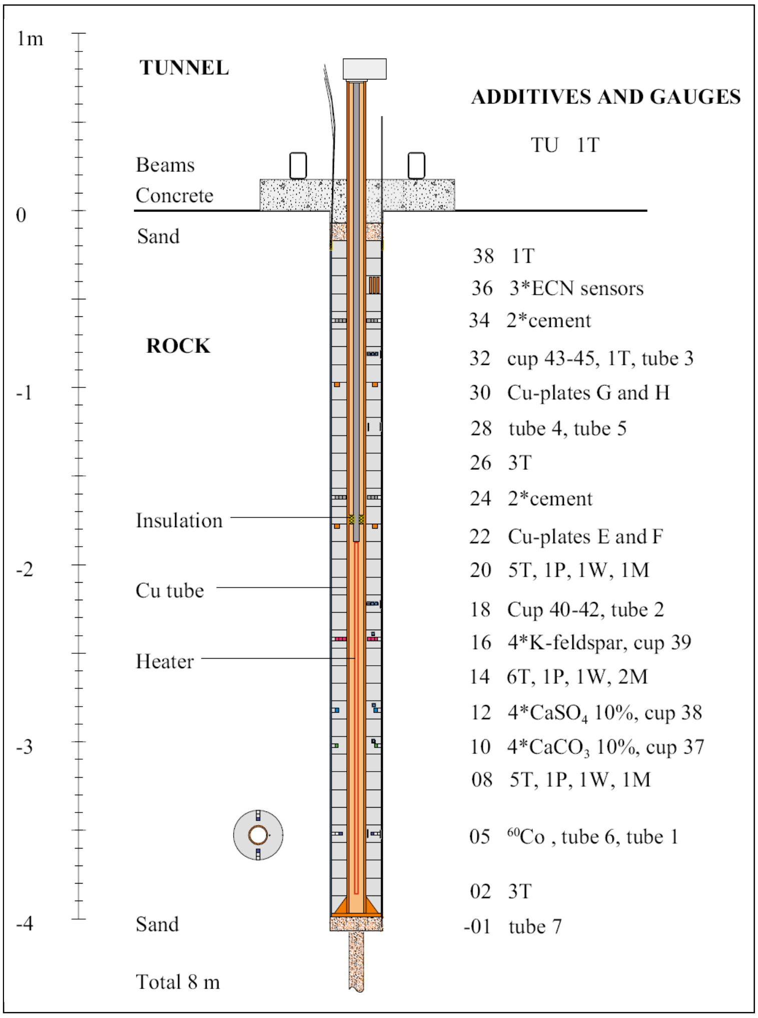
The Long Term Test of Buffer Material (LOT project): Copper Corrosion Tests

A quality assurance (QA) review of SKB's copper corrosion experiments performed as part of the LOT project is being undertaken on behalf of SSM. Table 1 sets out the findings of the first stage of the review, which was based on a meeting with SKB staff and contractors at SKB's Hard Rock Laboratory in Äspö on 1st December 2009.

Table 1. QA checklist for the copper corrosion tests that form part of the LOT project at Äspö.

1. Framework of Experiment	
1.1 Purpose and objectives	
What is being investigated?	The main LOT tests are investigating bentonite buffer properties and mineral stability in a repository-like environment. However, the LOT configuration provided an opportunity to include a number of supplementary tests to investigate other processes (copper corrosion, cation diffusion and bacterial behaviour). This quality assurance checklist is concerned with the copper corrosion tests.
What experiment is being undertaken?	Experiments are being undertaken in which copper tubes containing heater elements are surrounded by bentonite blocks and placed in boreholes at Äspö. There are two types of experiment in which the bentonite and copper tube "parcels" are exposed to different conditions: - standard or S-parcels (S1, S2, and S3) are exposed to expected repository conditions, - A-parcels (A0, A1, A2, and A3) are exposed to adverse repository conditions with the aim of accelerating reactions. Figure 1 shows a schematic illustration of the A2 test parcel that indicates the "additives" and sensors embedded in the bentonite blocks. The additives include copper coupons, ^{60}Co tracers, bacteria and chemicals. At the end of each experiment, the parcels are extracted and various laboratory tests are performed on the bentonite blocks (measurements of bentonite properties, tracer analysis, analysis of bacteria populations, and measurements of copper coupon corrosion).

	 Figure 1. Schematic drawing of the A2 test parcel (SKB, 2009, Figure 3-3); copper test coupons (plates) are placed in bentonite blocks 22 and 30.
Why is the experiment being undertaken?	The aims of the copper corrosion tests are to verify that the copper corrosion rate is less than 7×10^{-6} m yr^{-1} under initial oxic conditions (as indicated by corrosion modelling) and to identify corrosion mechanisms and products (SKB, 2000; SKB 2009).
What is the role of the experiment in the repository programme?	The data obtained from the copper corrosion tests will not be used directly in the SR-Site safety assessment, but the findings from the analysis of the retrieved parcels (A0, A1, A2 and S1) support SKB's understanding of copper corrosion rates and mechanisms under oxic conditions.

1.2 Resources and schedule	
Where is the experiment being conducted?	SKB's Hard Rock Laboratory at Äspö near Oskarshamn.
Who is conducting the experiment?	Clay Technology (Ola Karnland) is leading the LOT experiment on behalf of SKB and Posiva. The analyses of each recovered parcel have been undertaken by various organisations: • Bentonite mineralogy and physical properties – Clay Technology AB • Pore water chemistry – VTT (Finland) • Bacterial behaviour – University of Gothenburg and Microbial Analysis Sweden AB • Cation diffusion – Royal Institute of Technology (KTH) • Copper corrosion – Studsvik Material AB and Rosborg Consulting (using Clay Technology, Studsvik Nuclear AB and Stockholm University facilities) Bentonite mineralogy/chemistry for the A2 parcel was also analysed by independent laboratories: BGR in Germany, University of Bern in Switzerland, and G2R Laboratory and LEM from Nancy University in France. This additional work was financed by the collaborating organisations BGR, Nagra and Andra, respectively.
What is the schedule for the experiment?	Two one-year pilot tests (A1 and S1) were conducted in 1997 and 1998. Work on five more tests (S2, S3, A0, A2 and A3) was started in 1999 and parcel A0 was retrieved after one year in 2001. Parcel A2 was retrieved in early 2006, after just over six years of operation. The remaining parcels (A3, S2 and S3) are still in place and a LOT project meeting will be held during the spring of 2010 to discuss their extraction.
When will results be available?	The results of the two pilot tests (A1 and S1) were reported by SKB (2000). The results of the analysis of parcel A0 remain under review. The results of the analysis of parcel A2 were recently reported by SKB (2009).
What constraints do resources such as cost and timing place on experimental planning and design?	The time for resaturation constrains the scale of the test; full saturation would not occur in one year in a full-scale test. The smaller parcel size also facilitates extraction of the parcels in one piece. The copper coupon tests were designed to take advantage of the opportunity offered by the LOT project to study copper corrosion under repository conditions. The design of the coupons and the number of coupons used were constrained by the availability of bentonite blocks, given the need to accommodate other tests and gauges. SKB considered that the use of four copper coupons in two different bentonite blocks within each test parcel would be sufficient for the purpose of verifying copper corrosion behaviour.

1.3 Quality assurance	
What QA system and standards are used in the planning, design, execution, analysis, and reporting of the experiment?	The early experiments were not performed under SKB's present QA process. Work is currently carried out under SKB's management procedures according to project and activity plans. For example, extraction of the A0 parcel was carried out according to a specific quality plan. SKB describes the requirements for any work to be carried out by contracting organisations. The contractor then proposes a QA plan, which is discussed and approved by SKB. Once the work is finished, SKB confirms with the contractor that the work was carried out according to the QA plan. This process was followed for the A2 copper corrosion measurements undertaken by Rosborg Consulting (SKB, 2009). For the work financed by collaborating organisations BGR, Nagra and Andra, the contracting organisations are given access to LOT materials in order to undertake their analyses, but their procedures are not reviewed; appropriate QA procedures are assumed to be implemented.
How is the expert team selected/trained for the experiment?	SKB proposed the research groups to work on the experiments and asked Clay Technology (Ola Karnland) to design the experiments. Selection of the team was based on experience and skills known to be available at the research groups.
2. Design of Experiment	
2.1 Variables	
What are the dependent variables (i.e. those being observed)?	During the experiment the water content, water pressure, total pressure, and temperature distributions in the bentonite are monitored. The extent of copper corrosion under the observed conditions is measured following extraction of the coupons from the bentonite blocks. The temperature measurements are important with regard to interpreting the copper corrosion test results.
What are the independent variables (i.e. those that are varied to cause change in the dependent variables) and how are their values selected?	Heat sources maintain the copper tube surface temperature at about 90°C (S-parcels) and about 130°C (A-parcels), and generate a temperature gradient across the bentonite. The two bentonite blocks containing the copper coupons were exposed to temperatures of 30°C and 75°C respectively. Initially the temperature was set using a temperature control, before changing to input power control. The emplacement positions of the copper coupons in the parcels determine the temperature that each coupon experiences. The groundwater pressure in the rock and the rate of inflow to the copper coupons in the bentonite vary depending on conditions local to each test hole, resulting in different saturation levels around each coupon. The oxygen and chloride content of the bentonite around the coupons are also independent variables, although not controlled, and there is no knowledge of the rate of oxygen depletion.
What are the control variables (i.e. those that are held constant) and how are their values selected?	The same batch of MX-80 bentonite was used to produce each block used in each parcel. Therefore, similar initial pyrite concentrations were present in each block containing copper coupons.

2.2 Experimental techniques	
What experimental techniques and instruments are being used?	Experimental procedure: - the parcels, each comprising a copper tube surrounded by bentonite blocks, were lowered into 4-m long, 30-cm diameter boreholes; - the copper tubes contain heater elements over the lower 2-m length of the borehole (e.g., 600 W in the S1 parcel, 1000 W in the A1 parcel and 2000 W in the A2 parcel); - copper plates, cement, tracers (^{134}Cs and ^{60}Co), bacteria or additives were included in some bentonite blocks; - about 40 sensors (relative humidity, water pressure, total pressure and temperature sensors) were placed at different locations in the bentonite blocks in each parcel to allow continuous monitoring; - the system was pressurised until the end of the experiment, being fed with water from a nearby fracture. Parcel extraction: - the pilot parcels A1 and S1 were extracted using core drilling, but this required water cooling which flushed away some of the A1 bentonite and, therefore, parcels A0 and A2 were extracted using percussion drilling; - the bentonite rings containing the coupons were cut from the test parcels and were wrapped in plastic sacks from which the air was evacuated; - the samples were transported to Studsvik and stored prior to analysis; Analysis of copper coupons (SKB, 2009): - the bentonite blocks were cut apart or fractured to extract the copper coupons; - copper corrosion was analysed by SEM, EDS, XRD, microscopy and weighing; - measurements were made of the copper corrosion rate and type (pitting and uniform), the corrosion product formed, and the copper distribution in the bentonite. Note that the copper tube in each parcel does not form part of the experiment. Traces of copper corrosion products in the bentonite blocks next to the copper tube have been measured using ICP/MS, but these observations have not been used to estimate copper corrosion rates.
Are they standard techniques?	A lot of the equipment was newly constructed. The heaters were specially designed. Generally, standard components and sensors have been used, although titanium was used instead of the usual steel in some sensors to avoid corrosion. The laboratory copper coupon analysis methods are standard.
Are acceleration methods used?	The parcel diameter is smaller than in a canister deposition hole to shorten the resaturation time. The higher temperatures imposed in the A parcels increased the copper corrosion rates.
Have the techniques been validated and documented?	Results of the two pilot tests (A1 and S1) guided the design of the later tests. Descriptions, results and analyses of the pilot tests are provided in SKB (2000) and the results of the A2 parcel are documented in SKB (2009). The results of the A0 parcel test have not yet been published.

Are the techniques being used under normal conditions?	Equipment such as sensors is used under normal conditions and is expected to be reliable. However, some sensors have failed (including relative humidity sensors). The copper corrosion analysis techniques performed at the laboratory, after parcel extraction, are used under normal conditions.
Has equipment been calibrated and checked?	The copper tubes were checked for leaks when sealed. Equipment is calibrated before use and checked after use.
2.3 Uncertainty	
What are the key uncertainties in the experiment?	A key uncertainty is the timescale required to achieve the resaturated conditions needed to verify the chemistry model. The amount and distribution of oxygen in the system and the timescale for consumption of the oxygen are also important uncertainties for the copper corrosion analysis. It is thought that the warmest parts of the system are the last to be saturated and therefore the last to contain a gas phase (SKB, 2009).
2.4 Risks to success of experiment	
What are the risks to the success of the experiment and how are they mitigated?	The key risks to success of the corrosion analysis in the LOT experiment are: - Lack of control of resaturation during the LOT test. Rapid resaturation is preferred and water is fed throughout the experiment to the parcel. Saturated conditions are essential for verification of the chemistry model. - Risk of equipment failure (e.g., temperature control and/or sensor). Alarms are used in the monitoring system with associated response actions. - Damage to the copper coupon during its extraction from the bentonite block. All four copper coupons in the A1 parcel were damaged during the extraction process and were not analysed. Two coupons in the A2 parcel were damaged, although a partial analysis was undertaken of one of them. - Disturbances to final conditions after parcel extraction. In particular, the coupons could be exposed to oxic conditions resulting in further corrosion after extraction of the parcels. To reduce the opportunity for such corrosion, the copper coupons are retained in the saturated bentonite blocks. The blocks are only exposed for 10 minutes after extraction before being sealed in a nitrogen-rich environment and then transported to the laboratory. Generally, the corrosion analysis takes place within a month, although there is no maximum time in the QA plan. The coupons are extracted from the bentonite in the laboratory. Staff turn-over is also a potential risk, but experiments are well documented to mitigate against this risk.
What are the critical decisions in the experiment?	The critical decision is when to terminate the tests.
Is there duplication in the experiment?	There is duplication in blocks and between blocks - experiments are always over-specified. Copper coupons were placed in pairs in the bentonite blocks.

3. Conduct of Experiment	
3.1 Data collection and quality control	
How are data collected?	Data are recorded hourly and data collection is also event-triggered. The commercial and widely-used Orchestrator data acquisition software is used, which was checked at installation.
How are data stored (e.g., filing, indexing)?	Data are stored on a local project computer, with monthly transmission to Clay Technology. Clay Technology processes the data using Microsoft Excel, stores the data on CD-Rom and submits it to the SKB SICADA database. An indexing system is used for identifying tests, sensors, bentonite blocks and bentonite test sample locations. The raw copper corrosion measurement data were recorded on a Microsoft Excel spreadsheet and then entered on the SICADA database.
How are data checked (e.g., independently)?	Data collection is checked using a monitoring system with alarm functions. Data are checked by two independent SKB reviewers and Clay Technology (Ola Karnland) must approve the data before it can be entered into the SICADA database. No independent measurements are made.
How are data backed-up?	Regular backups are made onto a separate hard disk.
What quality control procedures are used?	Non-conformance reports are prepared when deviations occur. Quality checks are made on data entered into the SICADA database.
3.2 Records of experiment	
Are notebooks being used for the experiments?	Field notes, daily logs and database entries are made for the LOT Project. The copper coupon analysis was recorded in a Microsoft Excel spreadsheet directly, without the use of log books.
Are notebooks checked independently?	No.
Are planning, execution and analysis correspondence kept (e.g., emails)?	Important correspondence is kept and stored by Clay Technology or at Äspö. Activity plans are used. The SKB document handling system gives every document a unique number.
Are copies of records kept?	No.
3.3 Equipment	
Is equipment tested, inspected, and maintained?	The copper coupon corrosion analysis was performed at Studsvik Nuclear facilities and the equipment there is assumed to be tested and maintained.

4. Analysis and Reporting of Experiment	
4.1 Data interpretation	
What data interpretation methods are being used (models, software packages, model simplifications)?	The measured coupon weight loss from the copper coupons has been used directly to infer the copper corrosion rate during the LOT test.
How are uncertainties and sensitivities analysed?	The copper corrosion analysis has been reported without associated error quantification.
4.2 Reporting and review	
How are data and observations reported?	Many documents have been produced and are listed in a project document chart (an internal SKB document). Results have been published in scientific journals and in two PhD theses. SKB (2000) contains observations from the pilot tests and SKB (2009) records the analysis of parcel A2.
How are interpretations reported?	As above. SKB (2000) contains interpretations from the pilot tests and SKB (2009) for parcel A2.
How are limitations on the use of data and results reported?	Limitations on the use of the data have not been discussed. However, as the copper corrosion tests are a verification experiment, the data will not be used directly in the SR-Site safety assessment calculations. The understanding derived from this work will be discussed in the SR-Site Process Report, but the corrosion rate obtained will not be included in the SR-Site Data Report for use in the assessment.
How are reports reviewed (e.g. independently)?	Reports are reviewed and approved by SKB. An expert peer review of the A2 parcel report was performed and the review comments are recorded on the project folder.
How are review results managed/responded to?	The comment response process is managed by SKB.
5. Usability of Results	
5.1 Verification	
How are experimental outcomes checked against requirements of the experiment?	SKB performs checks and decides on whether further studies are required. The LOT copper coupon tests and weight loss measurements have provided the required information on copper corrosion. New copper corrosion experiments are underway and others are planned for the future, including laboratory experiments in which greater controls are exerted on conditions such as redox potential.
How are experimental results verified?	Observations are compared with expected results, such as from laboratory experiments or published data. The corrosion rates and process understanding have also been compared with the model and calculated corrosion rates reported by Wersin *et al*. (1994).

5.2 Use of results	
How are results abstracted for use in the repository programme?	The experiments are being analysed or are ongoing. Whilst measurements such as the bentonite swelling pressure may be used directly in the future SR-Site safety assessment, the copper corrosion data obtained will only be used to verify the corrosion process and a corrosion rate under oxic conditions of less than 7×10^{-6} m yr^{-1}.
Are results extrapolated for use on repository length and time scales?	The results are assumed to apply to repository time and length scales, although not directly.
What checks are made that data and results are used appropriately and within prescribed limitations?	The results are used to verify and validate an existing model. The model must be used appropriately. It would be made clear to anyone requesting the data that they should be cautious in its use and understand the uncertainties in it derivation.

References

SKB (2000). Long-Term Test of Buffer Material. Final Report on the Pilot Parcels. SKB Report TR-00-22. SKB, Stockholm, Sweden.

SKB (2009). Long Term Test of Buffer Material at the Äspö Hard Rock Laboratory, LOT Project. Final Report on the A2 Test Parcel. SKB Report TR-09-29. SKB, Stockholm, Sweden.

Wersin P., Spahiu K. and Bruno J. (1994). Kinetic Modelling of Bentonite-Canister Interaction. Long-Term Predictions of Copper Canister Corrosion under Oxic and Anoxic Conditions. SKB TR 94-25, Svensk Kärnbränslehantering AB.