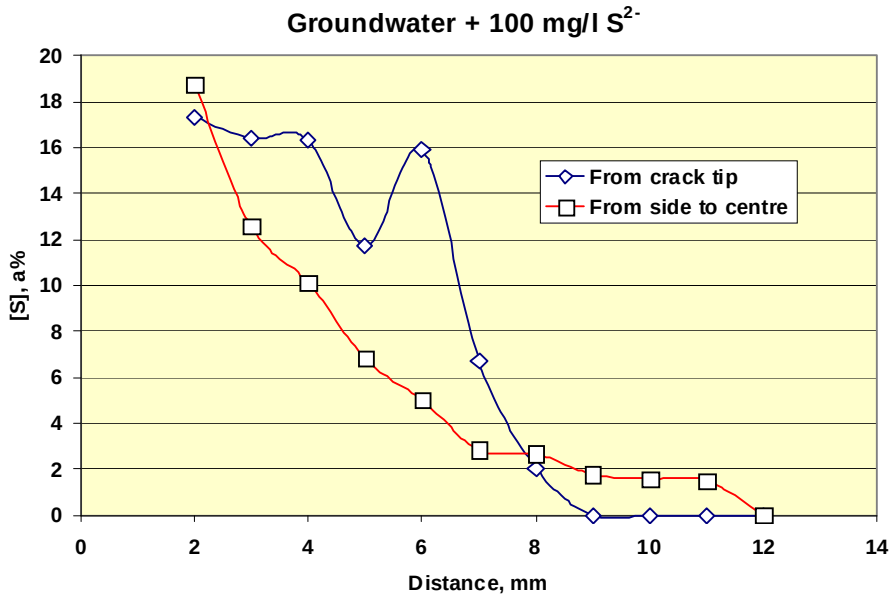

Sulphide induced stress corrosion cracking of copper – Final Report

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Confidentiality: Public

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Summary

Precracked CT-specimens of CuOFP have been exposed to groundwater with 200 mg/l, 100 mg/l and 10 mg/l sulphide. SEM/EDS studies of the fracture surface showed that during the exposure sulphur/sulphide had entered the material ahead of the precrack tip, with penetration rate of more than 1 mm per week. Optical metallography of sliced and polished cuts of exposed samples showed that sulphide inclusions could be found in all three dimensions of the material and not only in the crack plane, although the area fraction of the inclusions was normally the highest close to the crack plane. The surface fraction of inclusions did not vary strongly depending on the sulphide concentration. The occurrence of SCC in CuOFP when exposed to sulphide containing groundwater at room temperature could not be unequivocally shown.

The maximum sulphide concentration that may form at the bentonite/rock interface due to bacterial activity may be 400 – 450 mg/l at near neutral pH. At higher pH –values the maximum concentration may be much higher.

Transport of hydrogen sulphide in compacted bentonite in conditions of variable dry density was modelled by molecular diffusion and advection. Maximum sulphide flux values onto the copper canister surface were observed in advection cases where the concentration at source (rock/bentonite –interface) was set to 450 mg/l. In these cases the maximum flux was almost 200 000 $mgm^{-2} \cdot a^{-1}$.

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Preface

This report gives an overview on the results gained in the KYT2010 –research program project “Sulphide induced stress corrosion cracking of copper” executed between 1.1.2009 and 31.1.2011.

Espoo 25.1.2011

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 Japanese research group 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 (e.g. 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 were to evaluate the sulphide induced SCC risk of copper canisters under repository conditions. Technical targets were:

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

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

The experimental arrangement was designed, built and tested. The system consists of a pressure vessel made of austenitic stainless steel, the surfaces of which were passivated in high temperature water to produce a protective magnetite-type spinel-oxide layer on the surfaces. An Ag/AgCl/0.01MKCl -reference electrode with a stainless steel housing was used. The electrode sealing to the pressure vessel body was made by a Grafoil –box seal. The mechanical load was produced by a servohydraulic system, the pullrod of which was sealed to the pressure vessel body by flexible silicon. In preliminary tests the system was found to be air tight.

Despite of the air tightness, reactions of the sulphide containing groundwater with the pressure vessel walls and internal components of the loading arrangement were found to consume sulphide at a low but marked rate. As this was considered to possibly complicate the maintaining of the sulphide level in the groundwater during the exposure tests, the walls and internal components were covered with a lacquer.

The research method used wais 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 CuOFP material was provided by Posiva Ltd. The properties of the material (as given by Posiva Ltd) are shown in Table 1.

The base electrolyte used was the saline groundwater corresponding to Olkiluoto groundwater, see Table 2. The sulphide was added as Na_2S. The addition has to be made without oxygen contamination, and thus a local shield gas arrangement was developed based on a transformable Glow Box –system. The electrolyte also has to be transferred to the (oxygen free) pressure vessel without oxygen contamination. To enable this, a transfer system based on the use of nitrogen gas was developed.

The experimental system was ready and tested by June 2009.

***Table 1**. Properties of the CuOFP material studied (ref: Tube T62 top).*

Yield stress, MPa (0.2%).	39, 43, 50
Tensile stress, MPa	206-208
Tensile strain (A50)	51-54%
Hardness (HV5)	38-41
Grain size (μm)	120-150

Table 2. 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	

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

Detailed results from the experiments have been reported in the following intermediate reports:

1. Sulphide induced stress corrosion cracking of copper – Intermediate Report 1 (VTT-R- 07999-09), 30.10.2009 /3/
2. Sulphide induced stress corrosion cracking of copper – Intermediate Report 2 (VTT-R-00652-10), 22.1.2010 /4/ and
3. Sulphide induced stress corrosion cracking of copper – Intermediate Report 3 (VTT-R-10541-10), 14.1.2011 /5/.

In this task, three different levels of sulphide were used, 10 mg/l, 100 mg/l and 200 mg/l. The test matrix is shown in Table 3.

***Table 3**. Test matrix with time periods of individual test runs.*

Test Nr	Period	[S^{2-}], mg/l	Remarks	Covered in report Nr
1	7.9-1.10.2009	100		1 and 2
2	20-27.10.2009	100	Trials with pH-control	2
3	18-24.11.2009	100	Trials with pH-control	2
4	10.2-1.3.2010	10		3
5	29.4-16.6.2010	200		3
6	4-18.3.2010	0	Air/N_2 - environment	3
7&8	25.9-4.11.2010	200	Two specimens in one run	3

The main results from the experimental work were the following:

- The occurrence of SCC in CuOFP when exposed to sulphide containing groundwater at room temperature could not be unequivocally shown.
- The fatigue crack growth, which was used to form a pre-crack simulating e.g. a weld defect, was found to preferentially advance along grain boundaries.
- In some of the test runs, the electrical resistance of the specimens during the exposure time (as monitored by the Potential Drop –technique) was found to increase continuously, see. Fig. 1. The increase was, however, rather limited and could not be used as a convincing evidence for crack advancement during the exposure.
- Post-test optical microscopy of the fracture surfaces revealed a number of black spots up to several millimetres ahead of the crack tip, i.e. in the part of the specimen which had never been in direct contact with the environment.
- SEM/EDS studies of the fracture surface showed that in several areas sulphur concentration was up to 20at%. The sulphur concentration on the fracture surface was found to decrease as the distance from the crack tip increased and as the distance from the external side of the specimen increased. Fig. 2 shows results for specimen Nr 1 exposed to groundwater with [S^{2-}] = 100 mg/l.
- Optical microscopy of polished surfaces representing different sections of the exposed CuOFP specimens revealed a distribution of inclusions in the size range from 1 μm (resolution limit) to 70 μm. The unexposed reference sample showed no inclusions with the resolution limit used, see Fig. 3.
- In the optical microscopy of polished surfaces the surface fraction of the inclusions varied between 0 and $1.89*10^{-3}$ for the specimen Nr 1 exposed to groundwater with [S^{2-}] = 100 mg/l, and between 0.9 and $1.12*10^{-3}$ for the specimen Nr 4 exposed to groundwater with [S^{2-}] = 10 mg/l. A preference of higher area fractions closer to the fracture surface (crack plane) could be noticed (Fig. 4).
- The distance of the inclusions from the sulphide source, i.e. groundwater, indicated a diffusion rate of sulphide/sulphur in CuOFP of higher than 1 mm per week.

The main results were communicated in the form of a workshop presentation /6/ and a scientific publication /7/.

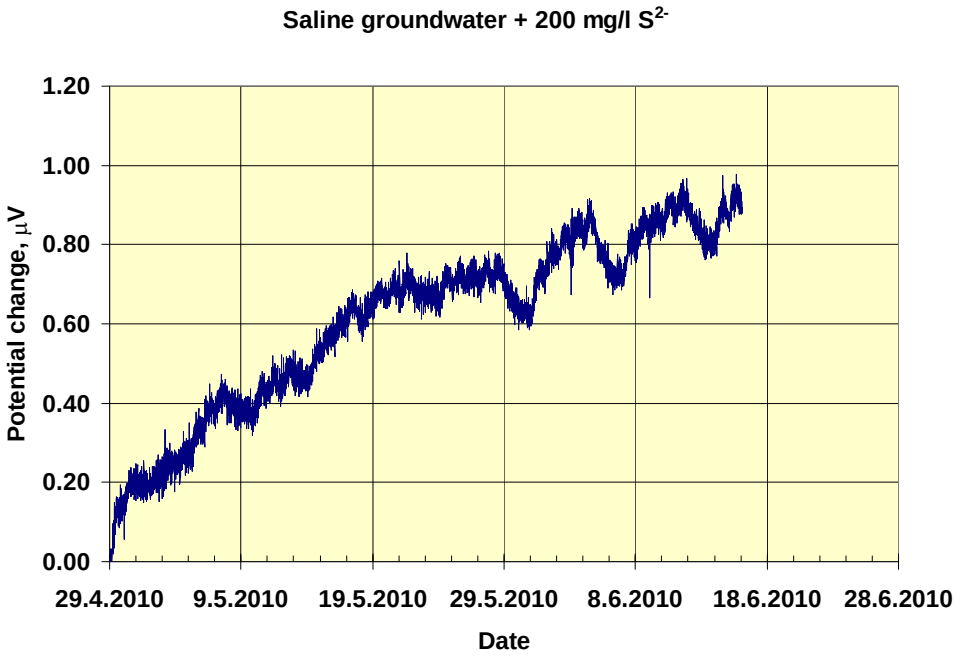

Figure 1. Potential Drop –signal of specimen Nr 5 as a function of time, [S^{2-}] = 200 mg/l.

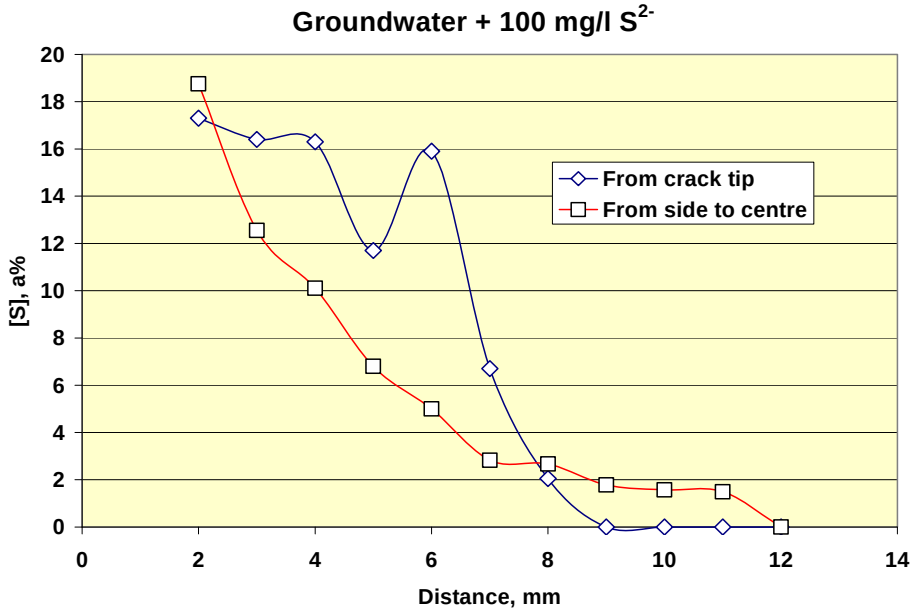

Figure 2. Sulphur concentration (at%) on the fracture surface of specimen Nr 1 (tested in groundwater with 100 mg/l S^{2-}) as found by SEM/EDS -analysis.

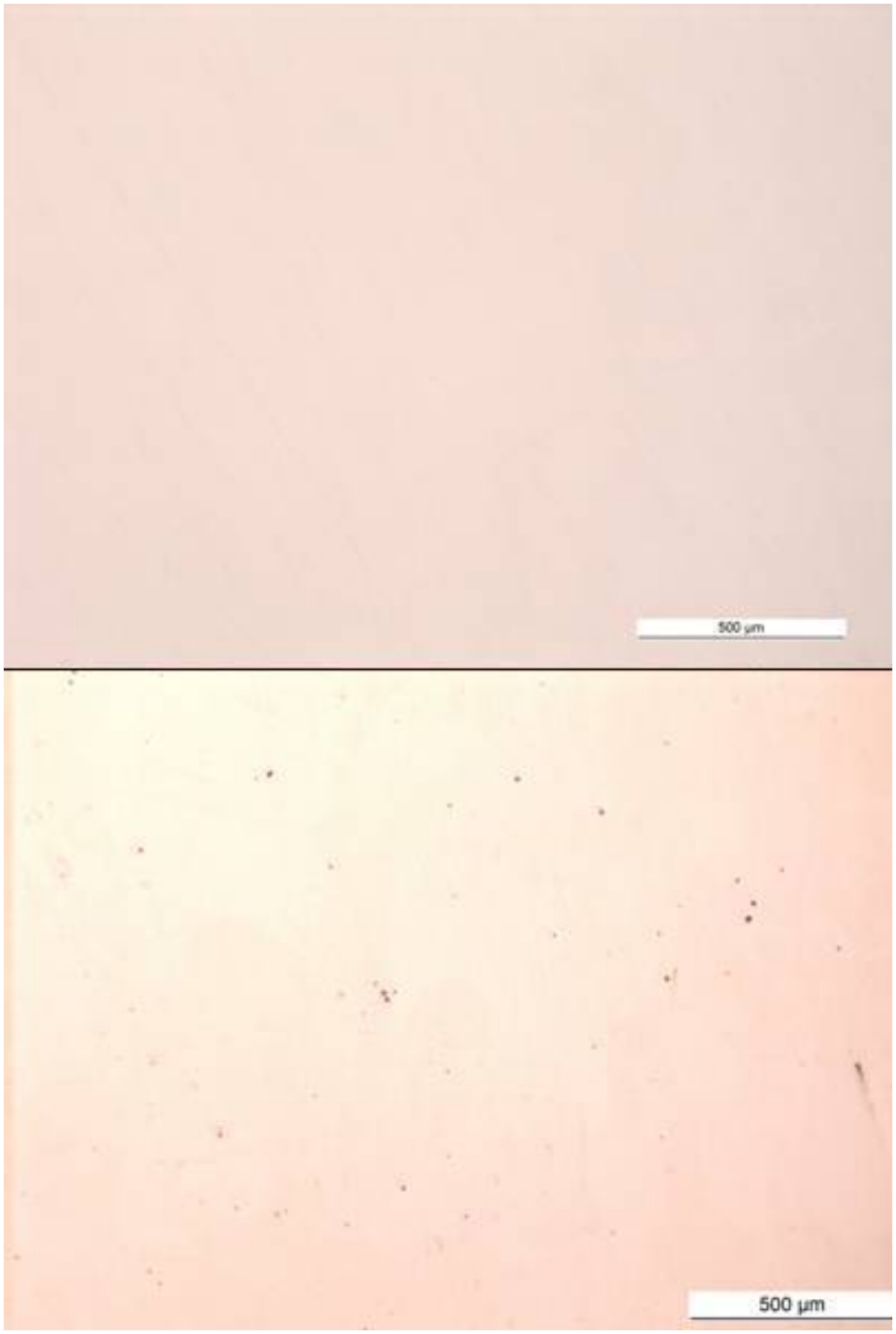

Figure 3. Comparison of polished surface of unexposed CuOFP (upper picture) and that of specimen Nr 4 exposed to groundwater with [S^{2-}] = 10 mg/l (lower picture).

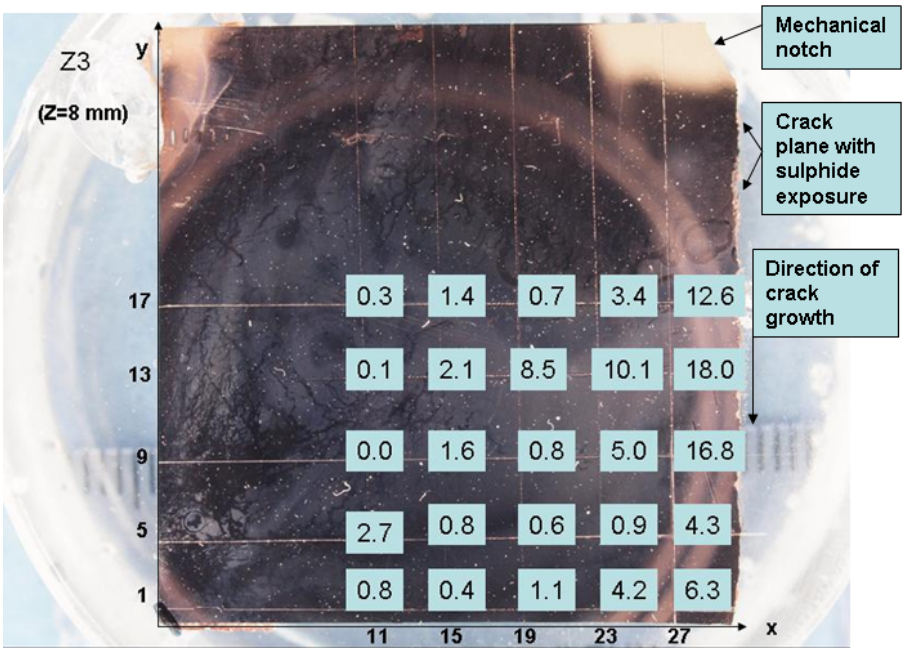

Figure 4. Area fractions of inclusions (x10^4) in slice Z3 (8 mm from outer surface) as a function of location.

Based on the results from this task it can be concluded that sulphide is able to enter CuOFP from sulphide containing groundwater at room temperature, presumably by grain boundary diffusion. The rate of in-diffusion is very high as indicated by the presence of inclusions in the CuOFP material several millimetres away from the sulphide source (groundwater) after less than four weeks of exposure.

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

Based on the performed literature survey the maximum sulphide concentration that may form at the bentonite/rock interface due to bacterial activity may be 400 – 450 mg/l at near neutral pH. At higher pH –values the maximum concentration may be much higher. The literature study has been published as a VTT Research Report /8/.

3.4 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. All model calculations were performed by COMSOL Multiphysics and Chemical Engineering Module in a laptop of 4 GB of memory and running under 32 bit Windows 7. The model has

been described in a scientific publication /9/ and in detail in a VTT Research Report /10/. The model can be used to estimate the sulphide concentration at the canister surface resulting from different 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.

An example of the outcome of the diffusion model calculations is shown in Fig. 5a and 5b. These results are for a scenario where sulphide is produced by bacterial activity in bentonite buffer itself: Concentration is low, the source, which may be quite near the copper canister surface (< 5 cm), is of limited size (below 1 mm). Sulphide concentration decreases rapidly with increasing distance from source, diffusion flux is high only on a very small surface area on copper canister and diffusion flux increases ten times higher in low density than in high density buffer. In this case the concentration at source was set to 1 mg/l.

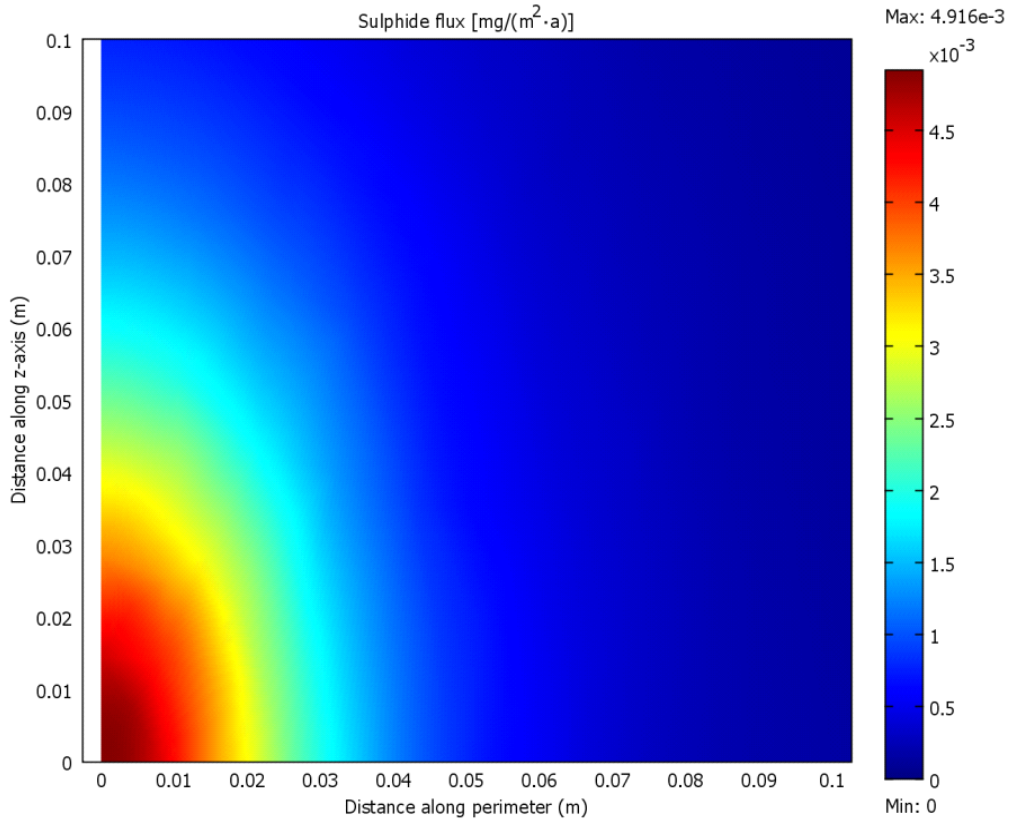

Figure 5a. Concentration isosurfaces (0.1, 0.01, 0.001 and 0.0001 mg/l on the source) and diffusion flux onto copper canister ($g/m^2/a$). Even 1/100 of the source concentration is observed only very near the source and flux onto copper canister decreases rapidly as the distance from source increases. Density of bentonite is 400 kg/m^3.

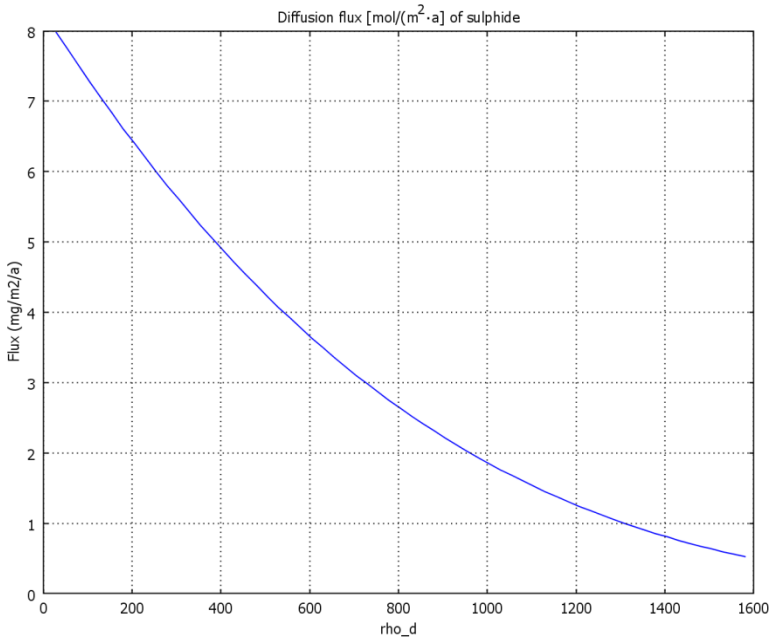

Figure 5b. Diffusion flux density in a corner (-0.525 m, 0.001 m, -0.001 m) nearest to source at surface of copper canister ($mg/m^2/a$) as a function of bentonite dry density (kg/m^3).

Maximum sulphide flux values onto the copper canister surface were observed in advection cases where the maximum flux was almost 200 000 $mgm^{-2}{\cdot}a^{-1}$.

Within this task the reaction rate constant for reaction of copper with sulphide in groundwater was determined experimentally. The reaction rate constant *k* was found to be

$$k = 2.3*10^{-7}\ gcm^{-2}s^{-1} = 7.3*10^{7}\ mgm^{-2}a^{-1}$$

The reaction was found to be zero-order with regard to sulphide concentration, i.e. the reaction rate does not depend on the sulphide concentration (at least within the concentration range in this test, i.e. 2 mg/l to 0.5 mg/l). The reaction product layer forming on the copper sheets, i.e. Cu_2S, seems not to be protecting as it does not have the ability to slow down the reaction rate.

The reaction rate constant is roughly two orders of magnitude higher than the maximum flux estimated to arrive at the copper canister surface /10/. Thus, even for the worst case scenario the diffusion rate of sulphide to the canister surface would always be expected to be rate limiting with respect to this reaction.

4 Summary and conclusions

Precracked CT-specimens of CuOFP have been exposed to groundwater with 200 mg/l, 100 mg/l and 10 mg/l sulphide. SEM/EDS studies of the fracture surface showed that during the exposure sulphur/sulphide had entered the material ahead of the precrack tip, with penetration rate of more than 1 mm per week. Optical metallography of sliced and polished cuts of exposed samples showed that sulphide inclusions could be found in all three dimensions of the material and not

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