Document ID 1921850, (1.0 Approved) **Reg no**	**Security class** Public **Document type** Notes **Author** 2020-12-03 Lotta Rubio Lind	**Page** 1(11)

Notes; Quality assurance - LOT meeting 2

Date: November 13th, 2020

Participants: *Galson Sciences Ltd*, Tim Hicks, Tamara Baldwin
SSM, Bo Strömberg, Henrik Öberg, Jinsong Liu, Michael Egan
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.

This meeting was the second 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)

Retrieval, sampling, handling of samples and analysis

1. Pre-characterisation

TR-20-14 states up front that copper coupons were 'not intended or prepared for detailed corrosion analysis', but the 1998 LOT test plan (IPR-99-01) stated that the copper coupons and 'interesting' parts of the central copper tubes will be analysed to evaluate the mean corrosion rate, and to identify pitting corrosion and corrosion products. Some detailed corrosion analysis has been undertaken, although various caveats are noted in TR-20-14, such as lack of pre-characterisation of the surfaces of the copper coupons and tubes.

   a.   Why was the pre-characterisation not done?
   b.   How significant are the uncertainties associated with this lack of pre-characterisation?

That is, do these uncertainties significantly affect confidence in results?

SKB's reply/comment:
   a.   The importance of pre-characterisation at the microscopic level was probably not realised at the time of initiation of the experiments. In the 1990s, SKB's assessment of localised corrosion was mainly based on literature studies of pitting of copper pipes, archaeological artefacts etc.
   b.   The uncertainty is difficult to quantify, but it should be noted that the reference coupons had pits of similar magnitude as the corrosion coupons, despite the fact that their average corrosion depth was only about 10% of the corrosion coupons. Similar results have been obtained by comparison of corroded and reference specimens in ABM 5 (TR-18-17), a test

parcel from another experimental series similar to LOT. It may be further noted that even newly prepared and polished coupons, displayed pits of tens of µm (TR-18-14).

It is thus possible that the topography observed in LOT is due to initially occurring defects of mechanical origin that has later been affected by the corrosion process.

Discussion: It was discussed if it is possible to distinguish between pits formed by corrosion and mechanically induced pits. In the report TR-18-14 it is obvious what has caused the pits on the unexposed (reference) coupons. But for the LOT experiment it is difficult to say for certain due to the lack of pre-characterisation.

Probabilistic modelling of localized corrosion during initially aerobic repository conditions was discussed in the context of field tests like LOT and Febex.

Differences between Febex and LOT were discussed; e.g the FEBEX experiment was probably exposed to oxygen for a longer time period than LOT, (both due to the clay volume and possibly due to leakage via cables).

It was concluded that SKB assesses the measured pit depths on the LOT specimens conservatively by assuming that all pits are results of localised corrosion.

2. Milled or polished side

What is the significance of having a milled side and a polished side to the copper coupons?

SKB's reply/comment: The polished side was probably intended for the evaluation of localised corrosion. The milled side was examined with LOM since it was judged to be potentially more reactive than the polished side and because it more closely resembles the rough KBS-3 canister surface (P-12-22, P-13-50, P-17-11).

Examination of cross-sectioned coupons with SEM was done on the polished sides for one coupon from each test parcel. It may be noted that newly prepared and polished coupons (SiC, grit size P4000), also displayed pits of tens of µm (TR-18-14).

Discussion: It was discussed if there would be any advantage of polishing the copper canister. It may be noted that the main reason for localised corrosion would not be surface topography but rather passivation of the surface. Also, in the repository (as well as in field tests), localised corrosion during initially oxygenated conditions is a process limited by mass-balance.

3. Deviations from activity plan

Were any deviations from the activity plan for division and retrieval of the parcels necessary?

SKB's reply/comment: With respect to retrieval, there was the previously discussed issue with rock edges between boreholes which prompted additional drilling of core holes (meeting 1, question 8).

There were no deviations from the activity plan for division of the parcels.

Discussion: SKB handled the challenges with the seem drilling straightness during retrieval without affecting the copper samples, but it did increase the costs slightly and it took more time to retrieve the test parcels. The corrosion analysis was controlled by internal steering documents at Kimab and Swerim ,not by SKB's activity plans. There were no major deviations from the original plan for the corrosion analysis. The pickling method used in the gravimetric analysis had to be

tested and adjusted (as described in TR-20-14), however, that was not totally unexpected and is not regarded as a deviation in that sense.

4. Hand tools

Hand tools were used to extract the coupons so as not to damage or scratch them. What tools were used and was damage avoided?

SKB's reply/comment: First of all, the original design drawings for the LOT parcels were used to identify the positions of the coupons. Next, a metal detector was used to verify the position to an accuracy of about a few cm.

Finally, a rubber hammer and a wedge made of wood were used to remove the clay. When the edge of the wedge came close enough to the position of the coupons, the remaining clay typically divided in a way that part of the coupon was exposed.

Discussion: Two lessons learned from earlier retrievals of large-scale field tests were that it is difficult to remove compacted bentonite clay and that it is easy to scratch or damage small specimens inside the bentonite. SKB used these experiences and took several precautions when extracting the copper coupons. For example, the position of the copper coupons were determined from the original drawings from the assembly of the test parcels and the exact positions were verified using a metal detector. In this way, the extraction took longer time but it was successfully done, all eight coupons were retrieved without any damage.

5. Calibration

Were there any issues identified with regard to calibration and are calibration records available?

SKB's reply/comment:
- Analytical balance (Rise KIMAB): Calibrated annually.
- XRD (at Rise KIMAB): Calibration of the instrument is done on regular basis by measuring Corundum NIST standard sample. The peak position identification and offset calculation is then done using EVA Diffraction program available by Bruker.
- SEM-EDS (at Rise KIMAB): Typically, the calibrations for magnification and energy positions in the EDS spectra are checked every year during maintenance. Normally, there is no need to correct them since they vary very little over time. For EDS you will know directly if the calibration is wrong, since all peak positions will be off. Either everything is wrong or nothing. An experienced operator will notice if anything is wrong.
- TEM (at Swerim): Magnification calibration, i.e. the scale bar for imaging and also for diffraction in the TEM, may not be more accurate than +/-5%. For diffraction, typically calibratation/normalization is done using a known phase before extracting the data, e.g. pure Cu.
- Regarding XRF for bentonite analysis, the instrument has an internal calibration named Omnian from Panalytical.
- SEM for bentonite had an internal calibration function.

Regarding test sensors there are also calibration protocols available.

Discussion: Overall the heating and temperature sensors have operated well. The heating system was updated with new components in September 2014 which resulted in a small drop in temperature, however, it does not affect test results in any significant way. This is reported in TR-20-11.

Calibration of scales at the laboratory at Äspö was discussed. SKB's water chemistry laboratory is an accredited laboratory and has routines for these types of calibrations which are also implemented in the Material research laboratory where the majority of SKB's internal bentonite analyses are done (the SEM is located at the Canister laboratory).

6. O content

The tube copper had a higher O content than the Cu-OFP used in the copper disposal canisters. What is the significance of the difference in Cu grade in terms of possible corrosion rates and mechanisms?

SKB's reply/comment: The difference is probably of low significance but we found it appropriate to mention. However, no conclusions in the report TR-20-14 are based on this difference. The main difference is the content of P and O. Cu susceptible to H sickness typically has ~10^2 wt-ppm O.

	O (wt-ppm)	P (wt-ppm)
Cu-OFP	<5	30-70
SS 5015-04	~30	150-400

Discussion: The difficulties of comparing different field experiments were discussed. SKB considers it difficult to compare coupons and pipes in the LOT experiment since they have to be examined with different method due to their size and degree of pre-characterisation.

SSM mentioned that preliminary results based on electrochemical potentiodynamic measurements suggest that pure copper is more prone to passivation as compared with OFP-copper. There are, however, still no definite results.

7. Reference materials

Regarding the reference materials:
   a. Was any pre-characterisation work done on the reference coupons and reference tube?
   b. Have estimates been made of the rate and type of any corrosion expected on the reference coupons and tube during dry storage? In Section C1.2, it is noted that there is cuprite on the reference coupons.
   c. Table 3-3 of TR-20-14 indicates that, during storage, the reference coupons corroded more than the test coupons. Was this expected, or is it possible that what is seen on the reference coupons are surface defects that could be present on manufacture?
   d. Would there be any benefit in looking further at the surface of newly prepared copper to understand its characteristics and surface defects on manufacture (as noted in Section 4.3)?

SKB's reply/comment:
   a. No pre-characterisation was made (see reply to Q1).
   b. Photos of the reference coupons and pipe are shown in Fig A-11 and A-16 in TR-20-14 and it's evident that some oxidation has occurred during storage.
   c. The reference coupons were analysed gravimetrically and the total mass-loss corresponded to 0.07 and 0.16 µm corrosion for the two coupons (Table 3-2, TR-20-14). The data in Table 3-3 are pits/defects; these are not necessarily related to corrosion as explained in reply to Q1 and Q2.
   d. In general, yes, to facilitate interpretation of future field tests. Especially older field tests in which the importance of microscopic pre-characterisation wasn't fully realized. Must be

done by preparing new coupons according to the same method as the corroded specimens, e.g. regarding cutting technique and polishing depth and/or fineness.

Discussion: It was discussed whether it would actually be useful to evaluate newly prepared surfaces, since it would require detailed documentation of the preparation of the specimens in order to be comparable.

SKB mentioned that the preparation of specimens of the MiniCan experiment is well documented, but for the LOT experiment SKB is not sure if it would be possible or even meaningful due to interpretation difficulties. The LOT coupons were prepared at Studsvik more than 20 years ago.

8. Microbes

Regarding microbes:
a. IPR-99-01 stated that microbial populations in groundwater will be analysed before emplacement and at the end of the experiment and that bentonite samples will be examined for microbial populations. Was information on microbial populations obtained?
b. How was information at the start of LOT recorded and stored, and was information about preparation of the bacteria samples managed separately to result in the information being lost?

SKB's reply/comment:
a. Microbes in Äspö groundwater have been studied in several projects and close to the LOT site is the Microbe site with measurements reported in *IPR-00-36 The microbe site, Drilling, instrumentation and characterization.* With respect to groundwater measurements, no specific measurements were made in LOT, so available data is from these nearby experiments. It should be noted that there are quite large local variations.
b. Data were stored in SICADA from the start. For example, there is 47 SICADA activity Ids stored regarding the first two pilot parcels. Information regarding bacteria in the bentonite plugs is not lost; the work which has been done is described in *TR-00-22 Long term test of buffer material. Final report on the pilot parcels* and *TR-09-29 Long term test of buffer material at the Äspö Hard Rock Laboratory, LOT project. Final report on the A2 test parcel.* Bacteria in the plugs at the termination of the pilot parcels are reported in TR-00-22, chapter 7. Furthermore, Appendix 1 in TR-09-29 covers the bacteria work for A2. By mistake data concerning bacteria placed on the copper coupons at installation were not stored. That work was part of LOT and was not managed separately (however done by another contractor, Micans, but it should be noted that SKB is always responsible for the final documentation).

Discussion: SKB have been in contact with he supplier that prepared the coupons with bacteria before test installation. It is considered likely that the bacterial media contained sulfate reducing bacteria (SRB), since these are considered as the microorganism having the most potential influence on the corrosion process, however, by mistake the documentation of this information has been lost.

It was discussed if any studies of bacteria could have been done on the sand that is underneath the test parcels but since copper does not interact with sand in the KBS-3 system, it has not been studied at this stage.

It was discussed why there was an 8 m pilot hole drilled when the test parcels are 4 m. Hydraulic testing is reported in TD-99-25 Äspö Hard Rock Laboratory, Long term test of buffer material, Hydraulic tests in five boreholes in the G-tunnel of Äspö HRL, however, it has not been

Document ID
1921850, (1.0 Approved)

Security class
Public

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documented why 8 m pilots were used, possibly to get a better picture of the area close to the experiments.

9. Saline water

The formation water supplied to the boreholes was observed to become more saline and alkaline over the duration of the test. Is there an explanation for these changes and could they influence copper corrosion mechanisms or bentonite behaviour in any significant way?

SKB's reply/comment: SKB has not done an in-depth analysis on the water in the area closest to LOT, however, 'upconing', when more saline, deeper, water rises towards the tunnel system is frequently observed at Äspö and is most likely the explanation also in this case.
With respect to affecting the bentonite the changes will have only marginal effect on the bentonite properties, see for example *TR-06-30 Mineralogy and sealing properties of various bentonites and smectite-rich clay materials*
There is very little Cl on the copper surfaces, typically <1 at-% and a few observations of up to ~3 at-% locally. This is similar to (or less than) what was found in LOT A2 (TR-09-29) and Prototype Repository (P-12-22).

Discussion: It was discussed why there is so little Cl at the copper surface. SKB states that the salinity is difficult to compare with previous test parcels since they were not analysed in the same way or to the same extent as LOT S2 and A3.

10. Monitoring corrosion potential

Why was monitoring of the corrosion potential of the copper or redox potential not attempted during LOT?

SKB's reply/comment: In general, the main focus of the LOT series was not copper corrosion. However, attempts were made to measure corrosion rates electrochemically by an electrode system installed in the test parcel LOT A2. Rate measurements were made but there was no recording of E_{corr} (Rosborg and Pan, Electrochimica Acta 53 (2008) 7556–7564).

E_h was regarded as practically unfeasible to measure in compacted bentonite in the 1990s, especially in a field test where it is difficult to install and maintain a reference electrode on long time-scales.

11. SEM cross-section analysis

Tube samples were chosen for SEM cross-section analysis based on visual appearance (Section 2.3). What criteria were used to judge the area to select?

SKB's reply/comment: It was decided to sample "type-areas" based o their visual appearance, for example light (Cu coloured), dark/black, and with grey deposits (could be bentonite and/or gypsum). This is shown in figures G1-G5 in TR-20-14. As exemplified for area 1 for the pipe sample from A3, several cross-sections were examined for each area (Fig G6 in TR-20-14).

Discussion: SKB believes that sampling "type-areas" was an appropriate way to choose samples for the analysis. It should be noted that the darkest parts are not necessarily the most corroded, since corrosion products may in some cases adhere to the bentonite surface in contact with the pipe.

SKB has examined parts that were exposed to temperatures relevant for the repository. The pipe sections in blocks 21-23 were also selected for practical reasons, that is, they were in the same bentonite blocks as the coupons. Other parts of the pipes have been stored at Äspö HRL and could still be analysed.

It was discussed whether the thermal gradient in the experiment can affect the corrosion depth (and rates). Due to this gradient the oxygen will be transported from the cooler part and it can cause a higher corrosion rate at the warmest part of the pipe. This could mean that the corrosion rate is overestimated for the warmer part, while underestimated for the cooler part, as compared with the situation without an axial thermal gradient along the pipe. It was noted that such an axial thermal gradient would not be present in the repository, where the temperature increase is caused by spent fuel residual heat rather than an electric heater.

12. Mass loss measurements

What is the accuracy of the mass loss measurements?

SKB's reply/comment: The accuracy of the gravimetric analysis done at Rise KIMAB was +/- 0.00009 g.

Discussion: The pickling process was discussed. It is a standardised methodology using a reference copper sample.

13. XRD results

Regarding the XRD results, Figure C-2 shows a peak at position 42 for coupon A3/K. The peak is attributed to Cu_2S, but isn't it Cu_2O? Also, on a close look, the peak at position 30 seems to coincide with a small Cu_2O peak rather than bentonite clay. Any correspondence with components of bentonite clay does seem very weak.

SKB's reply/comment: It is a mistake in the report, the peak at 42 corresponds to Cu_2O. Cu_2S peaks should be at 37, 46, and 48. Peaks are weak but present on several samples.

SKB agrees that the peak at 30 seems more like Cu_2O than bentonite, although we don't see that this is commented on in the report. Other peaks from bentonite are present in the diffraction patterns for some coupons, e.g. the peak at 22 for coupon A3/K and A3/I.

Discussion: The precision of the methods used was discussed broadly.

SKB clarified that the peak at 22 corresponds to bentonite. The bentonite is not evenly distributed over the coupon surface and the samples have to be washed with deionized water before the analysis otherwise the bentonite layer would be too thick.

14. C contamination EDS

What is the source of the C contamination noted in the EDS results (e.g. Figure C-46)?

SKB's reply/comment: The contamination is typically a few monolayers on the surface, covering the whole sample surface, but sometimes more. In SEM and TEM, the electron beam attracts adsorbed carbon and hydro carbons, so that carbon migrates to the beam and is there cracked and builds up a layer of carbon in the area which the beam scans. During an EDS analysis, the beam scans the same area for a long time, so a lot of carbon can build up. In SEM, the vacuum is lower, so even more carbon can end up on the sample from parts inside the chamber.

It may be noted that EDS data both including and excluding C is presented in Appendix C. There is no major impact on the evaluation of the levels of other elements due to C (See e.g. Fig C-46).

15. Zinc contamination

Has any reason been found for the detection of zinc in the reference coupons?

SKB's reply/comment: The source of Zn on the reference coupons is unclear, we did not identify a source of zinc, and nothing in the handling of the samples at Rise KIMAB should have contaminated the samples. Possibly, there was an unknown source for Zn in the laboratory at Clay Technology where the reference specimens were stored for over 20 years.

16. Bentonite composition or fingerprint

For the EDS analysis (Section 3.3), would it be possible to identify a bentonite composition or fingerprint that would enable the bentonite component to be removed from the EDS results to give clearer focus on the corrosion product composition?

SKB's reply/comment: Rise KIMAB has replied; the problem is that the quantification is not so accurate when there are several phases in the same position/pixel. Also, the bentonite doesn't seem to be homogeneously distributed. It contains a lot of small nanoparticles, so the composition is not the same in different positions. There is sometimes water present. What you get is only a mean composition, which may vary spatially. Therefore, you don't know what composition to deconvolute and the EDS results should mainly be used in a qualitative way.

17. EDS analysis Cu_2S

The EDS analysis (Section 3.3.1 and Appendix C) does appear to consistently indicate a Cu_2S phase at the surfaces of the coupons that were at cooler temperatures (block 30) but not at the surfaces of the coupons that were warmer (block 22). Is there any explanation for this? Is it statistically significant? The results for tube sample S2 (Figure 3-20) appear to contradict this so perhaps it is not significant.

SKB's reply/comment: There is some support of this observation in the EDS analysis made for larger areas (mm^2) of the coupons (Table 3-1). The same trend is not seen in the corresponding data for the pipes (Table 3-5), however, the data set is small.

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Table 3-1. EDS data of copper coupons at 100× magnification (at%).

Coupon	Block	O	Si	S	Cu	Ca	Fe
A3/I	22	50.8	12.1	2.0	22.6	3.1	0.4
A3/J	22	68.7	3.2	0.7	23.7	1.6	0.2
A3/K	30	28.7	5.7	7.8	53.9	0.3	0.2
A3/L	30	34.9	8.7	8.7	42.4	0.4	0.3
S2/M	22	40.2	10.5	2.2	37.3	0.5	0.3
S2/N	22	37.3	10.3	1.5	44.3	1.4	0.3
S2/O	30	38.7	9.3	5.9	38.5	0.5	0.3
S2/P	30	40.9	11.5	7.3	33.3	0.4	0.4

Table 3-5. Selected EDS data of copper pipe samples at 100× magnification (at%).

Sample area	O	Si	S	Ca	Fe	Cu
A3 pipe "white"	46.2	10.5	12.3	21.1	1.1	3.5
A3 pipe "dark"	29.1	16.9	4.2	1.2	1.1	38.2
S2 pipe "Cu"	16.4	7.9	1.3	2.1	0.7	61.6
S2 pipe "dark"	23.4	16.0	3.7	1.2	1.4	41.8

Discussion: It was concluded during the discussion that the small number of observations makes it difficult to draw any conclusions. It was mentioned that sulphide comes with the groundwater, which may not have been evenly distributed in the test parcels.

18. Diffraction analysis

The diffraction analysis (Section C1.4.3) appears to provide a means of identifying the composition of corrosion products, but the discussion is complex and the d values to compare with 1/d do not seem to be provided. Will a more detailed explanation and results be published?

SKB's reply/comment: Swerim has replied; It is not possible to unambiguously determine which phase(s) exist in the samples as there are so many small particles close to each other and each diffraction pattern obtained usually contains information from several different phases. When these phases have similar d-values and in many cases almost the same, it is not possible to distinguish which phase it is with our TEM equipment. This is further affected by the fact that it is not possible to get a better accuracy than about +/- 5% on all values. The accuracy does not depend on the calibration of the instrument but on a number of factors during measurement and postprocessing of data.

Discussion: SSM and SKB agree that TEM is an interesting method for trying to distinguish between different corrosion products. SKB will continue exploring this method.

19. Figure D-7 Cu_2S

In Figure D-7, it is not convincing that Cu_2S is being indicated as present on coupon S2/P. Is the figure showing the reflections discussed in Section C1.2 rather than a signal for Cu_2S?

SKB's reply/comment: Yes, but on peak 49 there is a small "shoulder", which is Cu_2S, according to Swerim. It is not very clear but it is an indication. SKB noted that the stoichiometry of Cu2S is

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also in agreement with the Cu:S ratio obtained from TEM-EDS, which supports the interpretation that Cu2S was formed.

20. The purpose of the H measurements

What is the purpose of the H measurements? Is it to provide evidence to support arguments that hydrogen embrittlement doesn't occur?

SKB's reply/comment: The purpose of the H measurements was to investigate whether there was any uptake of H in the copper material, which could potentially lead to embrittlement effects.

Discussion: It was discussed whether H-loading could occur in the experiment. During sulphide corrosion it would in principle be possible, but in this experiment the extent of sulphide corrosion was very low (which is expected due to the low sulphide concentration in the groundwater and the slow inflow of groundwater through the bentonite).

21. Timescale for oxygen consumption

Could the measured amount of corrosion and the expected rate of corrosion give an indication of the timescale for oxygen consumption in LOT?

SKB's reply/comment: The rate of corrosion has probably changed significantly during the initial period of exposure. Integrated corrosion rates are discussed in TR-20-14 for both coupons and pipes, however these will underestimate the initial corrosion rates and overestimate the long-term rates. Comparison with data from LOT A2 shows a clear decrease in the integrated corrosion rates for all types of copper surfaces.

It may be noted that laboratory experiments with copper in bentonite under aerated conditions reported gravimetrically determined corrosion rates of 100-200 µm/y for the first month at 50-80°C (Litke C et al., 1992. A mechanistic study of the uniform corrosion of copper in compacted clay and soil. AECL-10397, AECL, Canada.) This implies that the depletion of O_2 could be rapid. However, this doesn't mean that the environment becomes reducing, since Cu(II) may be present for longer periods (TR-10-67, TR-18-08).

Discussion: This issue was only discussed briefly and was planned to be discussed further at the third meeting (2020-11-27).

22. Coupon S2/P

Are there any further views on why coupon S2/P was less corroded than other coupons?

SKB's reply/comment: Not really, but it may be noted that the corrosion of gravimetric specimens in earlier LOT test parcels and the similar ABM 5 experiment showed variation both within and between test parcels, which is also discussed in section 4.2.1 in TR-20-14.

Discussion: Why this variation occurs was briefly discussed. It is unclear if variation in transport conditions or chemical variations can have an effect.

23. Correction factor (the issue was added at the meeting)

Discussion: The correction factor mentioned by Peter Szakalos was discussed. This means that corrosion estimated from measurements of copper in the clay needs to be multiplied with a factor in order to capture the total corrosion depth, i.e. including adherent corrosion products- SKB has measured copper in the bentonite adjacent to coupons and adherent corrosion compounds at the surface of the coupon samples. This was then compared with the mass loss of copper from the

sample. This method performs quite well, since the adherent layer of corrosion products was generally very thin (ca 1 µm). SKB did not apply a correction factor. It was also noted that the estimate of corrosion from copper in the clay is not a standard method.

This issue will be further discussed at the third meeting.