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# EIS study on aerobic corrosion of copper in ground water: influence of micro-organisms

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ABSTRACT

The nuclear waste disposal concept in Finland and Sweden is based on a multi-barrier system, where the solid spent fuel is placed in a cast iron container that is further enclosed in a copper canister. The copper canisters will be placed vertically in holes drilled in a deep bedrock which are then filled with a bentonite clay. The near-field environment of bentonite clay and groundwater is then expected to maintain integrity of the copper canisters for at least 100 000 years. The ground water at the final disposal depth contains micro-organisms with a vast metabolic potential, and it is known that micro-organisms may induce or accelerate the corrosion of metals. Therefore, it is of vital importance to understand the surface interactions of copper and the expected near-field environment. In this study, the results from two types of experiments that investigate the corrosion of copper in oxic ground water environment with and without micro-organisms and electrochemical impedance spectroscopy (EIS) as one of the key research methods are reported. First, long-term immersion experiments with a range of in-situ electrochemical measurements were designed to simulate the initial oxic stage of the deep geological nuclear waste repository in the presence of bentonite. Second, electrochemical laboratory tests were planned to improve understanding on the interactions between copper and the micro-organisms in ground water environment: copper specimens were incubated with micro-organisms for different time periods and then subjected to electrochemical measurements to provide data. The results collected from these two test series are reported and discussed here by focusing on the EIS data and its role in interpreting the surface processes. It is evident that EIS helps in understanding the influence of micro-organisms on the copper degradation process.

## 1. Introduction

The nuclear waste disposal concept in Finland and Sweden is based on a multi-barrier system, where the spent fuel from the power plants is contained within several overlapping protective systems. The solidified spent fuel is placed in cast iron inserts that are then nested within the exterior disposal canisters made of copper. The canisters will be positioned inside vertical holes drilled in the final disposal tunnels excavated in a crystalline bedrock in the depth of about 400-450 meters. The holes are then filled with a bentonite clay. The near-field environment of bentonite clay and ground water is expected to maintain the integrity of the copper canisters for at least 100 000 years. The natural ground water at the final disposal depth contains micro-organisms with a vast metabolic potential [1], and it is known that some micro-organisms may induce or accelerate the corrosion of copper [2–4]. Besides, it has been reported that the presence of bentonite may stimulate the microbial activity [5]. Therefore, in order to understand and evaluate the potential risks to the operational reliability of the disposal canisters, it is of vital importance to understand the surface phenomena of copper in the expected near-field environment.

One of the important practical issues when considering the interactions between copper and the surrounding environment is that the environmental conditions (temperature and oxygen content) change with time. During the early stages of disposal, warm oxidising period prevails, and conditions evolve with time to cool and anoxic when the temperature reaches that of the surrounding bedrock and the oxygen initially present is consumed by biological and chemical processes [1]. The evolution of the conditions may also influence the activity of microbial populations under the prevailing conditions [6]. For example, different microbial groups better thrive under oxidizing conditions than in anoxic circumstances. It is also known that the repository

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environment may contain residues of nitrogen compounds from explosives used in the excavation of disposal tunnels in the bedrock [7]; through their gamma radiolysis, e.g., nitric acid may be introduced in moist air, possibly affecting the performance of copper canisters. Nitrogen compounds as such may, e.g., cause stress corrosion cracking in copper and its alloys [8–11]. In the case of stainless steel, it has been demonstrated that nitrogen compounds may stimulate or retard the corrosion, or have limited effects, depending on the bacterial groups [12]. In particular, the presence of nitrogen compounds may contribute to the accommodation and enrichment of nitrifying bacteria that grow by consuming inorganic nitrogen compounds. It has also been reported that the most predominant microbial processes during the aerobic phase of the final disposal are those related to nitrogen cycle [13].

In this paper, the interactions between the copper surface and the expected near-field environment are examined, with a special focus being in the influence of micro-organisms on the aerobic corrosion of copper in ground water. The experiment was conducted in natural ground water retrieved from the planned repository site in the western coast of Finland. Electrochemical impedance spectroscopy (EIS) is used as one of the key research methods of the work. Two types of tests are conducted: immersion tests in the presence of bentonite and natural ground water and biofilm tests in the absence of bentonite using a pure culture of ammonia-oxidizing bacteria. The results may be utilised in evaluation of the behaviour of copper under initial aerobic stages of the disposal.

## 2. Experimental

### 2.1. Materials

The test material was an oxygen-free phosphorus-containing copper, OFP-Cu, i.e., the future external canister material, with the allowed amounts of elements as follows: O $<5$ ppm, P 30–100 ppm, H $<0.6$ ppm, S $<8$ ppm. In general, the oxygen level corresponds to that in oxygen-free electronic grades and phosphorus is added at 30–70 ppm for the adequate creep ductility [14]. The OFP-copper was supplied by the company responsible for the final disposal of spent nuclear fuel of the power plants in Finland, Posiva Oy. The tests involved specimens of two sizes. The specimens of 10 mm x 10 mm x 3 mm were used for *in-situ* electrochemical measurements in the immersion test; there were three identical Cu specimens for electrochemical measurements in each container. A conductive plastic-covered wire was soldered to the specimens to establish the electrical connection, after which all other areas of the specimens except for the front surface were covered by an insulating lacquer. The specimen size of 70 mm x 25 mm x 3 mm was used in the immersion tests for weight loss determinations and microstructural studies and in laboratory studies related to the biofilm growth and the associated electrochemical characterisation; each container involved ten parallel specimens of this size. All specimens were ground to 600 grit surface finish, rinsed with acetone and ethanol and heat sterilized at 160 °C for 2 h.

The ground water for the experiments was retrieved from the bore hole of the planned future nuclear waste repository site at the depth of 417 m. The water composition is shown in Table 1. The bentonite included in the test vessels was a MX-80 bentonite, the backfilling material in the KBS-3 concept. Here, it was delivered by Cetco as granules of the typical size range between 30 and 100 mesh. The bentonite was used either as such (one vessel) or as sterilised (two vessels). The sterilization was carried out with the dose of 15 kGy $\gamma$-radiation using a Gammacell facility.

**Table 1**
Composition for the used ground water. Only characteristics of significant contents are shown.

| Characteristic | Unit | Water composition |
|---|---|---|
| Alkalinity | $\text{mmol l}^{-1}$ | 0.184 |
| pH | | 6.91 |
| $S^{2-}$ | $\text{mg l}^{-1}$ | 0.271 |
| $Cl^-$ | $\text{mg l}^{-1}$ | 8350 |
| $NO_3^-$ | $\text{mg l}^{-1}$ | <4.0 |
| $NO_2^-$ | $\text{mg l}^{-1}$ | <4.0 |
| $SO_4^{2-}$ | $\text{mg l}^{-1}$ | <6.0 |
| Free $CO_2$ | $\text{mg l}^{-1}$ | 5.33 |
| $HCO_3^-$ | $\text{mg l}^{-1}$ | 11.2 |
| Total $CO_2$ | $\text{mg l}^{-1}$ | 13.4 |
| Ca | $\text{mg l}^{-1}$ | 1830 |
| Fe | $\text{mg l}^{-1}$ | 0.0081 |
| Mg | $\text{mg l}^{-1}$ | 28.4 |
| Na | $\text{mg l}^{-1}$ | 2800 |
| Si | $\mu\text{g l}^{-1}$ | 3270 |
| S | $\mu\text{g l}^{-1}$ | 4740 |
| Total N | $\text{mg l}^{-1}$ | 0.87 |
| $NH_4^+$ | $\text{mg l}^{-1}$ | 0.135 |

### 2.2. Methods

#### 2.2.1. Immersion tests

The tests were carried out in sterilized glass vessels, the volume of which was 3 L. The test involved three vessels, all of which contained bentonite. Two vessels contained natural ground water (one with sterilised bentonite and one with as-received bentonite), while one vessel (with sterilised bentonite) was made abiotic using glutaraldehyde. The test matrix is shown in Table 2. The bentonite clay was first added in the vessels so that it corresponded to roughly one third of the vessel volume (equivalent to 1200 g of bentonite in each case). After the bentonite addition, the vessels were filled with either natural ground water or ground water mixed with biocide (glutaraldehyde 25%, 0.3 ml per litre of ground water). Finally, test specimens and sterilized electrodes for the electrochemical measurements, were carefully placed in the vessels. The tests were performed in a heating chamber at the temperature of 37 °C under ambient atmospheric conditions, i.e., in the presence of atmospheric oxygen. The incubation period was 4 months.

#### 2.2.2. Electrochemical measurements

Open circuit potential (OCP) monitoring was carried out *in-situ* during the immersion tests using a two-electrode mode. Here, one of the Cu specimens of the size 10 mm x 10 mm x 3 mm was the working electrode, while an Ag/AgCl (0.15 M KCl) was a reference electrode. However, for consistency, all potential values presented in this work are given in a standard hydrogen electrode (SHE) scale. OCP records were collected every 5th minute in the beginning of the test period, but at 14 days of measurements, the sampling frequency was decreased to 30 minutes.

Electrochemical impedance spectroscopy (EIS) measurements were performed *in-situ* during the immersion tests using a three-electrode mode. One of the electrochemical specimens of the size of 10 mm x 10 mm x 3 mm was the working electrode in EIS measurements, with another similar Cu specimen acting as a pseudo-reference electrode; the use of Cu specimen as a pseudo-reference is justified by the fact that the experiments were continued beyond the 4 months test time reported here (up to 11 months). Platinum was used as a counter electrode. EIS spectra were collected roughly once a week by applying an alternating current potential of the root-mean-squared (rms) amplitude of 10 mV around the OCP of the specimens in the frequency range from 100 kHZ to 1 mHz. EIS measurements were carried out using a Gamry Instruments potentiostat model Reference 600TM and an