VTT TECHNICAL RESEARCH CENTRE OF FINLAND LTD

Projects:

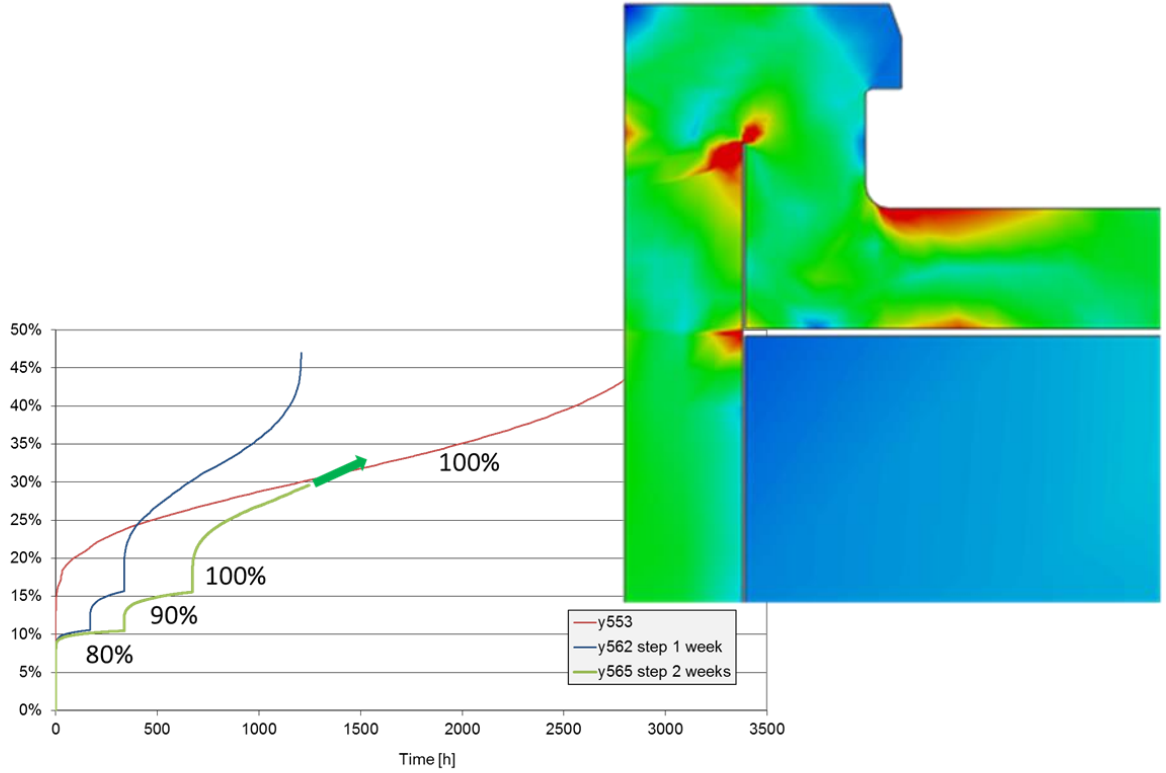
PRECO	Creep
MECHACOP	Mech. behaviour & H2
REPCOR	Corrosion
MICOR	Microbial corr. oxic
BASUCA	Microbial corr. anoxic

Coordinated project KAPSELI

KYT 2018 Final seminar

Finlandia house 29.1.2019

Juhani Rantala, VTT



Experimentally verified model based predictions for integrity of copper overpack (PRECO)

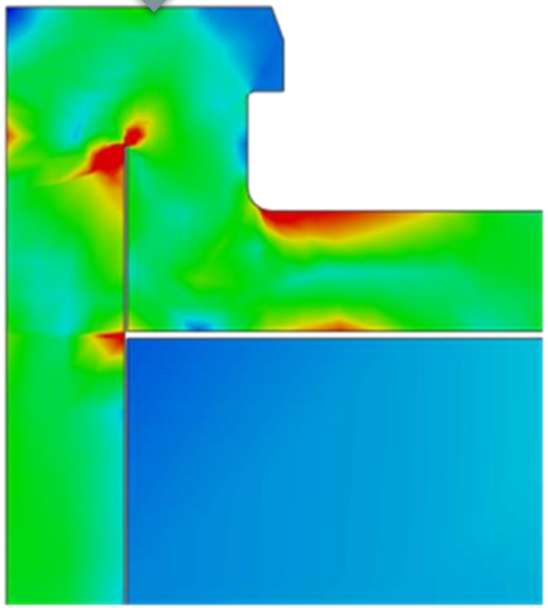
KYT 2018 Final seminar 29.1.2019

Juhani Rantala, VTT

PRECO-project

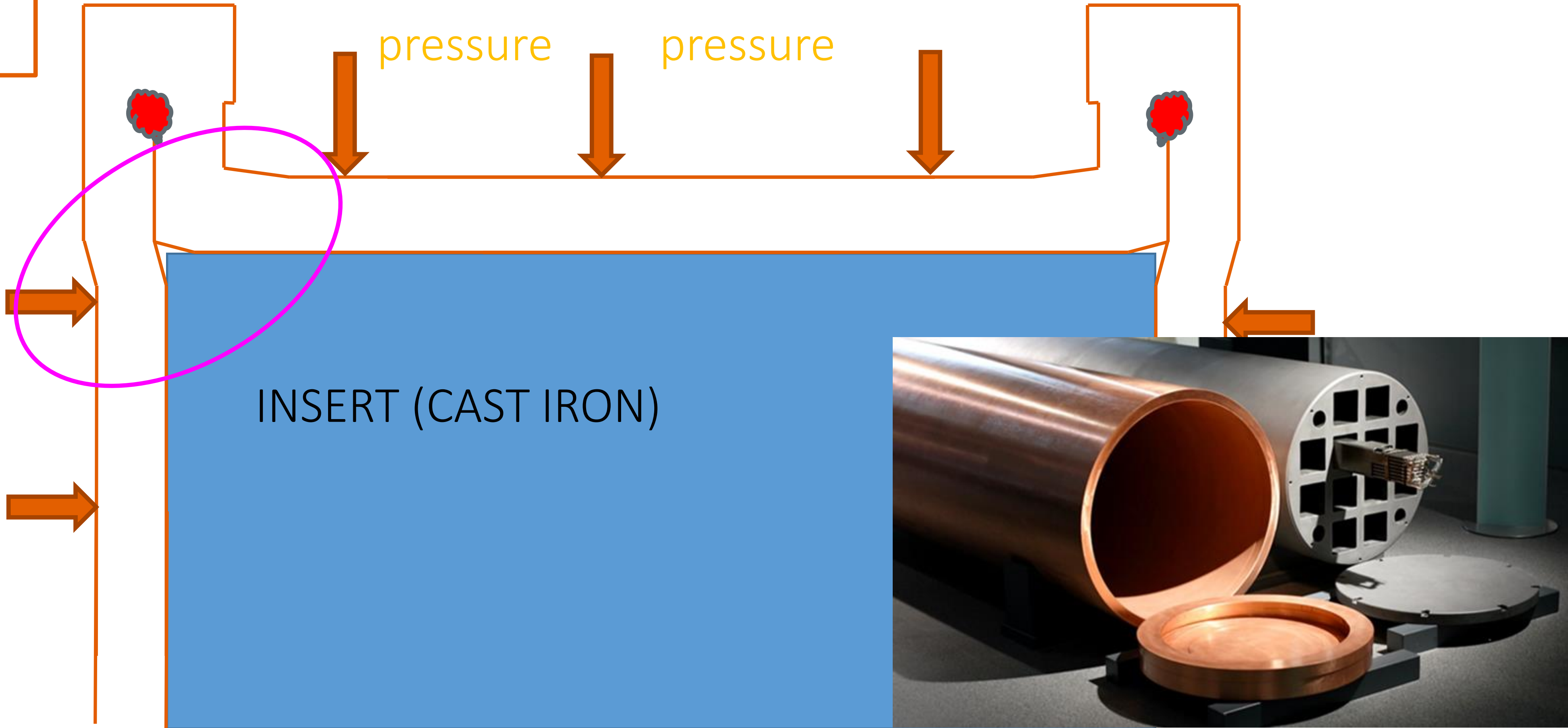
Creep &
Relaxation tests

Creep model
Relaxation model



Concentration of stresses and strains at the weld region

- Deformation capacity exceeded?
- Creep crack growth?
- Effect of relaxation?
- Load history dependence!

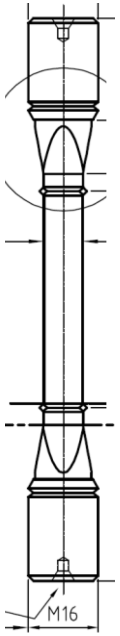


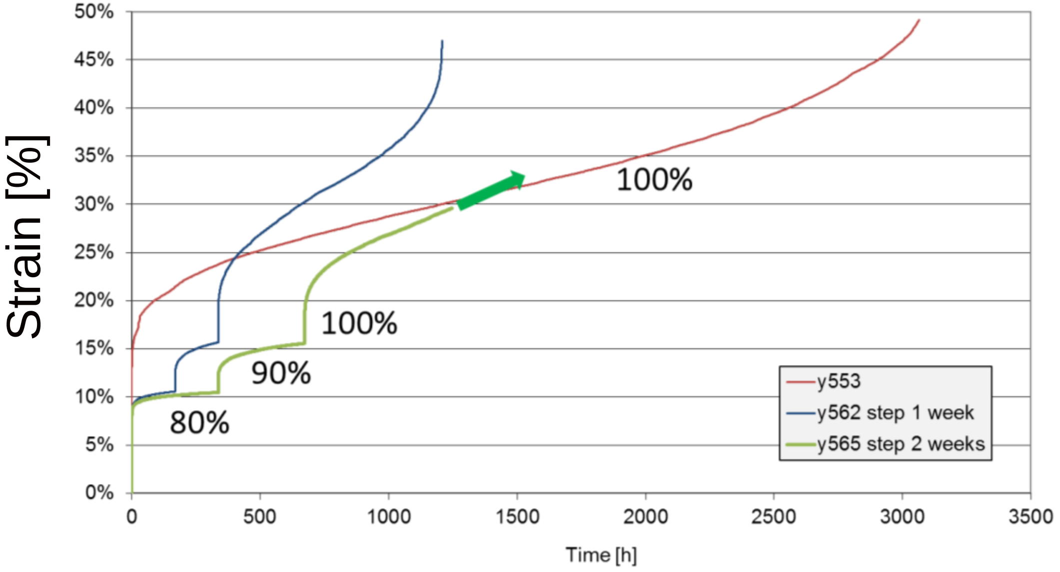
VTT

VTT

Creep and relaxation behaviour of Cu-OFP

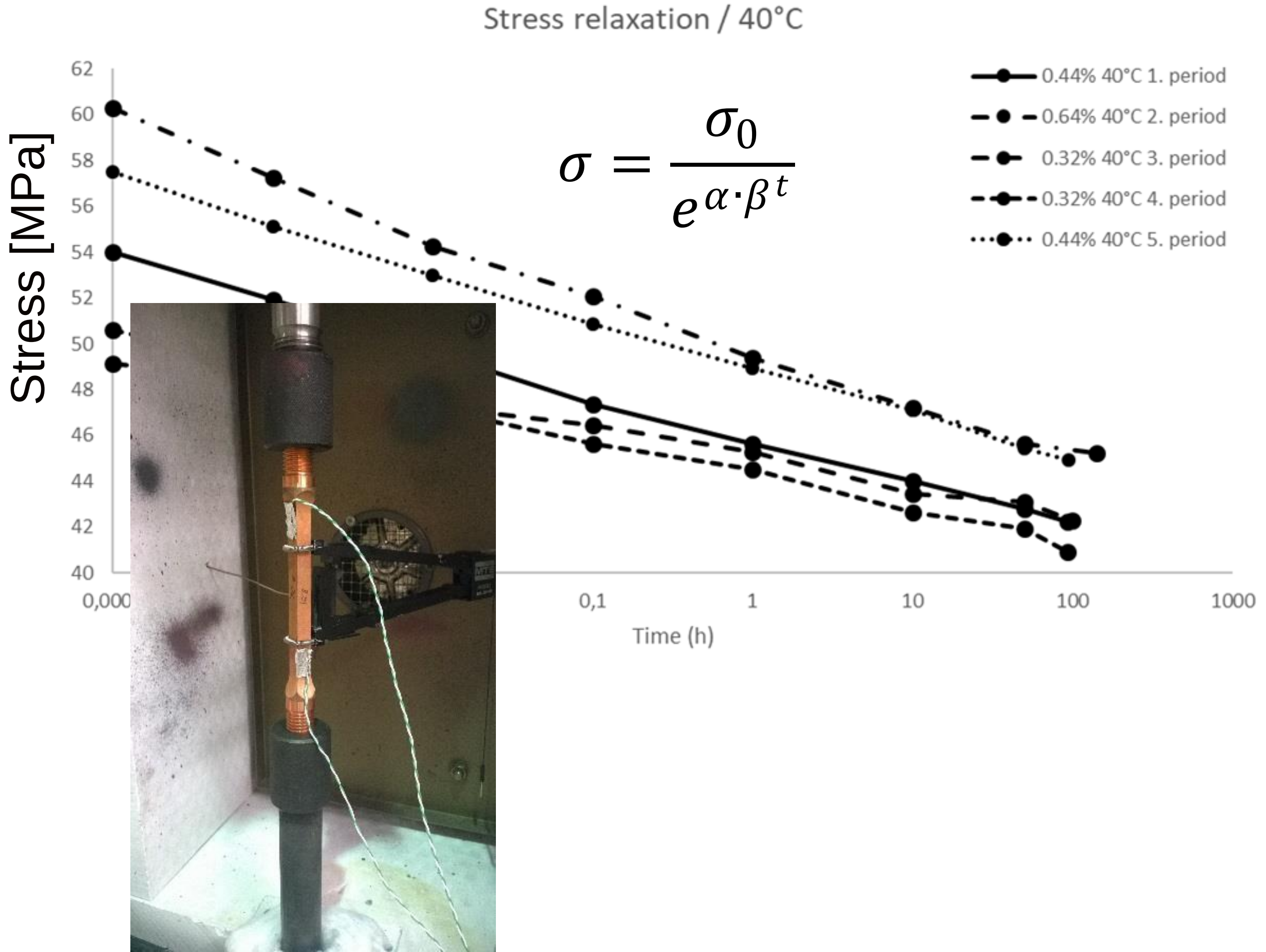
Loading history dependence!





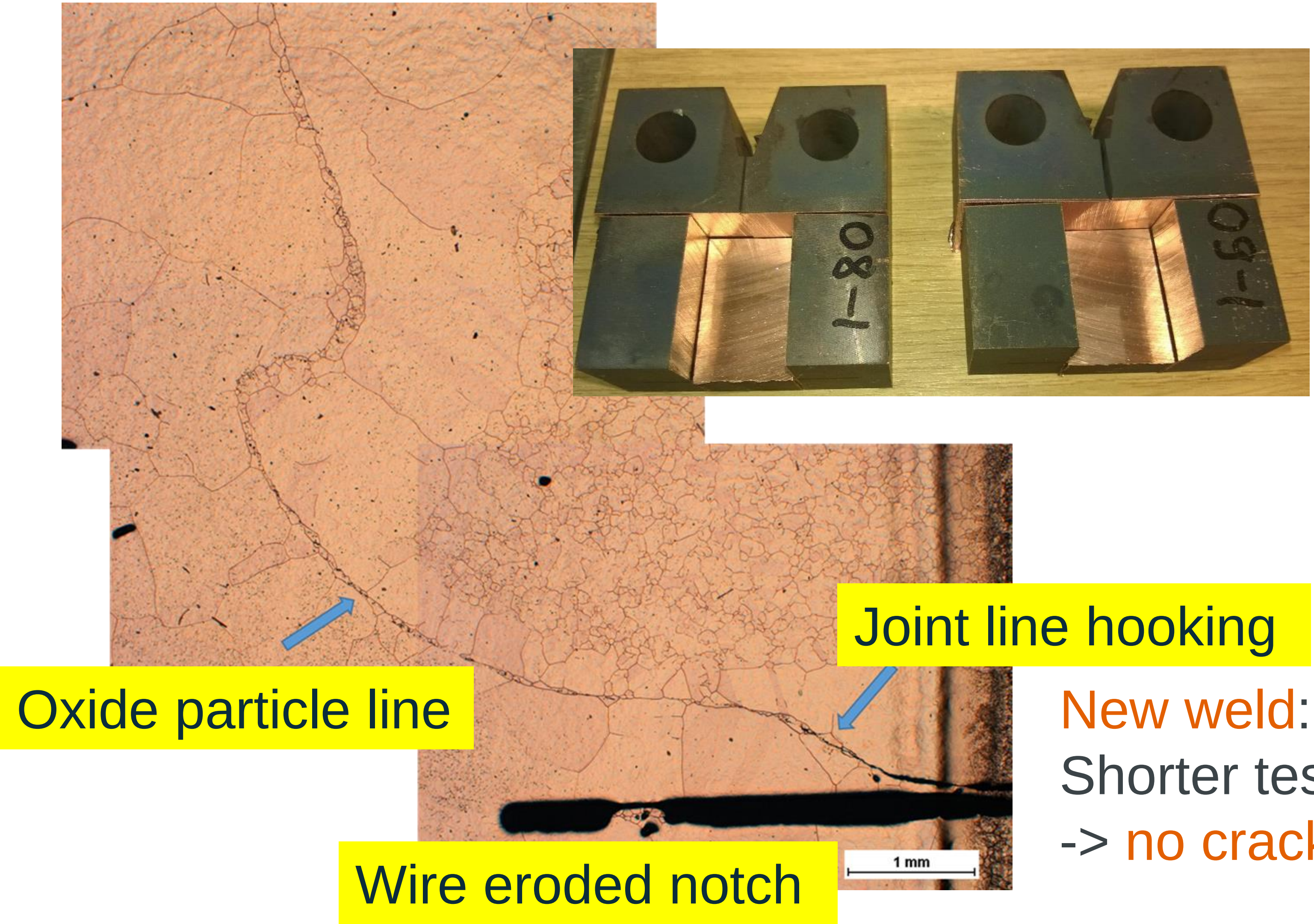
Bentonite swelling pressure will develop unevenly ->”step-loading” is likely to happen!

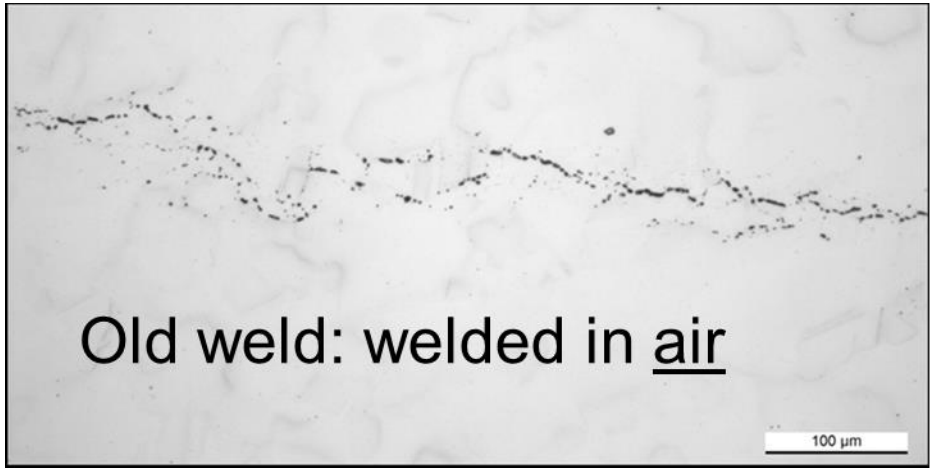
Relaxation testing at 40ºC, 60ºC and 80ºC and modelling -> implemented into FEA



$$\sigma = \frac{\sigma_0}{e^{\alpha \cdot \beta^t}}$$

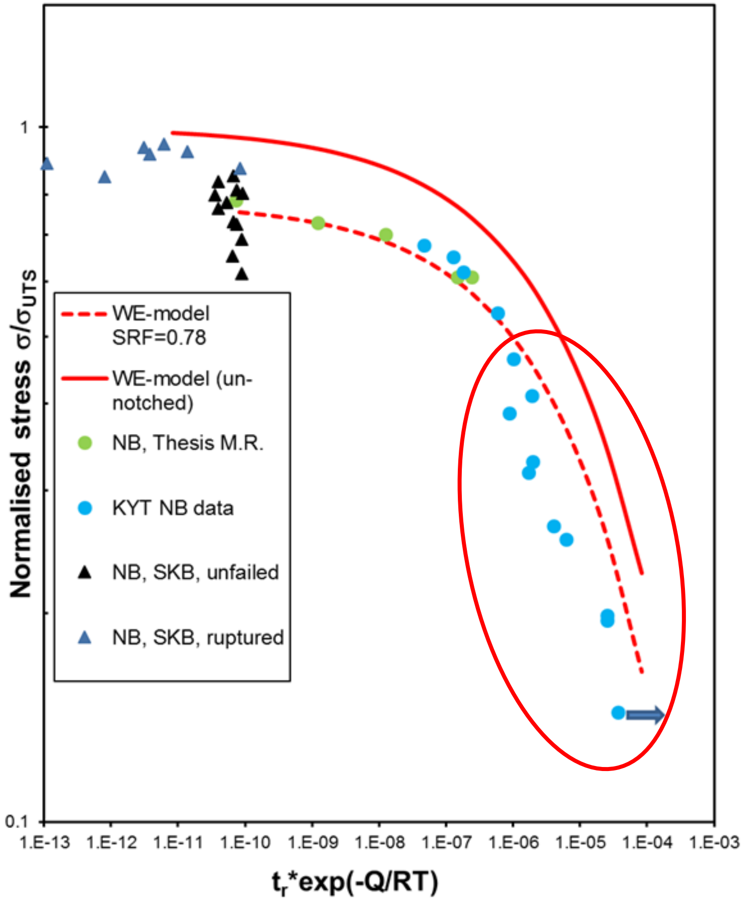
Cracking in the oxide particle zone



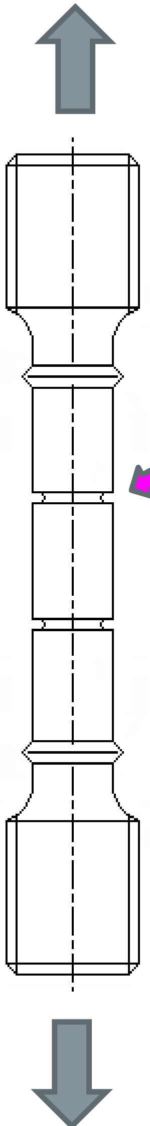


New weld: welded in argon atmosphere
Shorter test but much more heavily stressed
-> no cracking

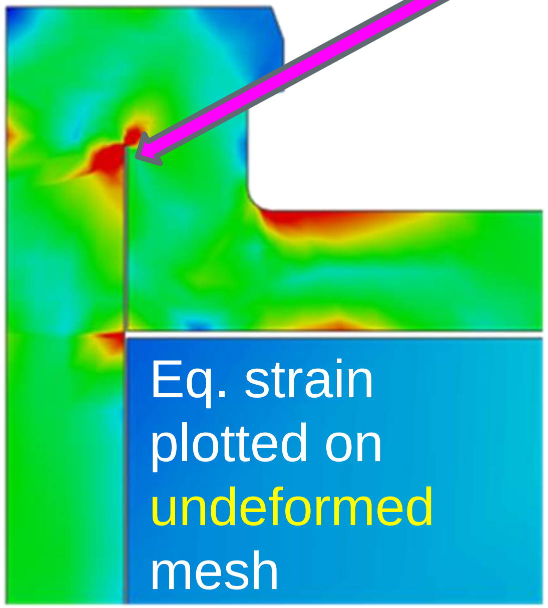
Effect of multiaxiality on the creep behaviour of Cu-OFP



Rupture time shortened and ductility reduced at low stresses due to multiaxiality



Multiaxial stress state



Critical question in KYT2022:
- will the ductility be exceeded?

Aalto-yliopisto
Insinööritieteiden
korkeakoulu

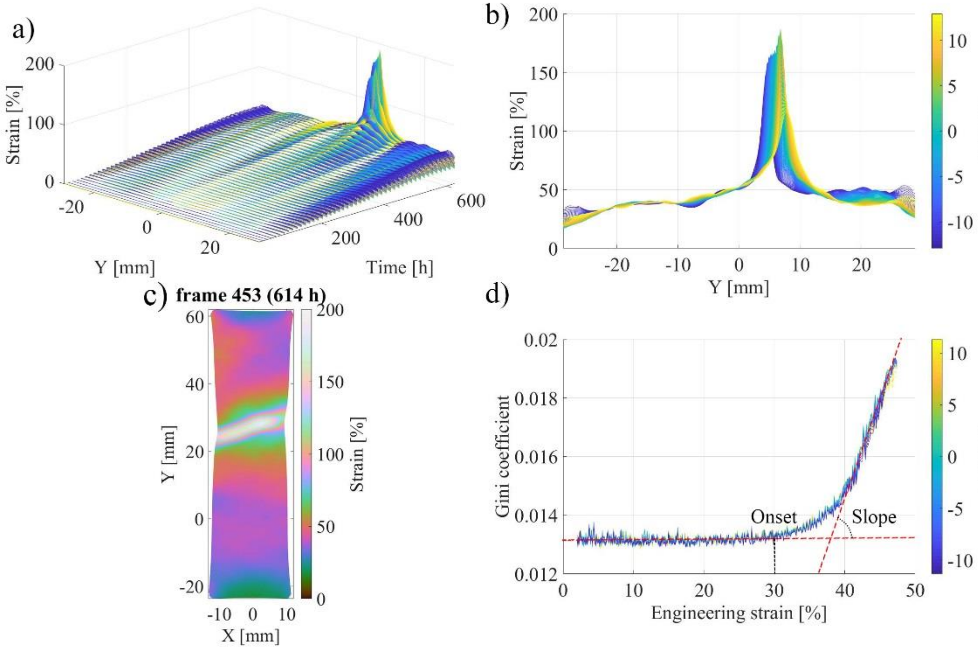
KYT2018
MECHACOP

Hannu Hänninen, Sven Bossuyt, Antti Forsström & Yuri Yagodzinskyy

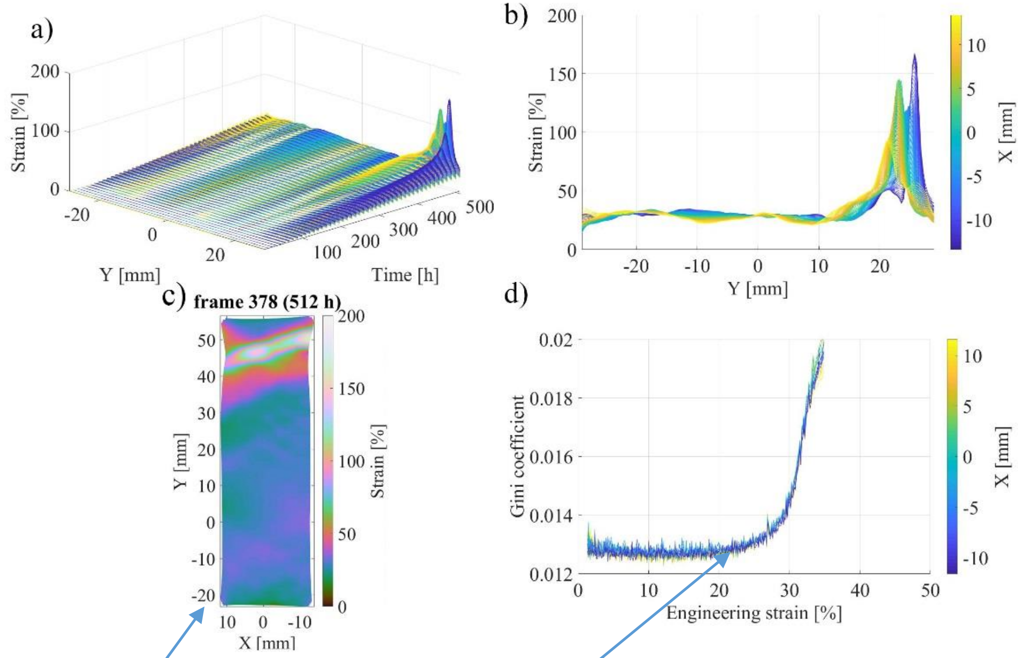
Final seminar 29.1.2019

Strain localization in FSW copper canister welds measured by optical strain measurement (DIC)

The old FSW weld was welded without shielding gas. Fracture occurs at the oxide line extending through the weld or at the weld boundary on the lid side of the canister.

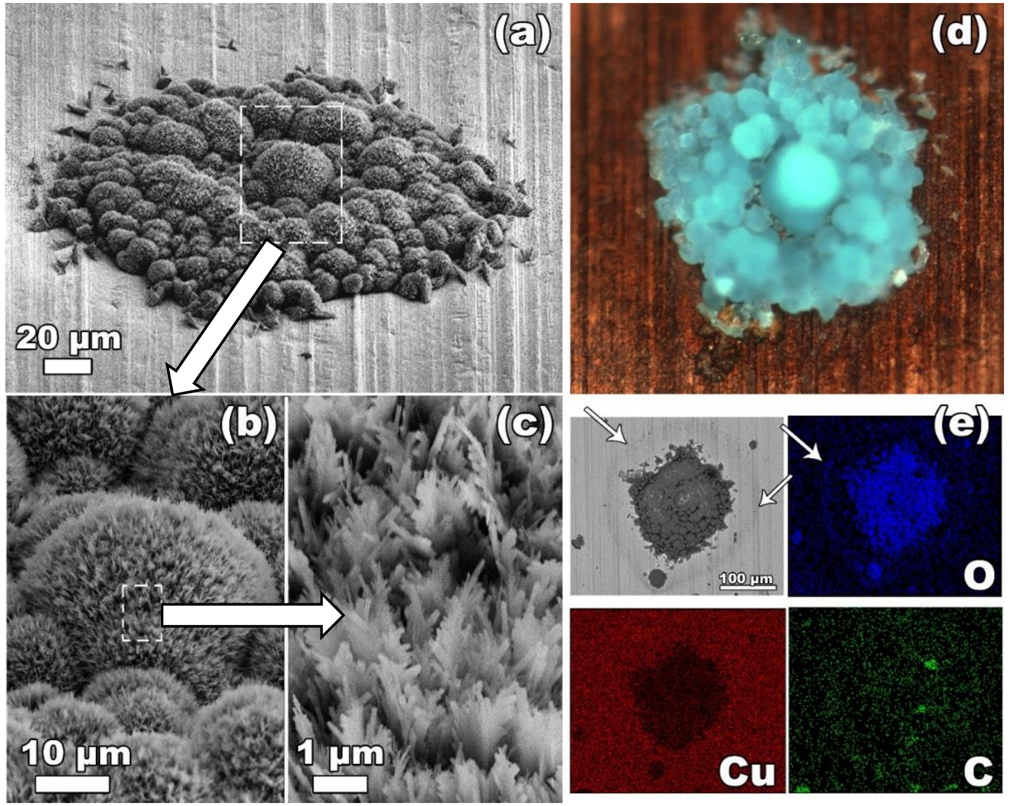


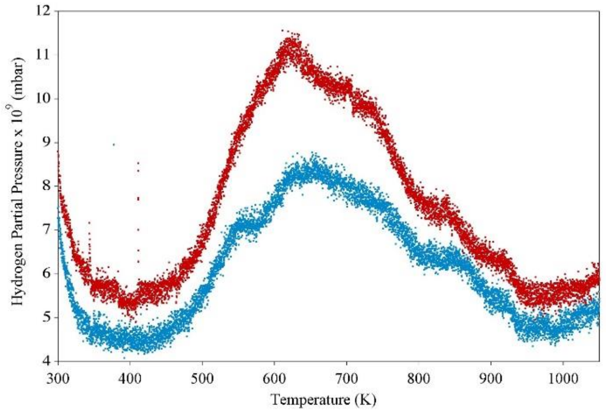
The new FSW weld was welded with shielding gas. Fracture occurs at the weld boundary on the lid side of the canister.



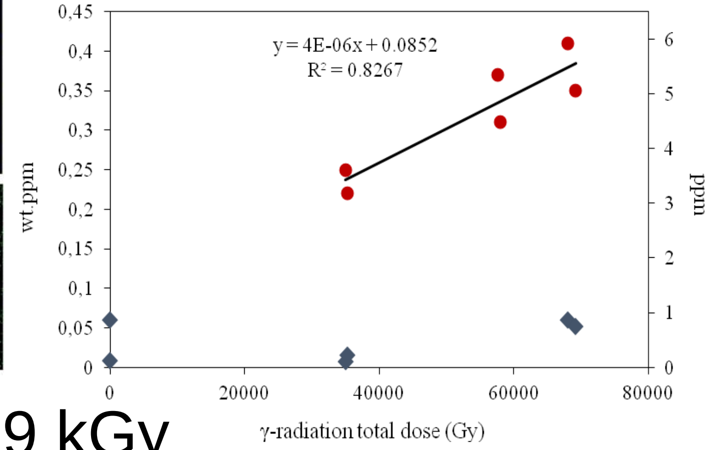
The new welds deformed less and localization of deformation begins earlier, even if end-effects from the specimen geometry are taken into account.

Cu exposed to water and γ-radiation, hydrogen uptake induced by γ-radiation





Hydrogen desorption of:
(●)γ-irradiated copper sample
(●)non-irradiated sample



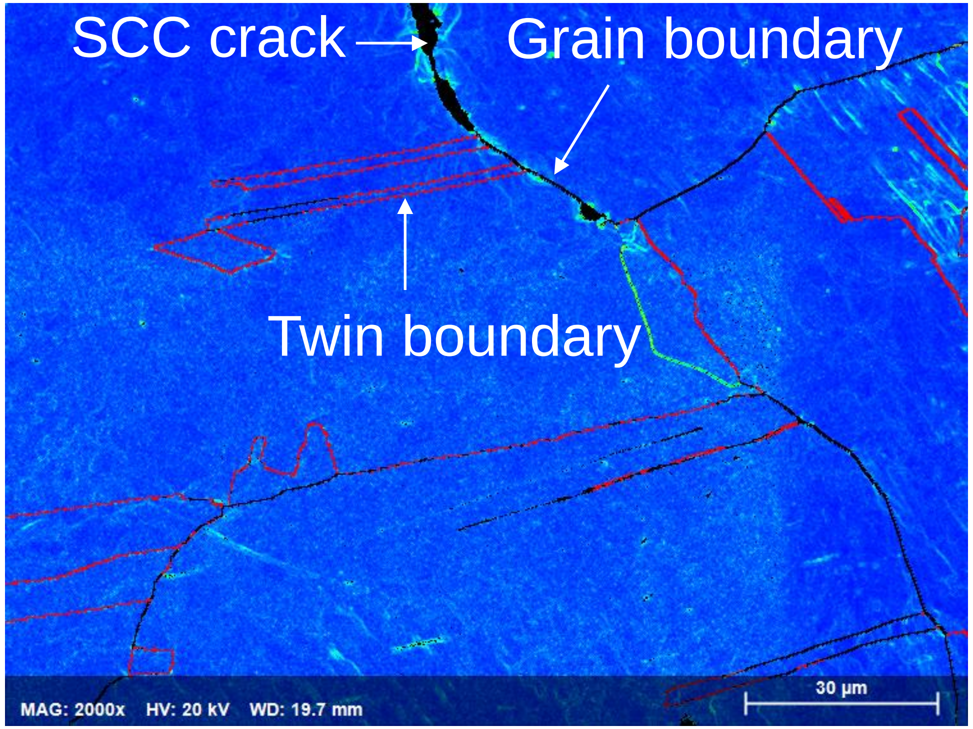
(●) Measured H-uptake and
(♦) adsorbed H_2O on copper surface, irradiated in water

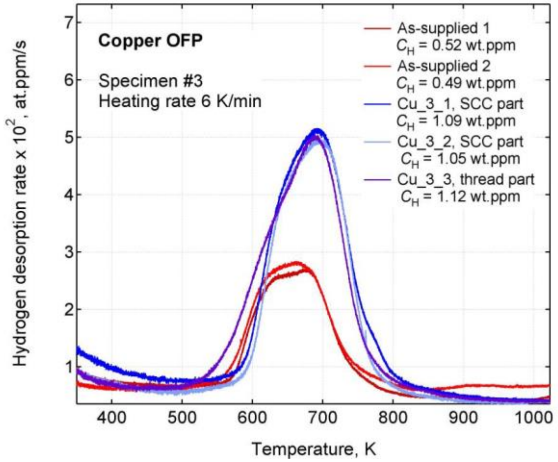
Dose rate: 0,135 Gy/s, total dose: 69 kGy

Islands of needle-shaped crystals formed on the surface of metallic copper in oxygen-free water after the γ-radiolysis. (a, b, c) scanning electron microscopy images taken at different magnifications, (d) optical image, (e) scanning electron microscopy backscattered image and corresponding energy dispersive X-ray maps obtained using K-lines of O, Cu and C.

SCC and hydrogen uptake of Cu in anaerobic sulphide containing solution

SCC cracks form along grain boundaries





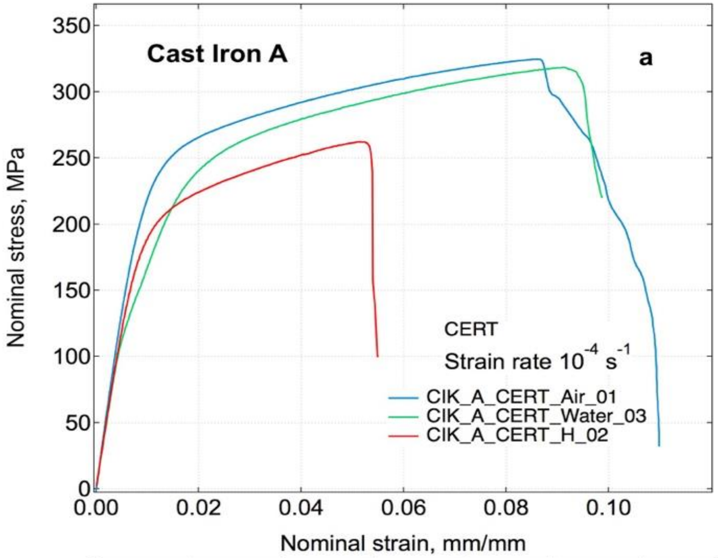
Hydrogen uptake:

- Base material: 0.5 wt.ppm
- SCC specimens: 1.0-1.2 wt.ppm

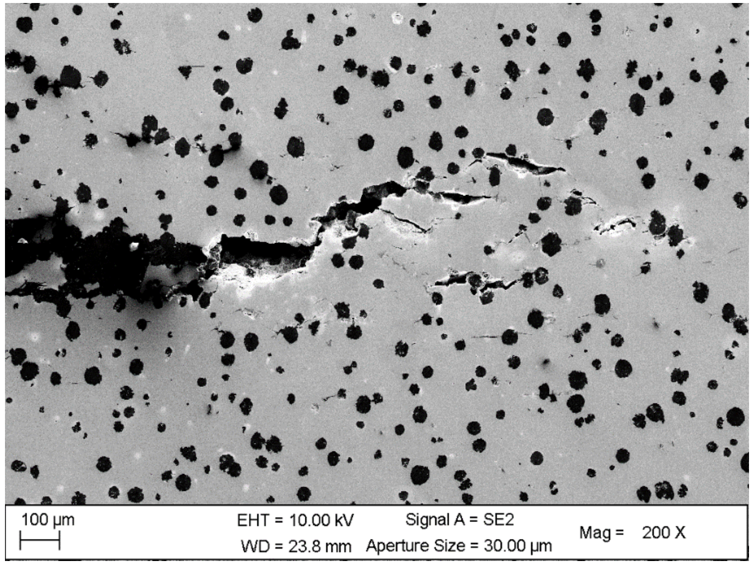
<u>SCC Test parameters:</u>

Temperature (° C)	90
NaCl (M)	0.1
Na_2S (M)	1×10^{-3}
Autoclave flow (l/h)	1
Strain rate (s^{-1})	1×10^{-7} to 5×10^{-7}
Max strain (%)	10
Test time (weeks)	2
pH	7.2

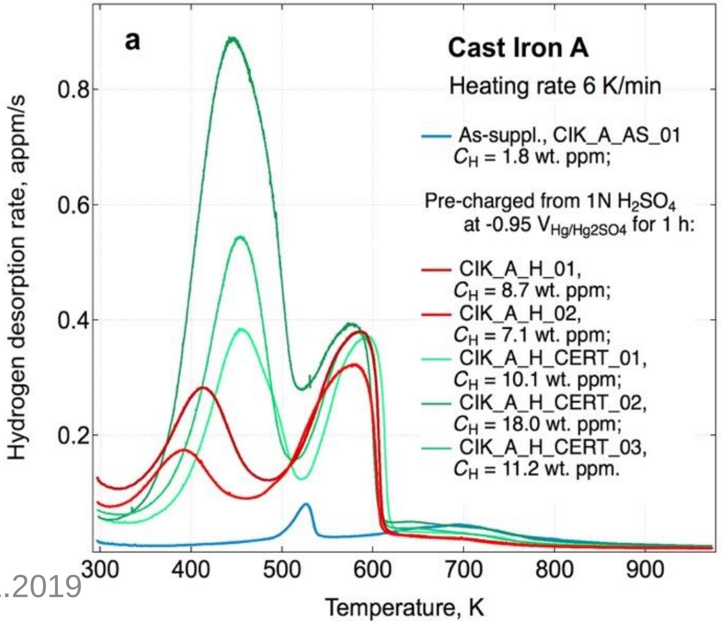
Hydrogen embrittlement of cast iron in continuous electrolytic hydrogen charging



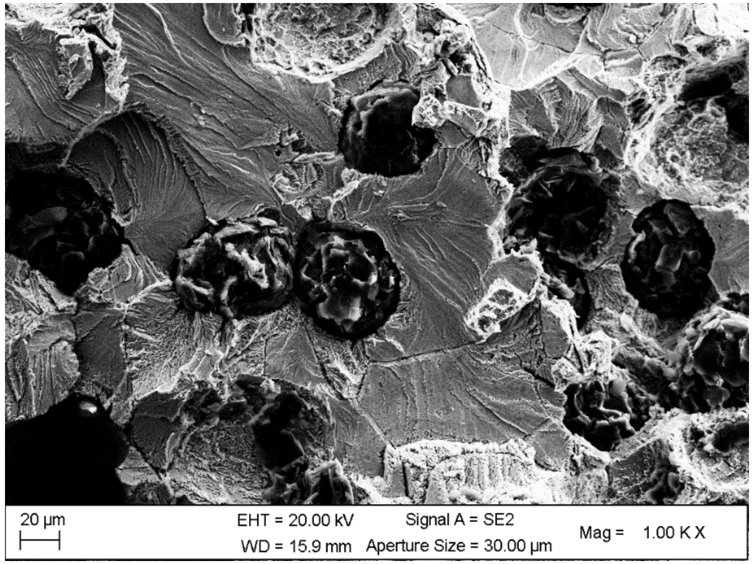
Hydrogen charging degrades the mechanical properties (red curve), when compared to air (blue) and water (green) tested specimens.



In hydrogen charging, several brittle cracks form along the main crack path.



Complex TDS peaks appear after hydrogen charging (red curves) and tensile testing (green curves), when compared to the as-supplied state (blue curve).



Hydrogen charging induces brittle cleavage fracture of cast iron.

Aalto-yliopisto
Insinööritieteiden
korkeakoulu

The effect of reaction product layers on copper corrosion in repository conditions (REPCOR)

Jari Aromaa*, Alexander Chernyaev, Vesa Lindroos,*
Marcus Olsio, Atte Tenitz, Mari Lundström
Aalto University
Hydrometallurgy and Corrosion Research Group

Background

- **Before emplacement of the canister in the disposal hole the copper surface will have an oxide film.**
- **The research question:**
  - **Can the oxide film increase copper corrosion rate in groundwater?**
- **The research tasks:**
  - **Produce oxide films on the surface of clean copper simulating the oxidation in air when canister surface is hot.**
  - **Characterize the oxide film composition and thickness**
  - **Measure the effect of oxide film on corrosion rate in different groundwater environments.**

Results – corrosion products

- Oxidation of copper in air produced oxide films in a couple of days that are tens or hundreds of nanometres thick.
- This is the currently estimated oxide film thickness before emplacement.
- The air-formed oxide films contained Cu_2O and some CuO.
- Pre-oxidized films continued to grow during immersion in air-saturated waters but dissolved in oxygen-deficient waters.
- Loss of the oxide film can increase risk of localized corrosion, where corrosion rate of bare copper areas increase due to adjacent remaining oxide film.

Results – corrosion rates

- The corrosion rate of fresh copper in oxygen-deficient water was few µm/year to few tens of µm/year.
- Change from oxygen-deficient to oxygen-saturated water can increase corrosion rate by two orders of magnitude.
- Pre-oxidized copper showed usually first rapid weight loss that evened out in tens of minutes, assumed to be due to reduction of the oxide.
- After the initial phase the corrosion rates were still 2-5 times higher than for fresh copper.
- The remaining oxide film was shown to increase corrosion rate and further tests will be done in KYT 2022 to confirm this in long-term tests up to 3-4 years.

MICOR

Microbially induced corrosion during the oxic stage of repository

Pauliina Rajala, Leena Carpén ja Elisa Isotahdon

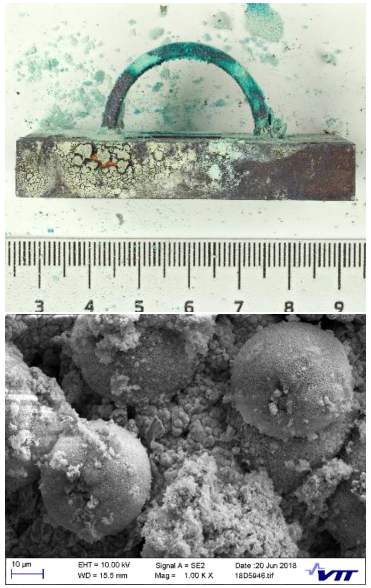
Image:Biofilm and corrosion products on the surface of sample

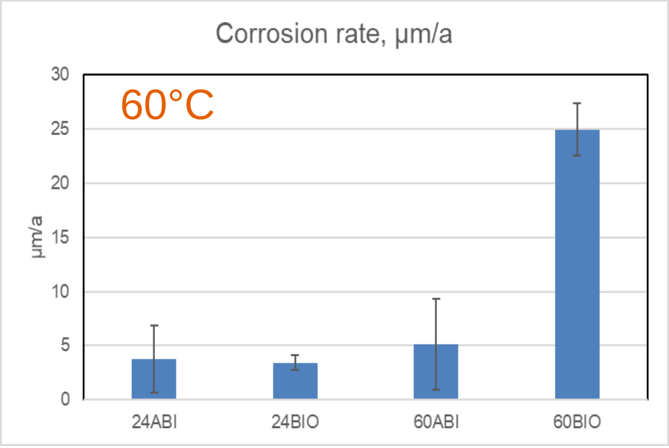
Aims of the project

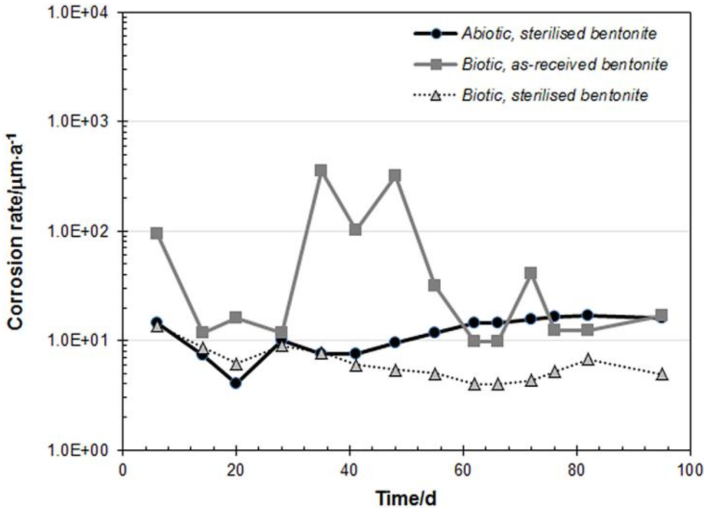
- Improvement of knowledge of microbial corrosion in Finnish final repository conditions
- Determination of the effect of **microbial action** on corrosion rate and corrosion mechanisms of copper in Finnish final repository conditions concerning the **oxic warm phase**
- Clarification of the properties and corrosion effect of the biofilm formed on copper surface in laboratory simulation
- To estimate the importance of oxic phase in long-term safety

Long-term laboratory tests with bentonite

- Cu-OFP: Weight loss samples, biofilm samples, electrochemical measurement –samples, U-bend samples for biotic environments
- **Biotic**: ONKALO-water + bentonite + microorganisms enrichment added, **Abiotic**: ONKALO-water + bentonite + glutaraldehyde (biocide) 0.3 ml/l
- 24°C, 37°C, 60°C
- Independent of the test environment (microbes, sterile) the corrosion behavior and surface phenomena were quite similar at 37°C
  - Corrosion was primarily general corrosion, average corrosion rates 13.2-17.6 µm/a in abiotic, 13.5-16.9 µm/a in biotic
- At higher temperature (60°C), corrosion rate was the highest in biotic environment, whereas at the lower temperature (24°C) corrosion rate in biotic environment was the lowest

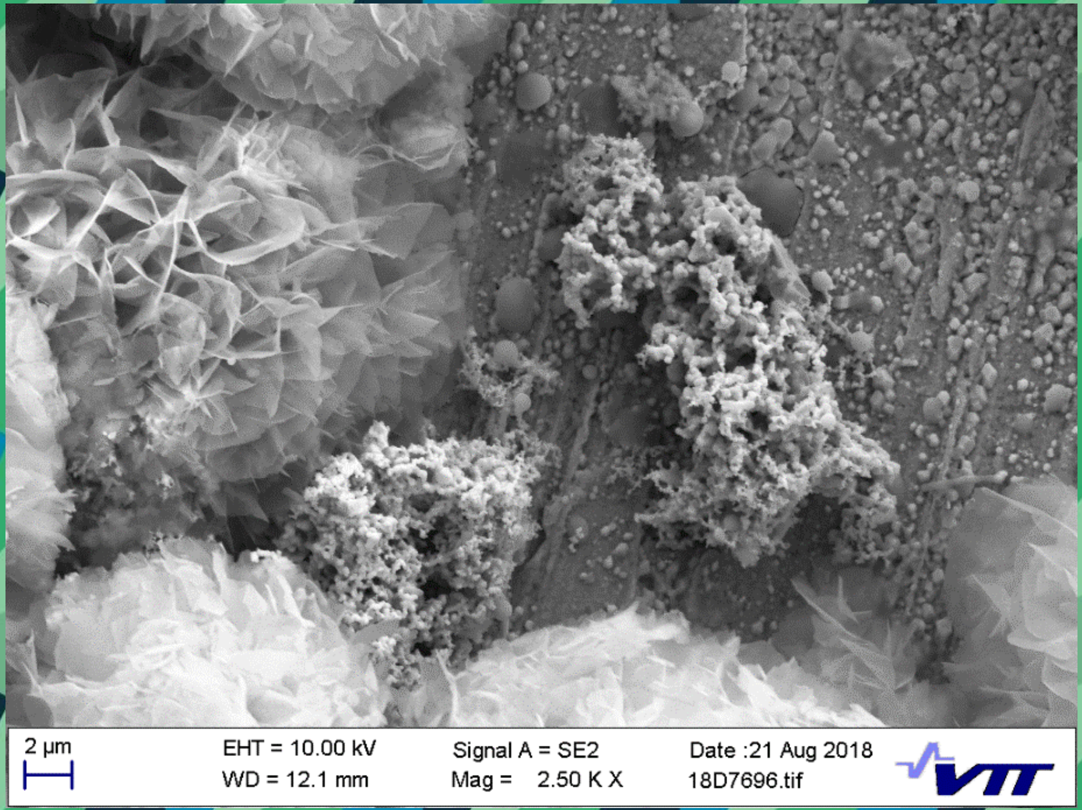






Important findings

- The electrochemical response of the Cu-specimens was heavily linked with the corrosion products
- The results demonstrate that groundwater chemistry and bentonite has an important role in the corrosion of copper under the early stage of repository
- Temperature affected the corrosion rate and corrosion product formation. The highest average corrosion rates, ca. 25 µm/a, based on weight loss were observed at 60°C test with microbes and the lowest in the 24°C test (3.5 µm/a)
- Based on the test results at 37°C, bentonite was a bigger source of microbes than the groundwater of the repository
- The results demonstrate that the role the biofilm formation plays in the corrosion of copper in oxic groundwater environment is very difficult to predict even in controlled laboratory conditions.



BASUCA

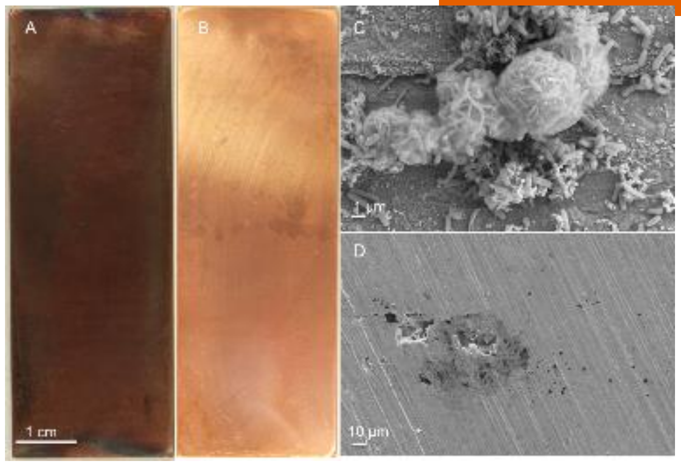
The effect of microbial activity on corrosion of copper in anoxic state of repository

Leena Carpén, Pauliina Rajala, Elisa Isotahdon

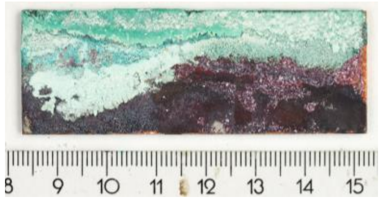
Aims and scheme of the project

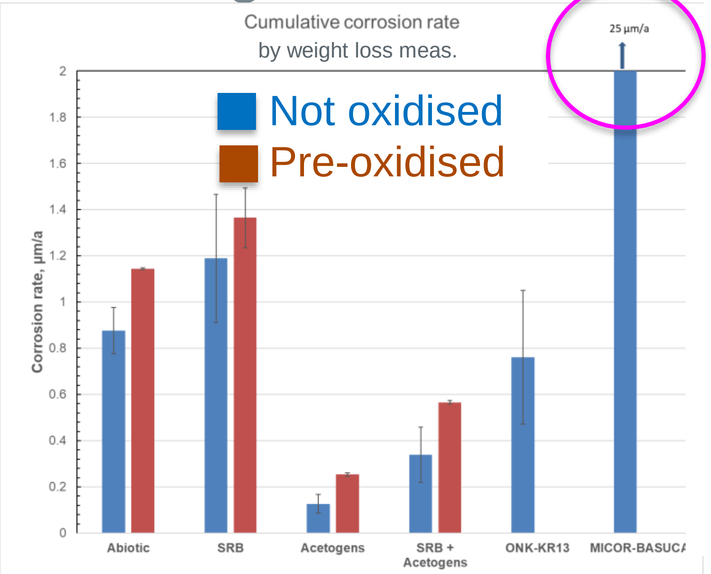
- Aim was to estimate and clarify the effects of microbiological activity on the corrosion behavior of copper in the nuclear waste disposal conditions in Finland
- The project is concentrated on the anoxic later stage of the disposal period and the effect of sulfate reducing bacteria (SRB), methanogens and acetogens in a simulated groundwater environment
    - temperature gradually stabilized to that of the surrounding bedrock (studied temperatures 10°C and 35°C)
    - all oxygen consumed
    - Cu in direct contact with ground water (chemistry stabilized with bentonite)
- Aims were achieved by creating a reliable and versatile laboratory environment where the corrosion of copper can be studied in the presence and absence of microbes

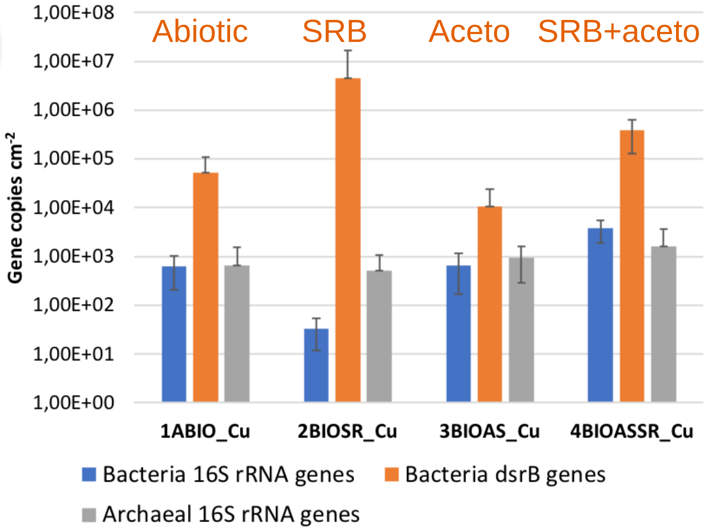
Experimental work



- Cu-OFP tested with 4 and 12 months tests
  - Electrochemical measurements, weight loss measurements, SEM/EDS, XRD, microbiological assays…
  - Some of the samples were pre-oxidized to simulate the oxic period
- Corrosion rates in biotic environments were either higher or lower than in sterile environment, suggesting that in some cases the biofilm increases but in other cases decreases the general corrosion rate
- Localized corrosion and initiation of SCC found
- MICOR-BASUCA combined test

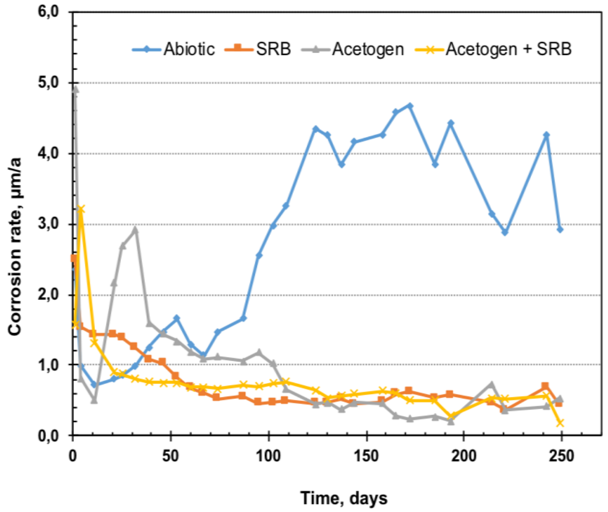


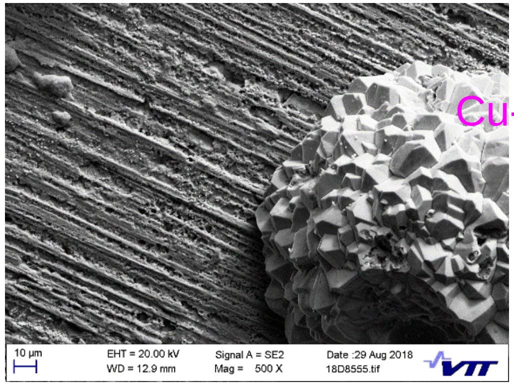




Important findings

- Test arrangement was successfully created that allows corrosion of copper to be studied at different temperatures in an oxygen-free environment both in the presence and absence of microbes.
- Improved understanding on the complex role of microbes in corrosion in the repository environment of Finland
- Localized forms of corrosion was observed in several environments
- Pre-oxidation influenced corrosion rates significantly – the role of oxic phase is evident on later corrosion behaviour of copper





Biofilm, bacteria