

Sulphide induced stress corrosion cracking of copper – Intermediate Report 2

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<p>Summary</p> <p>The experimental arrangement for studying sulphide induced stress corrosion cracking of CuOFP in simulated groundwater has been developed and tested. Three experiments with a target average sulphide concentration of $[S^{2-}] = 100$ mg/l has been made and revealed that CuOFP is susceptible to SCC under this concentration of sulphide. The verification of the SCC by SEM investigation was complicated by the appearance of exposed grain boundaries not only in the presumed SCC area but also in the prefatigue area. This finding will be examined in more detail during 2010.</p> <p>A literature survey of the maximum sulphide concentration that may form at the bentonite/rock interface due to bacterial activity shows that the maximum sulphide concentration at the bentonite/rock interface due to bacterial activity may be 400 – 450 mg/l.</p> <p>First version of a diffusion model for transport of sulphide through the bentonite to copper canister surface has been developed and it has been communicated in the form of a scientific publication and as a VTT Research Report.</p>	
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Preface

This Intermediate Report covers the progress made in the KYT2010 –research program project “Sulphide induced stress corrosion cracking of copper” till the end of January, 2010.

Espoo 21.1.2010

Authors

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1 Introduction

Copper canister is a central technical barrier for radioactive release from high level nuclear waste. Stress corrosion cracking (SCC) is a failure mechanism which has the potential capacity of damaging all the canisters in a relatively short time.

In 2007 a new Japanese research showed that also sulphide (S^{2-}) can cause SCC in pure copper under anoxic high chloride water conditions /1/. Sulphides may come to contact with the copper canister surface through three different processes: 1) transport via groundwater flow, 2) production at the bentonite/rock interface via sulphate reducing bacteria (SRB) and further transport and 3) through SRB activity within bentonite (pyrite reduction). In the groundwater sulphide concentrations are typically relatively low, 1-3 mg/l. The maximum value that can be formed through SRB activity at the bentonite/rock interface is not exactly known, but can be high, causing a high diffusion gradient through the bentonite. The sulphide concentration that forms because of SRB activity within bentonite is known to some extent as a function of bentonite density. According to experimental findings sulphides form within the bentonite even in fully compacted bentonite /2/. In scenarios where the density of bentonite locally decreases (e.g. piping, erosion-corrosion) the access of sulphide to the copper surface will be much easier.

2 Goal

The goals of the project are to evaluate the sulphide induced SCC risk of copper canisters under repository conditions. Technical targets are:

1. Develop an experimental arrangement for SCC tests in sulphide containing groundwater.
2. Determine experimentally the minimum concentration of sulphide in groundwater which can cause SCC in pure copper (CuOFP).
3. Evaluate the maximum sulphide concentration which can form at the bentonite/rock interface because of SRB activity.
4. Develop a diffusion model and make a quantitative estimate of the sulphide concentration reaching the surface of the copper canister in three different scenarios.

3 Results

In the following the results of the individual tasks are presented as of January 22, 2010.

Task 1. Experimental arrangement for SCC tests in sulphide containing groundwater

The experimental arrangement has been built and tested. The system (Fig. 1) consists of a pressure vessel made of austenitic stainless steel (1), the surfaces of which have been passivated in high temperature water, which produces a protective magnetite-type spinel-oxide layer on the surfaces. A Ag/AgCl (0.01MKCl) -reference electrode with a stainless steel housing is used. The electrode sealing to the pressure vessel body is made by a Grafoil –box seal. Pressure tight wire lead through (2) provides for potential measurement wires as well as for current leads for the potential drop (PD) system used for on-line crack length monitoring. The mechanical load is produced by a servohydraulic system (3), the pullrod of which is sealed to the pressure vessel body by flexible silicon. Pure 5N nitrogen gas (4) is used to purge the pressure vessel to remove air as well as to move the groundwater (5) into and out of the pressure vessel. All samples were taken and possible chemical additions made through an Athmosbag –system (6) to avoid any possibility of air contamination of the system.

This task has been completed.

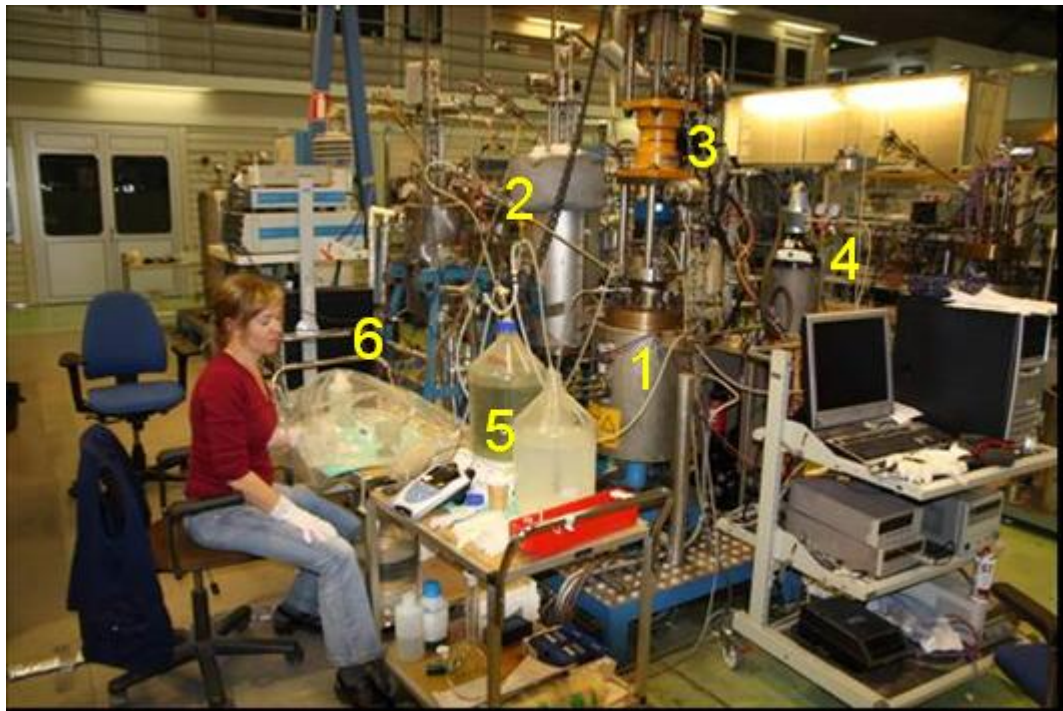


Figure 1. Experimental arrangement.

Task 2. Determination of the minimum sulphide concentration causing SCC in CuOFP

The research method used is constant load method with so-called Compact Tension (CT) –test piece, where the stress-strain state forming at the crack tip corresponds to the multiaxial stress-strain in the copper canister. A prefatigue crack was made in the test piece by high cycle fatigue in air.

The base electrolyte used was the saline groundwater corresponding to Olkiluoto groundwater (Table 1). The sulphide was added as Na₂S. Before the sulphide addition the pH of the base solution was increased to pH = 9 by NaOH to prevent the formation of H₂S during the following sulphide addition.

Table 1. The composition of the saline reference groundwater in anoxic condition

Element	Concentration	
	mg/l	mmol/l
Na ⁺	4800	208,8
K ⁺	21	0,54
Ca ²⁺	4000	100
Mg ²⁺	54,6	2,3
Sr ²⁺	35	0,4
B ³⁺	0,92	0,08
SO ₄ ²⁻	4,2	0,044
Cl ⁻	14500	412,7
F ⁻	1,2	0,063
Br ⁻	104,7	1,31
I ⁻	0,9	0,007
pH	8,2	

2.1 Test run 1 with 100 mg/l S²⁻

The first test was performed with a target level of 100 mg/l sulphide. Test was started on 04.09.2009, and the chemistry was let to stabilise until specimen was loaded on 07.09.2009. During the test the sulphide level and pH were measured regularly, see Fig. 2. Sulphide measurement was performed with ampules (CHEMetris VACUettes Kit K-9510D), which results in an accuracy of about ±10 mg/l of sulphide. The pH was measured with Thermo scientific Orion 5 Star Benchtop meter. During the period 15.9 ... 18.9 the sulphide level was found to be decreased. The level was restored each day to 100 mg/l by adding groundwater with 387 mg/l sulphide (storage electrolyte). The reason for the decrease most probably was a small persistent leakage in the silicon sealing of the pull rod of the servohydraulic loading device. After several additions of silicon the leakage was stopped. Smaller additions of sulphide were added later on, as measurement showed some consumption of sulphide. A plausible explanation for this is that copper reacts swiftly with the sulphide in the electrolyte. This hypothesis was supported by the finding that the surface of the test piece was covered with a thick layer of dark surface layer, presumably copper sulphide. Towards the end of the test larger decrease of sulphide was again noted, although no leakage was detected. The average level of sulphide during the test was 92 mg/l.

Because of hydrolysis of Na₂S through the reaction



the addition of sulphide produces an increase of pH. Table 2 shows the calculated pH as a function of sulphide concentration (in an otherwise unbuffered system).

Table 2. Concentration of sulphide and corresponding calculated pH

Test environment no.	pH		Concentration of S ²⁻	
	calculated		mg/l	mmol/l
1.	9,5		1	0,0312
2.	10,5		10	0,312
3.	11,5		100	3,119
4.	12,5		1000	31,19

When the test solution was prepared in the glass bottle, after the sulphide content of 100 mg/l was reached (and verified by ampule measurement), the pH of the solution was measured at pH = 10.9, i.e. 0.6 units lower than expected. After transferring the solution to the pressure vessel and re-measuring after 1 hour, the sulphide content was found to be the same, whereas the pH had decreased slightly to pH = 10.4, at which level it roughly stayed during the first week of the test, after which additions were necessary. The additions of sulphide (a total of 196 mg/l during the test period) resulted in an increase in pH as expected, with the final pH = 11.2.

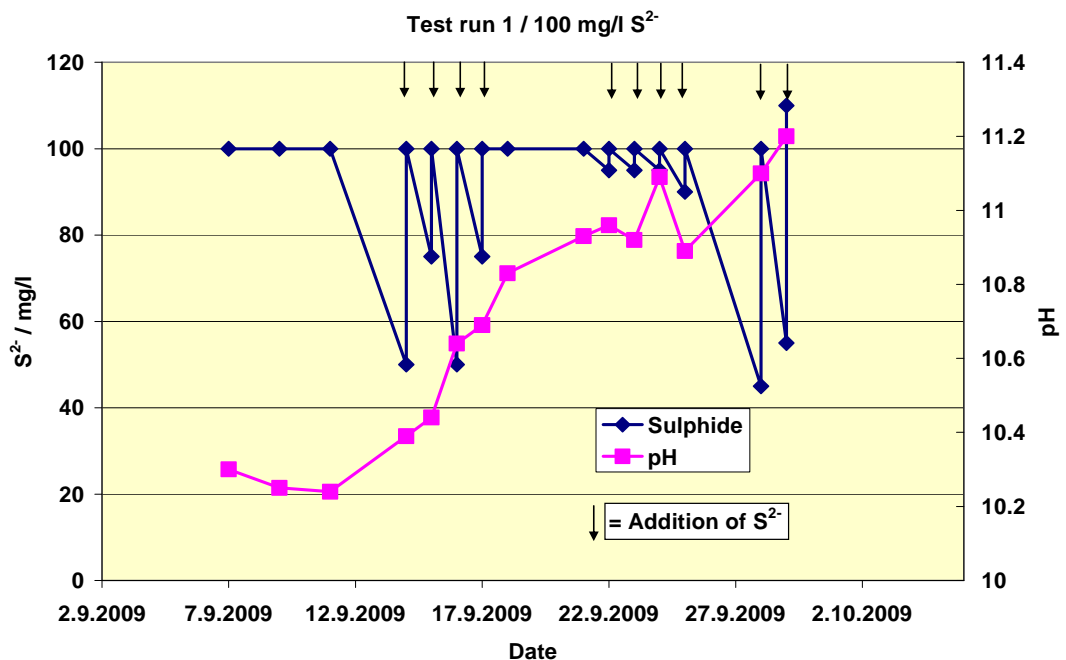


Figure 2. Sulphide concentration and pH as a function of test duration.

The potential of the Cu-specimen and Pt-plate (redox-potential) are shown in Fig. 3. The Cu-specimen potential is about $E_{Cu} = -0.65 V_{SHE}$ during most of the test period, increasing somewhat during the last five days of exposure. Potential of Pt-

plate (the redox-potential) is between $-0.3 V_{SHE} < E_{Pt} < -0.2 V_{SHE}$ for most of the test period, also increasing markedly during the last five days of exposure. Cu potential is quite low, about 0.1 to 0.2 V above the Cu/Cu₂S –equilibrium potential, and very close to the H₂/H⁺ –equilibrium potential (hydrogen line), see Fig. 4. Potential of Pt is rather close to the PtS/Pt –equilibrium potential, see Fig. 5. The marked increase of potentials of both Cu and Pt during the last exposure days indicates an air leakage, although visually nothing was observed. This would also explain the rather fast consumption of sulphide during the same period, see Fig. 2.

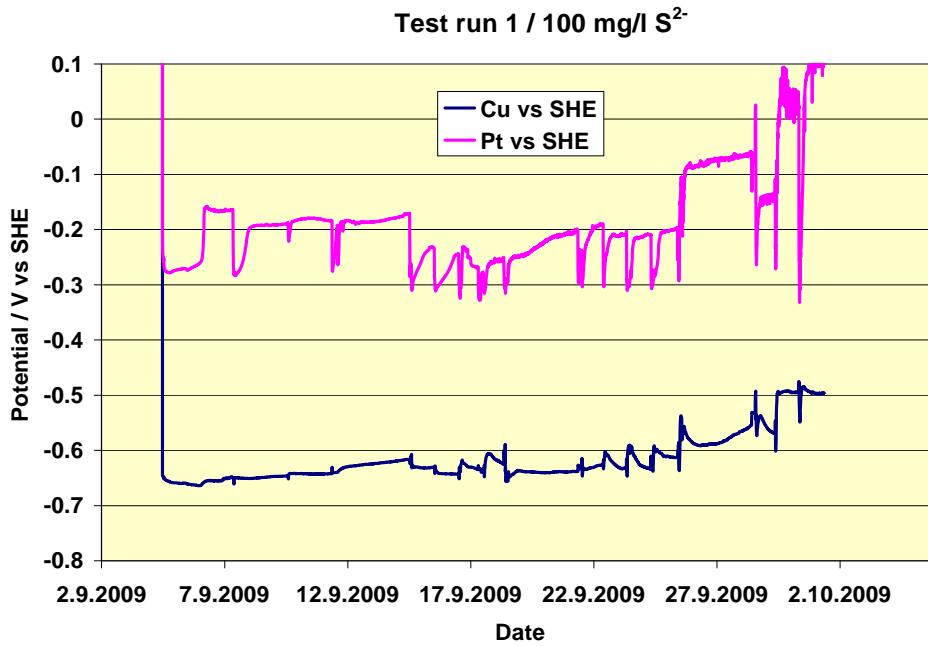


Figure 3. Potential of Cu-specimen and Pt-plate as a function of test duration.

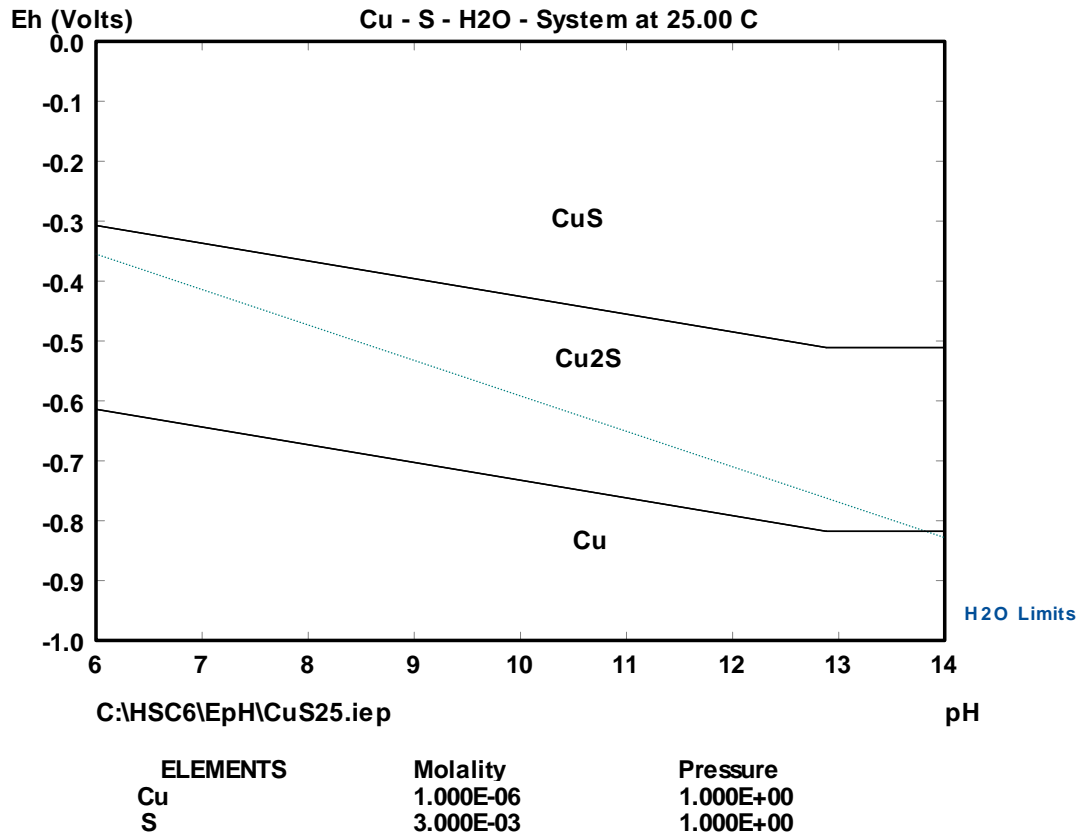


Figure 4. Potential–pH –diagram (Pourbaix-diagram) for Cu in sulphide environment.

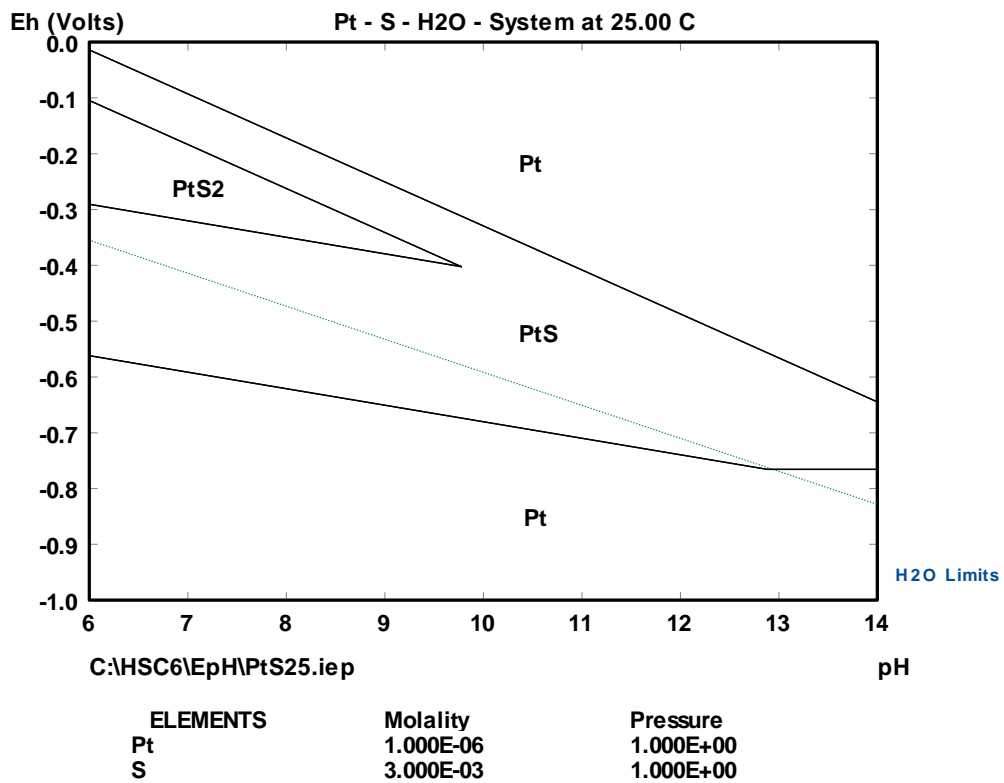


Figure 5. Potential–pH –diagram (Pourbaix-diagram) for Pt in sulphide environment.

The load and displacement of the Cu-specimen were recorded during the test. Displacement measures the opening of the CT-specimen, and is affected by the initial loading and following time dependent processes such as creep and/or crack growth. During the test the electrical resistance of the test piece was also followed by the so-called Potential Drop –method. An increase of the crack length during the test will result in a decrease of the cross sectional area of the test piece, which again is detected as an increase of the electrical resistance (in practise as an increase of the Potential Drop –voltage signal).

Load increase from the starting level of 0.2 kN to 3.75 kN resulted in an immediate increase of displacement from 0.01 mm to 0.45 mm, followed by a further slow increase to about 0.53 mm within the next two weeks, see Fig. 6. Further increase of load on 21.09.2009 to 4.0 kN resulted in an immediate increase of displacement to about 0.646 mm, followed by a slow increase to about 0.694 mm within the week. The immediate increase of displacement is accompanied by an immediate increase of the PD-signal in both cases, Fig. 7. This is because pre-fatigue crack surfaces are detached and current can no more go through them, which results in decrease of conducting cross-sectional area, increase of resistance and increase of measured potential. The PD-signal also tends to continue to grow slowly for a period after the load increase, and shows stable or even decreasing trend at some time intervals. It is proposed that when the Cu_2S –layer on the pre-fatigue crack surfaces grows thick enough, it meets the similar layer growing on the opposing surface and causes short-circuiting (Cu_2S is a rather good electronic conductor) which may result in a decrease of the voltage. Both the increase of displacement and the PD-signal indicate that stress corrosion cracking occurs during the test.

In fracture mechanical terminology, the increase of loading to 3.75 kN corresponds to a stress intensity of $K_I = 8,7 \text{ MPam}^{1/2}$, while the further increase to 4.0 kN corresponds to a stress intensity of $K_I = 9,1 \text{ MPam}^{1/2}$.

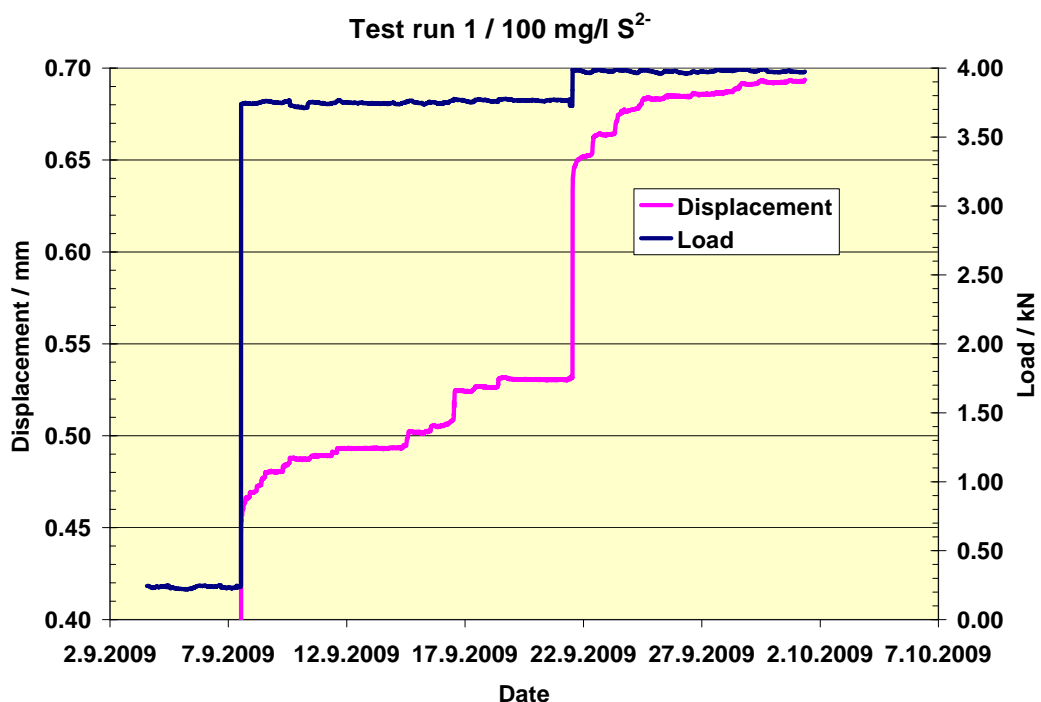


Figure 6. Load and displacement (crack opening) of the test piece as a function of time.

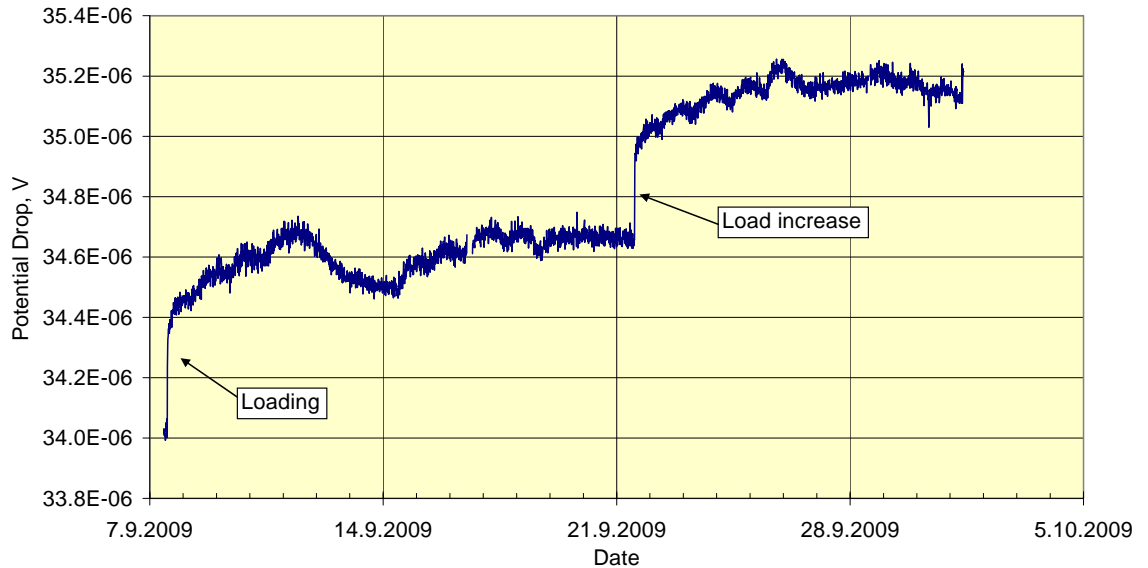


Figure 7. Potential Drop –signal of the test piece as a function of time.

After test termination the fracture surfaces were examined with both optical and scanning electron microscopy (SEM). The test piece is shown in Fig. 8 right after the test and after the specimen had been opened by further air fatigue. Figure 9 shows the digital picture of the fracture surface showing the pre-fatigue area, followed by an area of crack growth apparently after the first loading, and finally a reddish zone apparently formed as a result of the further load increase. Figures 10 to 12 (by SEM) show details of the areas. Fig. 10 shows normal air fatigue structure, ductile progress of the fatigue through the grains. Details (smooth plane-like surfaces of grains) typical of intergranular stress corrosion cracking (IGSCC) are seen in Figures 11 and 12. These constitute 50...70% of the fracture surface, whereas the rest of the surface appears to be structures typical of ductile fracture (possibly necks between the IGSCC-areas).

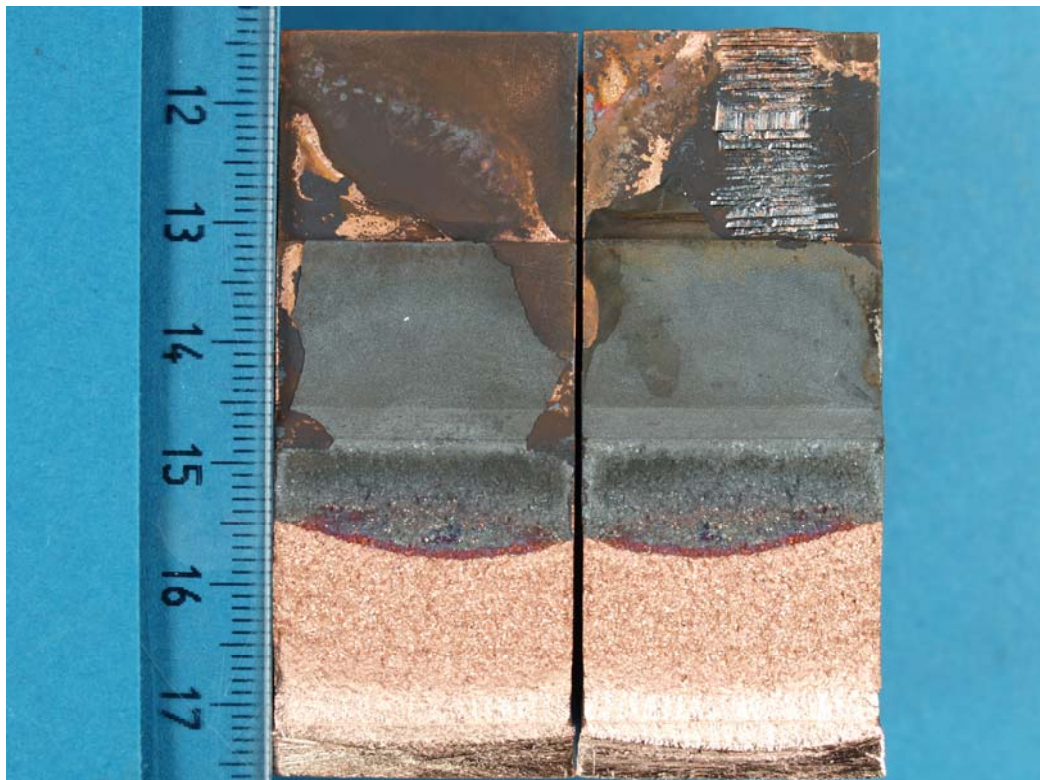
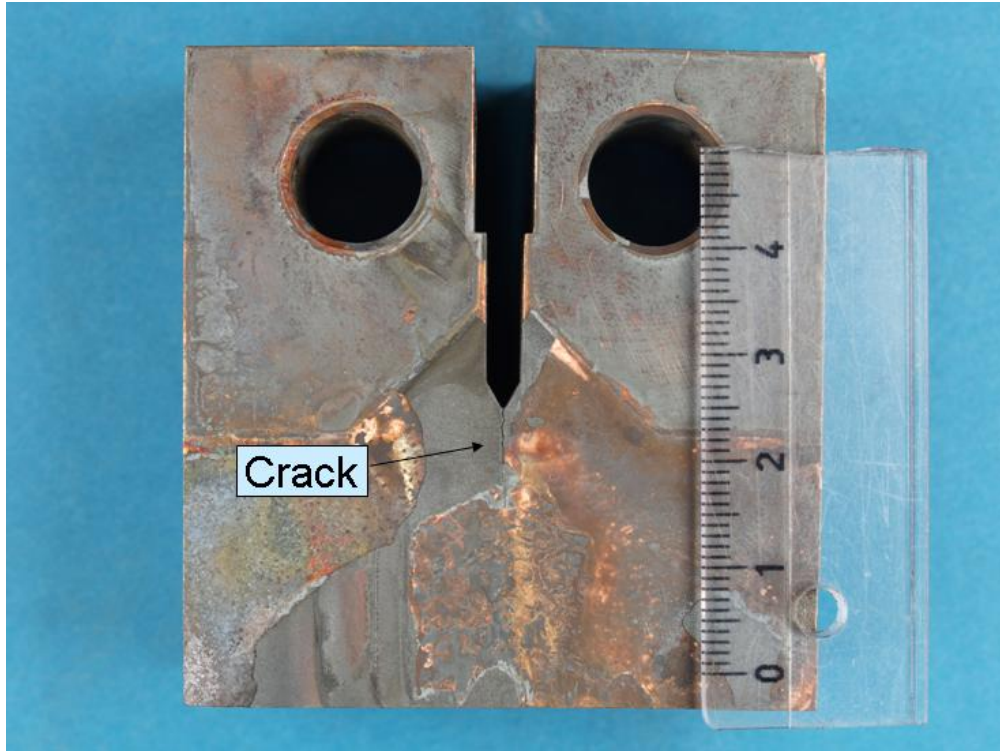


Figure 8. Test specimen after the test.

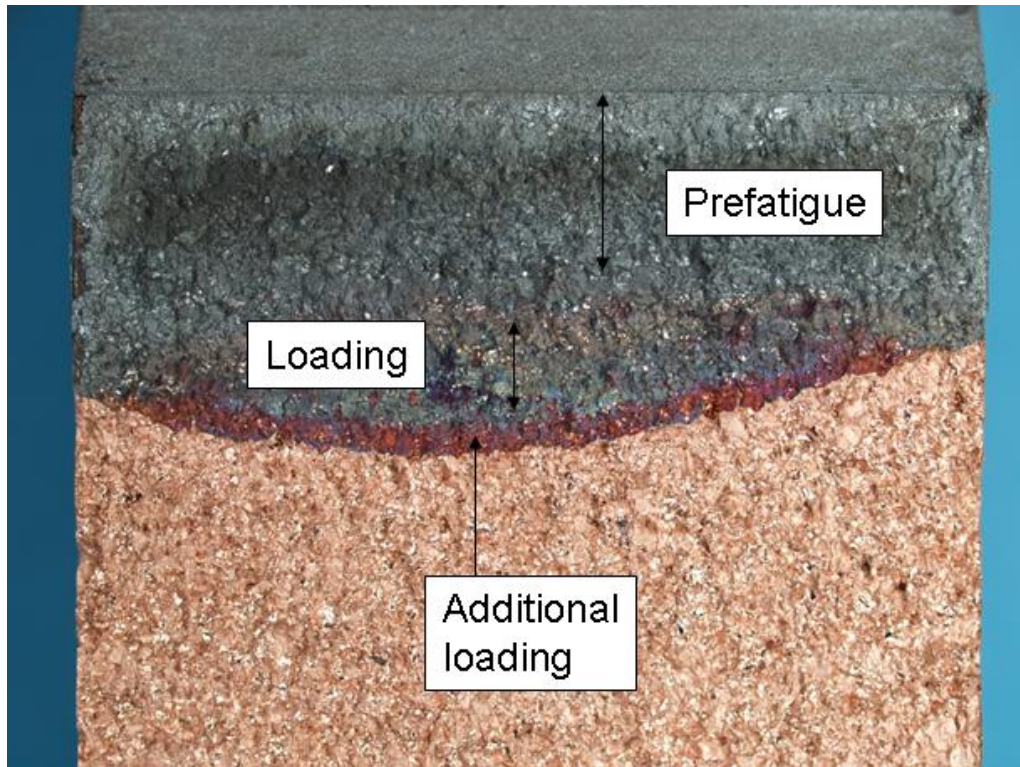


Figure 9. Digital picture of the fracture surface.

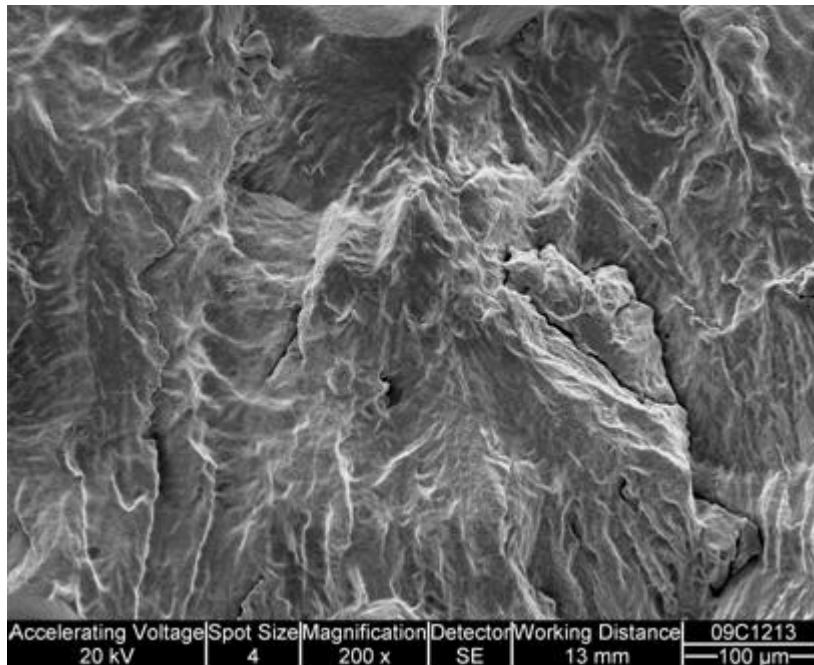


Figure 10. SEM-picture of the prefatigue area.

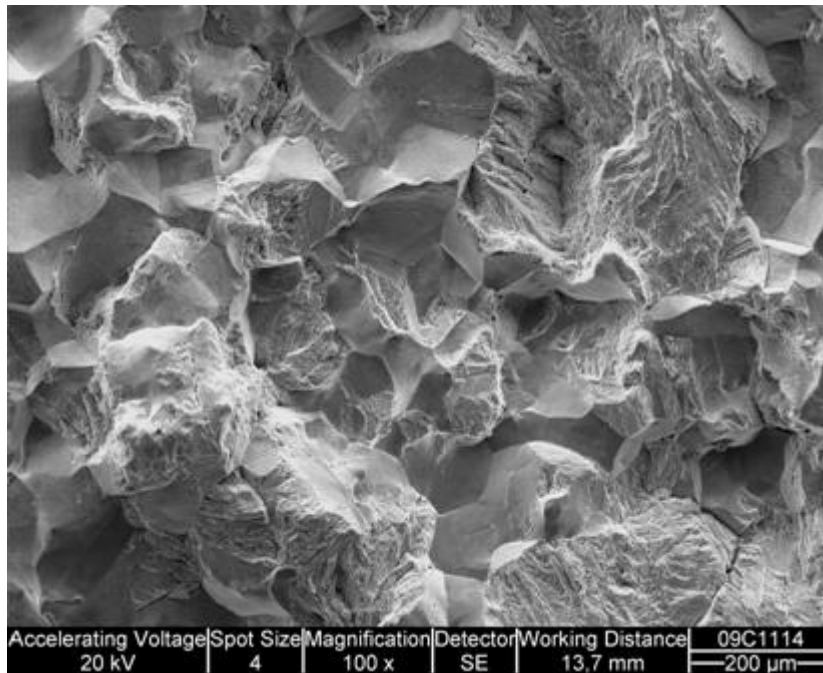


Figure 11. SEM-picture of the area after the pre-fatigue shown in Fig. 9 as "loading".

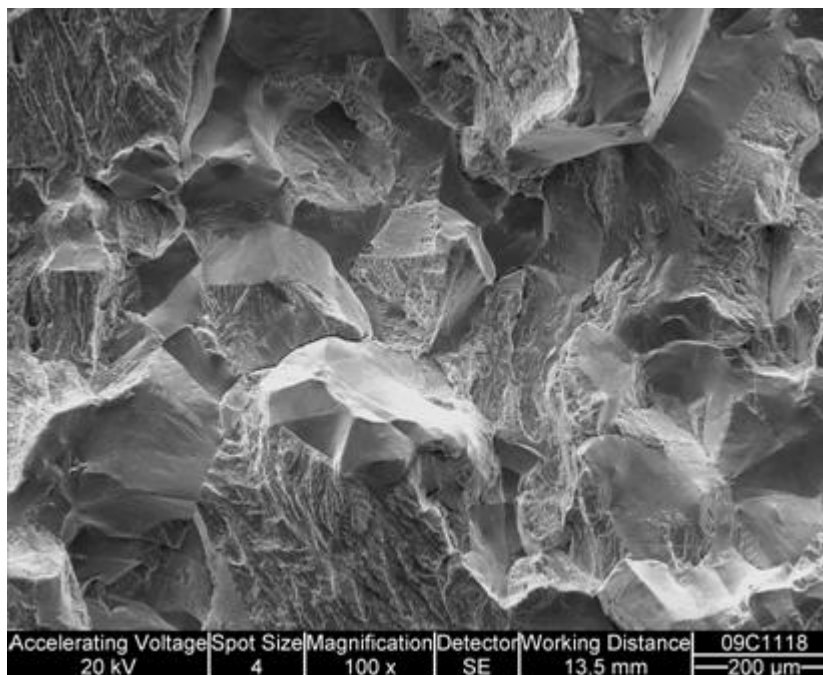


Figure 12. SEM-picture of the reddish area shown in Fig. 9 as "additional loading".

2.1 Test run 2 with 100 mg/l S²⁻

The second test run was performed with a slightly higher sulphide level in the beginning, i.e. S²⁻ = 130 mg/l, in order to compensate for the anticipated consumption of sulphide. Fig. 13 shows the pH and sulphide concentration as a

function of test duration. Loading to 4.5 kN was made on 20.10.2009 and test was terminated on 27.10.2009.

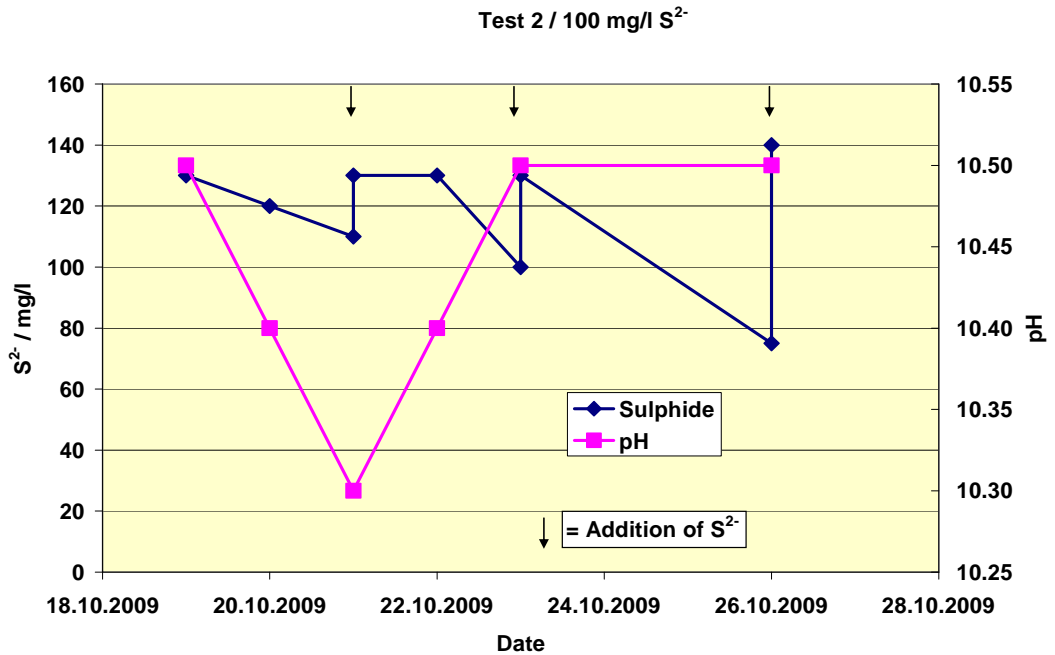


Figure 13. Sulphide concentration and pH as a function of test duration, Test run 2.

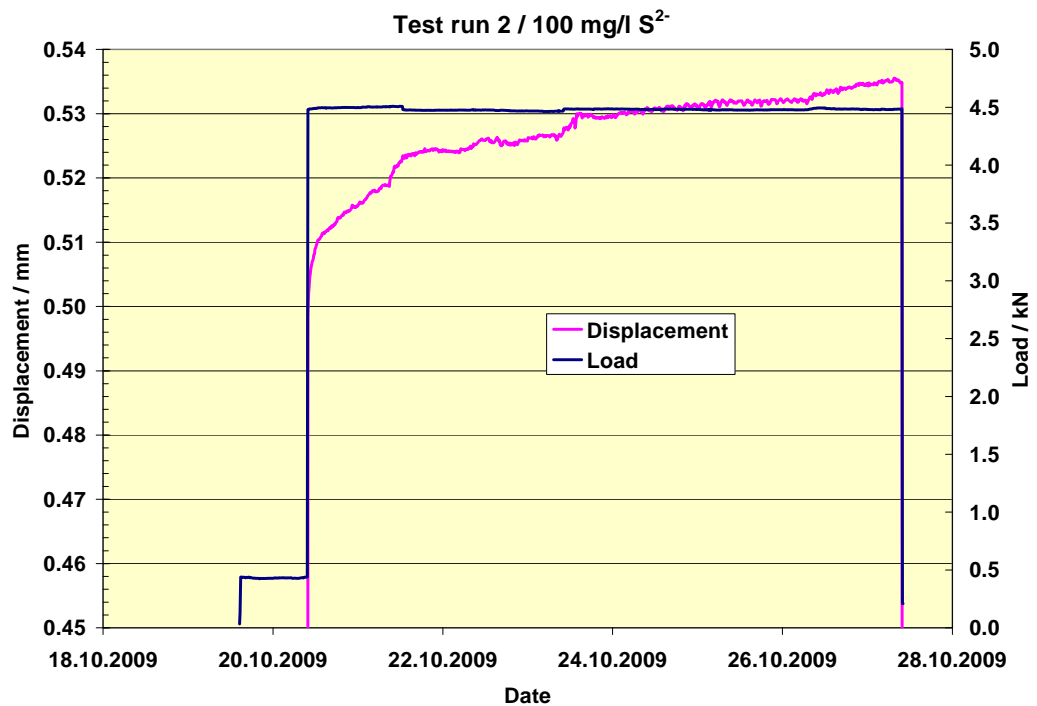


Figure 14. Load and displacement (crack opening) of the test piece as a function of time, Test run 2.

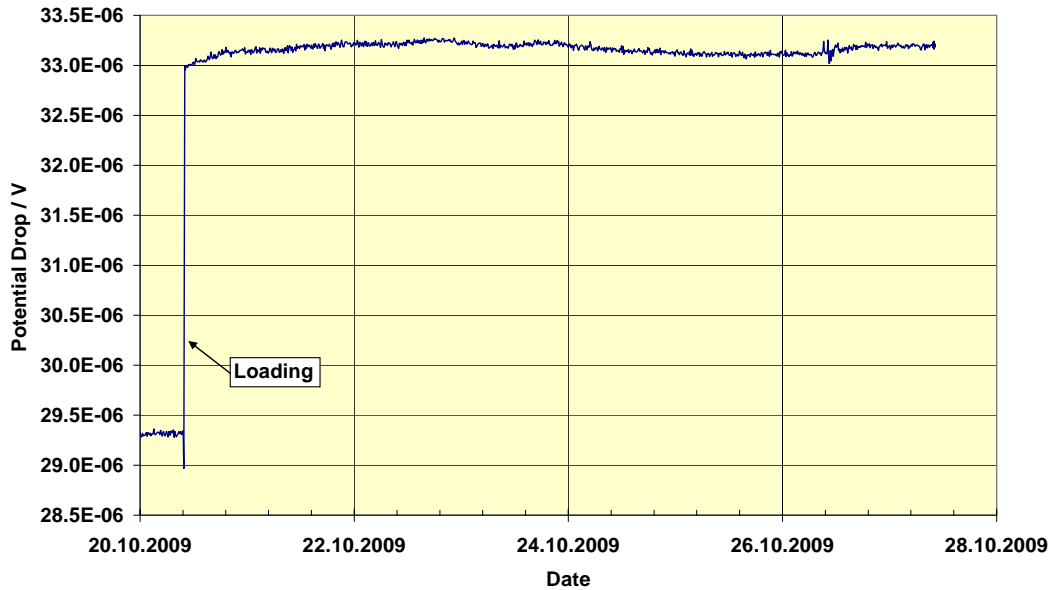


Figure 15. Potential Drop –signal of the test piece as a function of time, Test run 2.

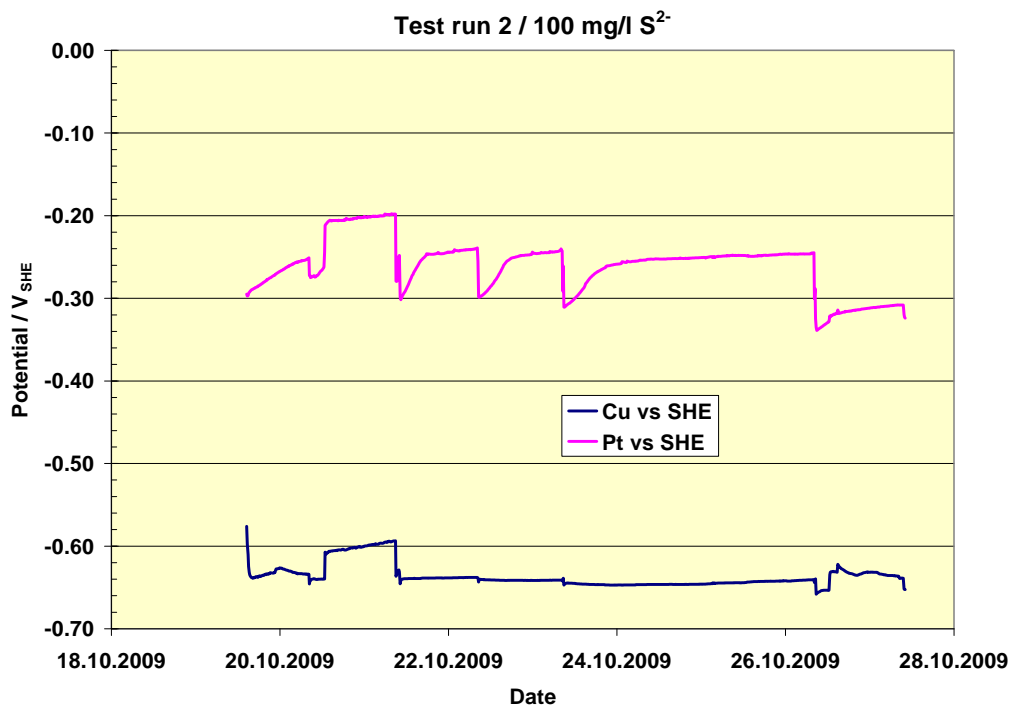


Figure 16. Potential of Cu-specimen and Pt-plate as a function of test duration, Test run 2.

The sulphide concentration was rather constant, resulting in an average level of 118 mg/l over the test period. The pH was also rather stable, averaging at about

pH = 10.4. The displacement continued to increase through the test period, Fig. 14, whereas the PD-signal was rather stable after the initial increase caused by loading and opening up the prefatigued crack, Fig. 15. The potentials of CuOFP and Pt were at the same levels as in Test run 1 and stable, Fig. 16, indicating that there were no air leakages during this test run.

The fracture surfaces are shown in Fig. 17, with red lines indicating the assumed crack extension during the test period and numbers from 1 to 3 indicating locations from which SEM-pictures were taken that are shown in Figs 18 to 20. In Fig. 18 (area 1 in Fig 17), occasional exposed grain boundaries can be seen in the prefatigue area (close to the machined notch) where rather high loads were used to initiate the prefatigue crack. Fig. 19 (area 2 in Fig 17) shows normal fatigue surface with striations and crack growth through the grains. Figs 20 and 21 (area 3 in Fig 17) show details (smooth plane-like surfaces of grains, 60-80% of the surface area) typical of intergranular stress corrosion cracking (IGSCC) similarly to Figs 11 and 12 in case of Test run 1.

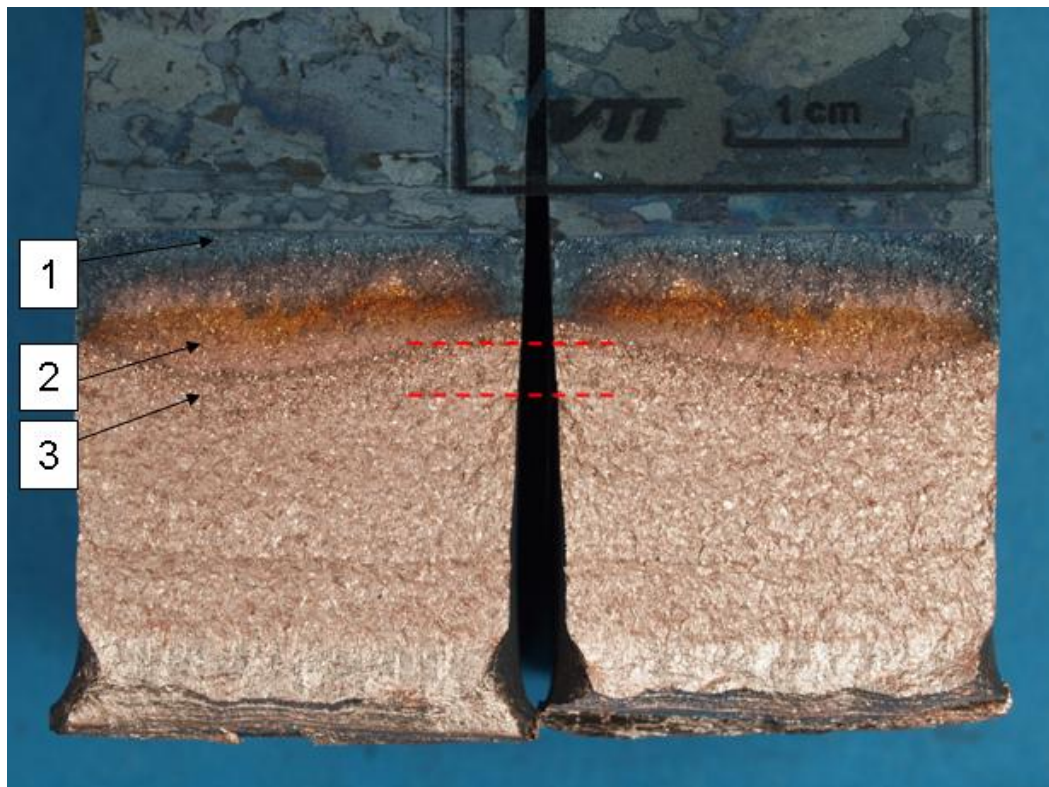


Figure 17. Digital image of the fracture surfaces, red lines marking the crack extension during exposure. Number 1 refers to the prefatigue area next to the machined notch, number 2 to the prefatigue central area and 3 to the presumed SCC crack extension area.

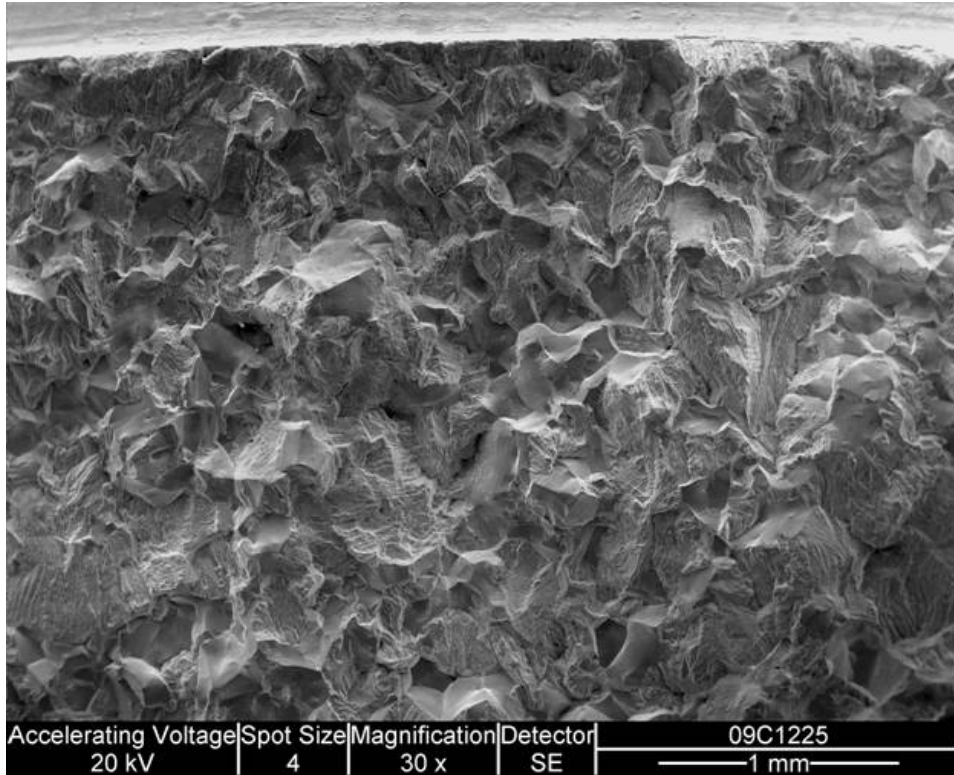


Figure 18. SEM-picture of the prefatigue area immediately after the machined starter notch.

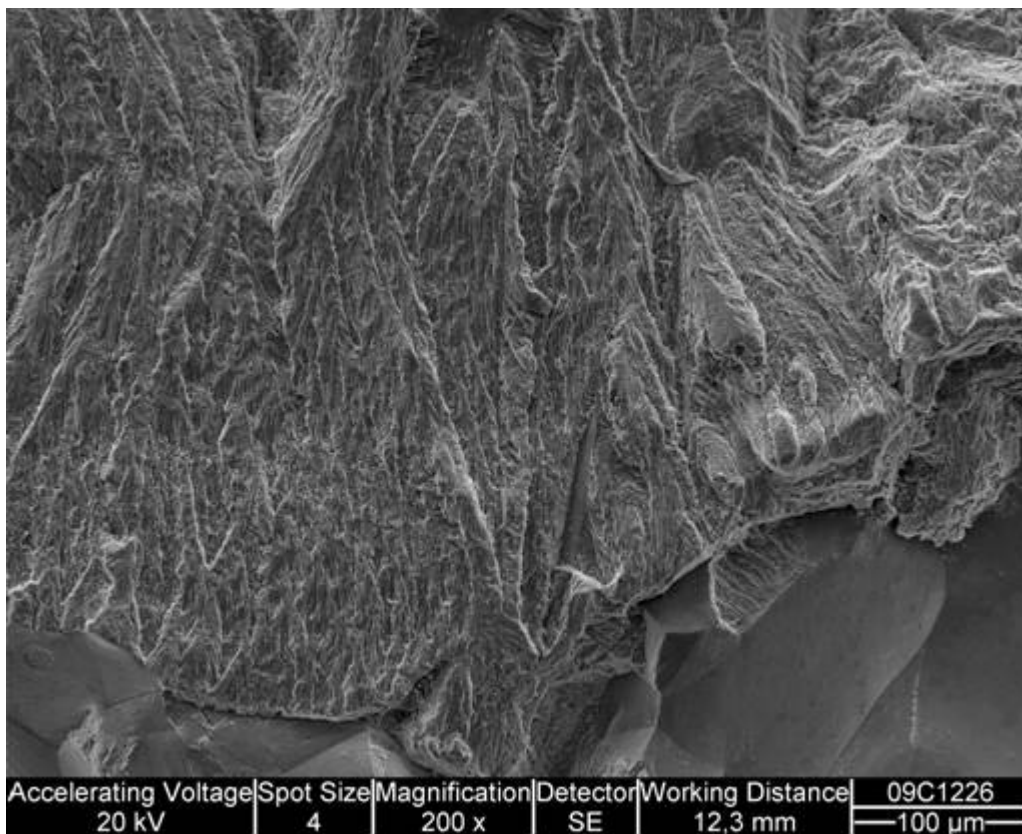


Figure 19. SEM-picture of the prefatigue area.

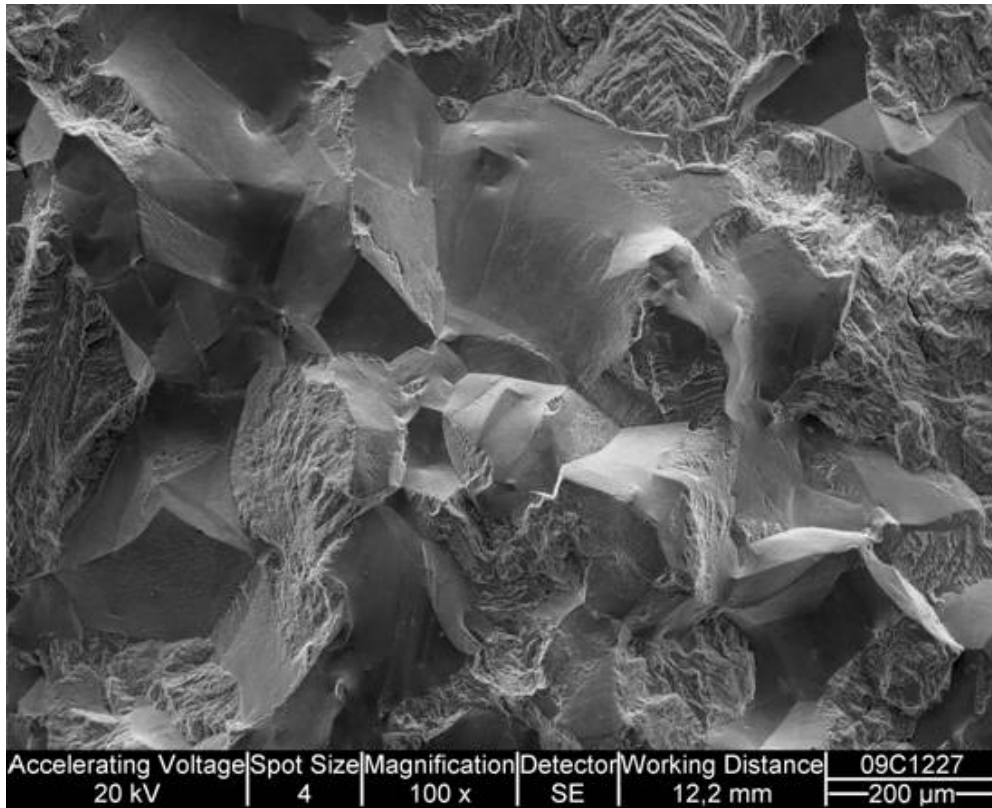


Figure 20. SEM-picture of the area after the pre-fatigue area, x100.

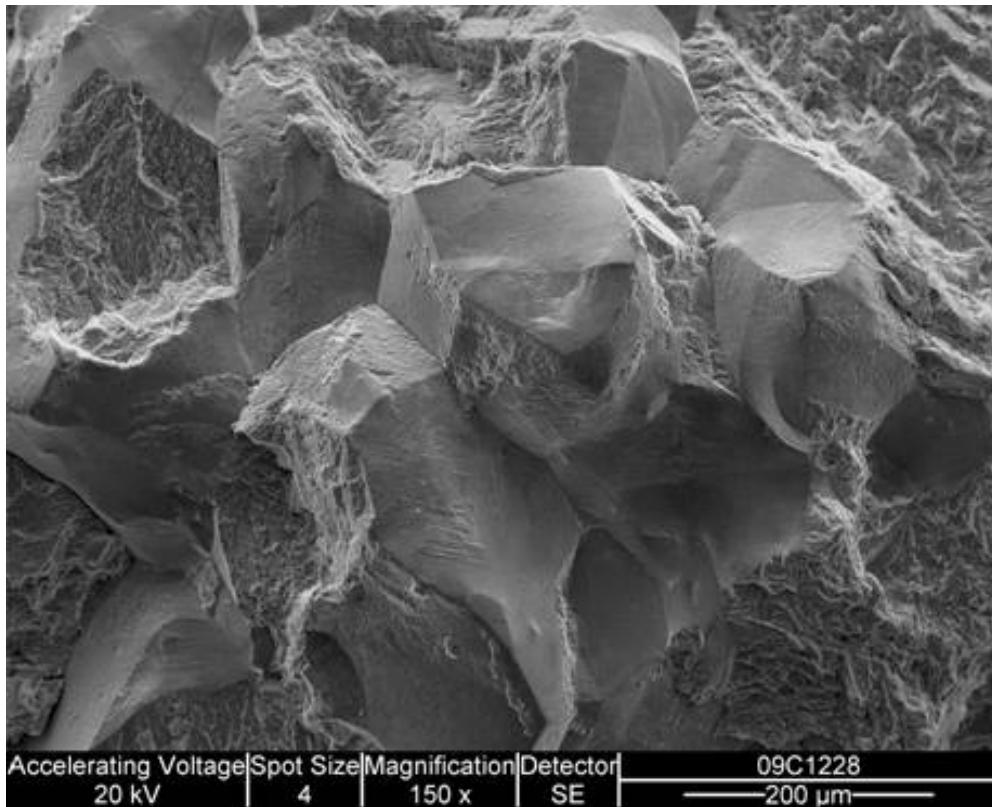


Figure 21. SEM-picture of the area after the pre-fatigue area, x150.

2.2 Test run 3 with 100 mg/l S²⁻

The third test run was performed as Test run 2 (with a slightly higher sulphide level in the beginning, i.e. S²⁻ = 130 mg/l) and with target pH of 8 < pH < 9, using sulphuric acid for pH reduction. The CuOFP –specimen was covered with lacquer (except for the precrack area) in order to limit the consumption of sulphide during the test. Loading to 4.5 kN was made on 18.11.2009 and test was terminated on 24.11.2009.

Fig. 22 shows the pH and sulphide concentration as a function of test duration. Attempts to keep the pH between 8 < pH < 9 were rather unsatisfactory, as at every check-up the pH was found to have risen to slightly above 10. At the end of the test when the test solution was extracted from the pressure vessel and let to settle in a glass bottle, a layer of solid particles (sediment) was found to form at the bottom of the vessel. The analysis of this sediment showed it was a mixture of CaCl and NaCl, see Fig. 23. It seems that there is a chemical reaction taking place in the solution which tends to keep the pH at about pH = 10.3.

The displacement continued to increase through the test period, Fig. 24, whereas the PD-signal was rather stable (as in Test run 2) after the initial increase caused by loading and opening up the pre-fatigue crack, Fig. 25. The potential of Pt was about 0.05 V higher than in the previous test runs, and that of CuOFP was about 0.2 V higher. Assuming that the pH on average was about 1.5 units lower than in the previous tests, the potentials should be about 0.05 to 0.08 higher, because of the pH –dependence of the equilibrium reactions, see Figs. 4 and 5. It is possible that the precipitation of (Na,Ca)Cl influences also the potentials.

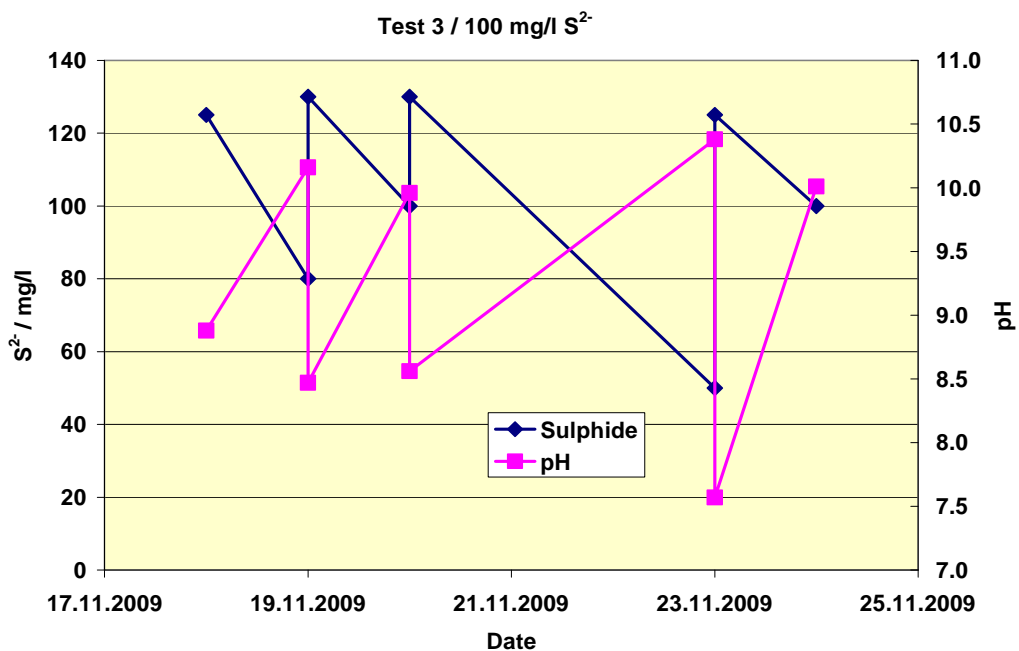


Figure 22. Sulphide concentration and pH as a function of test duration, Test run 3.

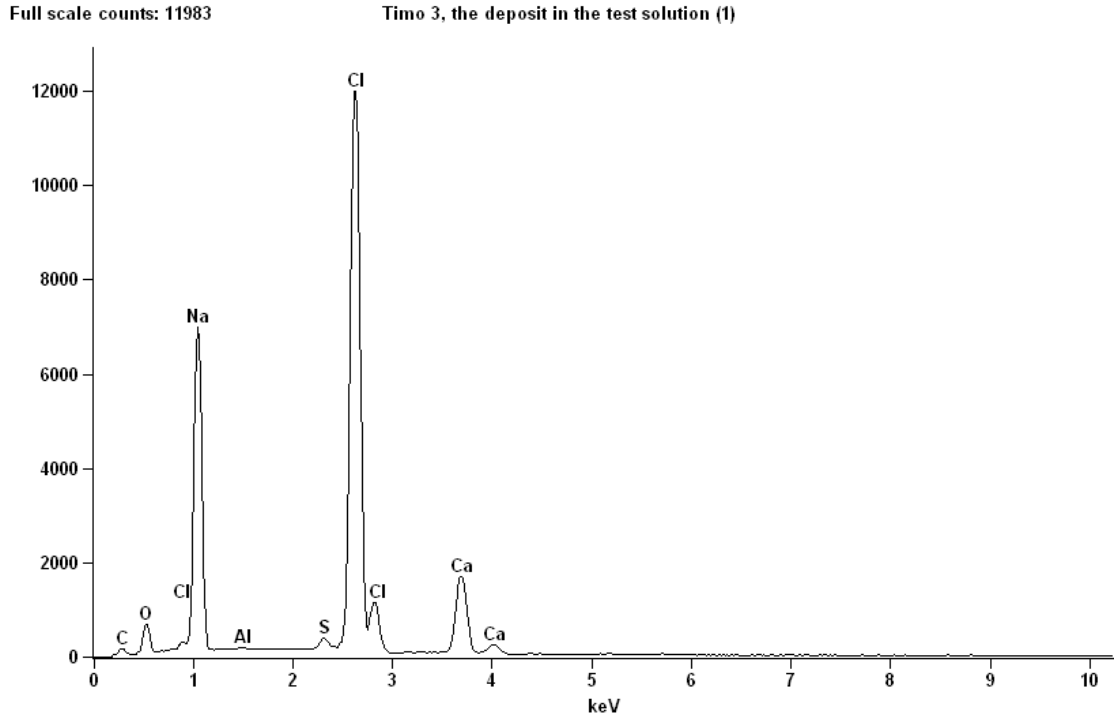


Figure 23. EDX-analysis of the sediment found after Test run 3.

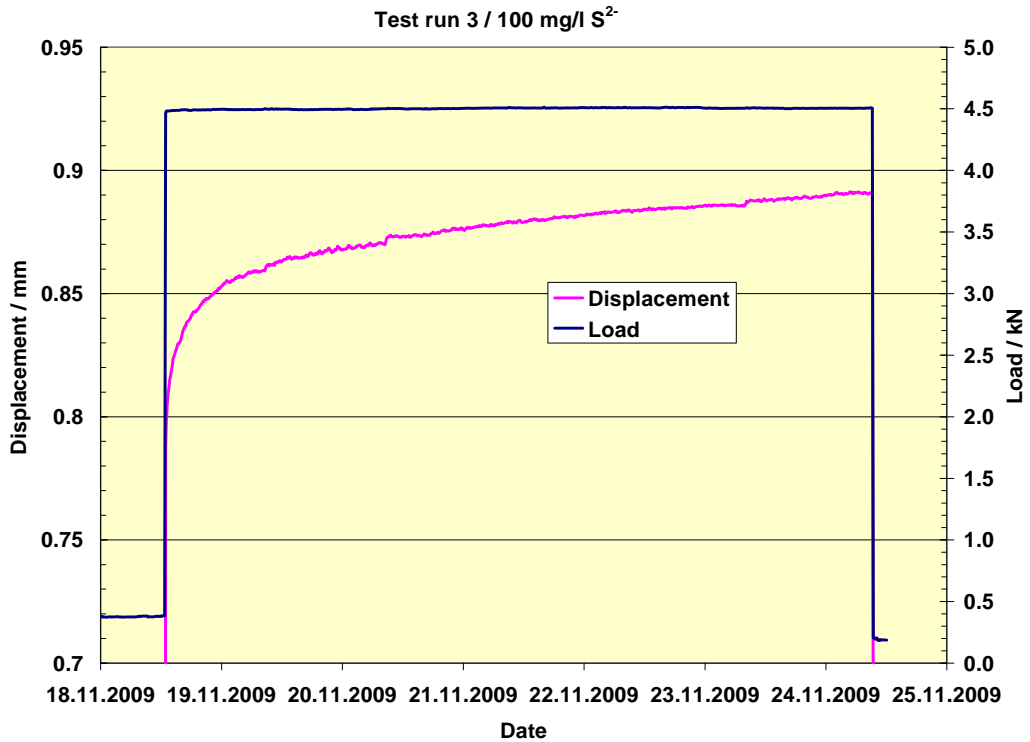


Figure 24. Load and displacement (crack opening) of the test piece as a function of time, Test run 3.

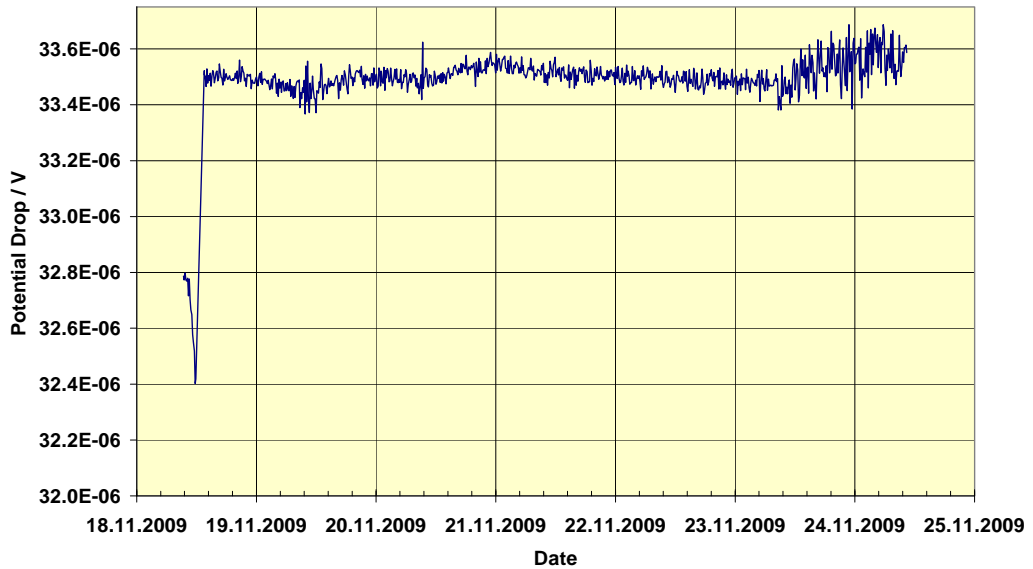


Figure 25. Potential Drop –signal of the test piece as a function of time, Test run 3.

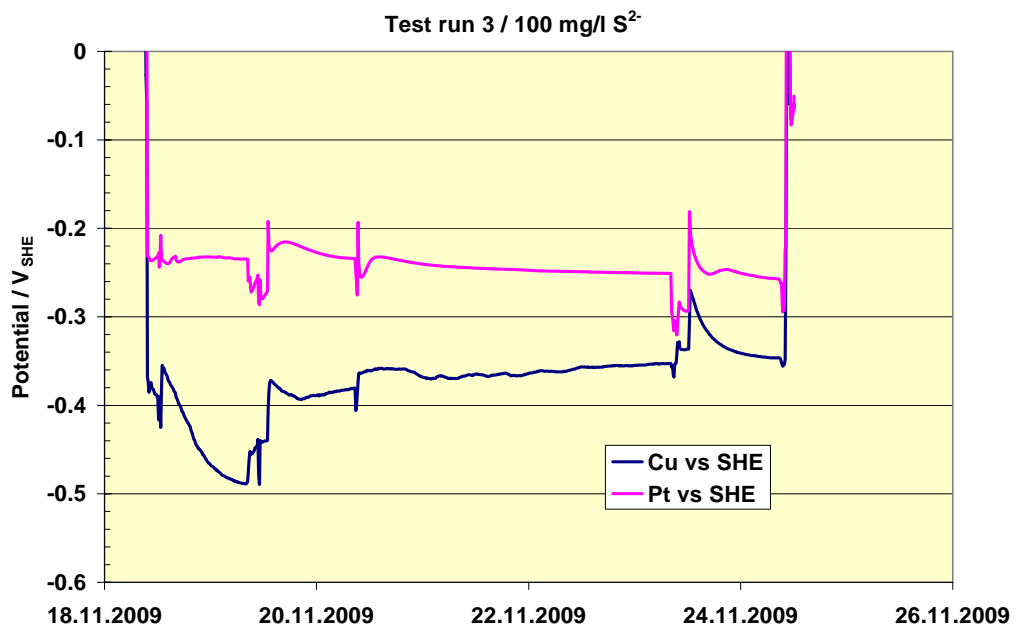


Figure 26. Potential of Cu-specimen and Pt-plate as a function of test duration, Test run 3.

The fracture surface showed a presumed SCC crack extension of about 2 mm, Figs. 27 and 28. SEM –examination revealed that the prefatigue area contained a substantial amount of exposed grain boundaries, Figs. 29 and 30. Moreover, the appearance of the presumed SCC area had roughly a similar amount of exposed grain boundaries as the prefatigue area. This is very odd, and makes it more difficult to draw conclusions on the SCC susceptibility of CuOFP, based on the SEM –investigation.

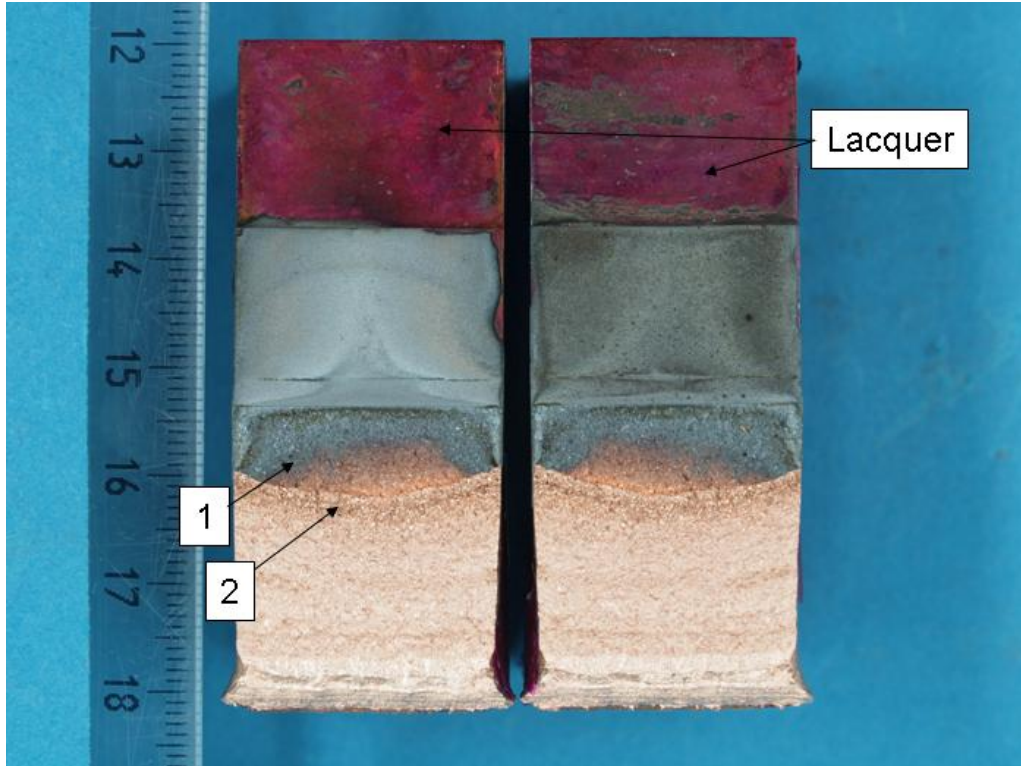


Figure 27. Digital image of the fracture surfaces. Number 1 refers to the prefatigue area and 2 to the presumed crack extension area.

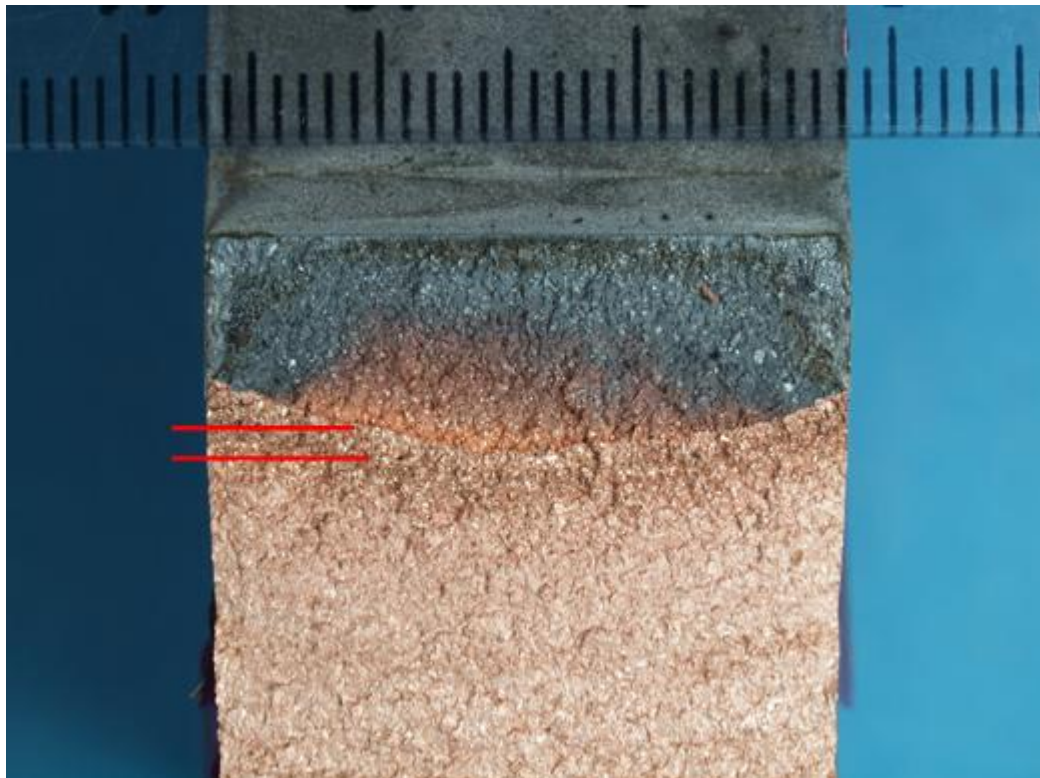


Figure 28. Digital image of the fracture surface. The red lines indicate the presumed crack extension length.

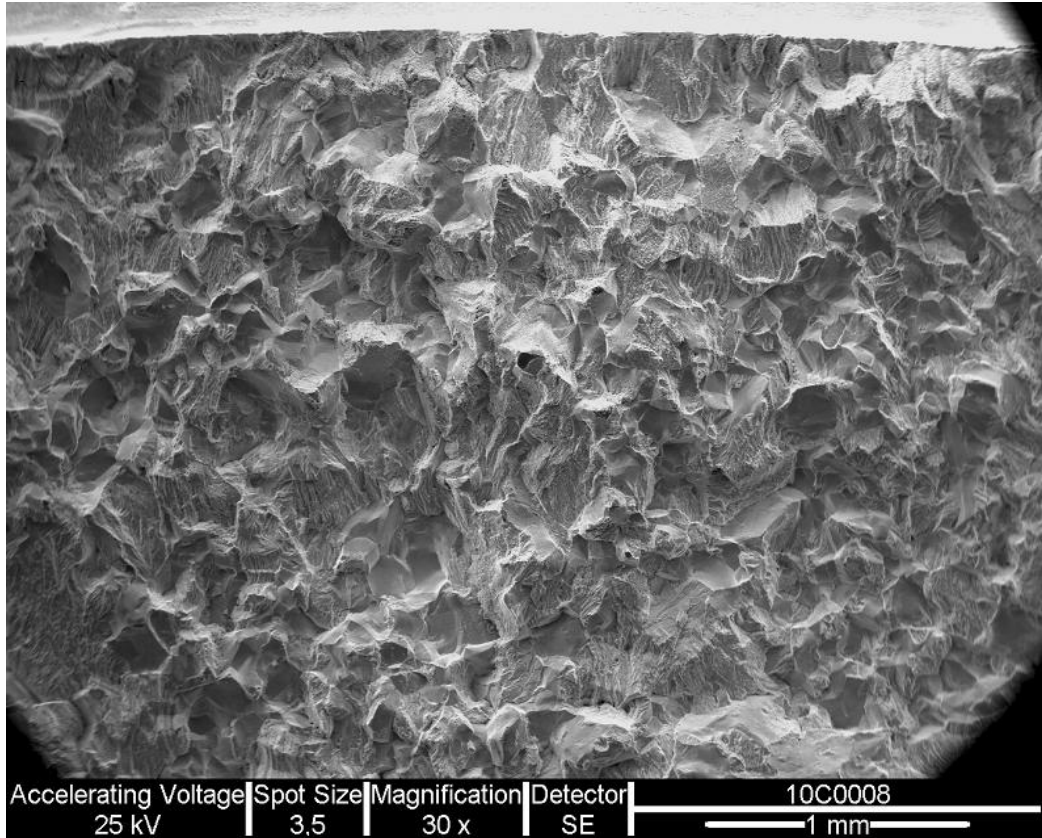


Figure 29. SEM-picture of the prefatigue area immediately after the machined starter notch (x30).

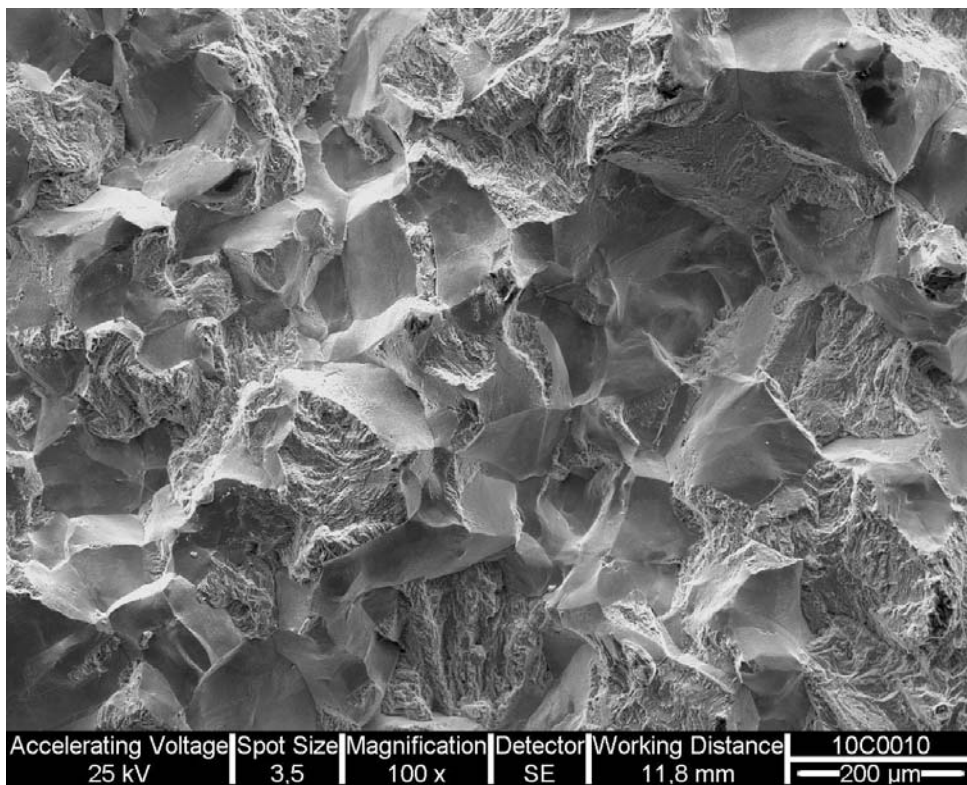


Figure 30. SEM-picture of the prefatigue area, roughly at the spot where the number 1 arrow is pointing in Fig. 28 (x100).

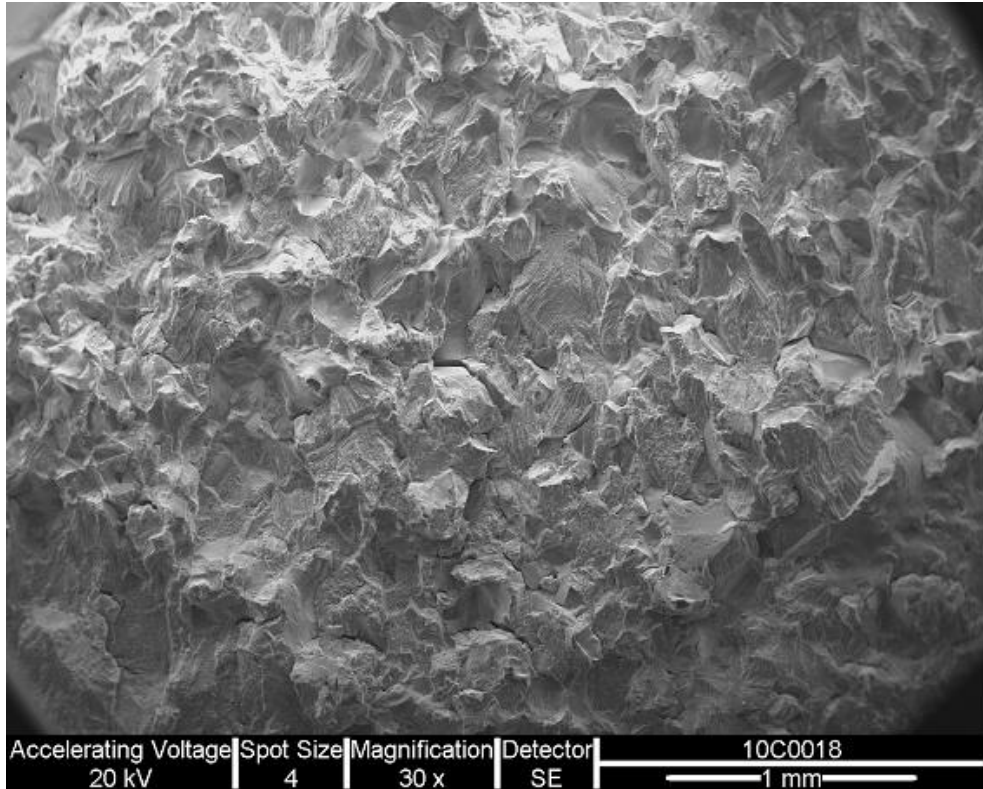


Figure 31. SEM-picture of the presumed SCC area, roughly at the spot where the number 2 arrow is pointing in Fig. 28 (x30).

A sulphide concentration of $[S^{2-}] \approx 100$ mg/l added in Olkiluoto –type groundwater causes SCC in CuOFP base metal.

Task 3. Evaluation of the maximum sulphide concentration at the bentonite/rock interface

In this task an estimate of the maximum sulphide concentration at the bentonite/rock interface and of the maximum physical dimension (size) of the bacterial colony is made based on literature and other experience. The literature survey is ready (VTT Research Report VTT-R-09242-09, “Sulphide induced stress corrosion cracking of copper – the effect of SRB activity”), and *based on it the maximum sulphide concentration at the bentonite/rock interface due to bacterial activity may be 400 – 450 mg/l.*

Task 4. Development of a sulphide diffusion in bentonite –model

In this task a diffusion model has been developed for transport of sulphide through the bentonite to copper canister surface. The model was developed with COMSOL Multiphysics –software. The model has been described in a scientific publication [3/ and in a VTT Research Report VTT-R-00662-10, (“Diffusion model for sulphide in compacted bentonite”). The model can be used to estimate the sulphide concentration at the canister surface resulting from the earlier

mentioned (Introduction) three scenarios. The model has bentonite density as a parameter, so that it can be used to estimate e.g. the effect of bentonite erosion on sulphide diffusion rate. *Further development of the model will be made in 2010.*

4 Summary and conclusions

The experimental arrangement for studying sulphide induced stress corrosion cracking of CuOFP in simulated groundwater has been developed and tested. Three experiments with a target average sulphide concentration of $[S^{2-}] = 100$ mg/l has been made and revealed that CuOFP is susceptible to SCC under this concentration of sulphide. The verification of the SCC by SEM investigation was complicated by the appearance of exposed grain boundaries not only in the presumed SCC area but also in the pre-fatigue area. This finding will be examined in more detail during 2010.

A literature survey of the maximum sulphide concentration that may form at the bentonite/rock interface due to bacterial activity shows that the maximum sulphide concentration at the bentonite/rock interface due to bacterial activity may be 400 – 450 mg/l.

First version of a diffusion model for transport of sulphide through the bentonite to copper canister surface has been developed and it has been communicated in the form of a scientific publication and as a VTT Research Report.

References

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