.

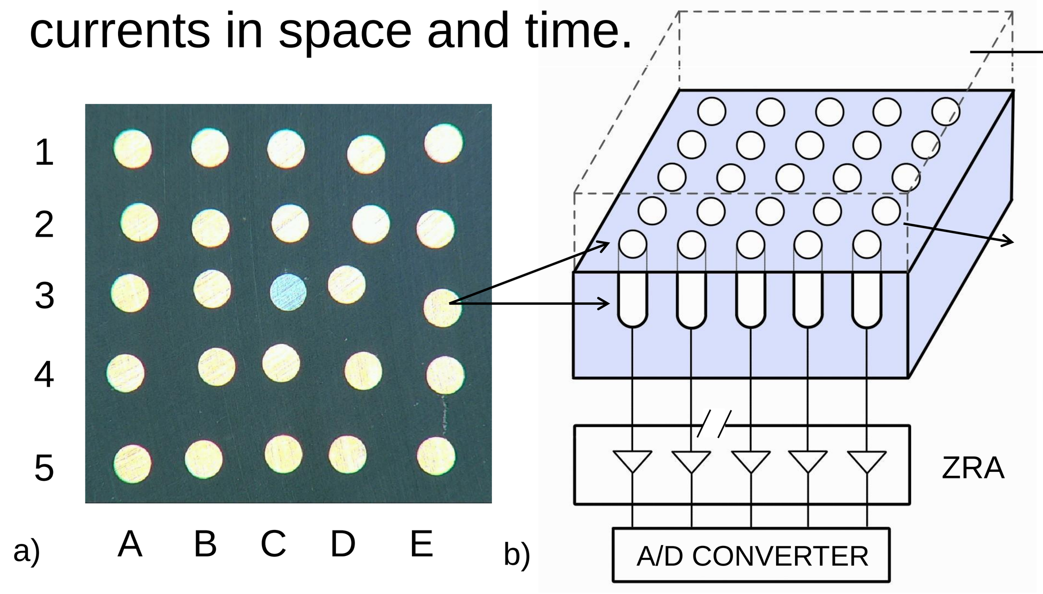

Figure 2: a) CMEA sample ratio CS/Cu = 1/24 and b) schematic presentation of the zero resistance ammeter (ZRA) system.

- **Surface characterization (FE-SEM, RAMAN spectroscopy)**

Bentonite mixture and time of exposure

- Bentonite/solution ratio = 1/1
- Bentonite: Na-montmorillonite (WMX-80)
- Chemical composition of solution: 0.2 M Cl^- + $5 \cdot 10^{-6}$ SH^-
- Exposure time: 155 days

ANOXIC ENVIRONMENT

RESULTS

CMEA measurements in bentonite mixture

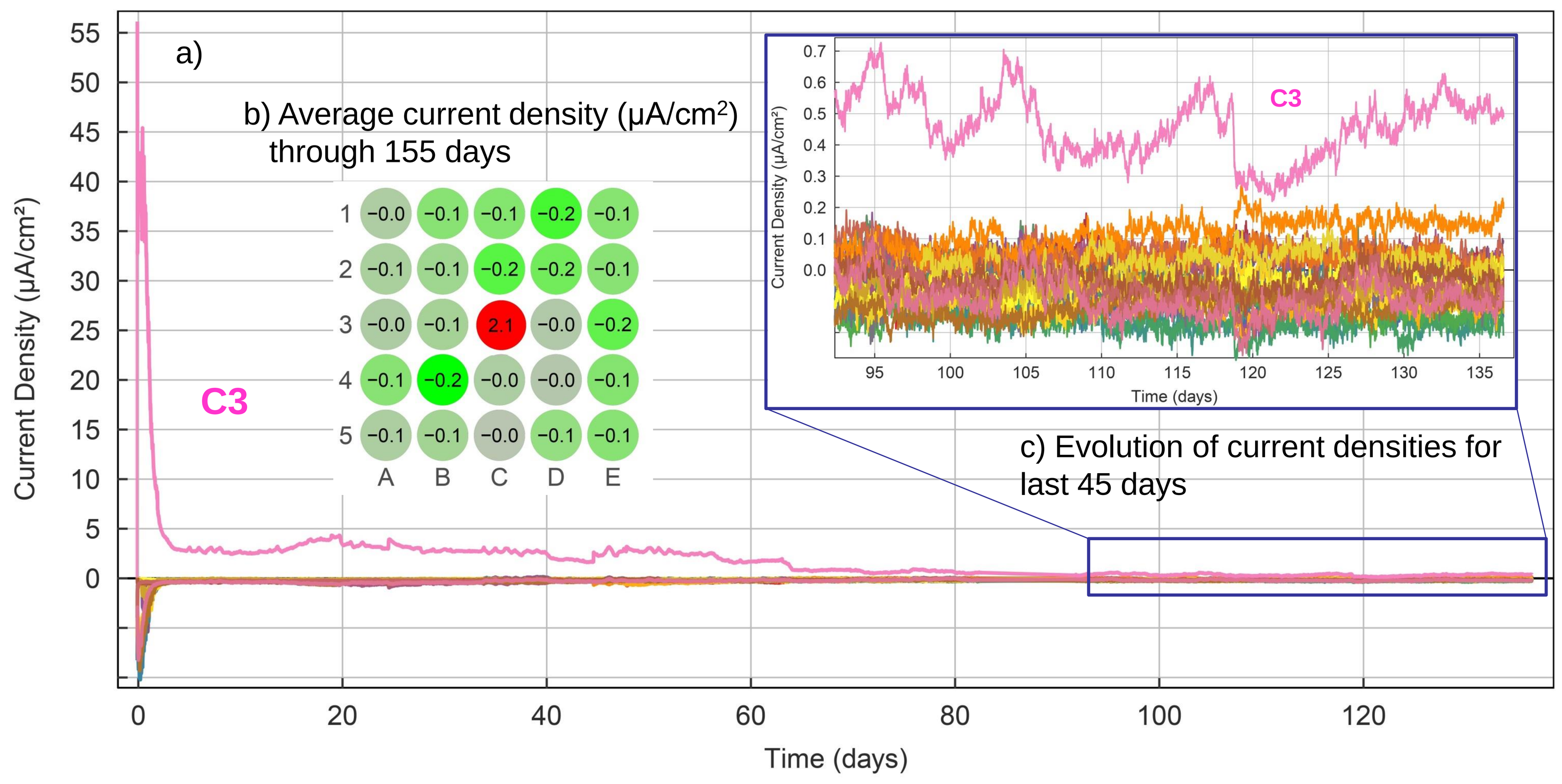

Figure 3: a) evolution of current densities in copper-steel coupled multi-electrode array (CMEA) over 155 days of exposure in bentonite mixture in an anoxic environment, b) average current densities over 155 days of exposure and c) evolution of current densities for last 45 days.

The current density of the steel electrode C3 dropped rapidly and after 93 days the current density fell to an average value of **0.5 μA/cm^2**. Tully et al.[1] investigated the influence of compacted bentonite on the corrosion of copper. It was found that over time (after 175 days) the corrosion rate falls below 1 μm/year. In the case of CS/Cu coupling, the average corrosion rate estimated from electrode activity towards the end of exposure, was **5.8 μm/year**, which is relatively low and **will decrease further**. The total volume damage to the steel electrode for the duration of 155 days was $1.7 \cdot 10^6$ μm^3, resulting in approx. 8.5 μm of corrosion damage. In the last 45 days of exposure the corrosion damage was about 0.7 μm.

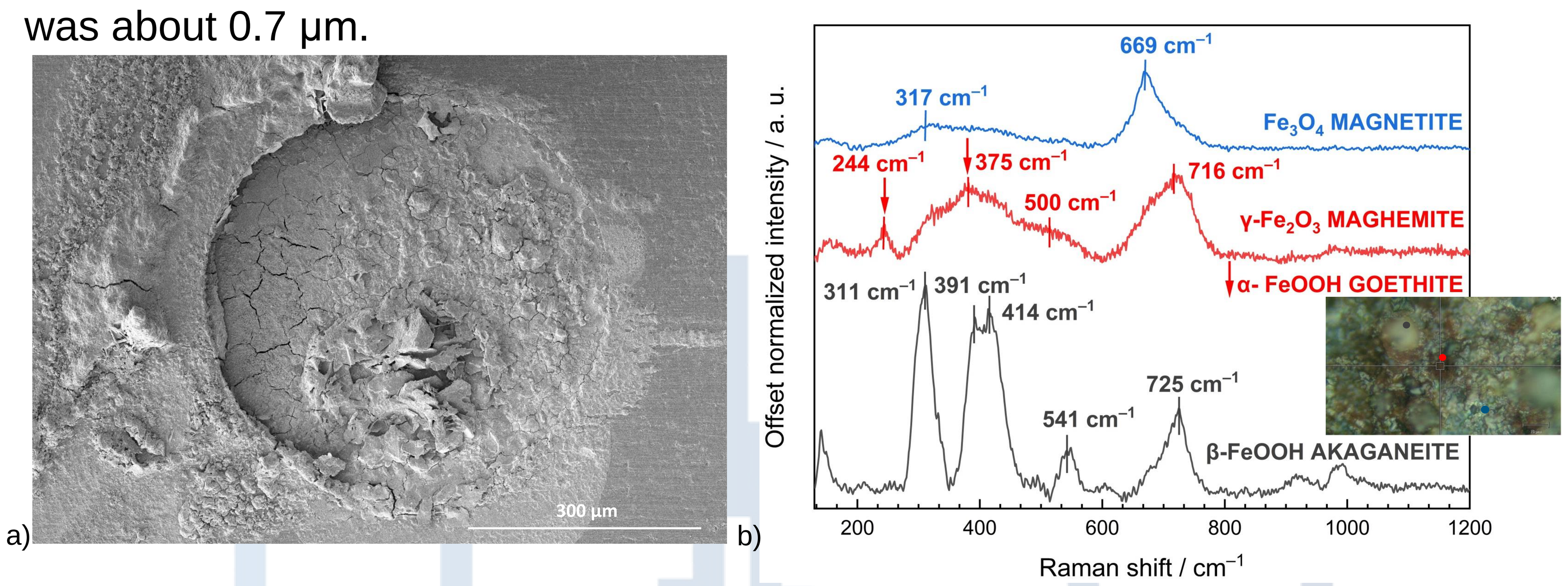

Figure 5: a) FE-SEM image of C3 steel electrode after 155 days of exposure to bentonite mixture in anoxic environment and b) RAMAN spectroscopy of various iron (hydroxyl)oxides formed on steel electrode.

CMEA measurements in solution 0.2 M Cl^- + $5 \cdot 10^{-6}$ SH^-

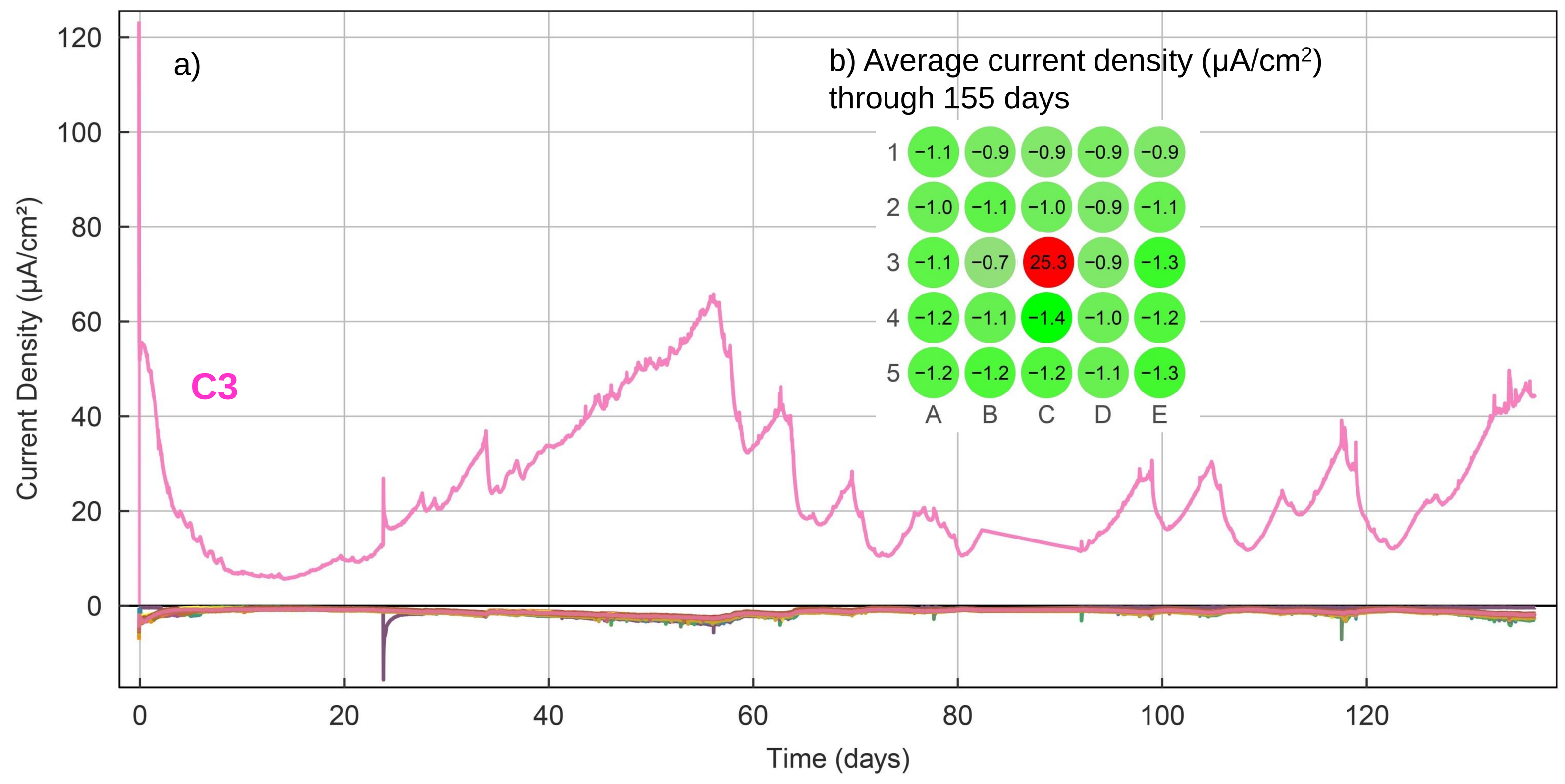

Figure 4: a) evolution of current densities in copper-steel coupled multi-electrode array (CMEA) over 155 days of exposure in solution in an anoxic environment and b) average current densities.

The anodic activity is **more intense** in the solution when compared to bentonite mixture in an anoxic environment. Kosec et al.[2] investigated galvanic corrosion under oxic conditions using the CMEA technique and very high corrosion rates were measured (15 and 20 mm/year). In this study in anoxic environment the current density at the steel electrode averaged **25.3 μA/cm^2** over 155 days. This value corresponds to an average corrosion rate of **290 μm/year**. The fluctuation of the current density over time indicates ongoing corrosion activity. The total damage volume on steel electrode was $20.7 \cdot 10^6$ μm^3, which corresponded to 105 μm of corrosion damage over 155 days. All copper electrodes were net cathodic.

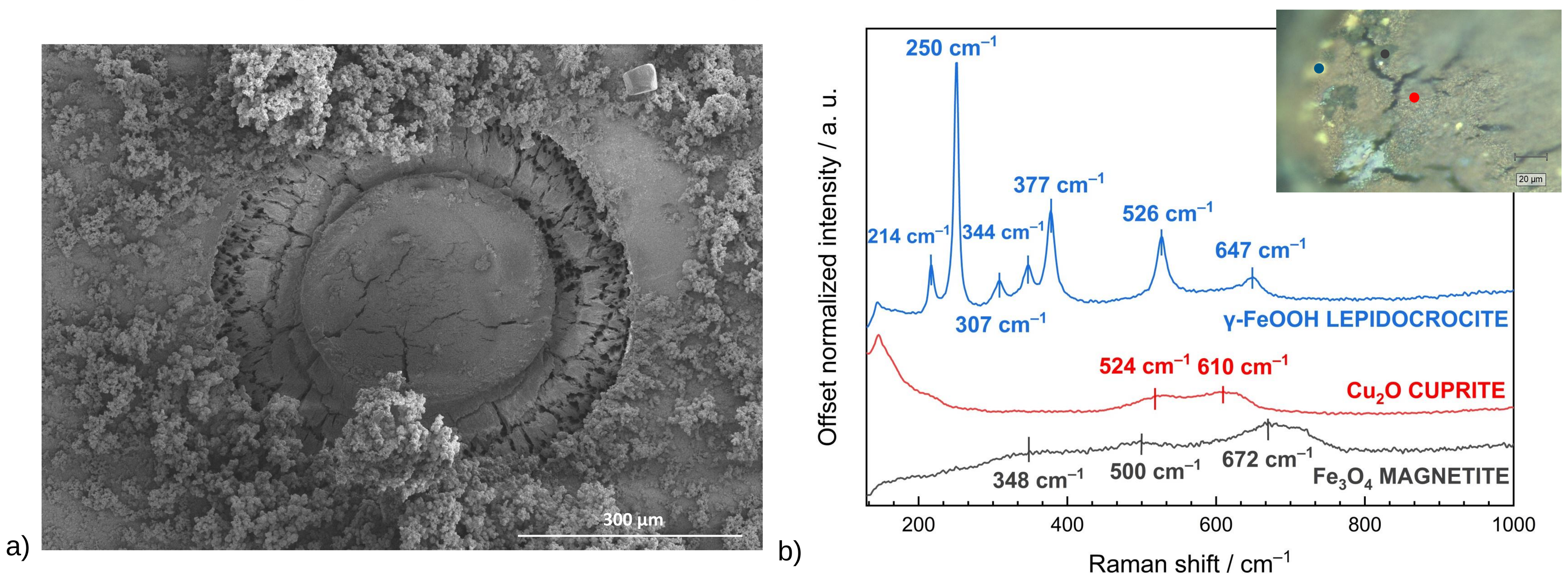

Figure 6: a) FE-SEM image of C3 steel electrode after 155 days of exposure to solution in anoxic environment and b) RAMAN spectroscopy on different corrosion products formed on steel electrode.

CONCLUSIONS

This study presents galvanic corrosion measurements using the CMEA technique in an anoxic environment with a carbon steel (CS)/copper (Cu) ratio of 1/24.
In **a bentonite mixture** in an anoxic environment, the corrosion rate for the steel electrode in the **last 45 days** was **5.8 μm/year**.
In **the solution** in an anoxic environment, the galvanic current of the steel electrode was **more intense**, resulting in a corrosion rate of **290 μm/year**.

ACKNOWLEDGMENTS

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REFERENCES

[1]Tully, C. S., Binns, W. J., Zagidulin, D. & Noël, J. J. Investigating the effect of bentonite compaction density and environmental conditions on the corrosion of copper materials. *Materials & Corrosion* maco.202313768 (2023) doi:10.1002/maco.202313768.

[2]Kosec, T. *et al.* Monitoring the galvanic corrosion of copper–steel coupling in bentonite slurry during the early oxic phase using coupled multielectrode arrays. *Materials & Corrosion* maco.202213689 (2023) doi:10.1002/maco.202213689.