SKB	**Document ID** 1920891, (2.0 Approved) **Reg no**	**Security class** Public **Document type** Notes **Author** 2020-11-27 Lotta Rubio Lind **Quality assurance** 2021-01-20 Lotta Rubio Lind (Approved)	**Page** 1(18)

Notes; Quality assurance - LOT meeting 3

Date: November 27, 2020

Participants:
Galson Sciences Ltd, Tim Hicks, Tamara Baldwin
SSM, Bo Strömberg, Henrik Öberg, Jinsong Liu, Michael Egan (participated the first part of the meeting)
SKB, Johannes Johansson, Magnus Kronberg, Magnus Westerlind, Lotta Rubio Lind

The meeting was held virtually using Skype.

SSM provided questions before the meeting which SKB gave written answers to and presented during the meeting. The questions and answers are all documented below. After each issue, the discussion that followed is summarized.

SKB was responsible for taking notes at the meeting. The notes were sent to SSM and SSM distributed the notes to Galson Sciences for a factual control before the notes were approved in SKB's document system.

It should be noted that SKB have added clarifying text after the meeting for issues 3, 8 and 18.

This meeting was the last in a sequence of three and the focus at the meeting was:

  (i)   Management system & project management (2020-11-05)
 (ii)   Retrieval, sampling, handling of samples & analysis (2020-11-13)
(iii)   Interpretation of results (2020-11-27)

Quality management system

1. Selecting suppliers

What evaluation criteria do you used when selecting SKB's external supplier companies (e.g. KIMAB, Swerim, Clay Technology)? Do you have minimum requirements for respective company expertise and profile?

SKB's reply/comment: SKB prefers that the suppliers are ISO-certified. A supplier evaluation is performed before contracting a new supplier and is renewed regularly to assure that the company still meets SKB's expectations. In the evaluation the different criteria are described in 1056110 – Inköpsinstruktionen (Purchase instruction), and these criteria regard:
- Economy
- Quality assurance
- Environmental impact

After delivery an evaluation of the new company used is done by the client according to a template provided by the procurement unit at SKB. For previously evaluated companies, additional evaluations should be made if called for by new experiences. These procedures are in place to ensure that past experiences are taken into account when considering a company for additional assignments.

Smaller companies and sole proprietorships do not necessarily have ISO-certifications and are then chosen for their unique expertise. The evaluation is then based on CVs, level of education, publications in the scientific literature, etc.

Discussion: SKB clarified that also for larger companies it can be specified which staff members at the supplying company that will perform the assignment. The competence of the individual is evaluated from CVs and descriptions provided by the companies. If the supplier, for some reason, has to change personnel for the assignment SKB has to approve the change. This is applicable for those assignments for which SKB requires specific personnel at the supplying company, and this procedure is stipulated the order.

2. Collaboration with consultants

How long has SKB collaborated with KIMAB, Swerim, and Clay Technology?

SKB's reply/comment: The relationship between SKB and these companies has a long history. SKB (and its predecessor the KBS-project) has collaborated with the Swedish Corrosion Research Institute (Korrosionsforskningsinstitutet) and the Swedish Institute for Metals Research (Institutet för Metallforskning) at the Royal Institute of Technology (KTH) since 1977. Corrosion studies were performed from 1977, and creep studies started in 1984. These two institutes then merged and formed KIMAB, later Swerea KIMAB. A couple of years ago the company was divided into Rise KIMAB and Swerim.

Clay Technology was formed in 1988 and SKB has been using the company from the beginning. The company was formed by parts of SGAB (Sveriges Geologiska AB, a state-owned company formed in 1982) with which SKB collaborated before Clay Technology was formed.

Discussion: It was discussed how many companies there are in Sweden that perform these types of corrosion and material analyses relevant for experiments such as the LOT project. SKB knows of other companies in Sweden that can perform parts of the analyses but Rise KIMAB (Swerim) is the only one that can undertake the whole assignment. Using suppliers from abroad (which is done for other assignments) was considered, however, this alternative may also enhance the costs due to, for example, travel expenses. It may be noted that it was initially discussed to involve an academic research group abroad, but it was considered difficult due to the need for careful handling of samples during transportation. If using several suppliers, the effort in coordinating the suppliers will increase.

3. Report procedures

Do contracting companies provide internal company reports to SKB which are then further processed within SKB to SKB TR- or R-reports?

SKB's reply/comment: Yes, in some cases, depending on the degree of involvement of SKB's experts in the actual work done. When SKB experts are involved in the work they are normally involved at an early stage of experimental planning, analysis and reporting. In such cases the SKB expert is usually a co-author of the report. For other reports the only post-processing is editorial, i.e. typesetting and printing of the report.

SVENSK KÄRNBRÄNSLEHANTERING AB

Discussion: It was discussed how the LOT corrosion report TR-20-14 was written. Since it was a close cooperation from the beginning, Rise KIMAB did not make a separate report, rather it was written jointly from the start by the SKB and Rise KIMAB authors (see further the list of authors of TR-20-14). This has been the procedure for several SKB reports produced in collaboration between SKB and other companies, e.g. Rise KIMAB. Swerim provided a separate report for the TEM analyses, which were done at a late stage during the work (it was an additional separate order), which was included in the report TR-20-14 as an appendix. This section (as all other appendices) were subject to peer review with the rest of TR-20-14. The analytical measurements and results are to be considered as independent results which are entirely reported, and the conclusions are written mainly by SKB personnel with the support of the supplier.

It was discussed that for some assignments the supplier provides SKB with a draft report that SKB publishes in a SKB report series (TR-, R-, P-). When receiving the draft SKB goes through the draft (delivery control) and have a dialog with the author in order to clarify any ambiguities in the report and in some cases a new version with clarifications is requested before a formal review is performed of the report. The review of reports in the SKB report series are handled in the same way no matter if it is a TR-, R- or a P-report and with the same requirements on the review. The number of reviewers depends on the availability of reviewers with the right competence, sometimes it is necessary to combine several reviewers to fully cover the content/extent of the report. When choosing the reviewer/ers it is also important that the reviewer haven't been involved in the writing of the report. The reviewer/ers can be an internal staff member or an external consultant. After the review and before publication the report is adjusted to the SKB layout.

It was discussed if SKB have a written policy concerning openness of results. It is widely known at SKB (a SKB culture) that we should publish all of our results from scientific assignments in order to maintain trust from the authority and society, however, at the meeting SKB could not say if the openness-policy was clearly stated in the management system at present and would doublecheck this which has been done in the text below:

Additional information after the meeting:
The SKB Policy refers to the four general principles that are expressed in SKB's Code of Conduct. One of the principles concerns *Openness*;

"Vår verksamhet drivs framåt av människor och samarbeten, och vi vet att transparens i ord och handling genererar förtroende och respekt. Vi är generösa med vad vi vet och delar gärna med oss av vår kunskap. Vi söker nya perspektiv, är innovativa och arbetar tillsammans med andra för att öka utvecklingstakten. När vi kommunicerar är vi proaktiva, transparenta, tydliga och relevanta."

"Our activities are driven by people and cooperation, and we know that transparency in words and deeds generate trust and respect. We are generous with what we know and willingly to share our knowledge. We seek new perspectives, are innovative and work together with others to increase the pace of development. When we communicate, we are proactive, transparent, clear and relevant"(unofficial translation).

Through the mandatory review of the RD&D programme reports, SSM oversees the development of management and disposal systems in the pre-licensing process. The review process includes opportunities for broad public participation in the development of the Swedish system for managing spent fuel and radioactive waste. The RD&D-programme can be found in the Management System for SKB in the part where the vision, goals and strategy of the company is described. In the latest SKB RD&D program published in 2019 it is stated in section *5.1.4 Review, openness and transparency* that:

SVENSK KÄRNBRÄNSLEHANTERING AB

"*SKB's research is conducted on the basis of the requirement that research results should be correct, traceable, reproducible and relevant for SKB's mission. To achieve this, SKB has developed and applies procedures for quality assurance of the execution of research projects and tasks. There are also special procedures for quality assurance of safety assessments, which include approval of research results, data and models for use in the assessments, see also Section 5.4.*

The fundamental principle is that SKB's research results will be published in the open literature to facilitate external review. Research results have, since the research programme was initiated in the 1970s, been published and will continue to be published in SKB's report series, which are available on SKB's website. Before they are published, the reports have undergone internal and/or external review in accordance with established procedures. Quality-assured data from SKB's site investigations, technology development and research are saved in databases and are available for the authorities in their review.

SKB also strives to publish relevant results in scientific journals and encourages its own personnel, as well as research institutions and consultants that SKB is collaborating with, to publish results. An independent review of the results is carried out through the peer review that takes place before publication. SKB's research results are also presented and discussed at scientific conferences and are published in the conference proceedings.

SKB is also working to disseminate research results outside the scientific community. For example by publication in popular scientific journals, publication on SKB's website and in SKB's paper Lagerbladet, themed evenings (mainly in Östhammar) and information at schools and universities."

4. External data deliveries

How are data deliveries from contractors controlled? That is, are data post-processed for recording in SICADA/use in reports?

SKB's reply/comment: Data is sent (by e-mail or via ftp) by the contractor and stored in SICADA, and a resource responsible for the work approves/releases the data in SICADA. With respect to post-processing, it depends on the data type. For example, temperature is stored as raw data, while other data are stored both as a raw data measurement files and calculated results in a template. For reports, calculated results are generally plotted or presented in tables. A general principle is that no data should be omitted. If it is obvious that e.g. a sensor is malfunctioning (for example showing unrealistic or unphysical values), it shall be documented that data from this sensor is removed and why.

Discussion: It was discussed how SKB handles identified errors in data already delivered and approved in the SICADA database. SKB replied that the supplier (internal or external supplier) then corrects the data sheet/table and send an updated version to the SICADA operators. The older version of data is then locked for use and only the updated data can be used/delivered for further use in, for example, modelling and reports. The SICADA operator also makes a SICADA bug-report in order to document the change.

It was also discussed how a contractor can access data from SICADA, this is done according to an instruction, using a template that is sent to the SICADA administration after which they provide approved data. If larger errors, errors that can affect model results and conclusions, are identified at a later stage, those who have received that data are informed about the changes made by the SICADA administration.

PDF rendering: DokumentID 1920891, Version 2.0, Status Godkänt, Sekretessklass Öppen

Interpretation of LOT corrosion analysis and test conditions

5. Corrosion - function of time

What can be said about the extent of copper corrosion in the LOT test as a function of time considering all available data? Are there clear causes for variability apart from the apparent dependence on temperature? Could there be non-quantifiable causes for variation related to the design of the experiments and, if so, which are expected to be the most significant?

SKB's reply/comment: Corrosion on the warmest parts of the pipes was estimated to be of the order of 10 µm, with a few µm deeper corrosion on the warmest parts of A3 (20 years) than for A2 (6 years). This is probably because O_2-induced corrosion proceeds beyond the depletion of O_2 itself, since the intermediate oxidant Cu(II) prevails on much longer time scales (King et al. 2010, King and Kolář, 2019). However, it can not be excluded that the available amount of O_2 differed between the test parcels. On the colder parts of the pipes, there was no significant difference between the A2 and A3 parcels.

For the coupons, gravimetric data is available from several test parcels and corrosion could be quantified with standardised methods. Two observations may be noted regarding variability;

1) The corrosion depths varied from 0.6 to 4.7 µm and were highest in the 1-year parcels (A0 and S1), intermediate in the 6-year parcel (A2) and lowest in the 20-year parcels (S2 and A3). The corrosion was thus inversely proportional with time, and correlation of measured corrosion depths (mass-loss) with temperature was very weak, indicating that there were other factors than time and temperature that controlled the corrosion in these experiments.

2) In the test parcel ABM 5 (another Äspö bentonite experiment, very similar to LOT), the variation in corrosion depth by mass-loss was 2.3 to 5 µm (Gordon et al. 2018), despite the fact that all specimens had the same temperature (ca 80 °C) and were exposed for the same time (5 years). It is not known exactly what causes this variability in LOT and ABM (within and between test parcels), but the most reasonable explanation is considered to be heterogeneous distribution or transport of O_2 and/or heterogeneous resaturation of the bentonite clay. When comparing the LOT and ABM test parcels it should be noted that the water supply systems were different. Concerning the different LOT parcels the natural flow from the boreholes may have contributed to spatial variations in the saturation process. Variations in the initial surface conditions of the copper specimens, especially for the pipes, can not be disregarded, e.g. regarding roughness and/or the initial oxide layer.

Discussion: It was discussed how the temperature gradient along the copper pipe and the gap between the bentonite and the pipe affects the results. Considering the gradient, the corrosion rates on the warmer parts would in the LOT case be overestimated and underestimated for the cooler parts. The coupons were imbedded from start (no gap) and there was no artificial temperature gradient and these effects can thus not be directly compared.

The general decrease of integrated corrosion rates between A2 and A3 (and S2) was discussed with reference to the report Johansson et al. (2014).

If there are other oxygen consuming processes in the experiment, such as microbial activity, was discussed. The conditions in the LOT experiment were not favourable for the microbes due to initial unsaturated conditions (low water content) and later high temperature and density so the oxygen consumption from bacteria should be considered low. This is further discussed in Issue 8.

6. Corrosion - highest temperatures

SKB has not measured the extent of corrosion on the part of the copper tube exposed to the highest temperatures. Why? What could be expected if these tube sections were analysed?

SKB's reply/comment: The corrosion of the warmest parts of the copper pipes has been measured based on the estimated concentration of copper in the bentonite (e.g. in block 9 and 11 for A3, see Table 3-19 in Johansson et al. 2020). Examination of the pipe surfaces was done for the pipes in blocks 21-23, since these were carefully handled during extraction of the coupons contained within the same bentonite blocks, in order to avoid damaging (scratching) the surfaces.

It may be noted that the temperature at the pipe surfaces examined metallographically was 70-80 °C for A3, which is not far from the peak temperature of 95 °C for any copper canister in the KBS-3 repository. On the other hand, the maximum temperature in A3 was 120 °C, which is higher than what is relevant for the canister in the repository. Initially, the canister surface in the repository will be ca 50 °C and it will take about a decade to reach the maximum temperature (95 °C) after which the temperature decreases slowly.

It is possible that the warmest part of the A3 pipe could be rougher or have slightly deeper pits than the examined part (depending on how the extent of these pits is influenced by corrosion). However, it should be noted that the deepest pits found on the pipe in A3 were only 25 µm, while the expected range of pit-depths during initially oxidising conditions in the KBS-3 repository would be up to a few hundred µm, and with a low probability of pits even up to ca 1 mm (Briggs et al. 2020). Pipe material from LOT S2 and A3 has been saved for the possibility of further metallographic examination. It is, however, unlikely that the confirmation of deeper pits on the warmest parts of the pipe in A3 would change any conclusions regarding localised corrosion under the initially oxidising conditions of the repository.

7. Copper in bentonite - XRF

Do the bentonite copper content measurements by XRF provide an accurate measure of the local extent of corrosion on the copper tube? Would consideration of corrosion products left on the copper tube significantly affect the results?

SKB's reply/comment: The estimate from the XRF analysis of clay near the coupons showed that the mass of copper found in the bentonite clay was in the range 0.011-0.018 g. This is not far from the mass-losses of the coupons which were in the range 0.009-0.024 g, and which correspond to corrosion depths of 0.6-1.3 µm. The "error" in this comparison would be the adherent corrosion products which are included in the gravimetric analysis but not in the Cu in clay analysis. However, the oxide films on the coupons were generally very thin, typically around 1 µm, at some positions less, and locally sometimes up to a few µm (see e.g. Fig 4-2 and Fig B-38 in Johansson et al. 2020). There was no apparent difference in oxide films on the coupons A3/K (50 °C) and S2/N (30 °C), as seen in the micrographs in Appendix B. It may be further noted that there was no obvious difference in the thickness of adherent corrosion products on the examined pipe samples (Appendices F and G in Johansson et al. 2020). Some micrographs show adherent layers of bentonite (high Si), while corrosion products were typically around 1 µm thick, sometimes less and locally sometimes more corrosion products in or near pits or surface defects. This was despite the fact that the temperature was higher in A3 (70-80 °C) than in S2 (50-60 °C), and despite the fact that both lighter and darker areas were examined for each test parcel (Figure G1-G5 in TR-20-14).

Laboratory studies in the Canadian program have shown that the estimate of corrosion from copper content in the clay, sometimes need to be multiplied by a factor to match gravimetric results. This factor has been estimated to range from 1 to 19 in the different experiments made

(Litke et al. 1992, King et al. 1997). While the experiments in Litke et al. (1992) used a 50:50 sand-bentonite mixture and had an initial O_2 inventory of ca 30 mol/m^2 copper area, the experiments in King et al. (1997) used compacted bentonite without sand and had less than 1 mol/m^2 copper, which is closer to the initial conditions in LOT. The factors derived in the study by King et al. (1997) varied in most cases within the range 1-1.7. The fact that many of these values were close to 1 is in agreement with the general picture from LOT in which the adherent oxide film was mostly very thin.

Discussion: It was discussed that the available amount of O_2 is important for the thickness of the oxide film. SKB has discussed the Canadian experiments with one of the authors and it was noted that in the study by Litke et al. (1992), the copper surfaces in many cases had an appearance with thick deposits of blue-green corrosion products, while the copper surfaces in King et al. (1997) appeared more similar to the copper surfaces in LOT.

It was also discussed that the steep copper profile in the bentonite clay is indicative of Cu(II) being adsorbed. This is discussed in the Canadian studies cited and further references therein. SSM brought up a discussion about the form of copper in the clay and mentioned that ion exchange between copper ions and Na and Ca in the bentonite is known to occur. The possibility of complexation was also mentioned by SSM.

8. Oxygen consumption - microbes

It has been claimed in the LOT context that the initial oxygen content available during the LOT-experiments was rapidly consumed by microbial processes before the oxygen had a chance to react with the copper. What is SKB's position regarding this claim? What knowledge can be gained from SKB's other experiments regarding microbial oxygen consumption, pyrite oxidation and other reactions in bentonite clay?

SKB's reply/comment: The bentonite clay in LOT was initially cold and unsaturated, conditions under which microbial O_2 consumption is very inefficient (Birgersson and Goudarzi 2018, Giroud et al. 2018). When the heaters were turned on the temperature of the copper surface increased rapidly from rock temperature to ca 40 °C and then continued to increase. As indicated by laboratory studies, copper corrosion under aerobic conditions and temperatures 50-80 °C can occur rather rapidly (Litke et al. 1992, King et al. 1997). This supports the view that O_2 may have been consumed by corrosion before the microbial consumption started. Oxidation of pyrite is not significant at rock temperature but is known to occur at 55 °C. The occurrence of pyrite oxidation would however be difficult to confirm, which is further discussed in the reply to Q9.

Discussion: The activation energy for the oxidation of pyrite was discussed and that there is a temperature effect on pyrite oxidation. Different corrosion experiments were also discussed, and whether any of the experiments have measured the corrosion that occurs at a very early stage. SKB mentioned that the Canadian studies cited in the response to Q7 measured corrosion already after one month, and depending on the conditions they sometimes measured rather high corrosion rates on this short timescale, as compared with the rates measured after several months or years in the same experiments. This shows that the initial corrosion may occur much more rapid than the integrated corrosion rates measured for longer exposures.

SKB has started two new experimental studies in order to improve the detailed description of corrosion during the very early stage. One of the experiments is a small scale laboratory test conducted at a lab in the UK. The aim of this experiment is to measure of corrosion at different stages during the depletion of O_2. The second is a medium scale test conducted at the Äspö HRL and aims to follow the development of the gas-phase composition in a setup with copper and

Document ID
1920891, (2.0 Approved)

Security class
Public

Page
8(18)

Notes; Quality assurance - LOT meeting 3

unsaturated bentonite clay. Both experiments will focus on unsaturated conditions. The UK experiment is expected to finish during 2022. The first part of the Äspö experiment will be reported during 2021.

It was discussed if other studies made, for instance on corrosion on copper roofs, could give more information on the early corrosion. SKB pointed out that such studies differ from repository conditions in several ways, for example regarding the availability of O_2, the chemical composition of rain water due to atmospheric pollutants, and temperature. It was further noted that in studies of such objects as for example copper roofs, corrosion is seldomly measured on shorter timescales.

Additional information after the meeting:
It may be noted that the first sentence in SKBs reply to Q8 was a bit unprecise. Neither of the cited studies (Birgersson and Goudarzi 2018, Giroud et al. 2018) concerned microbial effects in the clay so it should rather be said that any type of O_2 consumption was inefficient under the unsaturated conditions of the experiments. Concerning LOT, microbial activity is not expected to have occurred, initially due to the unsaturated conditions (see for example SKB TR-20-08), and later due to the high clay density and high temperature.

Regarding the studies of the composition of the gas-phase cited in the reply to Q8, it may be appropriate to clarify what was actually observed. The study by Giroud et al. (2018) reported on experiments where open glass vials were filled with granulated bentonite and placed into stainless-steel bottles, subsequently sealed and airtight. All bottles were kept at laboratory temperature of ca 23 °C. The partial pressure of O_2 decreased by a few percent over a time period of 15 days, however, the same pressure drop was seen also for inert gases like N_2 and Ar, and the results were therefore interpreted as sorption rather than a reaction. Similarly, Birgersson and Goudarzi (2018) reported on a test that was conducted in isothermal (room temperature or 50 °C), isolated conditions, and involved only bentonite pellets. The test showed no noticeable O_2 consumption at room temperature and very little at 50 °C over a period of 1 year. These studies show that, although inorganic reactions may consume O_2 trapped in bentonite clay under some conditions, the reactions are slow at low temperatures, at least for an unsaturated conditions.

9. Oxygen consumption - other processes

If all the oxygen was not consumed in the experiment, could a certain fraction of the available oxygen have been consumed by processes other than copper corrosion? If so what is an approximate estimate of this fraction? Is there a formation of sulphate which could indicate pyrite oxidation?

SKB's reply/comment: Formation of sulphate from pyrite oxidation is likely to occur, however a bit difficult to verify, as the bentonite originally also includes gypsum (Ca-sulphate) and the sulphate moves in the bentonite, typically towards the central heater. Possibly the total sulphate content could be measured. Another strategy could be to look for disappearance of pyrite in XRD, however this is not trivial as the pyrite content is low already at the start. In Callovo-oxfordian (COX) clay, which is a clay stone rich in pyrite, signs of pyrite oxidation in the field experiment ABM1 was observed based on increasing Fe(III)/Fe(II) ratio, however this was not studied in detail as it was not the purpose of the study (Svensson and Hansen, 2013).

10. Availability of oxygen

Could there have been a slow leakage of oxygen from the tunnel through seals, fractures in the rock, the EDZ, through holes next to cables and pipes etc.? (Onset of reducing conditions does not *per se* exclude in-leakage if the prevailing redox reactions consuming oxygen are reasonably well buffered).

SKB's reply/comment: The weld between the bottom plate and pipe was pressure tested with He gas before the experiments were installed (Sandén and Nilsson, 2020). It seems unlikely that significant leakage could have occurred through concrete and clay, however, considering the large number of cables going through the concrete and around the test parcels it can not be completely excluded that some leakage could have occurred.

Discussion: The importance of cables was discussed for the different experiments in order to better understand the potential for leaking of oxygen for the different experiments. The experiments FEBEX (Nagra) and Prototype (SKB have a fairly large number of cables going through the clay system and have shown that leakage of O2 may be difficult to avoid on the scale of the experiments. The LOT experiment has fewer cables installed but SKB cannot definitely rule out that leakage of oxygen took place. SSM pointed out that a slow in-leakage of O2 would generally be difficult to detect if there are processes (like for example corrosion) that consumes O2 and keeps the concentration within the experiment low. In a situation in which the consumption rate of O2 is more rapid than the supply by mass transfer, a scenario which cannot be outruled for the case of LOT, the O2 concentration could in principle not only be low but be close to zero. Such slow mass transfer could still have some relevance on time-scales of several years.

11. Added groundwater - influence on oxygen

Could groundwater added to the LOT experiments have consumed oxygen through its reducing capacity? Is there knowledge of the reducing capacity of this groundwater (e.g. Fe(II) content)? If so how could addition of groundwater have affected the oxygen content available for copper corrosion?

SKB's reply/comment: The Fe(II) concentration of the groundwater that is supplied to LOT is low (around 70 ppb). Since the exchange of groundwater with the LOT-packages is limited the Fe(II) can be assumed to have negligible effect on the oxygen consumption.

Discussion: SSM mentioned that one way to determine if Fe(II) have been oxidised during the experiments would be to look for ferric precipitates, since Fe(III) would be very insoluble under the prevailing conditions. Other reducing agents mentioned and deemed to be less important were dissolved manganese and hydrogen sulphide. It was concluded that Fe(II) should control the redox potential of the groundwater.

The water filling procedure was shortly discussed and it was clarified that no pumps were used, see issue 12 below.

12. Water filling procedure

Were all slots and gaps completely filled with groundwater at the onset of the experiments (i.e. when the heaters were switched on)? For how long were the slots and gaps open? What was the pathway for water to enter the gaps (i.e. from titanium tubes and rock)? What is known about the groundwater inflow rates in the "deposition holes"? Is it possible to identify any water conducting feature in spite of the drilling near the holes?

SKB's reply/comment: The (natural) water inflow rates were measured at different depths in the bore holes for the LOT test parcels. The general conclusions from the pilot hole characterization program were that the water inflow was low, and that the water inlet points were few in all holes (therefore it was decided to use groundwater from the nearby hole, see below). The average water inflow to the borehole where test parcel S2 should be installed was ca 1 ml/min, which is nearly two orders of magnitude higher than for the other boreholes (Table 2-1 in Sandén and Nilsson 2020).

Document ID
1920891, (2.0 Approved)

Security class
Public

Page
10(18)

Notes; Quality assurance - LOT meeting 3

Before the start of the heaters and the water filling procedure, the Ti-tubes were open to the Äspö tunnel for ca 4 months in the S2 and A3 test parcels (Table 3-1 in Sandén and Nilsson 2020).

After installation of the test parcels in the holes, there was a remaining air-filled gap between bentonite blocks and rock surface with a width of 10 mm, and another air-filled gap between bentonite blocks and the central copper tube with a width of ca 1 mm. These gaps were slowly water filled (on February 2, 2000) in parallel with the onset of heating. The filling was made with groundwater from the adjacent borehole (HG0038B01) by use of the fixed installed Ti-tube and bottom filter placed in the sand below the parcel and close to the rock wall. The valve connected to the bottom filter was closed at the time when the groundwater had reached the uppermost filter (filter in block 32), which until then was open to the Äspö tunnel. This filter was then instead connected to the groundwater supply. This inflow point is assessed to simulate a point inflow from a water bearing fracture in the rock. The test parcels have had access to pressurised water from this point inflow during the entire test duration.

Discussion:.It was discussed what determines the time to reach full saturation in the LOT experiments and that the high temperature at the pipe surface is an important factor. It was also discussed that the period before contact is established between the bentonite and the copper pipe surface could be important in the description of the development of corrosion in LOT.

In connection to Q10 it was discussed whether it is possible that leakage of air could have occurred through factures connected to the tunnel floor. SKB can not definitely exclude the possibility.

SSM made the point that there could be residual oxygen in bentonite and sand even after saturation that could diffuse to the copper surface.

SSM mentioned that the plugs in deposition tunnels may be a source of oxygen leakage during construction of the repository and this has been evaluated in one of the complementary investigations made by SKB after SR-Site

13. Water inflows in the LOT boreholes

Are there known differences between the LOT holes regarding water inflow and saturation? What is the time scale of full resaturation and is there an appreciable variability between the holes?

SKB's reply/comment: The natural flow was described in the reply to Q12. Reaching full saturation and swelling pressure of the bentonite clay generally took years. For blocks 8 and 14 in LOT A3, near the hottest part of the copper pipe, the process was particularly slow, taking 4 – 6 years to reach the final pressure (Sandén and Nilsson 2020). This can be compared with LOT A2, in which the saturation in blocks 8 and 14 took less than two years (Karnland et al. 2009).

Discussion: It was discussed if the slow resaturation of the bentonite near the warmest part of the copper pipe can result in the higher extent of corrosion there compared with the colder regions. The high temperature does not only influence the rate of O_2 consumption by corrosion, but may also keep the initial gap between copper and bentonite clay open for a longer time due to dryer conditions and thus slower resaturation, as compared with colder areas. It was concluded that it is plausible that both these effects of higher temperature have contributed to the distribution of corrosion over the copper surfaces in LOT.

SKB's position with respect to copper corrosion and alternative interpretations

14. Corrosion kinetics

At what point does the oxic corrosion of copper become diffusion controlled due to the formation of corrosion products? Is diffusion control of relevance (or mixed kinetics) as a rate limit for the initial phase of LOT with oxic corrosion?

SKB's reply/comment: Diffusion control could mean either anodic diffusion control (i.e. the diffusion of either copper cations across a passive Cu_2O film or of dissolved Cu(I) diffusing in the buffer pore water) or cathodic diffusion control (i.e. diffusion of O_2 either through the buffer or across a precipitated corrosion product layer). Different experiments have indicated different types of diffusion control. For example, measurements of the depletion of O_2 with time in King et al. (1997) clearly indicated diffusion-limited O_2 consumption, which suggests that the cathodic reaction is diffusion controlled. In that study, the limiting step was probably diffusion through the buffer, rather than through a thin corrosion product film, as the buffer was compacted in situ (i.e. there were no air-filled gaps). On the other hand, anodic transport control may have been possible in Litke et al. (1992) because of the high amounts of O_2 in the tests. While the experiments in King et al. (1997) may be applicable to the coupons in LOT, the situation for the copper pipes in LOT is more complicated due to the fact that air-filled gaps may have been present initially and when these had been depleted of O_2, the oxidant, O_2 or Cu(II), was only available by diffusion through the bentonite clay.

Discussion: The extent of different initial phases were discussed. The corrosion of the pipe surfaces may initially have been under kinetic control, while a similar initial phase for the coupons may have been much shorter (diffusion control is likely to have been rate limiting for a comparatively longer duration), since these were embedded in bentonite clay from the start. This is probably an important difference for the comparison of corrosion between pipes and coupons, although temperature variations were also important.

15. Corrosion - temperature dependence

What is the temperature dependence of copper corrosion rate for the relatively unexposed copper surfaces put in the LOT experiment (activation energy)?

SKB's reply/comment: For the copper coupons, the correlation of corrosion depth (or rate) with temperature was very weak. This may reflect that the corrosion was controlled by diffusion through the clay. However, it must also be noted that the temperature did not differ as much between the coupons as for the pipes. For the copper pipes, there was a clear temperature effect on the measured corrosion depths (and thus on the integrated corrosion rates) as shown in Figure 4-1 in Johansson et al. (2020). Since the integrated corrosion rates are determined for a very long period of time (20 years) during which the corrosion process goes through different mechanistic phases (O_2, Cu(II), sulphide) with different kinetics, it is unclear what a detailed kinetic analysis of activation energies based on integrated rates would mean.

Discussion: It was discussed if there are publications on reaction rates for oxygen and copper. SKB replied that there are such papers in the general scientific literature, see for example King et al. 1995 and references therein. SKB mentioned that the reports cited in response to Q7 contain kinetic data for O_2 induced corrosion of copper at a copper/bentonite interface.

16. Corrosion in sand

What are the differences in between corrosion of copper in sand and in bentonite (of relevance for interpretation of corrosion on the tube bottom plate)?

SKB's reply/comment: This has not been investigated, since sand is not a material that will be used in the KBS-3 repository, it was only used in the specific LOT experiments. The verification of solid Cu(II) corrosion products adherent to the bottom plate, but not on other copper surfaces in LOT, may be due to ion exchange between corrosion products and bentonite clay, which does not occur with sand.

Discussion: It was discussed how the contact with bentonite clay allows ion-exchange between corrosion products and the clay, which is not possible with sand. This could be an explanation for the accumulation of Cu(II) corrosion products that was observed on the bottom plates but not on any surfaces in contact with bentonite clay. SSM noted that evaporation at the warm copper surface may be important for the formation of chloride containing corrosion products. SKB pointed out that one circumstance that may be of importance is that one of the Ti-tubes ran out in the sand just below the bottom plate. It is not known if Cu(II) corrosion products were formed under the bottom plates of earlier test parcels, e.g. A2, but in general the appearance of the pipe in A2 resembled the pipes in S2 and A3. In A2, small amounts of the solid Cu(II) phase paratacamite were found on one of the coupons. This has not been found on the coupons in S2 or A3. SSM also made the point that there is a great deal of uncertainty about the saturation process but the sand beneath the bottom plates would have saturated quickly. SKB agreed in general but notes that this depends on how fast water reached the sand in the deep bottom hole.

17. Corrosion kinetics, oxic-anoxic conditions

It has been claimed in the LOT context that corrosion of copper will not slowdown in response to a shift between oxic and anoxic conditions. What is SKB's position on that?

SKB's reply/comment: Experimentally, it has not been possible to distinguish the time dependence of the corrosion rate in the presence of O_2 versus the presence only of Cu(II), although the latter phase is expected to be longer (King et al. 2010). However, when O_2 has been depleted and the resulting Cu(II) intermediate has reacted, the only oxidant available in the deep ground water environment is sulphide, for which transport limitations will control the long-term corrosion rate. The integrated corrosion rates that can be calculated from corrosion depths obtained from copper coupons and pipes in the LOT series, clearly indicate that the integrated rate is decreasing with time. This is discussed in sections 4.2.1 and 4.2.2 in Johansson et al. (2020). As regards the possibility of corrosion of copper in pure, O_2-free water, it is SKB's clear position that this process occurs to an extent that is compatible with established thermodynamic data, which is completely negligible in the LOT context, see further Hedin et al. 2018 and SKB 2019, Chapter 4.

18. Corrosion products, oxic-anoxic conditions

It has been claimed in the LOT context that the formation of the main detected corrosion product cuprite (Cu_2O) in LOT A2 and S2, and also other typical corrosion products in similar experiments (malachite $Cu_2(CO_3)(OH)_2$, para-atacamite $Cu_2Cl(OH)_3$) may be related to anoxic conditions. What is SKB's position regarding this issue? What are SKB's key arguments? Has knowledge of the thermodynamic properties of these phases been utilized to address such issues?

SKB's reply/comment: In order to form corrosion products, in such amounts to precipitate solid phases, some other oxidising species than water is needed (the dissolved copper oxidised by water is negligible; Hedin et al. 2018, SKB 2019). For this evaluation thermodynamic data is used to investigate what phases that can form under different conditions. For example, the copper oxide corrosion product Cu_2O is formed under conditions where the redox potential $Eh > 0$ V SHE (at 25 °C, for pH up to 8, and a total copper concentration in solution of 10^{-6} M). To form Cu(II) solid phases even higher potentials are required. This can be seen from Pourbaix diagrams (Puigdomenech and Taxén 2000), but can also be evaluated with more detailed speciation

calculations, that has been done e.g. for corrosion in high chloride concentrations (Lilja et al. 2021), still using the same type of thermodynamic data. The claims that the solid corrosion products are related to anoxic conditions, may depend on the used definition of "anoxic conditions". For the LOT experiment (as well as in the bentonite buffer in the repository) the redox potential would be determined most probably by iron compounds and be in the range of that in groundwater (around -0.2 V; SKB 2011), when all O_2 is consumed. Such potentials are not compatible with formation of either copper oxides or paratacamite (or malachite). The observation of oxides and paratacamite in LOT is though consistent with thermodynamic data for the initial conditions with O_2 (high Eh). (Malachite would be formed with a water composition with slightly lower chloride concentration and higher carbonate concentration.) Even if the development of reducing conditions does not support formation of e.g. paratacamite, this does not exclude that compounds already formed may remain kinetically stable also during reducing conditions.

Discussion: Regarding the terminology, SSM asked if the groundwater redox potential of -0.2 V (SHE) should be described as anoxic, reducing or if both descriptions are plausible. It is SKB's understanding that the terminology is not strictly defined and that both the terms anoxic and reducing could be used to describe the groundwater environment.

The thermodynamic and/or kinetic stability of different corrosion products formed in the presence of O_2, such as Cu_2O, $CuOH$, $Cu(OH)_2$ and $Cu_2Cl(OH)_3$), was discussed, for conditions under initial depletion of O_2, as well as for the long-term sulphidic repository environment. SSM has also pointed out, to which SKB agrees, that it is possible that the prolonged presence of solid phases normally associated with oxidising conditions (such as paratachamite) could be due to slow dissolution kinetics in combination with slow mass transfer, rather than kinetic stability for the conditions and time scale of these experiments. In this context there was also a discussion about thermodynamic stability of cuprite together with copper both in the presence and absence of other redox affecting species such as hydrogen gas and dissolved hydrogen sulphide.

SSM asked whether SKB could provide a reference for thermodynamic data on paratacamite, a polymorph of $Cu_2Cl(OH)_3$, which has been identified in field tests such as LOT. SKB replied that such data were applied for thermodynamic calculations underlying the safety assessment SR-Site (Puigdomenech and Taxén 2000).

Additional information after the meeting:
Since the meeting, SKB has looked into the data used in Puigdomenech and Taxén (2000) and a few things needs to be clarified. First of all, the data applied in Puigdomenech and Taxén (2000) was for atacamite, which is a different polymorph of $Cu_2Cl(OH)_3$. It is noted that SKB has not always been strictly consistent or precise when referring to the polymorphs of $Cu_2Cl(OH)_3$, as is also the case for older literature. Further, naturally found paratacamite often contains some zinc. However, as discussed by Pollard et al. (1989) the $\Delta G°_f$ (Gibbs free energy of formation) values for the three polymorphs of $Cu_2Cl(OH)_3$ are very close, with paratacamite being the most stable, closely followed by atacamite, and botallakite being the least stable of the three (there is a also other crystallographic variants, like clinoatacamite, Jambor et al. 1996). The difference in $\Delta G°_f$ between paratacamite and atacamite given by Pollard et al. (1989) was less than 7 kJ/mol and in the same paper, comparison was made with earlier studies showing the same trend in the relative thermodynamics of the polymorphs. The value for $\Delta G°_f$ assigned to atacamite in Puigdomenech and Taxén (2000), lies within the range of values for atacamite and paratacamite given in other studies (Woods and Garrells, 1986). The subtle differences between the $\Delta G°_f$ values reported for the polymorphs of the $Cu_2Cl(OH)_3$ does not change the stability area to any noticeable extent. It has thus no implication for the interpretation of the observation of $Cu_2Cl(OH)_3$ in LOT or the thermodynamic evaluation of corrosion products to be expected in the spent fuel repository.

The structure, thermodynamics, and chemical stability of the CuOH phase mentioned above, has been studied experimentally as well as by theoretical methods, see further Soroka et al. 2013 and Korzhavyi et al. 2012.

19. Corrosion products- Cu(II) phases

In King's review, a presence of Cu(II)-phases is suggested. According to established knowledge, ordinary copper corrosion in an oxic environment involves formation of a double-layer of Cu_2O and CuO on top of the metal, with the monovalent oxide forming closest to the metal surface. To what extent does the presence of the buffer affect these reactions? What is the significance of an absence or presence of Cu(II)-phases for the interpretation of LOT? It has been claimed in the LOT context that a lack of Cu(II) suggests that corrosion has been anoxic. What is SKB's position on this issue?

SKB's reply/comment: As elaborated on in the answer to Q18, the oxidation state of corrosion products, more oxidising conditions (more positive Eh) supports the formation of Cu(II) compounds (e.g. CuO in fresh water or paratacamite, $Cu_2(OH)_3Cl$, in chloride-rich groundwater), while less oxidising conditions (less positive Eh) results in the formation of Cu(I) corrosion products (e.g. Cu_2O or $CuCl_2^-$). In aerobic systems, it is common to get a bilayer structure with a Cu(II) phase on top of Cu_2O, and this was found in the copper-bentonite experiments in both Litke et al. (1992) and King et al. (1997). The bentonite tends to adsorb the Cu(II) and, hence, lower the tendency for Cu(II) precipitation at the copper surface. In Litke et al. (1992) the initial $[O_2]$ was high (30 mol/m^2 Cu) and the average corrosion depth was ca 40 µm, and precipitated Cu(II) was clearly visible as blue-green corrosion products. In King et al. (1997), the initial $[O_2]$ was lower (<1 mol/m^2 Cu) and the fraction of Cu(II) in the corrosion product was in the range 1-56%, while the steep copper profiles in the bentonite clay adjacent to the copper surfaces implied the presence of Cu(II) adsorbed in the clay. LOT seems to be more similar to King et al. (1997), i.e. no visible adherent Cu(II) products but steep Cu profiles in the adjacent bentonite clay. See also answer to Q16.

20. Hydrogen embrittlement

One of key issues raised by the Swedish Land and Environment Court is hydrogen embrittlement of copper. Are there any results of relevance to this issue for the LOT S2 and A3 phases?

SKB's reply/comment: Analysis of hydrogen levels in the copper pipes from LOT S2 and A3 (section 3.4.2 in Johansson et al. 2020), shows that hydrogen is only present in or near the surface of the material, which is also where corrosion products and bentonite deposits are present. Comparison of bulk levels of hydrogen of the S2 and A3 pipes with a reference pipe showed very low levels of hydrogen and no significant difference between the pipes. Having said this, it may be noted that the only process which could hypothetically lead to hydrogen uptake by copper under the conditions in LOT, is the long-term corrosion by sulphide (H_2S/HS^-), and as is evident from the results in Johansson et al (2020), the extent of sulphide corrosion in LOT was very limited.

Discussion: The form of hydrogen in the surface deposits was discussed. The role of hydroxide groups and water associated with bentonite deposits and corrosion products was discussed, as well as the amount of adsorbed water on particles and surface deposits. SKB mentioned that results similar to LOT have been obtained in a Round-Robin study of the performance of the Leco method for hydrogen measurements on uncorroded copper specimens (Granfors 2017).

21. FEBEX - LOT

Are there any key findings from the FEBEX experiments that are of relevance for the interpretation of the LOT results?

SKB's reply/comment: The results from FEBEX are regarded as part of the general scientific knowledge of copper corrosion under early repository conditions dominated by O_2-induced corrosion (Wersin and Kober 2017). The results, e.g. regarding corrosion products and corrosion morphology, are discussed in Johansson et al. (2020) and will be integrated in the safety assessment PSAR for the spent fuel repository.

A few detailed results may be worth mentioning in this context. The mass-loss of the FEBEX coupon 4A2 corresponded to an average corrosion depth of 8.5 µm, while the deepest pit observed on the FEBEX coupon 4A1 was ca 90 µm. These numbers are both larger than the corresponding values for the coupons in LOT, which may be due to a combination of higher temperature, larger clay volume (more O_2) and an extended oxic period in FEBEX as compared with LOT. It may be noted that FEBEX differed from LOT in several aspects, for example there was no sulphur on the coupons in FEBEX (while low levels of sulphur were found on all copper surfaces is LOT), there were clear signs of blue-green Cu(II) corrosion products on the coupons in FEBEX (not present generally in LOT S2 or A3), and FEBEX is thought to have had a longer oxic period initially (possibly due to leakage from the tunnel).

Concluding remarks by SKB

In the context of the above questions from SSM, SKB would like to make the following summarizing points regarding the interpretation of copper corrosion in the LOT series:

Purpose with the LOT experiment
- Since the LOT experiments were designed with the purpose to study the behavior of bentonite clay under repository-like conditions, the experiments can only give limited information about copper corrosion. In order to be clear about this, a number of limitations of LOT, if considered as a corrosion experiment, are discussed in Section 1.5 in Johansson et al. (2020).
- There is no information available concerning the initial development of redox conditions in the LOT experiments, and, consequently, the development of the corrosion process can not be described in detail.

Oxygen consumption
- There is a large uncertainty considering the amount of O_2 (from air) that has been available for corrosion.
- It is considered likely that the copper pipe surfaces consumed a large fraction of the initially available O_2 when the heaters were turned on and during the following months during which the temperature of the pipes increased from 40 °C to 90 °C or higher.
- It is considered likely that the copper pipes consumed most of the O_2 in the unsaturated clay system faster than chemical processes in the clay (e.g. oxidation of pyrite) since the copper surface had a higher temperature than the outer parts of the bentonite blocks.
- Microbial consumption of O_2 is not regarded as efficient in unsaturated bentonite clay.

Evaluation of corrosion
- Since the roughness of the copper surfaces in LOT were not characterized prior to the experiments (one of the limitations of LOT if regarded as a corrosion experiment), localized corrosion can only be pessimistically evaluated by assuming that the topography observed is solely due to corrosion. However, even under that assumption, the observed pits are consistent with the expected corrosion morphology under initially oxidizing conditions in the repository.

Document ID
1920891, (2.0 Approved)

Security class
Public

Page
16(18)

Notes; Quality assurance - LOT meeting 3

- Given the uncertainties due to the limitations of LOT as a corrosion experiment, the results are consistent with the conceptual corrosion model applied by SKB in the assessment of post-closure safety for the spent fuel repository.
- A group of researchers has suggested that copper corrodes in pure O_2-free water, i.e. by reactions between copper and water molecules, to an extent that by far exceeds that predicted by established science and thermodynamic data (Hultquist et al. 2015). It is emphasized that this hypothesis can not be evaluated in a complex field test like LOT, in which air (O_2) was initially available and since groundwater is not pure water. This hypothesis has instead been thoroughly evaluated in careful laboratory experiments, which have been published in the scientific literature, see further Hedin et al. 2017, 2018, Ottosson et al. 2017, and references therein.
- One of the observations made in LOT S2 and A3 was a slightly difference appearance and the formation of Cu(II) corrosion products under the bottom plates of the test parcels. This difference between the bottom plate and other copper surfaces in the test parcels is attributed to different reactivity at the copper-sand interface, as compared with the copper-bentonite interface. Since a copper-sand interface will not be present in a KBS-3 repository, these observations are not regarded as directly applicable to the assessment of copper corrosion in the spent fuel repository.
- The detailed evaluation of corrosion in SKBs safety assessment is based on numerous studies (laboratory experiments, models, and field tests) of different aspects of copper corrosion under repository conditions (radiation, O_2, sulphide, microorganisms, groundwater etc) and is not dependent on a single experiment like LOT, especially since it was not designed for detailed studies of corrosion.

References:

Birgersson M, Goudarzi R, 2018. Investigations of gas evolution in an unsaturated KBS-3 repository. SKB TR-18-11, Svensk Kärnbränslehantering AB.

Briggs S, Lilja C, King F, 2020. Probabilistic model for pitting of copper canisters. Materials and Corrosion. doi:10.1002/maco.202011784.

Granfors M, 2017. Round-robin of hydrogen content in copper determined by melt extraction and gas analysis. SKB R-17-15, Svensk Kärnbränslehantering AB.

Giroud N, Tomonaga Y, Wersin P, Briggs S, King F, Vogt T, Diomidis N, 2018. On the fate of oxygen in a spent fuel emplacement drift in Opalinus Clay. Applied Geochemistry 97, 270–278.

Gordon A, Pahverk H, Börjesson E, Johansson A J, 2018. Examination of copper corrosion specimens from ABM 45, package 5. SKB TR-18-17, Svensk Kärnbränslehantering AB.

Hedin A, Lilja C, Johansson A J, 2017. Copper corrosion in pure water – scientific and post-closure safety aspects. Proceedings of the 16th International High-Level Radioactive Waste Management Conference, Charlotte, NC, 9 – 13 April 2017. American Nuclear Society.
Hedin A, Johansson A J, Lilja C, Boman M, Berastegui P, Berger R, Ottosson M, 2018. Corrosion of copper in pure O2-free water? Corrosion Science 137, 1–12.

Hultquist G, Graham M J, Kodra O, Moisa S, Liu R, Bexell U, Smialek J L, 2015. Corrosion ofcopper in distilled water without O2 and the detection of produced hydrogen. Corrosion Science 95, 162 – 167.

Jambor J L, Dutrizac J E, Roberts A C, Grice J D, Szymański J T, 1996. Clinoatacamite, a new polymorph of $Cu_2(OH)_3Cl$, and its relationship to paratacamite and "anarakite". The Canadian Mineralogist 34, 61-72.

Johansson A J, Svensson D, Gordon A, Pahverk H, Karlsson O, Brask J, Lundholm M, Malmström D, Gustavsson F, 2020. Corrosion of copper after 20 years exposure in the bentonite field tests LOT S2 and A3. SKB TR-20-14, Svensk Kärnbränslehantering AB.

Karnland O, Olsson S, Dueck A, Birgersson M, Nilsson U, Hernan-Håkansson T, Pedersen K, Nilsson S, Eriksen T, Rosborg B, 2009. Long term test of buffer material at the Äspö Hard Rock Laboratory, LOT project. Final report on the A2 test parcel. SKB TR-09-29, Svensk Kärnbränslehantering AB.

King F, Quinn M J, Litke C, 1995. Oxygen reduction on copper in neutral NaC1 solution. Journal of Electroanalytical Chemistry 385 (1995) 45-55.

King F, Ryan S R, Litke C D, 1997. The corrosion of copper in compacted clay. AECL-11831, AECL, Canada.

King F, Lilja C, Pedersen K, Pikänen P, Vähänen M, 2010. An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geologic repository. SKB TR-10-67, Svensk Kärnbränslehantering AB.

King F, Kolář M, 2019. Copper Sulfide Model (CSM). Model improvements, sensitivity analyses, and results from the Integrated Sulfide Project inter-model comparison exercise. SKB TR-18-08, Svensk Kärnbränslehantering AB.

Korzhavyi P A, Soroka I L, Isaev E I, Lilja C, Johansson B, 2012. Exploring monovalent copper compounds with oxygen and hydrogen. PNAS 109, 686 – 689.

Lilja C, King F, Puigdomenech I, Pastina B, 2021. Speciation of copper in high chloride concentrations, in the context of corrosion of copper canisters. Materials and Corrosion, 72, 293-299. https://doi.org/10.1002/maco.202011778

Litke C D, Ryan S R, King F, 1992. A mechanistic study of the uniform corrosion of copper in compacted clay and soil. AECL-10397, AECL, Canada.

Ottosson M, Boman M, Berastegui P, Andersson Y, Hahlin M, Korvela M, Rerger R, 2017. Copper in ultrapure water, a scientific issue under debate. Corrosion Science 122, 53 – 60.

Pollard A M, Thomas R G and Williams P A, 1989. Synthesis and stabilities of the basic copper(II) chlorides atacamite, paratacamite and botallackite. *Mineral. Mag.* **53**, 557-563.

Puigdomenech I, Taxén C, 2000. Thermodynamic data for copper. Implications for the corrosion of copper under repository conditions. SKB TR-00-13, Svensk Kärnbränslehantering AB.

Sandén T, Nilsson U, 2020. Installation, monitoring, dismantling and initial analyzes of material from LOT test parcel S2 and A3. Results from field test. SKB TR-20-11, Svensk Kärnbränslehantering AB.

SKB 2011. SKB, 2011. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project. SKB TR-11-01, Svensk Kärnbränslehantering AB

Document ID
1920891, (2.0 Approved)

Security class
Public

Page
18(18)

Notes; Quality assurance - LOT meeting 3

SKB, 2019. Supplementary information on canister integrity issues. SKB TR-19-15, Svensk Kärnbränslehantering AB.

Svensson P D and Hansen S, 2013. Redox Chemistry in Two Iron-Bentonite Field Experiments at Äspö Hard Rock Laboratory, Sweden: An XRD and Fe K-Edge XANES Study. Clays and Clay Minerals 61(6). p.566-579.

Soroka I L, Shchukarev A, Jonsson M, Tarakina N V, Korzhavyi P A, 2013. Cuprous hydroxide in a solid form: does it exist? Dalton Transactions 42, 9585 – 9594.

Wersin P, Kober F (eds), 2017. FEBEX-DP. Metal corrosion and iron–bentonite interaction studies. Nagra Arbeitsbericht NAB 16-16, Nagra, Switzerland.

Woods T L, Garrells R M, 1986. Phase Relations of Some Cupric Hydroxy Minerals. Economic Geology 81, 1989-2007.