Corrosion of copper in sulphide containing environment

NKS Seminar 25.5.2022
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Nuclear waste disposal, Sweden and Finland

- KBS-3 concept with the outer canisters made of OFP-copper are part of the multi-barrier system ensuring the long-term safety of disposal
- The corrosion behaviour of OFP-copper in environments simulating groundwater environment in oxic and anoxic phases has been widely studied

Sulphide S^{2-}

- One of the open issues remained is related to sulphides as potential threat to copper stability in anoxic environments
- During the disposal process, possible sources of sulphides could arise from sulphate-reducing bacteria, mineral decomposition or groundwater itself (Fennoscandian bedrock is very sulphidic)
- Sulphide may lead to corrosion of copper forming copper sulphides and the presence of sulphur may promote the adsorption of detrimental hydrogen on copper surface.
- **The role of sulphide films is not unambiguous**

New modern methods, new information

- ***NKS-COCOS*** - ***Co****rrosion of* ***co****pper in* ***s****ulphide containing environment: the role and properties of sulphide films* - project 2019-2021
- Collaboration between VTT Technical Research Centre of Finland and KTH Royal Institute of Technology
  - Both have background in studies in national research programs
- COCOS project aimed to provide information on the behaviour of copper in the expected repository conditions and focus on the role of sulphide

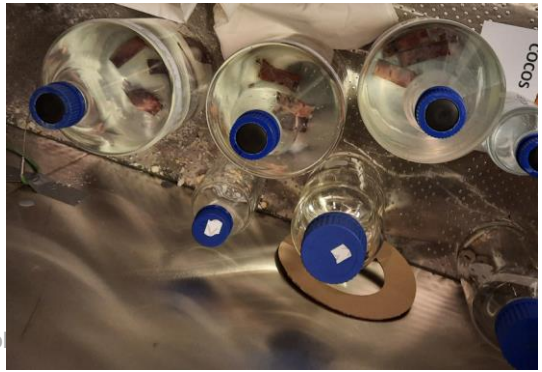
Experiments in COCOS

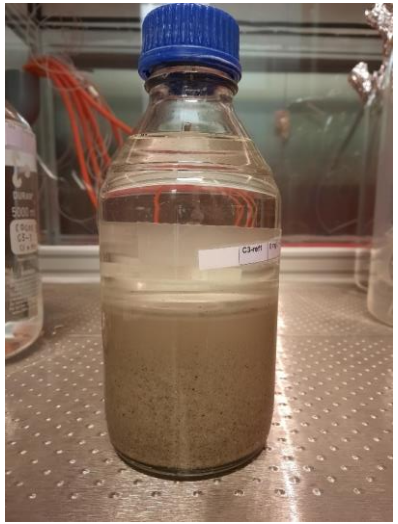
- Environment
  - Simulated anoxic groundwater with added sulphide 0..640 mg/L, for most part 32 mg/L (10^{-3} mol/L)
  - 3 long test campaigns:
    - COCOS1 4 months 2019-2020
    - COCOS2 9 months 2020-2021
    - COCOS3 4 months 2021
- Material
  - OFP-Cu sheet
  - Pre-oxidation to simulate the oxic phase

Table 1. The chemical components of the simulated groundwater.

	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

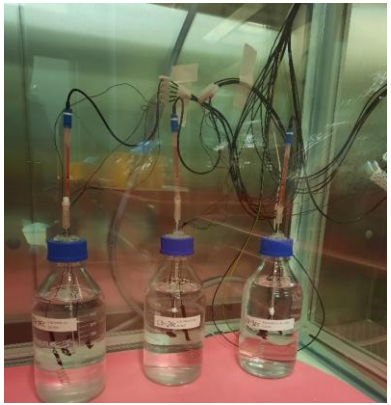
*Original Na content; actual amount is dependent on the addition of Na_2S.

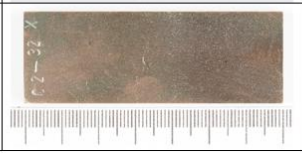
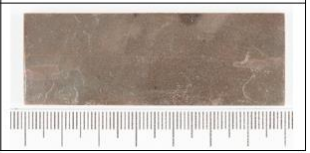


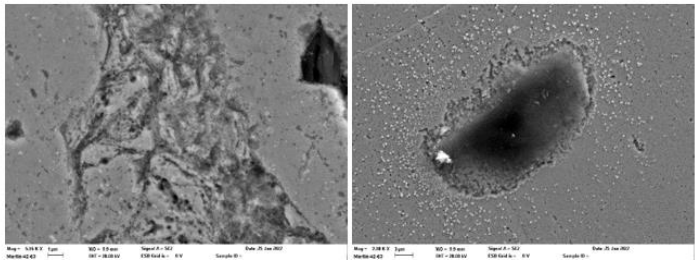


Experimental methods in COCOS

- Electrochemical measurements
  - Monitoring on-line
  - Open circuit potential, LPR, Tafel, EIS
- Mass loss samples
  - Corrosion rate
- Analysis of the water after test
- Characterisation of copper samples with microscopical methods (OM, SEM+EDS, EBSD, Raman), X-ray diffraction, SIMS, GD-OES

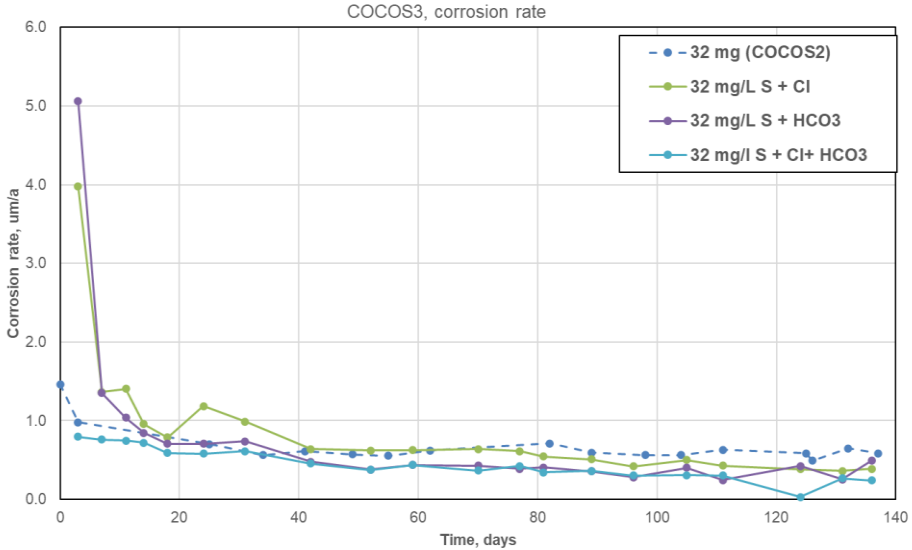


Test	Example surface of pre-oxidised sample	Example surface of non-pre-oxidised (ground) sample
C2-1 0 mg/L S		
C2-2 3.2 mg/L S		
C2-3 32 mg/L S		

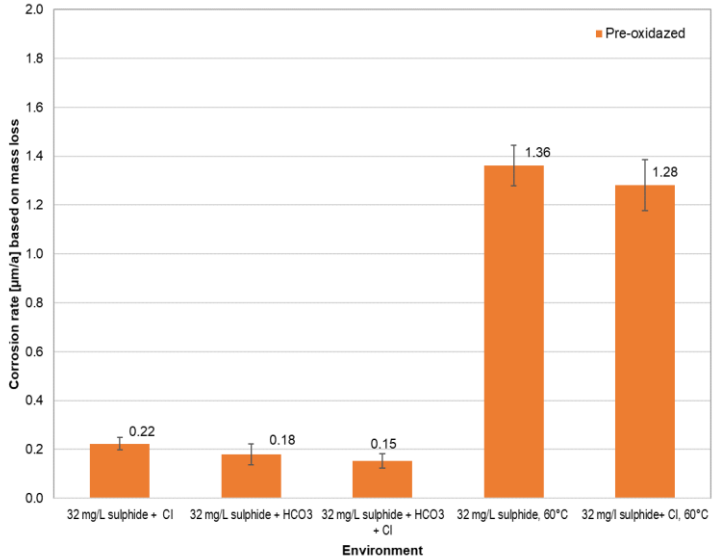


Corrosion rate measurements

Momentary corrosion rate based on electrochemical measurements



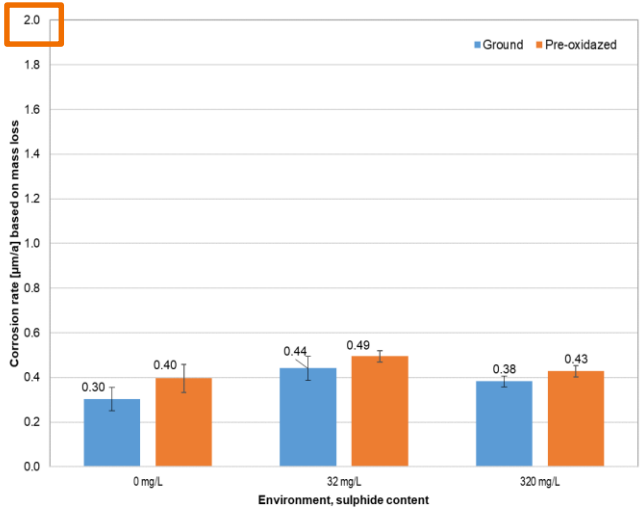
Cumulative corrosion rate based on mass loss (after removal of surface layer)

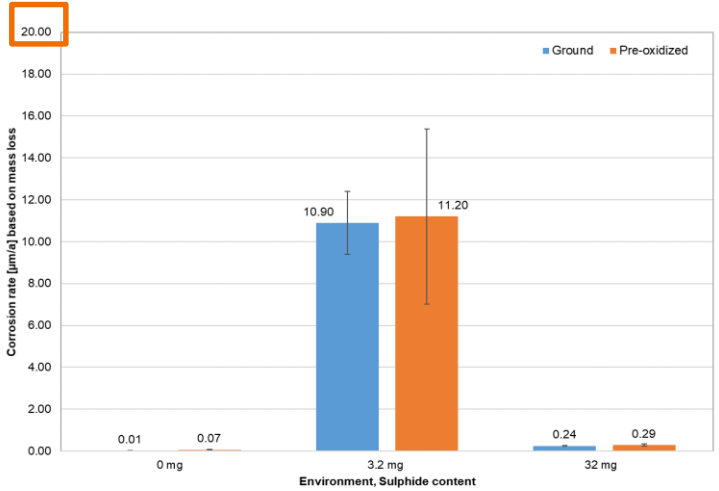


Corrosion rate vs sulphide content

Not proportional!

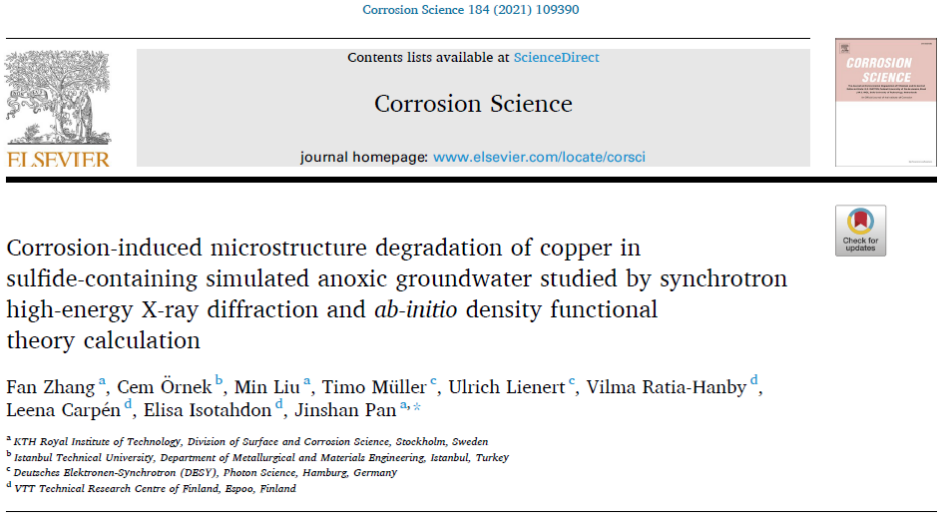
Role of surface film formation, certain amount of sulphide needed to form the film





Synchrotron high-energy X-ray diffraction (HEXRD) studies

- HE-XRD measurements combined with *ab initio* DFT calculation
- HE-XRD:Heterogeneous lattice deformation in microstructure of copper
- DFT: absorption oh H and S on Cu surface and lattice relaxation
- The exposure caused significant lattice deformation that can be explained by hydrogen infusion
- The risk of hydrogen induced stress corrosion cracking of copper when exposed to sulfide-containing groundwater



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Corrosion-induced microstructure degradation of copper in sulfide-containing simulated anoxic groundwater studied by synchrotron high-energy X-ray diffraction and *ab-initio* density functional theory calculation

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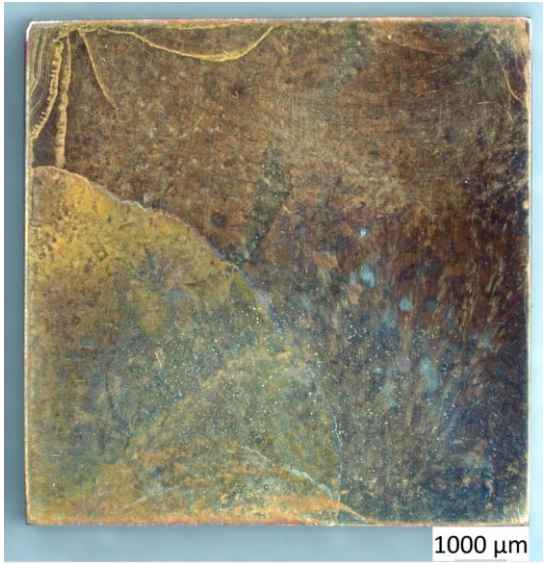
Conclusions from COCOS project

- Thick surface film formation was not detected after exposure with traditional methods after sulphide additions
- Sulphide additions do not proportionally increase corrosion
- High-energy XRD studies showed that the exposure in sulphide containing water caused significant lattice deformation in copper samples
- New sophisticated methods are needed to discover the small changes in microstructure and thin surface films
- Future studies on sulphide environments with focus on possible hydrogen intake to discover the mechanisms better



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beyond

the obvious

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