

Memorandum concerning the use of results from the LOT project at the Swedish National Council for Nuclear Waste seminar "Mechanisms of Copper Corrosion in Aqueous Environments"

Compiled by Ola Karnland and Martin Birgersson (project management for the LOT project)

Background

Eleven of totally eighty five PowerPoint slides in the presentation of Dr. Peter Szakálos referred to the ongoing LOT-project. The majority of these slides contained incorrect information to such an extent and of such character that we find it necessary to point this out. We would like to stress that the following comments concern obvious factual errors, and are not a question of different interpretations of the results.

LOT-tests

In the LOT project, test parcels are used which simulate KBS-3 repository-like conditions, and test parcels in which harmful processes are accelerated. All test parcels are placed in bore-holes at 450 m depth in the SKB Rock laboratory in Äspö, Sweden. In each test parcel there is a central, heated copper tube which simulates the copper canister in a repository. The copper tube is surrounded by bentonite, which contains measuring equipment and various test materials. At installation, the bentonite contains air, which is entrapped when the bentonite starts to absorb ground-water from the surrounding rock. The air is thereby successively concentrated at the central copper tube. The oxygen in the air is expected to react with the copper and with minerals in the bentonite. The test parcels are retrieved after different exposure times in the rock, and comprehensive analyses and tests are performed. The main purpose with the LOT-project is to study the bentonite clay properties and long term stability. In addition, minor special studies are performed concerning copper corrosion, cation diffusion and bacterial activity in the bentonite. In total, 9 independent laboratories in 5 countries were involved in the analyses of the latest retrieved test parcel (A2). Specially designed and well characterized copper coupons are used in the corrosion study and not the central copper tube. The main reasons for this are to achieve correct boundary conditions and to use a relevant copper quality. A central tube of copper is used to admit analyses of possible impact of released copper on the bentonite. More detailed information is available in the SKB reports TR-00-22, TR-09-29 and TR-09-31.

Comments on Dr Szakálos' presentation.

Item 1

Results from the German laboratory BGR concerning copper content around the central copper tube in the LOT A2 experiment were used in the presentation, and it was stated:

"A significant part of the copper in bentonite are precipitated as Cu- and Cu(Fe)-sulphides, representing ca 4 $\mu\text{m}/\text{y}$ in corrosion rate. Considering the total amount of copper in corrosion product, bentonite and groundwater it is most likely that the copper corrosion rate is at least 10 $\mu\text{m}/\text{y}$ (pitting corrosion not taken into account)."

Comment 1

All analysis methods (ICP/AES, ICP/MS, XRF and μ XRF) used to determine the copper content in the bentonite reflect the total amount of copper in the material. To compensate for additional copper content in “*bentonite and groundwater*” is thereby incorrect, and the speculative quantification “*it is most likely that the copper corrosion rate is at least 10 $\mu\text{m}/\text{y}$* ” lacks any support. The statement concerning pitting is unnecessary since no pitting is found in the LOT corrosion study.

Evaluated as mean corrosion rates, the measured copper content in the bentonite gives 1.1 $\mu\text{m}/\text{y}$, 2.7 $\mu\text{m}/\text{y}$, 1.2 $\mu\text{m}/\text{y}$, and 1.2 $\mu\text{m}/\text{y}$ according to BGR’s data series. The corresponding values based on data from ANDRA (France) is 1.7 $\mu\text{m}/\text{y}$, and from SKB 1.8 $\mu\text{m}/\text{y}$, 1.3 $\mu\text{m}/\text{y}$, and 0.14 $\mu\text{m}/\text{y}$.

Item 2

The presentation contained a diagram, which illustrated the copper content in the bentonite around the central copper tube at a specific level in the A2 test. The diagram shows an interpolation between 3 selected data points from one of BGR’s data series.

Comment 2

The BGR study includes 2 additional data sets with more than 1600 data points in total, and the full set of data gives a good conception of the distribution of copper in the bentonite. However, the presented interpolation between the three selected data points differs qualitatively from this distribution.

Item 3

It was stated in the presentation that the KTH group and other researchers, including SKB’s, have measured corrosion rates between 3 and 20 $\mu\text{m}/\text{y}$ in oxygen-free water at room temperature: (presented in Swedish):

”Vi och andra forskare (inkl. SKB) uppmäter 3-20 $\mu\text{m}/\text{år}$ ”

In another section of the presentation it was stated that corrosion rates between 1 and 20 $\mu\text{m}/\text{y}$ have been measured in oxygen-free water, which is confirmed by the SKB LOT experiments:

“We have shown experimentally that copper corrodes in oxygen-free water 1-20 $\mu\text{m}/\text{y}$. These results have been confirmed from SKB’s own long term exposures (LOT)”

In a third section of the presentation, it was claimed that corrosion rates of copper in the LOT experiments are between 10 and 20 $\mu\text{m}/\text{y}$:

“This laboratory study confirm the LOT in-situ exposure, i.e. the general corrosion rate of heated copper is 10-20 $\mu\text{m}/\text{y}$ ”

These results were compared with a theoretical corrosion rate in oxygen-free water of 0.003 $\mu\text{m}/\text{y}$, and the huge difference was pointed out.

“SKB safety analysis: 0.003 $\mu\text{m}/\text{y}$, i.e. 1.000- 10.000 times lower than the measured corrosion rates”

Comment 3

A direct comparison between the copper corrosion rates in oxygen-free water and in the LOT experiments is not meaningful, since the LOT test parcels in this context contains a huge amount of air. The bentonite also contains a limited amount of sulfides which initially contributes to the corrosion. In the test plan for the LOT project, a maximum mean corrosion rate of 7 $\mu\text{m}/\text{y}$ was predicted under oxic conditions. The measured mean corrosion rates, in the parcels retrieved so far, are between ~ 0.3 and ~ 4 $\mu\text{m}/\text{y}$.

Summarizing comments

The main topic of the seminar was under which conditions and to what extent copper corrodes in oxygen-free water, which was also the title of Dr. Szakálos' presentation (*“Thermodynamics and kinetics of copper corrosion in oxygen free water”*). It is therefore surprising that results from the LOT-experiments were used to such an extent in arguing around this process, keeping in mind the huge amount of oxygen initially present. Particularly remarkable is that the dominating oxic corrosion was completely neglected, and that all measured corrosion was ascribed to oxygen-free conditions. Further, it is inexplicable how it repeatedly could be stated that the LOT experiments confirm copper corrosion rates of up to 20 $\mu\text{m}/\text{y}$ in oxygen-free water when the measured mean corrosion rates are between ~ 0.3 and ~ 4 $\mu\text{m}/\text{y}$ and include oxic corrosion. A conclusive comment is that the entire treatment of results from the LOT experiments in the presentation was lacking a reasonable scientific stringency.