



## Review meeting LOT experiments (ii)

- (i) Management system & project management
- (ii) **Retrieval, sampling, handling of samples & analyses**
- (iii) Interpretation of results.

# Question 1 – Pre-characterisation



1. 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 precharacterisation?

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

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, SKBs assessment of localised corrosion was mainly based on literature studies of pitting of copper pipes, archeological artifacts 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 in the ABM 5 test parcel (TR-18-17). It may be further noted that even newly prepared and polished coupons, displayed pits of tens of  $\mu\text{m}$  (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.

# Question 2 – Milled or polished side



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

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  $\mu\text{m}$  (TR-18-14).

# Question 3 - Deviations activity plan



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

With respect to retrieval, there was the previously discussed issue with rock edges between boreholes which prompted additional core holes (meeting 1, question 8).

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

# Question 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?

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.

# Question 5 - Calibration



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

Analytical balance (Kimab): calibrated annually.

XRD (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 (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 (Swerim): Magnification calibration, i.e. the scale bar for imaging and also for diffraction in the TEM, may not be more accurate than  $\pm 5\%$ . For diffraction, we typically calibrate/normalize against 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

# Question 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?

The difference is probably of low significance but we found it reasonable to mention. No conclusions in the report are based on this difference.

The main difference is the content of P and O.

Cu susceptible to H sickness typically has  $\sim 10^2$  wt-ppm O.

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

# Question 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)?

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 and it is 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  $\mu\text{m}$  corrosion for the two coupons (Tab 3-2, TR-20-14). The data in Tab 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 pre-characterisation wasn't made properly. 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.



# Question 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?

Microbes in Äspö groundwater has 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 ones were made in LOT, so available data is from these nearby experiments. It should be noted that there is quite large local variations so it does not entirely answer the original question.

- a. 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?

Data was stored in SICADA from the start. For example, there is 47 SICADA activity logs stored regarding the first two pilot parcels.

Bacteria information on 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 is reported in TR-00-22, chapter 7. And Appendix 1 in TR-09-29 covers the bacteria work for A2.

Regarding the bacteria placed on the copper coupons at installation it was not stored, i.e., a mistake was made at that time. That work was part of LOT and was not managed separately (however done by another contractor).

# Question 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?

We haven't 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 noticed 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).

# Question 10 – Monitoring corrosion potential



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

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  $E_{\text{corr}}$  (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.

# Question 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?

It was decided to sample “type-areas” based on 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.



# Question 12 - Mass loss measurements?



What is accuracy of the mass loss measurements?

The accuracy of the gravimetric analysis done at Rise Kimab was  $\pm 0.00009$  g.

# Question 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  $\text{Cu}_2\text{S}$ , but isn't it  $\text{Cu}_2\text{O}$ ? Also, on a close look, the peak at position 30 seems to coincide with a small  $\text{Cu}_2\text{O}$  peak rather than bentonite clay. Any correspondence with components of bentonite clay does seem very weak.

It is a mistake in the report, the peak at 42 corresponds to  $\text{Cu}_2\text{O}$ .  $\text{Cu}_2\text{S}$  peaks should be at 37, 46, and 48. Peaks are weak but present on several samples.

Agree that the peak at 30 seems more like  $\text{Cu}_2\text{O}$  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.

# Question 14 - C contamination EDS



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

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 where 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 other 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).

# Question 15 – Zinc contamination



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

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 Tech where the reference specimens were stored for over 20 years.



# Question 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?

Kimab: 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.

# Question 17 - EDS analysis Cu<sub>2</sub>S



The EDS analysis (Section 3.3.1 and Appendix C) does appear to consistently indicate a Cu<sub>2</sub>S 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.

There is some support of this observation in the EDS analysis made for larger areas (mm<sup>2</sup>) 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.

**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

# Question 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?

Swerim: 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 effected by the fact that it is not possible to get a better accuracy than about  $\pm 5\%$  on all values. The accuracy does not depend on the calibration of the instrument but on a number of factors during measurement and post processing of data.

# Question 19 - Figure D-7 $\text{Cu}_2\text{S}$



In Figure D-7, it is not convincing that  $\text{Cu}_2\text{S}$  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  $\text{Cu}_2\text{S}$ ?

Yes but at 49 there is a slight “shoulder” on the peak, which is  $\text{Cu}_2\text{S}$  we believe. It is not very clear but it is an indication.

# Question 20 - 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?

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.

# Question 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?

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  $\mu\text{m}/\text{y}$  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  $\text{O}_2$  could be rapid. However, this doesn't mean that the environment becomes reducing, since  $\text{Cu(II)}$  may be present for longer periods (TR-10-67, TR-18-08).

# Question 22 - Coupon S2/P



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

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.