

## **Comments to Karnland and Birgerssons memorandum regarding the Swedish National Council for Nuclear Waste seminar "Mechanisms of Copper Corrosion in Aqueous Environments"**

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Karnland and Birgersson have made questionable comments regarding our presentation at the National Council for Nuclear Waste seminar "Mechanisms of Copper Corrosion in Aqueous Environments" (16<sup>th</sup> of November 2009).

Firstly we find it odd that Karnland and Birgersson claim that we had eighty five (85) PowerPoint slides in our presentation at the seminar. This is remarkable since we had only twenty four (24) slides in our public presentation. Of the unpublished extra material, in total 61 slides, only a few were shown during the afternoon discussion. Despite this fact, all 85 slides seem, most unfortunately, represent the background material for Karnland and Birgersson's memorandum.

In response to Karnland and Birgersson we want to discuss and clarify some important issues regarding the scientific basis of our presentation – a presentation that is supported by facts from published scientific material.

Of some 30 years research, the LOT-project is the only one that has semblance to a full-scale test in a repository environment and for which results have been published. Even here some crucial parameters are still lacking such as mechanical load, salt concentration due to water evaporation, irradiation and radiolysis of water. The project is performed with groundwater in the Äspö hard rock laboratory, approximately 450 m down in the Swedish bedrock. However, the results obtained in the project so far have not been according to SKB AB's expectations, especially regarding copper corrosion:

- No copper was found on the expected smectite exchange sites in the bentonite clay<sup>1</sup> (From Abstract in Appendix 6)
- Instead, a large amount of copper corrosion products<sup>1</sup> was found to precipitate on the huge surface area created by the bentonite particles thus indicating severe corrosion<sup>2</sup> (see page 5). According to our judgement the maximum corrosion rate on the heated central copper tube could at least be 10 µm/year during the five year exposure (discussed below).

It is stated in Ref. 1 (Appendix 6, page 9) regarding copper detected in the bentonite at different distances from the central copper tube in the LOT-project: "First of all a surprisingly high content of Cu was found even within the 1<sup>st</sup> cm indicating that a) Cu corrosion occurred and b) led to penetration of Cu into the bentonite. Even the 50 mg/kg which were observed in the 40 mm sample" likely result from Cu migration."

It must, therefore, be concluded that the copper canister and the bentonite clay are not independent "barriers" since they both interact by a simultaneous degradation process, i.e. by dissolution-precipitation copper corrosion<sup>2</sup> (page 5).

In a situation with a limited amount of water or low flow rates of water (irrespective whether the conditions are oxic or anoxic), such as in a repository environment, it is thermodynamically expected that a solid corrosion product will be formed also on the copper surface. This was confirmed by Rosborg within the LOT-project<sup>3</sup> and by King in laboratory studies<sup>4</sup>.

Karnland and Birgersson, on the other hand, calculated the copper corrosion rate in the memorandum *only based on the copper detected in the bentonite*, omitting the corrosion products on the copper surface, which is obviously wrong. By comparing the weight loss measurement of the copper coupons and the measured amount of copper in the bentonite, it is clear that a significant part of the copper corrosion product is formed on the copper surface<sup>3,4</sup>, as expected.

Thus the maximum copper corrosion rate could easily be higher than 10 µm/year at the heated part of the central copper tube in the LOT project as mentioned above. In fact, King reported much higher copper corrosion rates than 10 µm/year in his laboratory study in bentonite/groundwater. After two years, the corrosion rate stabilises at as high levels as 20 µm/year in the temperature range 50-100°C<sup>4</sup>. Furthermore, it was concluded in the same study that “O<sub>2</sub>-transport was not rate-limiting” and that a significant part of the copper detected in the bentonite was a result of corrosion by a dissolution–precipitation process.

It was believed some 20 years ago that dissolved oxygen in bentonite pore water in a deep repository would be consumed very slowly, i.e. over several years. However, it has been found in more recent years that oxygen is consumed within days or first weeks of exposure<sup>5-8</sup>. For instance, in Ref. 5, SKB report TR-01-05 (the REX project) entitled “O<sub>2</sub>-depletion in granitic media” it is stated in the abstract regarding the studies in the Äspö hard rock laboratory: “The results from the in-situ experiments were confirmed by those of the replica experiment performed in the CEA laboratory in France. Both were concordant in showing time scale for O<sub>2</sub> uptake in the order of days.” In Ref. 7 it is shown (Fig. 2) that oxygen is consumed within six days irrespective bentonite/water temperature. The same behaviour is observed in a POSIVA study in bentonite/saltwater, see Ref. 8, pages 12-13. In another SKB project, “Mini Can” it is stated on page 48, Ref. 9, that “anoxic condition existed in the boreholes” nevertheless the measured copper corrosion rates was again several µm/year, as shown in Figure 6-33.

An important conclusion from the above is that copper corrosion by dissolution-precipitation in a deep repository environment is mainly an anoxic process following the rapid oxygen consumption with formation of anoxic corrosion products such as CuS, (Cu,Fe)S and Cu<sub>2</sub>O and complex copper chloride hydroxides, as detected in the LOT-project<sup>1,3</sup>.

A more important scientific fact is that copper corrosion rates are *always* reported to be in the µm/year range irrespective of copper quality or oxic/anoxic condition<sup>2,10</sup>. Thus SKB’s safety analysis underestimates the copper corrosion rate by a factor of between 1000-10.000 times, as pointed out in our presentation at the seminar.

## References

- [1] SKB TR-09-29, LOT project, parcel A2. Appendix 6, S. Kaufhold, R. Dohrmann, BGR, Germany.
- [2] SSM Dnr: 2009/2639. IN\_2009-12-15. Comments to the BRITE report. Also available at: <http://www.mkg.se/kth-forskarna-svarar-pa-myndighetens-brite-rapport-om-kopparkorrosion>
- [3] SKB TR-09-29, LOT project, parcel A2, Appendix 3. B. Rosborg, Rosborg Consulting.
- [4] F. King et al. Corrosion Science, vol. 33, no 12, p 1979 (1992)
- [5] SKB TR-01-05, "O<sub>2</sub>-depletion in granitic media".
- [6] C. Lazo et al. Mater. Res. Soc. Proc. 757, (2003) pp. 643-648.
- [7] T. Carlsson et. al, Mater.Res. Soc. Symp. Vol.1124 (2009)
- [8] POSIVA WR 2007-62. Copper Corrosion in Bentonite.
- [9] SKB-TR-09-20 "Miniature canister corrosion experiment"
- [10] C. Leygraf and S. Seetharaman, answers to questions about copper corrosion raised by Kärnavfallsrådet, [http://www.karnavfallsradet.se/sites/default/files/dokument/10-03\\_Copper\\_corrosion\\_in\\_deoxygenated\\_water.pdf](http://www.karnavfallsradet.se/sites/default/files/dokument/10-03_Copper_corrosion_in_deoxygenated_water.pdf)