Comments to the quality assurance review draft report of the SKB´s LOT experiment (SSM2020-5740-39, SSM reg nr, 2020-3872, ärende nr SSM2020-5740)

The quality assurance (QA) report was performed by T.W. Hicks and T.D. Baldwin at the consultant company Galson Science Ltd and J.R. Scully at the University of Virginia.

The SSM assignment

Unfortunately, it was not included in the assignment from SSM to identify the missing parts in the study that are of scientific importance for the evaluation of the SKB´s LOT-experiment. These topics and tasks should be identified and highlighted as mandatory issues for SKB to perform and implement before the LOT-study could finally be accepted. Only a QA-report is unfortunately not good enough in this case.

Important missing issues in the LOT-report

We have already made comments concerning the missing issues in the LOT-report, which was submitted to SSM 2020-11-23, see Appendix 1. There we highlighted some omitted metallographic studies which could be done with a workload corresponding to one week or so. Additionally, the question of how fast oxygen gets depleted in the LOT-test site should also be evaluated, that could easily be performed retroactively on site within some few weeks. If SSM is interested in guiding and securing that the LOT-project will be of more scientific importance for the KBS-3-model, then these issues must be addressed to SKB.

The QA-report

Concerning the draft QA-report, the main conclusion seems to be that it is not possible to judge whether SKB's implications concerning copper corrosion is right or wrong. That conclusion is based on the information in the LOT-report and by additional information, mainly protocols from SKB-meetings.

If the consultants had considered deeper knowledge in ground water microbiology in general and facultative bacteria in particular, they should have been more critical. Especially concerning SKB´s explanation that remaining oxygen must have been the cause to the severe copper corrosion during the 20-year long exposure in groundwater at 500 meter depth. With today's knowledge about groundwater microbiology, it is clear that the LOT-exposures were exclusively anoxic from a corrosion point of view, as we have already pointed out in Appendix 1. With this knowledge it would have been quite easy to understand that the anoxic copper corrosion had been most problematic with respect to the KBS-3 model, especially since there were not much of sulphides present to explain the partially catastrophic copper corrosion rates.

The hydrogen problem

It should be stressed that the direct reaction between copper metal and water molecules in an anoxic environment enables the fast degradation processes of stress corrosion cracking (SCC) and hydrogen embrittlement. Gunnar Hultquist (KTH) has shown that when copper metal is surrounded by an anoxic environment it will be subjected to hydrogen uptake (hydrogen charging), see Appendix 2. However, there will not be any severe hydrogen charging in the

case with the central copper tube in the LOT-study since the inside of the copper tube contains oxygen (air) which act as an effective sink for the diffusing hydrogen through the tube wall.

Pitting corrosion

From the QA-report summary: "*However, observations of thicker corrosion products in pits and the lack of detailed analysis of surface anomalies versus pitting leaves open the possibility that copper pitting has occurred.*" The authors of the QA-report seem surprised that pitting corrosion has occurred on unalloyed copper exposed to anoxic groundwater. The sulphide content was obviously quite low in the LOT-site, but the chloride content was not low. The groundwater at 500 m depth contains more chlorides than the Baltic sea. In the complex chemistry of groundwater, it is not surprising that unalloyed copper is subjected to pitting corrosion. Especially when accepting the fact that copper does react with water molecules as well, albeit slow in pure water. However, in the aggressive groundwater it is thermodynamically expected that unalloyed copper forms oxides, hydroxides, carbonates, nitrates, sulphides and sulphates and combinations thereof. It is just a question of time before the onset of localized corrosion occurs, and 20 years is obviously more than enough to develop pitting corrosion as was also observed earlier, see Appendix 1.

From the QA-report summary: "*However, any copper corrosion by sulphide attack would far exceed the corrosion depths of penetration that have been estimated could occur by anoxic corrosion in pure water in saturated bentonite. Thus, corrosion by sulphide attack is of greater concern in safety assessments than any postulated corrosion in oxygen-free water.*" This is a wrong statement since groundwater with low sulphide content still contains other corrosive species including a high chloride content (see above) which obviously creates severe copper corrosion, especially when heated, which is unfortunately not included in the safety analysis.

Conclusions

SSM should make requests to SKB concerning minor complementary work (metallography and O_2-depletion measurements) instead of focusing on a QA-report. However, when accepting the scientific knowledge of microbial activity and fast oxygen consumption in the ground water, our earlier statement remains: *The LOT-study shows, under all circumstances, that the anoxic copper corrosion rate in Swedish groundwater is catastrophic with respect to the KBS-3 model and this conclusion can be made without further considering the radiation induced corrosion (radiolysis), stress corrosion cracking and hydrogen embrittlement.*

In more general terms, it is disturbing that SKB has not made any successful studies concerning copper corrosion in the Äspö hard rock laboratory. The copper corrosion has in all studies (LOT, Prototype and MiniCan) been 100-1000 times faster than anticipated by the KBS-3 model. The explanation by SKB has always been the same: oxygen must have been present in the exposures since the copper corrosion was too high. This "explanation" is not valid anymore since it is scientifically proven that the oxygen depletion takes place fast in the groundwater by microbial activity. The question now should be how SSM can approve the KBS-3 model without any relevant and successful copper corrosion studies in the submitted application?

The most important comments to the SKB LOT-report TR-20-14

There are two major problems with the SKB report TR-20-14 [1].

i) SKB has excluded scientific facts concerning microbial activity in the ground water and used flawed thermodynamics when they claim that the partially severe copper corrosion in the LOT-project can be explained by oxygen gas from the air.

ii) SKB has omitted to study the most corroded parts of the central copper tubes and the bottom plates.

i.   Consumption of dissolved O_2 in anoxic and anaerobic groundwater

All groundwater is anoxic, i.e. without dissolved oxygen gas and it always contains microbial activity that keeps the environment anaerobic. There are detailed studies performed in Äspö hard rock laboratory, for instance the REX-project [2] that shows that added or trapped oxygen is consumed within days by microbial activity or as soon as the studied system or experimental set-up is filled with natural ground water. A full-sized repository tunnel reaches an anoxic state within a few month [3]. Any added oxygen represents fast energy for the microbes in the groundwater, as explained by prof. K. Pedersen.

SKB filled the quite small LOT A3 and S3 test volumes directly with pressurized groundwater via titanium tubes. Therefore, it can be concluded that an anoxic state occurred instantly, especially when considering the 20-year time frame of the LOT-project. It is impossible that the injected natural groundwater via the titanium tubes could have contained dissolved oxygen as SKB implies on page 63. The statement on page 71 has as also no scientific support and is obviously wrong with today's knowledge: *"Estimates of the initially available volume of air in macroscopic gaps and porous materials in the test parcels, were consistent with the interpretation that entrapped O_2 is the main oxidant behind the corrosion."*

SKB uses the identified corrosion products as another evidence for oxic corrosion, from page 9: *"The EDS analysis indicated high levels of chlorine and the XRD showed good agreement with the diffraction pattern of $Cu_2(OH)_3Cl$, an expected corrosion product of copper in the presence of O_2 and chloride (Karnland et al. 2009)."* This is based on flawed thermodynamics since both copper oxides [4] and $Cu_2(OH)_3Cl$, paratacamite [5] are thermodynamically

stable in both anoxic and oxic environments and thus proves nothing in this case. In the potential-pH diagram in part II on page 35 in ref. [4] it is shown that both Cu_2O and CuO are stable in anoxic water. Paratacamite is for instance found naturally in anoxic groundwater/brine bearing sandstone and quarts [6].

To summarize, the detected corrosion in LOT A3 and S3 can only be explained with anoxic copper corrosion by natural groundwater.

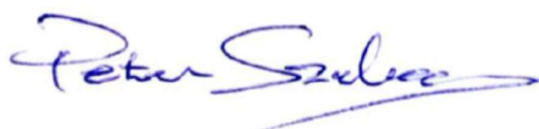### ii.   The most important metallographic evaluations are omitted

The hottest part of the central copper tubes, which are expected to corrode the most, corresponds to bentonite blocks 8-15, see Fig. 2-2 in the report. SKB has omitted to present any metallographic cross-section from the hottest part (block 8-15). Only the copper content in the bentonite, which is recalculated to some non-relevant and underestimated corrosion rates are included in the report, see Table 3-19. The highest corrosion rate from Table 3-19, only based on copper content in bentonite, corresponds to 13,8 µm during 20 years for the A3-parcel. However, this must be complemented with several metallographic-cross-sections of the central copper tube in the hot part (block 8-15). The pitting corrosion might be up to 100 µm as observed in a similar repository study with approximately the same exposure time, see the FEBEX-report [7].

The most corroded part of the copper structures are the bottom plates which were exposed directly to the anoxic groundwater. Based on the appearance of the bottom plate from parcel A3, see Figure 3-1 to the left and compare it with the bottom plate from the S3-parcel to the right, it can be estimated that the deepest pits may be in the range of 0.5-1 mm on the A3-parcel which were heated to around 80°C, see Fig. 1-3 to the right. It is of paramount importance to make several metallographic cross-sections of the bottom plates and measure the variation in total thickness. No cleaning of the corrosion products should be done since SKB argues in the report that the removal of the corrosion products might create up to 50-60 µm deep pits, see page 68. This is obviously a wrong statement if a correct cleaning process has been performed.

Considering the depth of the pits observed it should be remembered that the current LOT-experiments were performed without any radiation. In view of previous experience [8] one can expect that the extent of localized corrosion is accelerated further in the presence of γ-radiation. Hence, it is impossible to predict the actual corrosion effects in the LOT-experiments if γ-radiation would have been present.

Concluding remark

This LOT-study shows, under all circumstances, that the anoxic copper corrosion rate in Swedish groundwater is catastrophic with respect to the KBS-3 model and this conclusion can be made without further considering the radiation induced corrosion (radiolysis), stress corrosion cracking and hydrogen embrittlement.

Tekn. Dr. Peter Szakálos   Prof. em. Christofer Leygraf

References

[1] A. J. Johansson et al.,"Corrosion of copper after 20 years exposure in the bentonite field tests LOT S2 and A3", SKB TR-20-14 (2020).

[2] I. Puigdomenech et al., "O_2 depletion in granitic media: The REX project" SKB TR-01-05 (2001).

[3] Müller H. et al., "Implementation of the full-scale emplacement (FE) experiment at the Mont Terri rock laboratory. Swiss J. Geosci. 110:287–306 (2017).

[4] P. Szakalos and C. Leygraf, Part II, Technical note SSM-2019:22 (2019).

[5] P.Szakalos and S. Seetharaman.", Corrosion of Copper Canister" Page 13 in Technical note SSM 2012-17 (2012).

[6] Y.Cao et al., "Paratacamite from Gypsum Veins in Sandstones of the Kuqa Basin, Xinjiang, China: Implications for a New Epigenetic Cu Enrichment Mechanism", Resour. Geol. Vol. 66, No. 2: 114–126 (2015)

[7] Wersin P. and Kober F, FEBEX-DP, Metal Corrosion and Iron-Bentonite Interaction Studies. Arbeitsbericht NAB 16-16 (2017).

[8] Åsa Björkbacka, Radiation induced corrosion of copper, Doctoral Thesis, KTH Royal Institute of Technology, Stockholm, Sweden, ISBN 978-91-7595-710-4 (2015).
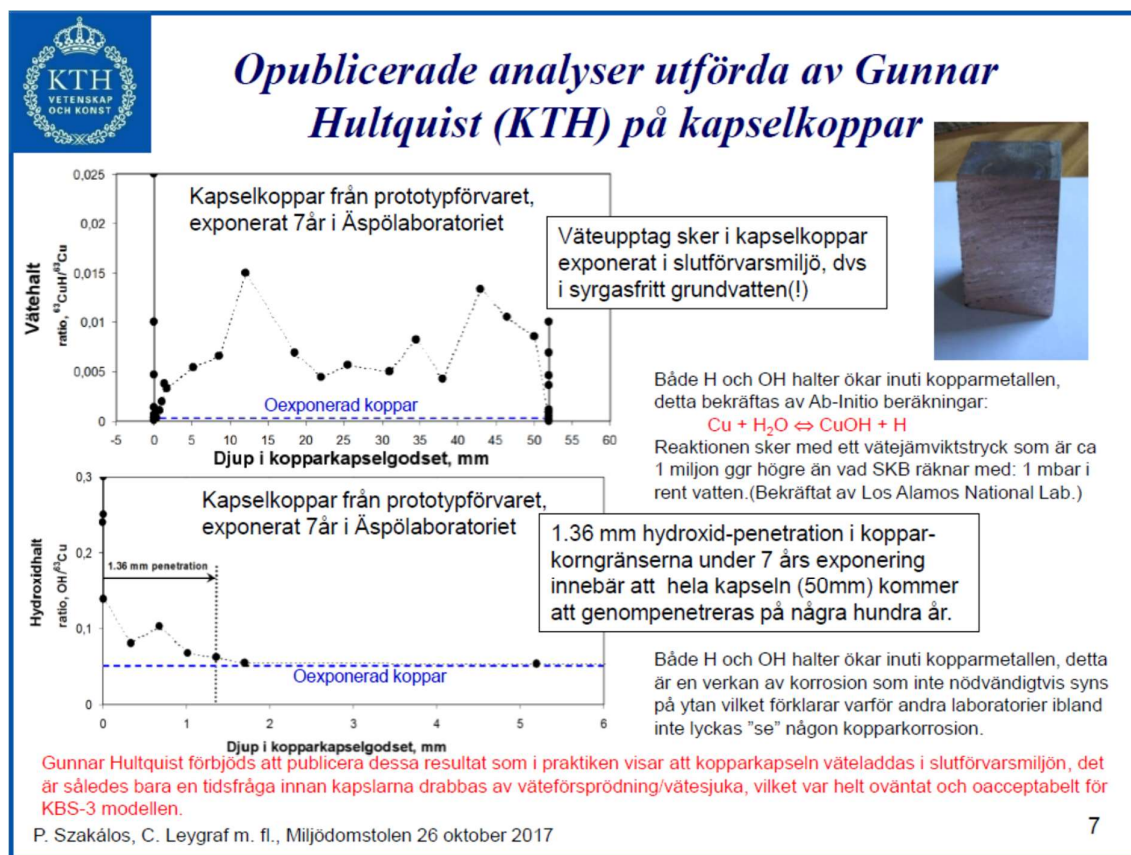
Gunnar Hultquist (KTH) has shown that the full-size copper canister in SKB´s prototype repository was subjected to severe hydrogen uptake, throughout the whole thickness of 50 mm, during seven years of anoxic exposure in groundwater and bentonite in the Äspö hard rock laboratory (upper curve). The dotted blue line corresponds to the normal hydrogen content in SKB-copper. The relatively low hydrogen contents close to the outer and inner surfaces, around 0 mm and 50 mm, are a consequence of post-exposing the copper to oxygen (air) which act as an effective hydrogen getter. The lower curve shows the uptake of OH in the grain boundaries of the canister copper. This is evidence of internal corrosion which may not be visible on the copper outer surface. By extrapolation based on the OH-profile it can concluded that the whole canister may be penetrated by OH within 250 years. However, hydrogen embrittlement and cracking of the copper canisters is expected much earlier.