Corrosion of copper in geological repository for nuclear waste - The effect of oxic phase on the corrosion behaviour of copper in anoxic environment

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Abstract
The high level nuclear waste disposal concept in Finland is based on multi-barrier system with waste canisters made of copper. Due to the good corrosion properties of copper, canisters are assumed to have lifetimes exceeding 100 000 years. The groundwater at the disposal site is anoxic and thus the corrosion is assumed to be extremely slow. However, prior to reaching the anoxic stage, copper canister will face a shorter oxic stage, when Cu-oxide scales are formed on the surface of copper. In addition, the colonization and activity of microbes on the surface or in the vicinity of the copper canister can result in microbially induced corrosion (MIC) that may initiate and accelerate several corrosion mechanisms, depending on the microbes present. In order to simulate the whole lifespan of canister, both stages (oxic and anoxic) as well as presence of microbes, should be taken into account in the laboratory experiments. In this study, pre-treatments of copper samples were made to simulate the oxic warm phase before exposing samples in long-term measurements in anoxic environment. As a pre-treatment prior to anoxic test, samples were pre-oxidized in air. Pre-oxidation was performed by controlled heating in the laboratory furnace in air. Another oxic pre-treatment was done by exposing samples to oxic long-term test prior to anoxic test. The anoxic long-term test was performed using synthetic groundwater. Inoculation of sulfate reducing bacteria (SRB) and acetogenic bacteria both enriched from the disposal site was added to the water used. The average corrosion rates of pre-oxidized samples were systematically higher than non-pretreated samples in all environments. Results indicate that the role of the oxic stage may be significant when evaluating corrosion behaviour of copper. Scanning electron microscopy (SEM) characterization revealed different corrosion products. Presence of microbial community and their activity was quantified using molecular biological methods.

Keywords
nuclear water disposal, copper, anoxic conditions, MIC

Introduction

The high level nuclear waste disposal concept in Finland is based on multi-barrier system [1]. The waste (spent fuel) will be disposed in a cast iron container that is enclosed in a copper canister. Canisters will be surrounded by bentonite clay buffer in a geological repository. Copper is chosen as corrosion barrier for the cast iron canister because of its corrosion resistance is assumed to be extremely good under anoxic conditions. The disposal canister plays a major part of the multi-barrier concept and it should have a lifetime exceeding 100 000 years to prevent the release of radioactive nuclides to the surrounding environment.

In the anoxic groundwater at the disposal site the corrosion of copper canister is thus assumed to be extremely slow, but in reality, prior to reaching the anoxic final stage, copper canister will face short oxic stage, when oxide scales are formed on the surface on copper. Also, the natural ground water in the final disposal site contain different micro-organisms that live also in anoxic environments [2]. It is known that some of those micro-organisms may induce or accelerate the corrosion of copper by different mechanisms and then the term of microbially induced corrosion (MIC) [3-5] can be used. When the lifetime and corrosion resistance of copper canister in final disposal is estimated, there are important practical aspects such as the activity of the microbes

that must be taken into account. The interactions between copper and the surrounding environment is complex, since the environmental conditions, mainly temperature and oxygen content, change with time [6].

Several studies for copper corrosion in repository conditions have been made to simulate both the oxic and anoxic phases [7-8] using different temperatures, water chemistries and microbial enrichments to cover all corrosion risks. In this study, we use the temperature of 37°C simulating the phase when the temperature of the canister surrounding has not yet reached the temperature of bedrock, but the oxygen around canister has been consumed. The role of oxic phase is simulated by pre-oxidation of samples.

Materials and methods

Copper coupon were made from oxygen-free phosphorus-containing copper grade (OFP-Cu). Material was provided by the Finnish nuclear waste management company Posiva Oy. Specimen size of 70 mm x 25 mm x 3 mm was used. All specimens were ground to 600 grit surface finish, rinsed with acetone and ethanol and heat sterilized at 160°C for 2.5 hours. The length, width and thickness of the specimen coupons were measured and weighed with the accuracy of 0.1 mg. Part of copper samples were pre-oxidized (90°C, 7 days). As a reference, also two samples that were previously exposed to aerobic immersion test (60°C, with real groundwater of disposal site + microbe enrichment, 155 days) were exposed in this anoxic test.

Specimens were exposed to simulated groundwater at 37°C for 252 days in anaerobic immersion test. The chemistry of the synthetic water (Table 1) was calculated to simulate the groundwater of disposal site also including the effects of bentonite clay, which will be used as buffer material surrounding copper canister. Conductivity of water was 2190 mS $m^{-1}$and pH was adjusted to 7.9. The experiments were performed in gas tight glass vessels with a volume of 12 L. Vessels were acid washed, rinsed with ddH_2O and heat sterilized. Argon gas flushing was used before and during the transfer of oxygen free simulated groundwater into the vessels. Inoculations of sulfate reducing bacteria (SRB) and acetogenic bacteria enriched from the disposal site (groundwater retrieved from a deep borehole, 405-414 m) were added to test vessels to accelerate the microbial corrosion. A sterilized abiotic environment was used in one vessel for comparison. Vessels were placed in an airtight anaerobic chamber and regularly flushed with argon.

Table 1. Chemical components in synthetic water used in tests, pH was adjusted to 7.9.

	K	Ca	Cl	Na	SO_4	Br	HCO_3	Mg	Sr	Si	B	F	Mn	PO_4	lactate
mg/L	54.7	280.0	5274.0	3180.2	595.0	42.3	13.7	100.0	8.8	3.1	1.1	0.8	0.2	0.1	1

After the exposure the morphology and composition of the biofilm and the corrosion layers were examined with a field scanning electron microscope (FE-SEM) Zeiss ULTRAplus. Weight losses were determined and corrosion rate (µm/a) was calculated.

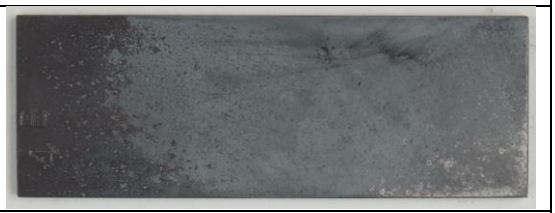
In each biotic environment, the biofilm formed on the sample surface during exposure was evaluated after the test by microbiological methods. The copper coupons for microbiological studies were removed from each environment aseptically under argon flow and stored at -80°C in sterile plastic tubes until DNA extraction. The biofilm was extracted from the surface of the copper coupons by bead beating the coupons in 10 mL sterile PBS and nonionic surfactant (1 µL in 1 mL-1 PBS) for 20 minutes at 150 rpm agitation, followed by ultra-sonication for 3 min.

The released biomass was then collected on 0.22 µm pore-size filtration units for subsequent DNA extraction. The DNA was extracted from the filters using DNA isolation kit (PowerWate, Qiagen). The abundance of bacteria (based on 16S rRNA gene), sulfate reducing bacteria (based on the dsrB gene) and archaea (based on 16S rRNA gene) on the coupon surface was evaluated by quantitative PCR as previously described [4].

Results and discussion

Specimens after the 253 days tests were photographed. The images of samples from each environment with and without the pre-oxidation treatment are shown in Table 2. General corrosion and pitting corrosion was observed to some degree in all samples. More loose corrosion product was formed on the surface of pre-oxidized samples. Visually, the samples from environment with both SRB and acetogens were different as they were darker in color. As a reference, the images of sample from combination test is shown. The corrosion damage is significantly much more severe, since green patina layer has been developed in the surface.

Table 2. Photographs of non-oxidized and oxidized samples after the exposure.

Test environment	**Non-oxidized**	**Pre-oxidized**
Simulated water		
Simulated water + SRB		
Simulated water + acetogens		
Simulated water +SRB + acetogens		
Samples from the combination test (aerobic phase + anaerobic phase), two examples		
Simulated water + SRB		

Cumulative corrosion rates were calculated from the weight losses of samples after corrosion loose products were removed by pickling. Corrosion rates and their standard deviations are shown for each studied case in Figure 1. In every environment, the pre-oxidized sample suffered more weight losses indicating higher corrosion rates. The increase caused by pre-oxidation in corrosion rate was quite similar for all environment, approximately 0.2 µm/a, although the relative increase differed between 15% to 100%. This indicates that pre-oxidation did not just accelerate the corrosion, but corrosion mechanisms were changed. The deviation between parallel samples were higher in non-oxidized samples. As a reference, the calculated corrosion rate for the combination test sample was more than 10 times higher, 25 µm/a, than those of other specimens.

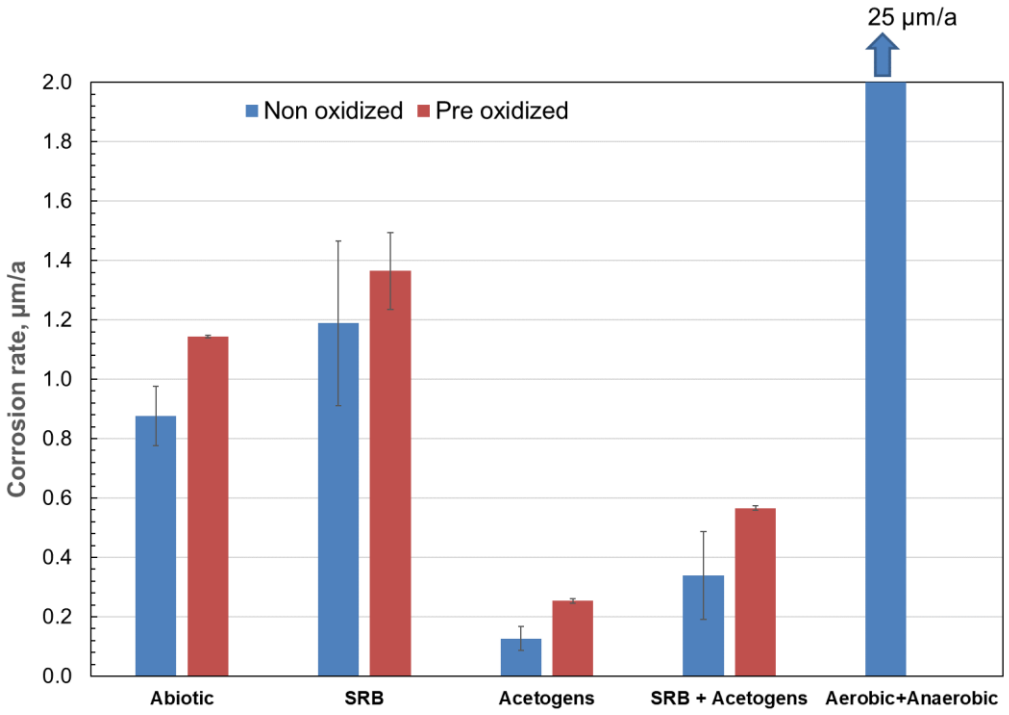
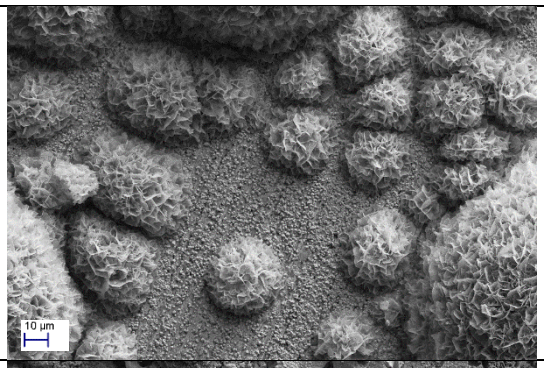
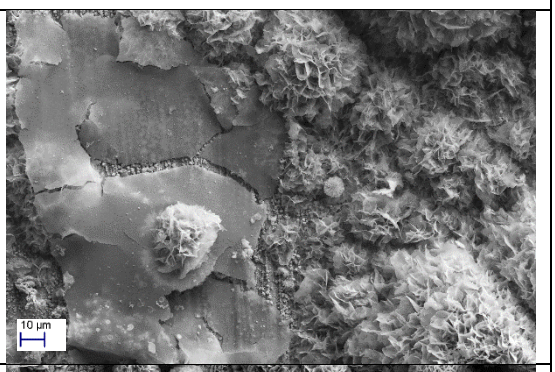
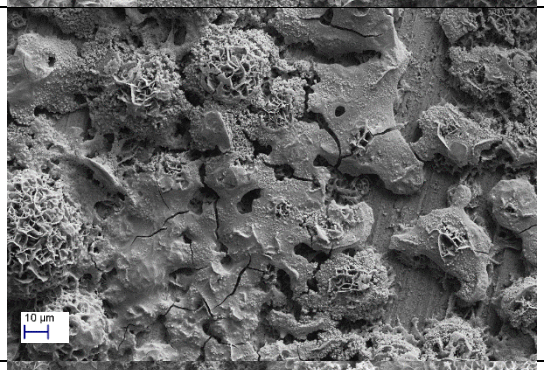
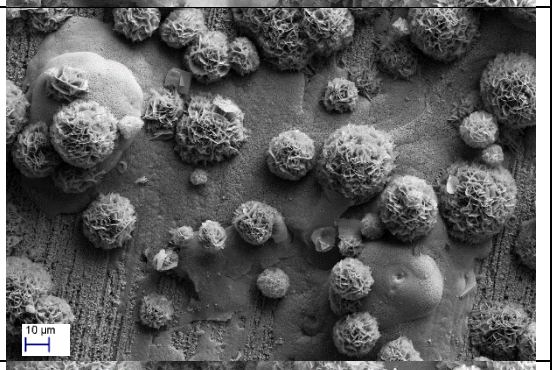
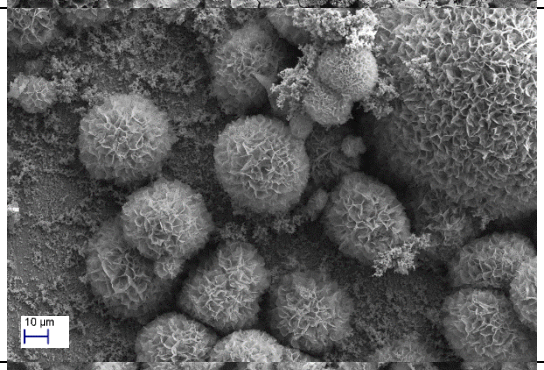
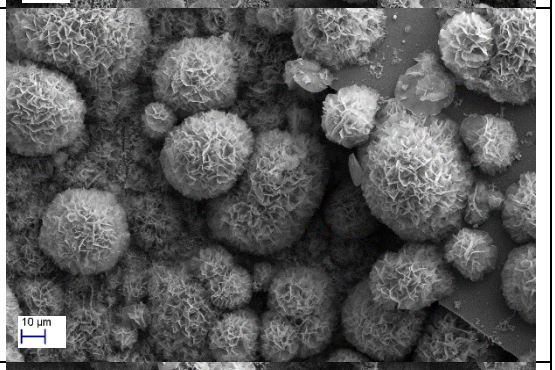
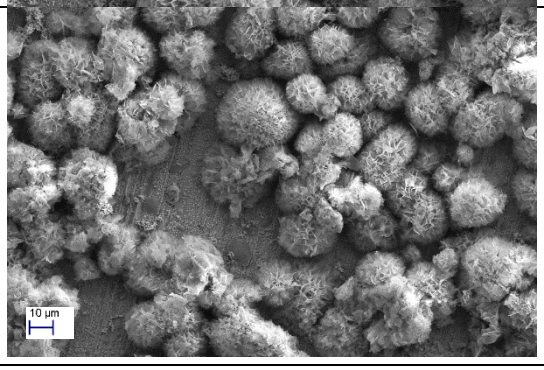
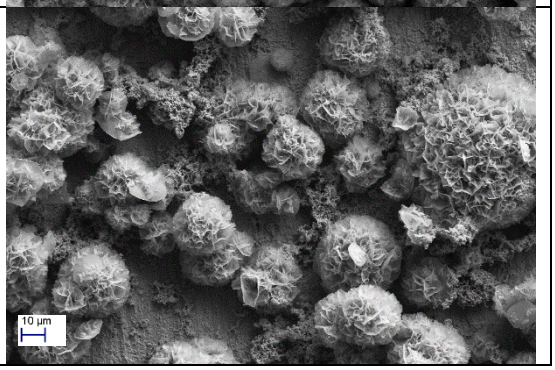


Figure 1. Average cumulative corrosion rates based on weight loss measurements

The pitting type local corrosion was dominant form of corrosion. In pre-oxidized samples more loose corrosion product on the surface was detected, indicating uniform corrosion of oxide layers formed in oxic stage. SEM imaging was conducted to samples with the biofilms formed during exposure (Table 3). Round deposits were detected on all surfaces, but more of flaked oxidized deposit in the pre-oxidazed samples.

Table 3. SEM-SE images of the samples after exposure (before cleaning).

Test environment	**Non-oxidized**	**Pre-oxidized**
Simulated water		
Simulated water + SRB		
Simulated water + acetogens		
Simulated water +SRB + acetogens		

The number of bacterial and archaeal community in surface of copper coupons was quantitated based on copy numbers of bacterial and archaeal 16S rRNA genes and the number of SRBs was estimated based on *dsr*B gene copy numbers (Figure 2). The overall number of both bacteria and archaea was highest in SRB + acetogen environment were both enrichments were added. The number of SRBs was highest in the SRB only environment (10^6 copies of *dsr*B) compared to the acetogens or acetogens + SRB environments (10^4 and 10^5 copies of *dsr*B). The highest number of SRBs was detected on the surface of the same specimens where also pitting corrosion

was most abundant and we can assume that the pitting is a consequence of surface processes induced by SRB.

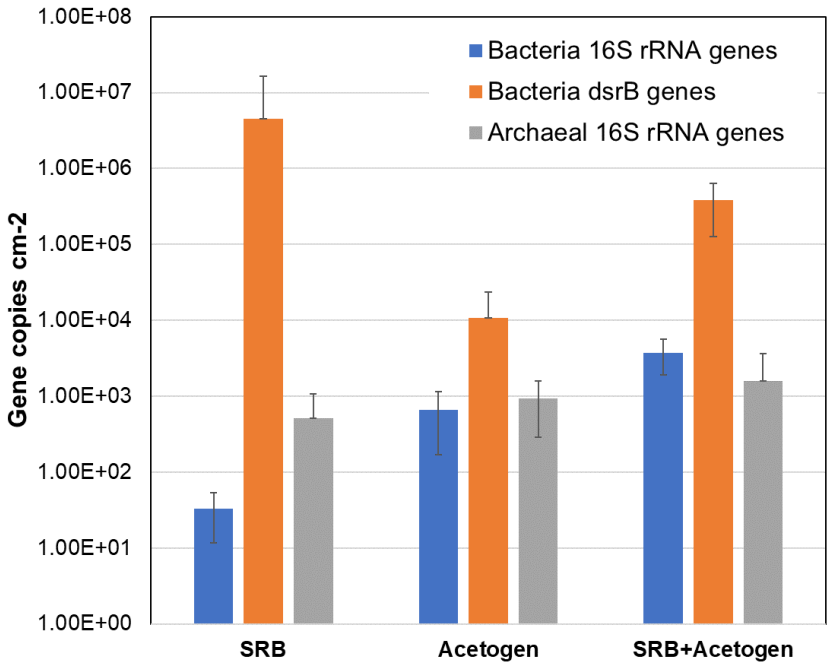


Figure 2. Mean numbers of analysed bacterial 16S rRNA, dsrB of SRBs and Archaeal 16S rRNA gene copies on cm^{-2} biofilms on copper surfaces after exposure

In the presence of SRB the average corrosion rates calculated on the basis of weight losses were the highest of the biotic environments and in the presence of acetogens the corrosion rate was the lowest. In the SRB environment where corrosion rate was higher, also the number of microorganisms was highest.

Conclusions

Pre-oxidation treatment increased the corrosion rate of copper samples in each studied environment indicating that the oxic period in the early stage of repository has impact on the corrosion of copper in later anoxic stage.

All measured corrosion rates were below 1.4 µm/a. The increase of pre-oxidation in corrosion rate was about 0.2 µm/a. Pre-oxidation should be taken as standard procedure prior to exposure to anoxic environments, because otherwise the scenario is not realistic. However, selecting proper pre-oxidation method in laboratory should be studied more closely.

The microbe enrichment used, SRB, acetogens or both SRB+acetogens, had an evident effect on the corrosion rate of copper. The effects of microbes were both corrosion accelerating or hindering, when compared to the abiotic (sterile) environment. The biofilm generated in the presence of acetogens protects rather than contributes (general) corrosion. The environment with SRB (and no acetogens) resulted in highest weight losses indicating the highest corrosion rates. However, in both abiotic and biotic environments, localized pitting type corrosion was detected.

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