IN SITU COPPER CORROSION EXPERIMENTS IN ÄSPÖ HARD ROCK LABORATORY.

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ABSTRACT

Svensk Kärnbränslehantering AB (SKB) has for several years conducted in situ experiments in the Äspö HRL. These experiments include studies of atmospheric corrosion of copper in the underground laboratory atmosphere and aqueous corrosion of copper in various types of groundwater that are present at different depths in the underground laboratory. The first of these experiments were started in the 1999 and they are scheduled to run for three years, although intermediate sampling will be possible during that time period.   In addition to these experiments, copper exposed to compacted wet clay. One such experiment that had run for one year has been finalized and evaluated. Real-time monitoring of corrosion attack by means of the electrochemical noise and other electrochemical techniques may offer interesting possibilities to estimate the kind and degree of corrosion in a sample or component, and further visualize the corrosion resistance of pure copper in repository environments. As a pilot effort, three cylindrical copper electrodes for such measurements, each of about 100 cm^2 surface area, have been installed in a test parcel in the Äspö Hard Rock Laboratory and electrochemical measurements using InterCorr's SmartCET system were initiated in May 2001 and the first results are reported.

INTRODUCTION

Svensk Kärnbränslehantering AB (SKB) plans to encapsulate the spent nuclear fuel from electricity production in canister with an outer 50 mm thick copper shell for corrosion protection and a cast iron insert for mechanical stability. These canisters will be buried in deposition holes

bored from the bottom of the access tunnels at a depth of 500 to 700 m in granitic rock, surrounded by a 35 cm thick bentonite buffer. Figure 1 shows an outline of such a repository.

In 1986, SKB presented the first plans to build an underground rock laboratory at Äspö in its research program and the construction work was completed in 1995. The activities at the Äspö Hard Rock Laboratory (HRL) can be seen as a dress rehearsal for the siting and construction of the future deep repository for spent nuclear fuel. The laboratory offers a realistic environment for a great variety of experiments and tests under the conditions that will actually prevail in a deep repository.

Some of the conditions expected in a repository can be difficult to realize in a laboratory. The Äspö Hard Rock Laboratory, therefore, offers a unique possibility to perform corrosion testing under fully realistic commissions. SKB has, therefore, initiated a number of experiments in HRL. Of these, a pilot study has been finalized and reported (1), some preliminary results from an ongoing test has been reported (2), while other experiments have not been described before.
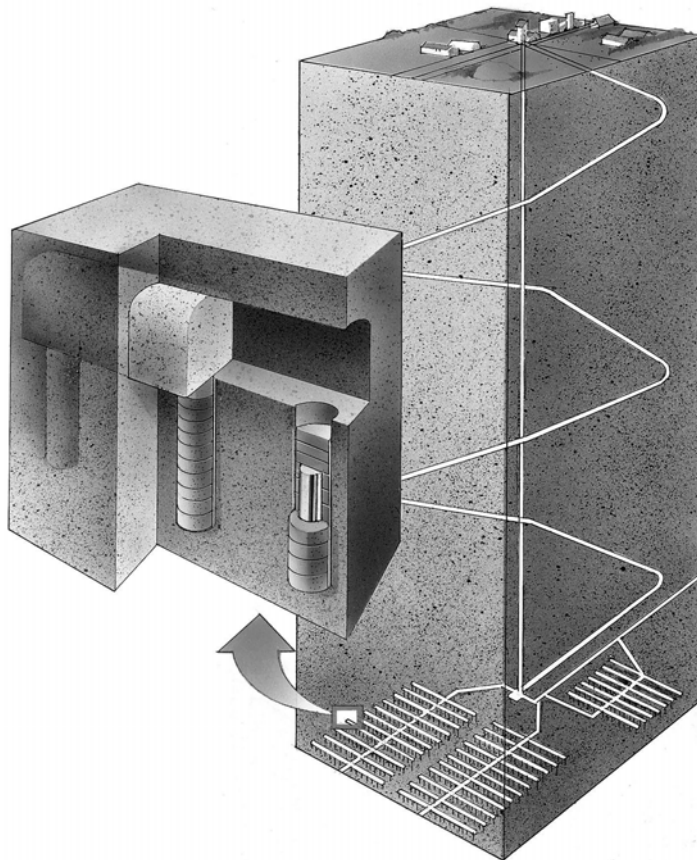

Fig. 1. The layout of a repository for spent nuclear fuel in granitic rock

EXPERIMENTAL

The LOT Experiment

The primary aim of the "Long Term Test of Buffer Material" (LOT) (1) experiments in the Äspö HRL is to is to study the mineralogical stability and behavior of the bentonite clay. However, additional testing has been included, of which the investigation of corrosion on copper coupons in bentonite blocks is one. Among there can be mentioned radioactive tracers to study cation diffusion, microorganisms to study their viability in compacted bentonite clay, and copper coupons to study copper corrosion. The test parcels, which consisted of a central copper tube with heater elements and prefabricated bentonite blocks, were placed in core-drilled bore holes with a diameter of 300 mm and a depth of 4 m in granitic rock at a depth of 450 m below ground at the Äspö HRL. The final density of the bentonite clay, at full saturation and after swelling in the test holes, was calculated to be 2000 kg/m^3. The test coupons for the pilot test parcel S1 were cut by travelling-wire electric discharge machining from a plate of pure copper (99.992 % Cu) with a deliberate addition of 50 ppm P. The nominal dimensions of the coupons are 50x23x1 mm. The pilot parcel with the copper coupons was emplaced in late 1996 and retrieved in 1998 and the coupons were analyzed after a total time of exposure of 16 months of which about 12 months was at the final temperature heater temperature (max 90°C).

A new test parcel was emplaced in at the end of October in 1999. This parcel had three cylindrical copper electrodes, each of 98.7 cm 2 surface area, embedded near the top of the test parcel where the temperature is about 24°C. The purpose of this arrangement was to monitor in real time the corrosion attack by means of the electrochemical noise and other electrochemical techniques. These real-time monitoring started in May 2001 and is performed with linear polarization resistance (LPR), harmonic distortion analysis and electrochemical noise (EN) techniques using InterCorr's SmartCET system. An excellent overview of the application of electrochemical noise techniques in monitoring corrosion processes can be found in ref. 3.

The LPR technique polarizes the electrodes by a small amount (±10mV) using a sine-wave perturbation in the linear region in the E-I curve around the corrosion potential, and the current response is measured. It is a useful measurement of the corrosion rate when corrosion is relatively uniform, but it has some limitations. The assumption is made that the system under study has reached a steady state when the measurement is made (which is true in this application), and the measured polarization resistance is a composite of the solution resistance and charge-transfer resistance. In this application, the solution resistance is low, which provides a greater confidence in the derivation of corrosion rate from the polarization resistance. Corrosion rates are calculated using the Stern-Geary relationship (4).

Harmonic distortion analysis relies on the non-linear nature of electrochemistry and is related to electrochemical impedance spectroscopy, in that an alternating potential perturbation is applied to one sensor element in a three-element probe, measuring a resultant current response. The technique applies an AC signal typically of about 0.1 Hz to the cell and a measurement is made of the 1st, 2nd and 3rd harmonic as well as the fundamental of the current response. Using these results, the polarization resistance and Tafel slopes are mathematically calculated (5-6).

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Electrochemical noise (EN) is the generic term used to describe the low amplitude, low frequency random fluctuations of current and potential observed in many electrochemical systems, and has been used to characterize both corrosion rate and mechanism (7-13). EN data is taken at a frequency of one reading per second and statistical analyses are employed to compute the EN resistance (12), which is analogous to the polarization resistance obtained from LPR measurements. General corrosion rates are calculated from the EN resistance using the Stern-Geary method (4). However, EN measurements also provide information on the type of corrosion. The localization index (LI) is defined as the ratio of the standard deviation of the current noise to the root mean square of the EN current (I_{rms}), which provides an indication of the stochastic distribution of microscopic events. For uniform corrosion, the LI is typically 10^{-2} or less. When localized corrosion occurs, the raw data typically exhibit stochastic transients and the LI tends to approach unity (13).
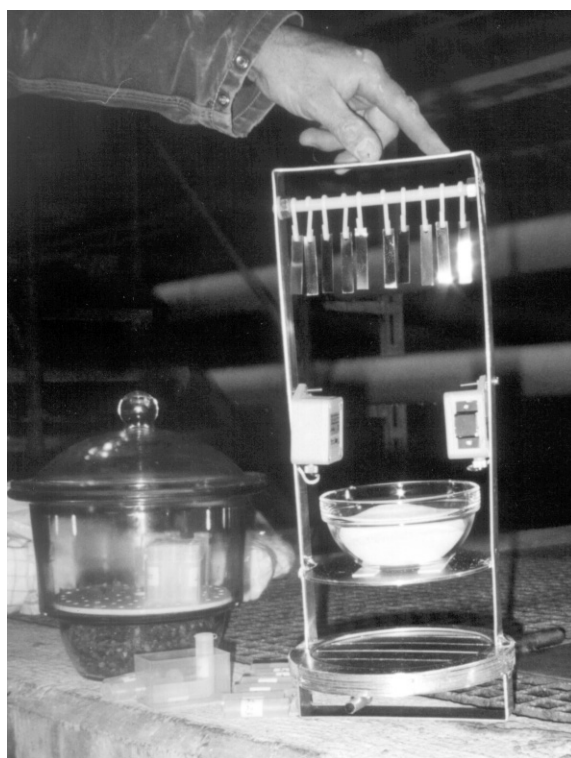

Fig. 2. The experimental setup for the atmospheric corrosion tests

Atmospheric Corrosion Tests

In this experiment, copper coupons are exposed to the underground atmosphere while they are protected from convection and from liquid by exposure inside a cylinder that is closed upwards and open downwards. Three different set-ups are used. In exposure (a) no further measures to control the environment are taken. In exposure (b) loosely stacked bentonite blocks are used to control the humidity. In exposure (c) the whole assembly is heated to about 75°C through an electric heating coil. The temperature is measured periodically. Since the corrosion of copper

may be sensitive to light, the exposure chambers will be protected from excess light by a dark cover. The purpose of these experiments is to simulate the environment around the copper canisters before the repository is fully saturated. They were started in the summer of 1999 and they will run for three years. No results are, therefore, available at this time. The experiment set-up is shown in Figure 2.

Aqueous corrosion tests

Corrosion of copper in the absence of molecular oxygen or other oxidizing agents at pH the pH of groundwaters is possible only in the presence of sulfide. The corrosion then takes place at such a low corrosion potential that hydrogen evolution is possible. This low potential excludes the formation of copper species not bound to sulfide. The known dissolved complexes between copper and sulfide are very weak, so the only corrosion product will be one of more solid copper sulfide.

The volume of the corrosion products is inevitably larger than the volume of the corroded metal because of the low solubility. Because of volume increase there is likely to be some geometric interference between grains of corrosion product at the corroding surface. The corrosion products have been known to crack, form scales and fall off the surface.

Copper corrosion in sulfide containing waters can be studied in the laboratory. However, making the exposures on site at the Äspö HRL offers unique possibilities to study the corrosion in natural sulfide containing waters that for long time have been under reducing conditions. These waters will be more representative for the conditions expected in a repository than any synthetic groundwater or groundwaters collected on site and transported to the laboratory, since natural deep groundwaters are normally not stable under surface conditions.

Two exposures are currently in progress, one in reducing water with high sulfide content (SA1480A) and one in reducing water with high chloride content (SA2880A) (See Table I). The water is fed from sealed-off fractures inside rock to the exposure cells, where copper coupons are exposed to the natural water at the same hydraulic pressure as in the rock in order to maintain the natural water composition. The cells are so designed that the copper corrosion potential, the redox potential and pH of the water can be measured. The current tests were started in May 2001 and will run for at least three years. No results are, therefore, available at this time.

Table I. Chloride, sulfate and sulfide contents in aqueous corrosion test in Äspö

ID Code	Cl^-	SO_4^{2-}	HS^-
SA1420A	2860	292	0.07
SA2880A	14500	643	< 0.01

RESULTS

The LOT Experiment – Pilot Test

The pilot test parcel was extracted by overlapping core drilling outside the original bore hole, then lifted and disassembled. The visual inspection after field exposure did not reveal any significant differences between the surfaces of the copper tube and the copper coupons, with the exception of mineral precipitation on the warmest parts of the tube. Two coupons were analyzed, one, coupon A, representing temperature conditions around $50^{o}C$ and the other one, coupon D, representing temperature conditions around $25^{o}C$.

Coupon A was released from bentonite by mechanical breaking. Coupon D and a few centimeters of covering bentonite were impregnated with resin for SEM/EDX analysis. The corrosion rate of coupon A was determined through mass loss and was found to be 3 μm per year. This average corrosion rate is not fully adequate to characterize the corrosion, since the visual inspection indicated that the corrosion attack might have been uneven. Optical and SEM micrographs, however, did not reveal any sign of pitting. The corrosion pattern was rather complicated and several corrosion products were present, such as cuprite (Cu_2O) and malachite ($Cu_2CO_3(OH)_2$). The fact that cupric species are found clearly indicate that at least part of the corrosion attack took place under rather strongly oxidizing conditions. It is, therefore, not possible to draw any conclusions considering the long-term corrosion rate, since the observed corrosion attack may have occurred mainly during the initial phase of the experiment.

The LOT Experiment – Final Test

A value on the Stern-Geary constant is required to calculate the corrosion rate from the measured linear polarization resistance (LPR) data (4). The field equipment used allows the Stern-Geary constant to be estimated by means of harmonic distortion analysis of the current response from the sine wave LPR potential polarization (5), without the need for a reference electrode. A Stern-Geary constant value of 6.5 mV was determined and was used to calculate the corrosion rate from the LPR and EN data. The resulting rate of general corrosion was 1.7 μm per year (see Figure 3).

The localization index is shown in Figure 4. The localization index (LI) is defined as the ratio of the standard deviation of the current noise to the root mean square of the electrochemical noise (EN) current (I_{rms}). The electrochemical noise data reveals a slight tendency to localized corrosion. With purely uniform corrosion the pitting function" to be in the region of 0.05 or less (13). Here it is approximately 0.12. While this is far from values >9 for obvious pitting, it is not as low as expected from purely uniform corrosion.

Care must be taken when comparing the corrosion rate found in the pilot study and the rate determined from the electrochemical noise measurements. Even though they are rather close, 3 μm per year and 1.7 μm per year, respectively, we expected the corrosion rate in the electrochemical noise experiment to be even lower, since the entrapped oxygen in the parcel should have been consumed by now. The corrosion products on the pilot test coupon also indicated that at least part of the corrosion had taken place under quite oxidizing conditions since

cupric species had formed. The current test parcel is not due for retrieval until 2004 and no direct comparison can be made until then.
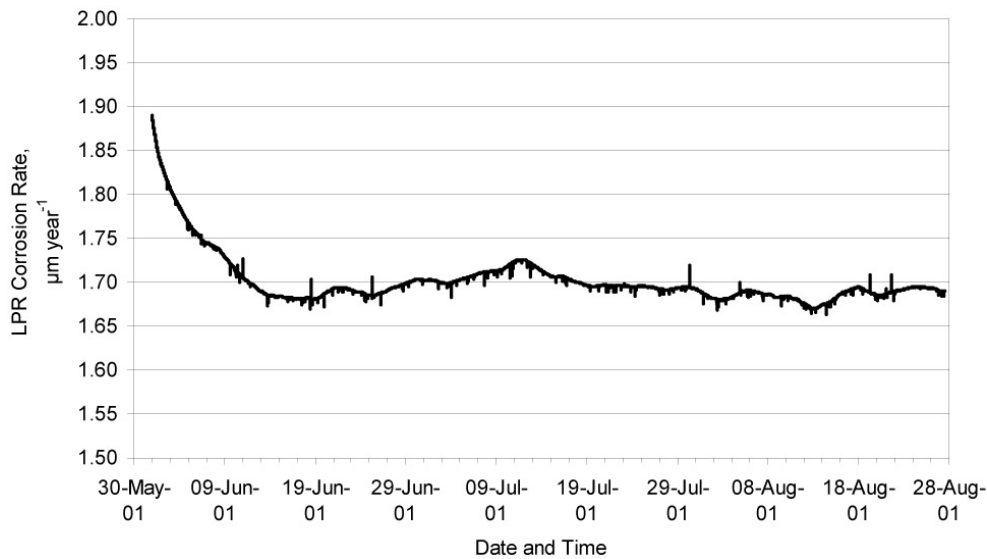

Fig. 3. The corrosion rate obtained from linear polarisation resistance measurements (using a Stern-Geary constant of 6.5 mV).
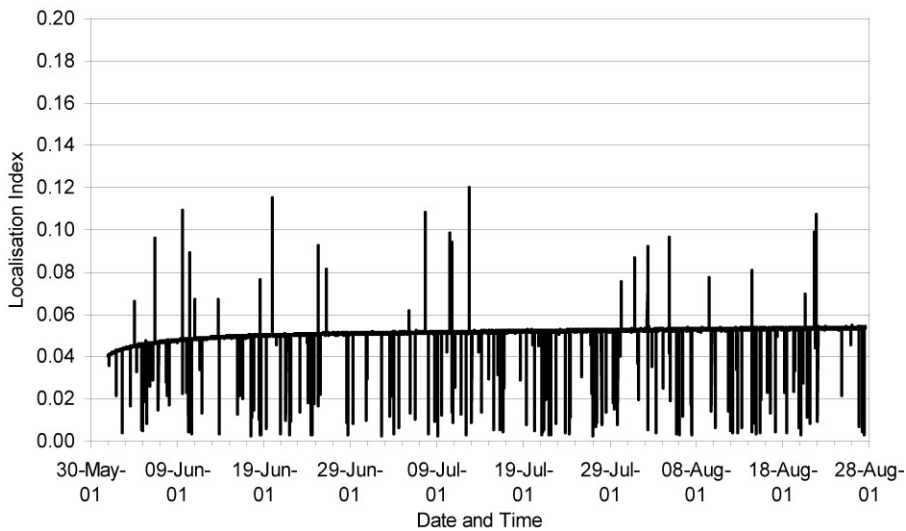

Fig. 4. The localization index (ECN/root mean square of the current).

The electrochemical noise data indicate a slight tendency to localized corrosion on the copper electrodes. Oxygen is a pre-requisite for pit propagation and the observed tendency toward localized corrosion could in fact indicate that the system has, contrary to expectation, not yet

gone reducing. Optical and scanning electron microscopy on a copper coupon exposed in the pilot test did not reveal any signs of pitting after about one year exposure. It was observed, however, that the corrosion products were not the same all over the specimen surface (1).

Even if efforts were made to avoid crevices, it cannot be ruled out that tiny crevices may exist at the lead connections to the electrodes. The presence of such crevices might be the reason for the observed tendency to localized corrosion, and thus an artifact in the corrosion monitoring. Crevice corrosion of pure Cu is, however, uncommon and In long-term irradiated corrosion tests under simulated conditions of a Canadian repository, no crevice corrosion was observed on either creviced U–bend of creviced planar samples (14). Another, maybe more probable explanation for the apparent slight tendency to localized attack could be the fact that for very low general corrosion activity one might expect that under these conditions, corrosion events are stochastic (random) and statistically can represent pit initiation so the localization index could produce indications of nascent pitting. If localized corrosion is present, it is expected that the localization index will increase further as pits grow; if the measure is an artifact of the technique it will remain constant.

CONCLUSIONS

- The gravimetrically determined average corrosion rate of copper in bentonite block S122 over a period of about one year (at a temperature of about 50°C) was estimated to 3 μm per year.

- The corrosion rate of copper in bentonite block A236 after one year exposure (at a temperature of about 24°C) shows a prevailing value of about 1.7 μm per year from the linear polarisation resistance technique (using the Stern-Geary constant value 6.5 mV measured at Äspö).

- The electrochemical noise data shows a tendency towards some low-level localised corrosion, such as nascent pitting.

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