LOT – Investigation of copper coupons from test parcel A0

Report compiled by Bo Rosborg based upon experimental work performed at Studsvik Nuclear AB and information obtained from Ola Karnland, Clay Technology AB.

Summary

Coupons of pure copper have been exposed in bentonite blocks 22 and 30 in LOT test parcel A0 at the Äspö Hard Rock Laboratory from December 1999 to November 2001 (in total 498 days at full temperature). The conditions have been similar to those in a KBS-3 repository. Objective: Determine nature and extent of copper corrosion.

This report documents the investigation of copper coupons A022A and A030C after exposure. The coupons have milled surfaces but for one polished side, and contain a deliberate microhardness indentation on the latter.

The copper coupons showed about the same weight loss, in spite of the fact that coupon A022A has been exposed at about 80°C and coupon A030C at about 35°C, and the average corrosion rate was estimated to less than 4 µm per year.

The nature of the corrosion can be classified as a somewhat uneven general attack; the corrosion attack is on the microscale somewhat uneven and different corrosion products are formed along the surfaces of the coupons, however, any obvious signs of pitting cannot be claimed.

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Background information

The test series “Long Term Test of Buffer Material” (LOT) has been initiated at the Äspö Hard Rock Laboratory with conditions similar to those in a KBS-3 repository (1). The main purpose is to study the behaviour of the bentonite clay. Wyoming bentonite with the commercial name MX-80 has been used. However, additional testing has been included, and the investigation of corrosion on copper coupons exposed in bentonite blocks is the subject of this report.

Objective: Determine nature and extent of copper corrosion.

Attempt: "Quantitative information about the mean corrosion rate. Qualitative information about pit corrosion and corrosion products." (2)

Hypothesis: The average corrosion rate is less than 7 μm per year.

A pilot test series has earlier been performed and evaluated (1). The average corrosion rate of a copper coupon in LOT test parcel S1 exposed at about 50°C was estimated to less than 3 μm per year (3-4).

The present investigation concerns LOT test parcel A0 (2). The copper coupons exposed in bentonite blocks no A022 and A030 were obtained from Ola Karnland, Clay Technology AB, and handed over by Ulf Nilsson at Äspö on September 6, 2002. The two coupons in bentonite block A022, copper coupons A022A and A022B, were already loose from the bentonite block, however, copper coupons A030C and D were still inside an intact bentonite block.

Background information about the copper coupons is found in Appendix A. The nominal dimensions of the copper coupons were 60 x 15 x 1.5 mm. The bentonite blocks no A022 and A030 have been exposed at temperatures of about 80°C and 35°C respectively. Test parcel A0 was emplaced on December 16, 1999. Power to the heater was first turned on February 2, 2000. Full temperature lasted from June 16, 2000, up to October 18, 2001. The test parcel was retrieved on November 27, 2001. The total time of exposure is 710 days and the time of exposure at full temperature is 498 days.

Four test parcels are still exposed and will be retrieved later (2). In one of them, that is test parcel A2, real-time corrosion monitoring is performed apart from exposure of copper coupons (5). Preliminary this test parcel will be removed during 2004.

This report forms an input to the final report concerning the evaluation of the exposure of LOT test parcel A0 to be compiled by O Karnland, Clay Technology AB.

Experimental procedure

For the sequence of actions performed during investigation of copper coupons A022A and A030C, see Appendix B.

Copper coupon A022A was photographed in its bentonite piece as received (item 1). (Coupon A022B was archived in its plastic container for later transport to Clay Technology.)

Copper coupon A030C was removed from bentonite block 30 by first sawing loose "a piece of cake" and then breaking loose the coupon from this part (item 3). (The remaining part of the block was archived for later transport to Clay Technology.)

The coupons went first through a few steps of cleaning in deionized water. (The water from each cleaning step has been saved for possible later examination of loose corrosion products.)

In the previous investigation a reference coupon was selected to follow the exposed coupons through all cleaning procedures for the purpose of comparison (3). However, this time no reference coupon was used, but saved for later investigations of copper coupons within the LOT project, and in particular the coupons in test parcel A2.

The main reason for exposure of the coupons in water overnight was to get rid of adhesive bentonite. When the coupons were removed from the water, they were flushed with water which was also saved.

The coupons were stored in a desiccator before each weighing operation and a control weight was used.

Finally the coupons were exposed to 10 % H_2SO_4 solution, first dipped in the solution for 10 min and then ultrasonically cleaned in the same solution during another 5 min (6). After treatment in this solution the copper coupons were examined in a scanning electron microscope (SEM).

Corrosion rates

The results from the weighing of copper coupons A022A and A030C are compiled in Appendix C.

The average corrosion rate of the copper coupons has been calculated from the following data:

weight loss – copper coupons A022A and A030C showed weight losses of 86 and 83 mg respectively

surface area – 20.25 cm^2 for both; the actual sample dimensions deviated somewhat from the nominal, however, they gave the same surface area

density of copper – 8.94 g/cm^3

time of exposure – 498 days at full temperature (in total 710 days)

The average corrosion rates on coupons A022A and A030C are 3.5 and 3.4 µm per year respectively, that is less than 4 µm per year (conservatively based on the time of exposure at full temperature).

Thus, the copper coupons showed about the same corrosion rate in spite of the fact that coupon A030C was exposed at a higher temperature of about 80°C compared to about 35°C for coupon A022A.

Observations

Macrophotographs taken after the different steps of cleaning in deionized water and 10 % H_2SO_4 solution are found in Appendix D. Microphotographs from the scanning electron microscopy are found in Appendix E.

After breaking loose the copper coupons from the bentonite, corrosion products could be seen on parts of the bentonite surfaces facing the copper coupons, see Appendix D. Apparently bare copper surfaces were also seen.

Corrosion products were removed from the coupons during the different steps of cleaning in deionized water, see the macrophotographs in Appendix D and also the weight losses given in Appendix C. Different corrosion products were seen on the surfaces of the coupons.

Examination of the coupons in microscopes revealed a somewhat uneven corrosion attack. However, any signs of active pits could not be found.

Surprisingly enough it was not easy to find the microhardness indentation mark on the polished side of the coupons after exposure, in spite of the fact that the average corrosion rate was estimated to be less than 4 µm/year and the indentation marks are more than an order of magnitude larger, see Appendix E. However, the milling marks were still quite clear after exposure.

In summary, the nature of the corrosion can be classified as a somewhat uneven general attack; the corrosion attack is on the microscale somewhat uneven and different corrosion products are formed along the surfaces of the coupons, however, any obvious signs of pitting cannot be claimed.

Acknowledgements

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