

Comments regarding the two remaining papers, referred by SKB as concerning anoxic copper corrosion

These two papers was previously sent to the expert panel and referred as follows by SKB:

- 5) Application of an On-line Corrosion Probe and a Reference Electrode for Copper Corrosion Studies in Repository Conditions
I. Betova, J. Heinonen, P. Kinnunen, C. Lilja, E. Ruokloa, T. Saario,
Mat. Res. Soc. Symp. Proc. Vol. 807, p. 429-434
- 6) Corrosion of copper in 1 M NaCl under Strictly Anoxic Conditions
M. Bojinov, T. Laitinen, K. Mäkelä, M. Snellman, L. Werme
Mat. Res. Soc. Symp. Proc. Vol. 807, p. 459-464

We like to add papers (5B) and (6B) since they add important information regarding Refs. (5) and (6).

- 5B) STUK-YTO-TR 206 (2004)
- 6B) POSIVA report 2003-45

It is stated in (6) that the corrosion is notable up to 3-4 days of exposure at room temperature and then it becomes negligible. This is based on an "On-line Corrosion Probe and a Reference Electrode for Copper Corrosion Studies in Repository Conditions"

However, there are some questions regarding the "On-line Corrosion Probe" that should be discussed. The corrosion or penetration depth is a function of the copper probe resistance and the instantaneous corrosion rate is a function of the differential coefficient (derivative), see Ref. 5B, page 13.

The POSIVA report (6B) was the base for the publication (6). Fig. 4 in Ref. (6) is the same as Fig. 12 in Ref. (6B) and it is understood that this 3-day graph is a cut from the 30 day exposure data as shown in Fig. 10a and 10b.

By cutting out the first 3-days corrosion data and exclude the rest of the 30 days data, it might give the impression that the probe works satisfactory in measuring the corrosion rate. However the total picture is quite disappointing as the derivative and thus the corrosion rate varies

roughly in the range of $-50 \mu\text{m}/\text{year}$ to $+50 \mu\text{m}/\text{year}$ during the 30 day exposure as seen in Fig 10, Ref 6B.

Additionally, there is no correlation between weight loss measurement and the “On-line Corrosion Probe” results. In page 5, Ref. (6) it is stated that the total weight loss was 12.1 mg at RT after 30 days exposure and that “Assuming that the total weight loss occurs during the first 5 days of exposure, we estimate the penetration depth of corrosion as $1.6 \mu\text{m}$, in good agreement with the wire probe results” However, in Ref. 6B, pages 9 and 11 it is clear that the exposed surface area was $3 \times 14 = 42 \text{ cm}^2$ (RT-exposure) which gives $12.1 \text{ mg} / 42 \text{ cm}^2 / 8.9 \text{ g cm}^{-3} \times 10 = 0.32 \mu\text{m}$ in penetration depth. This means that the probe, overestimated the corrosion rate by five times ($1.6/0.32 = 5$) in this particular example.

The error is even larger when studying the 80°C exposure with Oxisorbe. In Chapter 2, “Methods”, in Ref (6B), it can be understood that six samples were exposed at 80°C , i.e. $6 \times 14 = 84 \text{ cm}^2$ exposed copper surface. In Ref. (6), page 3 it is stated that the weight loss is 14.6 mg thus: $(14.6 \text{ mg} / 84 \text{ cm}^2) \times (365/6) \times 10 = 11.8 \mu\text{m}/\text{year}$.

It is stated on page 3 in Ref. (6) that the average corrosion rate during the 6 days exposure was $11.8 \mu\text{m}/\text{year}$ (OK!), i.e. $0.19 \mu\text{m}$ in penetration during six days. The probe, see Fig. 2, Ref. (6), indicate a penetration depth of $4.7 \mu\text{m}$ which is roughly 25 times higher.

It is notable that the corrosion probe of copper corroded which resulted in a total failure already after 3.5 days during one exposure at 80°C as discussed in both reports, Refs. (6) and (6B).

The experimental conditions in Refs. (5) and (5B) are similar with Cu exposed in highly saline groundwater, HSGW (1.52M chloride) and compacted bentonite at different pressures. The “On-line Corrosion Probe” was used in both reports. In Ref. (5B), page 13, it is stated that the corrosion takes place during the first 100h and is “practically zero at exposure times exceeding 100h”. The corrosion depth in Fig. 6a is around $1.7 \mu\text{m}$ during the first 100h or around $150 \mu\text{m}/\text{year}$ (positive values). The corrosion depth in Fig. 7a is around $-0.35 \mu\text{m}$ during the first 100h or $-31 \mu\text{m}/\text{year}$ (negative values!). The only difference between the exposures is the degree of bentonite compaction, 4,5 and 10 MPa respectively. The situation is confusing and the “On-line Corrosion Probe” seems again unreliable.

The last example is seen in Fig. 2 in Ref. (5) where it can be seen that the corrosion, according to the “On-line Corrosion Probe” takes place

during the first 3 hours with a penetration depth of 4.7 μm . This corresponds to a corrosion rate of 13700 $\mu\text{m}/\text{year}$ during the initial period and after that, the corrosion rate is assumed to be zero. Again, the reliability of the probe should be questioned since these corrosion kinetics are astonishing. One conclusion that should be drawn is that the "On-line Corrosion Probe" is not reliable in complex environments like saline groundwater with or without bentonite clay and not over time.

General comment:

We have published five peer-reviewed papers and one comment regarding anoxic copper corrosion. SKB has referred to two publications in peer-reviewed journals that was claimed to being conducted in anoxic or O_2 -free water solutions, (T.E. Eriksen et al. Corr. Sci., Vol. 29, No. 10, p. 1241,1989) and (J. P. Simpson and R. Schenk, Corr. Sci. Vol. 27, No 12, p. 1365, (1987), both papers has been disregarded since the conditions was not anoxic.

SKB has now referred to two MRS-publications, Refs. (5) and (6), which both relies on an "On-line Corrosion Probe". The reliability of this probe in complex environments is seriously questioned.

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