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The Swedish nuclear waste program and the long-term corrosion behaviour of copper

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ABSTRACT

The principal strategy for high-level radioactive waste disposal in Sweden is to enclose the spent fuel in tightly sealed copper canisters that are embedded in bentonite clay about 500 m down in the Swedish bedrock. Besides rock movements, the biggest threat to the canister in the repository is corrosion. 'Nature' has proven that copper can last many million of years under proper conditions, bentonite clay has existed for many million years, and the Fennoscandia bedrock shield is stable. The groundwater may not stay the very same over very long periods considering glaciations, but this will not have dramatic consequences for the canister performance. While nature has shown the way, research refines and verifies. The most important task from a corrosion perspective is to ascertain a proper near-field environment. The background and status of the Swedish nuclear waste program are presented together with information about the long-term corrosion behaviour of copper with focus on the oxic period.

1. Background and requirements [1–2]

1.1. Origin of the nuclear waste

1.1.1. Nuclear power plants in Sweden

In Sweden light water reactors have been in commercial operation since 1972. Today ten are in operation: three boiling water reactors at Forsmark, three boiling water reactors at Oskarshamn, and one boiling water and three pressurized water reactors at Ringhals. The two boiling water reactors at Barsebäck have been shut down prematurely for political reasons, the first in 1999 and the second in 2005.

1.1.2. Sites of waste generation

All Swedish nuclear power plants and present waste management facilities are situated on the coast (Fig. 1). The waste is handled and transported in solid form. The spent fuel is first stored in water pools at the nuclear power plants for at least nine months and then transported to an interim storage facility, where it will be stored for about 30 years, until it will be encapsulated in copper canisters and finally deposited in a deep repository.

1.1.3. Waste volumes

The amount of nuclear waste is visualized in Fig. 2. The estimate is based upon 40 years operation of the nuclear power plants. The spent nuclear fuel occupies about 20 000 m^3 out of the total quantity of radioactive waste amounting to 250 000 m^3.

1.2. A brief history of the Swedish nuclear waste program

1.2.1. The Nuclear Power Stipulation Act of 1977

In the Nuclear Power Stipulation Act of 1977 the politicians stated that utilities would not be allowed to load fuel into a new reactor before it had been shown that it was possible to arrange a final storage of the waste 'in an absolutely safe way'. The law offered two alternatives for the spent nuclear fuel: (i) reprocessing and final disposal of the high-level waste and (ii) final disposal of the nuclear fuel without reprocessing.

1.2.2. The KBS-project

The KBS-project was commenced when the Stipulation Act was passed. (**KBS** stands for **K**ärn**b**ränsle**s**äkerhet = Nuclear Fuel Safety.) The goal of the project was to arrive at a method for disposal of the nuclear waste.

For several years the project worked with vitrified waste from reprocessing. In the 'third report', published in 1983, a method for 'direct disposal' was presented [3]. The KBS-3 report recommends a final repository in the Swedish crystalline bedrock with barriers of natural materials.

1.2.3. The Nuclear Activities Act of 1984

In the Nuclear Activities Act of 1984 the Swedish Government states that the KBS-3 method 'in its entirety has been found essentially acceptable with regards to safety and radiation protection'.

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Fig. 1. Sites of nuclear waste generation in Sweden.

The utilities licensed to operate nuclear power plants have full responsibility for safely managing all nuclear production waste and for waste resulting from the dismantling of the facilities. The utilities are responsible for preparing a program 'for comprehensive research and development and other measures required to safely handle and finally dispose of the radioactive waste from the nuclear power plants'.

1.2.4. Svensk Kärnbränslehantering AB

The mission of Svensk Kärnbränslehantering AB (SKB, the Swedish Nuclear Fuel and Waste Management Co) is to manage and dispose of spent nuclear fuel and other radioactive waste. The present owners are E.ON Kärnkraft Sverige AB, Forsmarks Kraftgrupp AB, OKG Aktiebolag, and Vattenfall AB.

SKB presents an R&D programme every three years.

1.2.5. The nuclear waste fund

The nuclear power utilities pay a special fee for future expenses for safe management of spent nuclear fuel and decommissioning and dismantling of nuclear reactors. The size of the fee is based on a certain amount per kWh of electricity delivered by the nuclear power plants and is about a tenth of a euro cent for every kWh. The fund finances SKB activities.

1.2.6. Reviews

The Swedish Nuclear Power Inspectorate (SKI) and the National Radiation Protection Institute (SSI) oversee SKB's work. (These organizations will merge on July 1, 2008.)

The Swedish National Council for Nuclear Waste (KASAM) submits an independent assessment of the state of knowledge in the field of nuclear waste to the Government every three years.

1.2.7. Political decisions and pronouncements

- The waste from the Swedish nuclear power plants must be disposed of within the country's borders.
- Sweden will not dispose of fuel from other countries in its repositories.
- The spent fuel will not be reprocessed.
- The waste must not be passed on to future generations, but rather be managed and disposed of today.

1.3. The KBS-3 method

The lifetime engineering challenge: How to prove a million years life of an engineering barrier for storage of nuclear waste? This is definitely not a straight-forward task and rather looks like an insurmountable task. Sheet anchor: 'Seek advice from Mother Nature'.

Also, the lifetime engineering challenge is not merely a technical issue: The laws and rules of both nature and society must be respected.

1.3.1. Outline of a KBS-3 repository

The principal strategy for high-level radioactive waste disposal in Sweden is to enclose the spent fuel in tightly sealed copper canisters that are embedded in clay about 500 m down in the Swedish bedrock (Fig. 3) [1]. A multiple barrier principle is applied: the canister isolates, the buffer seals and the rock protects. SKB has chosen to build the repository with materials that occur naturally in the earth's crust. The idea is that the repository should imitate nature as closely as possible.

The canister of pure copper isolates the spent fuel from the surrounding environment. Its reference design is shown in Fig. 4

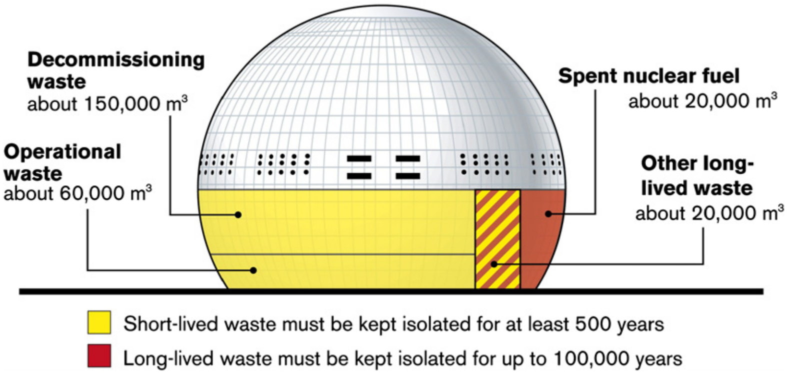


Fig. 2. Waste volumes compared to the size of the 'Globen' stadium in Stockholm.

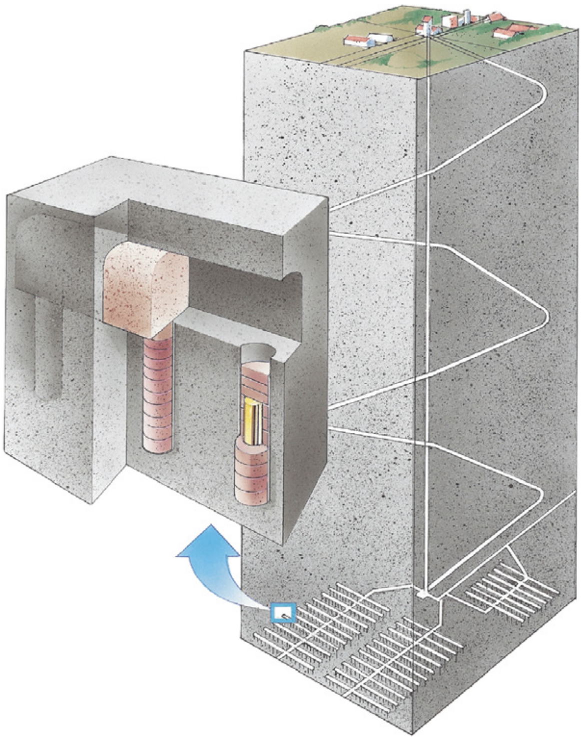
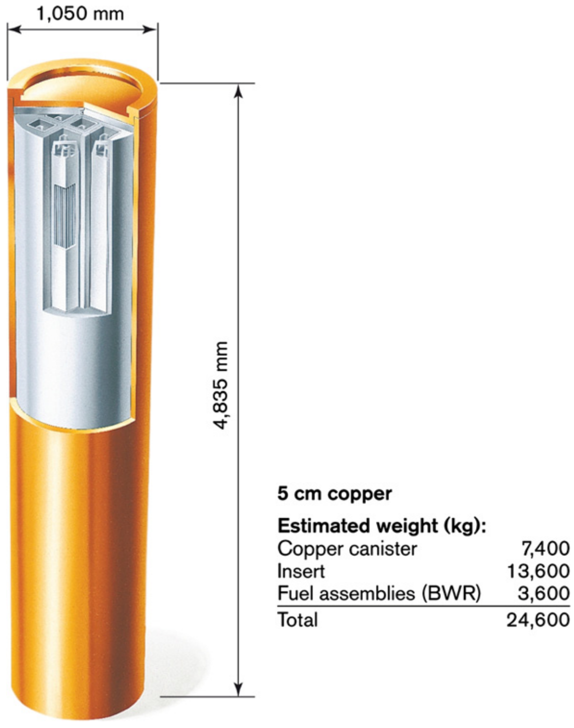


Fig. 3. A KBS-3 repository.

[4]. It has a 50 mm thick copper casing combined with a pressure-bearing insert of nodular cast iron, and is designed for a maximum outside temperature below 100 °C The canister is surrounded by a layer of bentonite clay that protects the canister against small movements in the rock, absorbs water while swelling, prevents direct contact with the groundwater, and acts as a filter trapping radionuclides. The rock protects the canister and the buffer from mechanical damage and offers a stable chemical environment – its primary purpose. The rock also delays transport of radionuclides.



Estimated weight (kg):

Copper canister	7,400
Insert	13,600
Fuel assemblies (BWR)	3,600
Total	24,600

Fig. 4. The copper canister.

1.3.2. Natures own laboratory

Analogues of a final repository exist at many places in the world, see Fig. 5. By studying nature we can find out how copper, bentonite clay, rock and uranium dioxide behave both under different conditions and over different periods of time.

'Nature' has proven (i) that copper can last many million of years under proper conditions – native copper has been preserved for nearly 200 million years in a compacted clay environment which is similar to the repository near-field environment [5], (ii) that bentonite clay has existed for many million years – Wyoming bentonite clay for instance was formed during Cretaceous, i.e. more than 65 million years ago [6], and (iii) that the Fennoscandia bedrock shield is stable – the bedrock of interest was formed during the Precambrian period, i.e. more than 545 million years ago [7].

The 'fossil forest' of 1.5 million year old tree stumps that has been found in Dunarobba in Italy [1] demonstrates the benefit of using clay as a buffer. The stumps have been protected by clay, which isolated them from the oxygen in the air and, therefore, prevented them from rotting.

1.3.3. Supporting information

Supporting information for the lifetime prediction of the copper canister has been gained from

- examination of natural and archaeological analogues,
- field and laboratory testing,
- modelling of the corrosion behaviour, and
- thermodynamic considerations.

1.3.4. View

For excellent reasons we know that copper will last if proper environmental conditions are established and maintained. The bentonite will most likely transform from sodium bentonite to calcium bentonite. This will have an effect on the bentonite properties, but not in any dramatic way. A suitable bedrock site will be found.

The groundwater may not stay the very same over very long periods considering glaciations, but this will not have dramatic consequences for the canister performance. (An open issue: After glaciations it cannot be completely ruled out that low ionic strength water from the melting glacier may push down to the repository level. If this happens during sufficiently long time, this water may erode away the bentonite in the 'worst' scenario.)

2. Waste handling facilities

Pictures of existing and outlines of future waste handling facilities, and further information about the facilities, can be found on www.skb.se.

2.1. Existing facilities

2.1.1. Transportation system

The ship M/S Sigyn was launched in 1982. Together with transport casks and containers for operational waste, spent nuclear fuel, and core components, it comprises a complete transportation system for the nuclear waste.

Fig. 5. Natures own laboratory (www.skb.se).

2.1.2. Final repository for radioactive operational waste

The final repository for radioactive operational waste (SFR) handles short-lived low- and intermediate-level waste. It is an underground rock facility located at Forsmark about 50 m beneath the seabed and has been in operation since 1988. Its disposal capacity is 63 000 m^3 waste.

2.1.3. Central interim storage facility for spent nuclear fuel

The central interim storage facility for spent nuclear fuel (Clab) is also an underground rock facility with storage pools located at Oskarshamn about 30 m under ground. It handles interim storage for the high level nuclear waste for about 30 years and has been in operation since 1985. Its storage capacity is about 20 000 boiling and 2500 pressurized water reactor assemblies. After a recently finished extension the capacity will soon be increased with 60%.

2.2. Future facilities

2.2.1. Encapsulation plant

The preferred location for the encapsulation plant is directly adjacent to Clab. The encapsulation capacity will be 200 filled canisters per year.

The copper canisters will be fabricated in a separate canister factory.

2.2.2. Deep repository for spent nuclear fuel

Site-investigations for a deep repository for spent nuclear fuel are in progress, see below. Its location is yet to be decided. The initial operation will be 200–400 canisters and the regular operation will be about 6000 canisters with a capacity of 200 canisters per year.

2.2.3. Final repository for long-lived low- and intermediate-level waste

For practical reasons a final repository for long-lived low- and intermediate-level waste will also be built. It will be located at the deep repository for spent nuclear fuel.

3. R&D facilities

While nature has shown the way, research refines and verifies.

The SKB R&D facilities are not only used for research and development purposes, but also important for demonstration of needed equipment and training of staff for operation of the future waste handling facilities.

3.1. The Canister Laboratory

The 'Canister Laboratory' is located in the harbour of Oskarshamn and has been in operation since 1998. It is the centre for further development of the encapsulation technology and related safety issues. Its primary purpose is to develop methods for welding the lid onto the copper canister and inspecting the weld for quality. The potential of high vacuum electron beam welding and friction stir welding has been explored.

3.2. The Äspö Hard Rock Laboratory

The 'Äspö Hard Rock Laboratory' is located on an island in the archipelago next to the Oskarshamn nuclear power plant. The geological investigations for the facility started in 1986, construction in 1990 and operation in 1995. The laboratory offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository. In Fig. 6 pictures of the laboratory above and below ground are given. As seen in the picture a number of experiments are performed on different places in the underground laboratory [8]. Three of these are briefly described here:

3.2.1. The retrieval experiment

The main purpose of the 'Canister Retrieval Test' was to demonstrate and gain experience from retrieval of a copper canister. An electrically heated full-scale canister was emplaced in the fall of 2000 and retrieved after five years exposure early in 2006. The bentonite next to the canister had been saturated with groundwater.

3.2.2. The prototype repository

The 'Prototype Repository' is a deposition tunnel with six full-scale canisters deposited in the same manner as in the future deep repository; the inner section was backfilled and sealed in 2001, the outer in 2003. The outer section will be examined after 5–10 years; the inner will remain intact for up to 20 years.

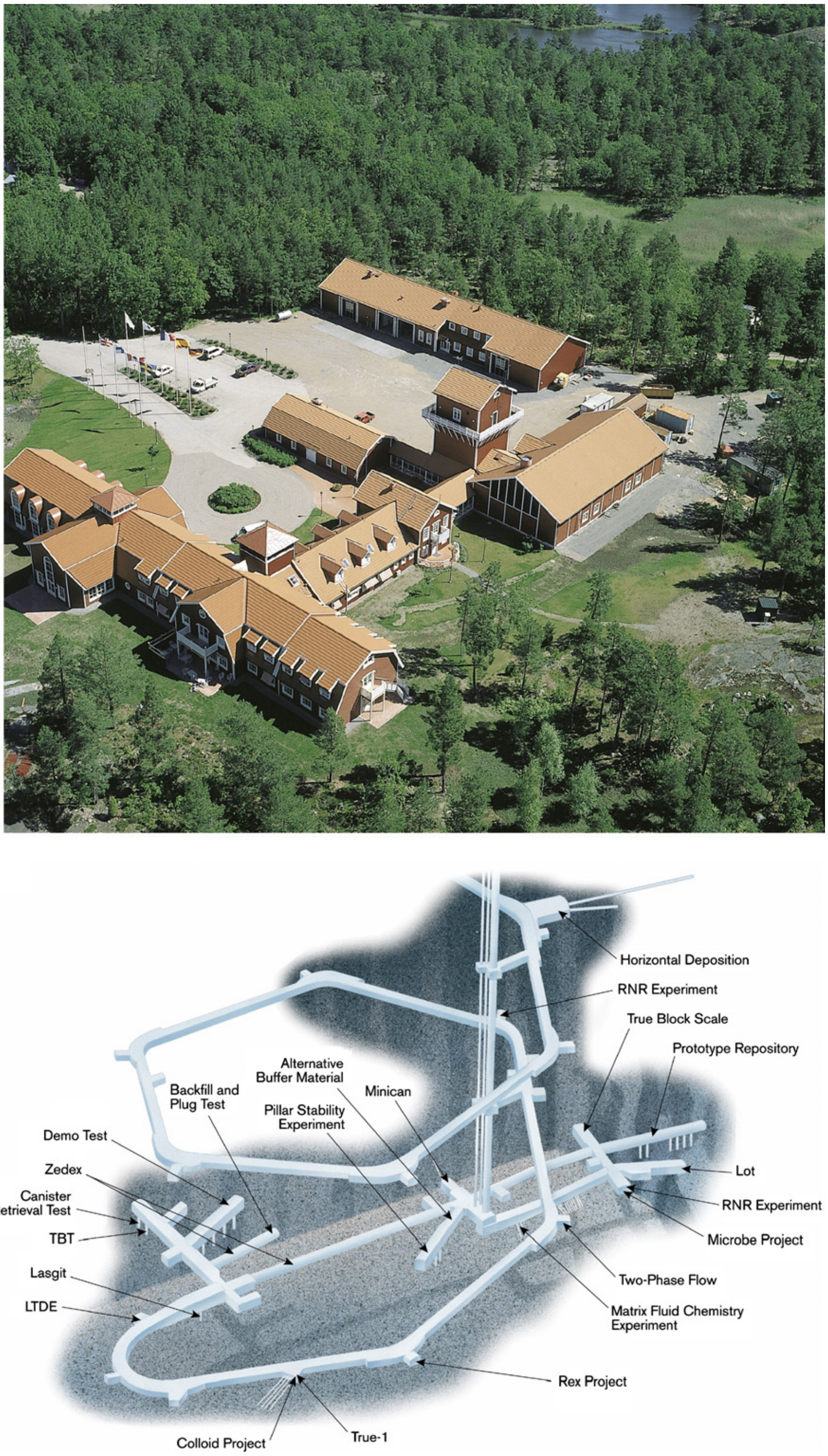


Fig. 6. The Äspö Hard Rock Laboratory above and below ground.

3.2.3. The LOT experiment

The 'Long Term Test of Buffer Material' (LOT) project is intended to show how the bentonite behaves in an environment similar to that in the future deep repository. The test series comprises seven test parcels, which will be run for 1, 5 and 20 years. Four test parcels have so far been retrieved [9]. The test parcels contain copper coupons for corrosion studies. In LOT test parcel A2 real-time monitoring of copper corrosion has also been performed, see Fig. 7 and below.

4. Status of the Swedish nuclear waste program

SKB has so far experience from full-scale manufacturing of 15 complete canisters [10]. Some of them are used for experiments in the Äspö Hard Rock Laboratory and some are on display at exhibitions. The number of canister components that has been manufactured as of July 2007 is given in Table 1 [10e].

The site investigations for the final repository were commenced in 2002. They were concluded in 2007.

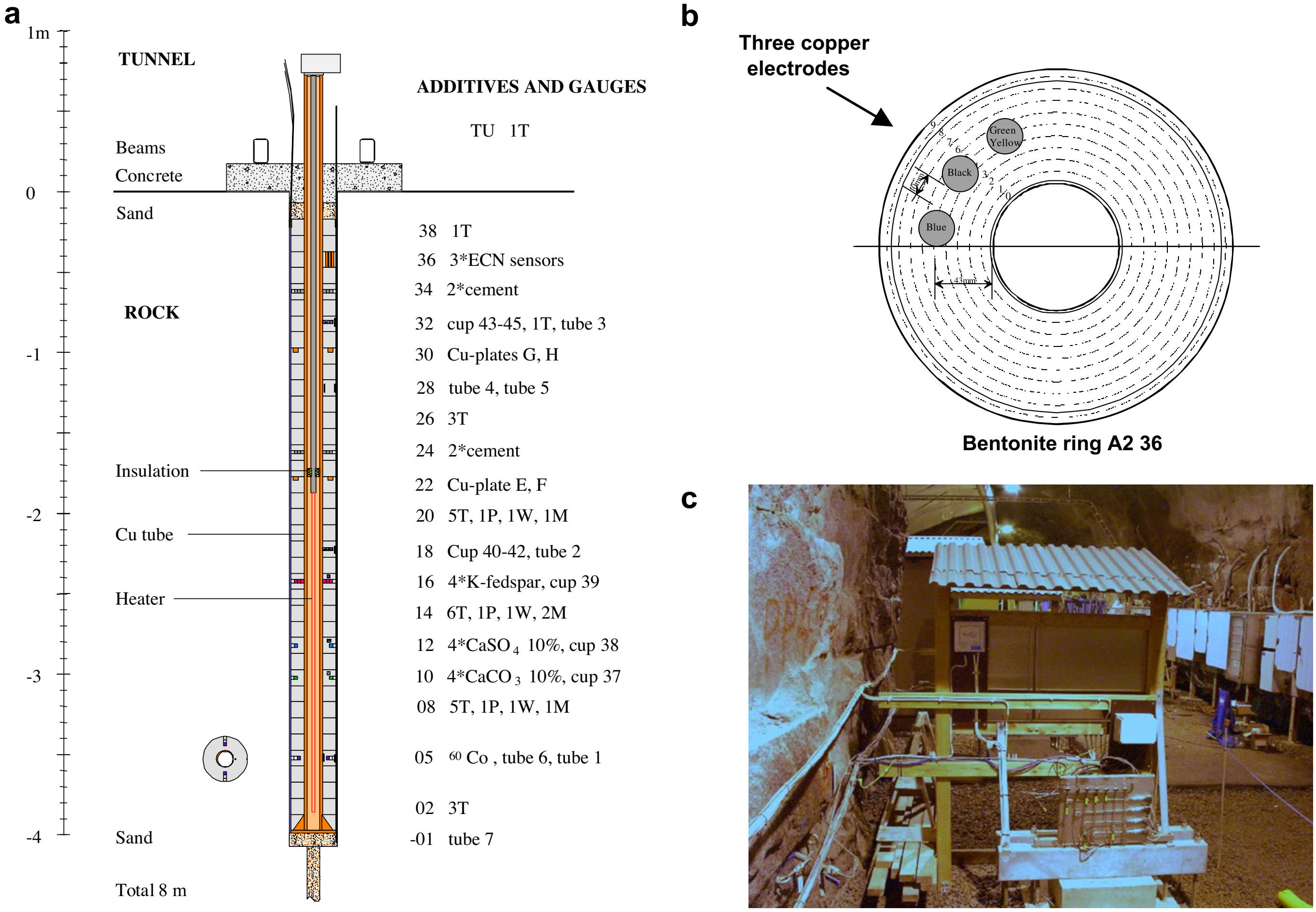


Fig. 7. (a) LOT test parcel A2, (b) position of electrodes, (c) top of LOT test parcel A2 with part of the instrumentation.

A timetable for the final repository is given in Table 2. The application to build an encapsulation plant was submitted in 2006 and the application for building the deep repository will be submitted in 2009. A deposition permit is expected in 2017. Then a trial operation with 200–400 canisters will start followed by an evaluation before the regular operation.

It is believed that SKB's mission is completed in 2060.

5. The long-term corrosion behaviour of copper

Besides rock movements, the biggest threat to the canister in the repository is corrosion. Copper will last if proper environmental conditions are established and maintained.

We knew (i) that copper can show high corrosion rates in some environments, (ii) that copper can reveal local corrosion under certain conditions, such as in some tap-water systems (treated shallow groundwater), (iii) that deep groundwater can vary considerably in salinity, and (iv) that glaciations will occur. Thus, the most important task from a corrosion and R&D point of view is to ascertain a proper near-field environment.

Two pertinent questions in a diagnosis for further efforts on the long-term corrosion behaviour of copper: (i) How to verify proper environmental conditions? and (ii) How to ascertain proper environmental conditions?

5.1. Past assessments

Assessments of the long-term corrosion behaviour of copper and predicted canister lifetimes have been made [11–13].

5.1.1. The 1978 assessment

The Swedish Corrosion Institute performed an assessment of the long-term corrosion behaviour of copper in 1978 and concluded that copper canisters would remain intact for a period exceeding 100000 years in a deep repository in the Swedish bedrock [11a]. An extension of this assessment was performed in 1983 [11b].

5.1.2. The 2001 assessment

As a follow-up to the 1978 assessment another assessment was published in 2001 [13]. It concluded '... that copper provides an excellent corrosion barrier in an underground repository' and '... it is apparent that corrosion is not the limiting factor in determining the canister design wall thickness'.

5.2. The material-environment system

After emplacement the copper canister, the bentonite clay and the granite rock form the barriers for the nuclear waste. From a corrosion perspective the material-environment system can be taken as involving (i) the copper canister, (ii) the groundwater, (iii) the bentonite clay, and (iv) the near-field environment. This environment will change with time.

Microorganisms are found in the rock and are of importance.

The copper canister will be subjected to many environments on its way from fabrication to final disposal. It is pertinent to find out the corrosion behaviour of copper in these environments, that is scrutinize the 'environmental envelope'.

Table 1
Manufacturing of canister components (number of components as of July 2007)

Component	Method/category	Number
Copper tube	Rolling/welding	13
	Extrusion	24
	Pierce and draw	10
	Forging	7
Forged lid/bottom		191
Nodular cast iron insert	BWR	46
	PWR	5
Steel lid for insert		19
Complete canisters		*15*

5.2.1. The copper canister

The copper canister (Fig. 4) will be fabricated from pure oxygen-free copper with a deliberate addition of approx 50 ppm P to improve creep properties [4]. A nodular cast iron insert is used to provide mechanical strength. The dimensions and waste load of each canister have been chosen such that the temperature on the outer surface of the canister never exceeds 100 °C. Friction stir welding is an attractive sealing method from a corrosion point of view [14].

Copper has a wide stability range in oxygen-free water [15].

Besides showing adequate corrosion resistance the canister material and its corrosion products must not appreciably impair the performance of the buffer.

5.2.2. The bentonite clay

The main mineral constituent in bentonite clay is montmorillonite, which has a sheet like crystal structure [6]. As an example, Wyoming bentonite sold under the commercial name MX-80 is dominated by natural sodium montmorillonite clay (∼75% by weight), which is responsible for the desired physical properties. The remaining part consists of quartz (∼15%), feldspars (∼7%), carbonates (∼1.4%), sulphides (∼0.3%), and organic carbon (∼0.4%). The mean mineralogical composition of the montmorillonite part is given by

$$\underbrace{(Al_{3.10}Fe^{3+}{}_{0.4}Fe^{2+}{}_{0.02}Mg_{0.48})}_{\text{octahedral cations}} \quad \underbrace{(Si_{7.92}Al_{0.08})}_{\text{tetrahedral cations}}$$

$$\underbrace{O_{20}(OH)_4}_{\text{structural O/OH}} \quad \underbrace{(Na_{0.48}Ca_{0.04}Mg_{0.02})}_{\text{exchangeable cations}}$$

The cation exchange capacity is around 0.8 eq/kg bulk. The natural exchangeable cations are sodium (∼85%), calcium (∼10%), magnesium (∼4%) and small amounts of potassium (∼0.3%). The specific surface area is around 550 m^2/g material and the grain density is around 2750 kg/m^3.

A high salinity of the groundwater will not deteriorate the properties of bentonite [16].

5.2.3. The rock

The foremost function of the rock is to protect the canister and the bentonite from any possible damage from the surface. It also provides a stable environment and retards transport of radionuclides up to the ground surface.

5.2.4. The groundwater

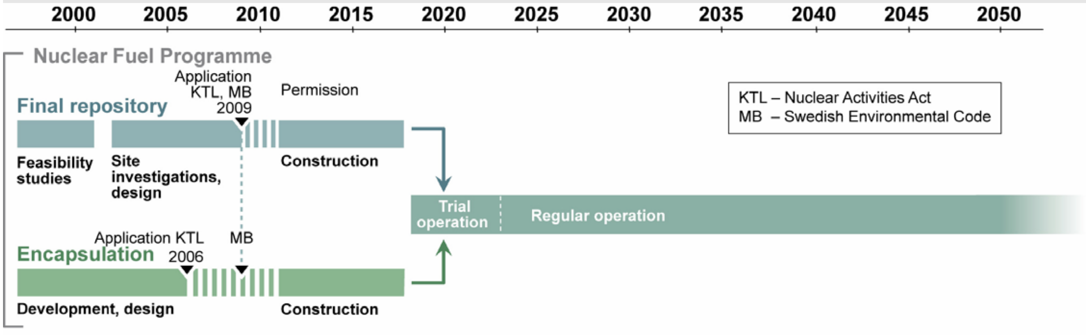
Groundwater in granite rock in Sweden is saline, oxygen-free and reducing below a depth of 100–200 m [13,17]. The redox potential below this depth ranges between −200 and −350 mV SHE and the water has a pH ranging from neutral to mildly alkaline (pH 7–9). The chloride concentration in the groundwater can vary within very wide limits, ranging from 5 mg/dm^3 to 50 g/dm^3. Groundwater analyses from different parts of Sweden show sulphide concentrations ranging from <0.01 mg/dm^3 up to 1 mg/dm^3, with 0.1 mg/dm^3 as a typical value. Dissolving sulphide minerals are one source of sulphide in the groundwater, but sulphide will also be produced by a specific group of microorganisms, the sulphate-reducing bacteria, which are common in deep groundwater [13].

Tables 3a and 3b give predicted groundwater compositions for a repository at Forsmark and Oskarshamn respectively.

5.2.5. The near-field environment

Initially, a limited amount of air will be left in a KBS-3-type repository after emplacement, which during the water saturation phase partly will be trapped by the low permeability rim of groundwater-saturated bentonite. After water saturation the chemical environment in the immediate vicinity of the canister is determined by the composition of the bentonite pore water. This is, in turn, determined by the interaction between the bentonite and the groundwater in the surrounding rock. The entrapped oxygen will be consumed through reactions with minerals in the rock and the bentonite and also through microbial activity. After the

Table 2
Timetable for the final repository in Sweden



- Application to built an encapsulation plant submitted in 2006.
- Application for building the deep repository will be submitted in 2009.
- Deposition permit expected in 2017.
- Then trial operation with 400 canisters followed by evaluation.
- Finally regular operation.
- SKB's mission completed in 2060.

Table 3a
Predicted groundwater composition for a repository at Forsmark (contents in mg/dm^3)

	At emplacement	After saturation (<100 years after emplacement)	10000 years into the future
pH	6–8	7.0–7.9	7–9
E_{redox}[*]	0 to −400	−200/−250	−200 to −300
Na^+	300–2000	1700	100–1000
K^+	2–13	13	2–10
Ca^{2+}	150–1650	1650	20–1000
Mg^{2+}	17–110	110	4–100
HCO_3^-	50–300	47	20–40
Cl^-	500–5000	5500	200–5000
SO_4^{2-}	40–400	370	1–400
HS^-	0–10	<0.01	0–1

[*] mV SHE.

Table 3b
Predicted groundwater composition for a repository at Oskarshamn (contents in mg/dm^3)

	At emplacement	After saturation (<100 years after emplacement)	10000 years into the future
pH	6–8	7.7	8–9
E_{redox}[*]	0 to −400	−300	−200 to −300
Na+	1000–3000	2100	100–2000
K^+	5–20	8	2–10
Ca^{2+}	1000–3000	1890	20–2000
Mg^{2+}	10–200	42	1–40
HCO_3^-	10–1000	10	10–20
Cl^-	300–10000	6410	200–5000
SO_4^{2-}	100–600	560	1–400
HS^-	0–10	0.15	0–1

[*] mV SHE.

oxygen has been consumed in the repository, corrosion will be controlled completely by the supply of dissolved sulphide to the canister.

Results show that oxygen in the repository is consumed more rapidly than was first thought [18–19]. While early work estimated the oxic → anoxic transition to be in the range 10–300 years, recent studies predict that all oxygen in the groundwater may be gone after only one year after closure. It is above all the presence of bacteria and reactive minerals that are responsible for this reduction.

5.2.6. Microorganisms

Since SKB's investigations of life in the bedrock at Äspö started, microbiologists have identified many new species [20]. There are fewer bacteria down in the bedrock than on the surface. Microorganisms in the bedrock were earlier mostly considered a danger for the copper canister, since sulphate reducing species could lead to increased sulphide levels and increased corrosion. Now they are also considered helpful due to their oxygen removing capacity. Microorganisms can consume oxygen and, thus, hamper the corrosion of the copper canister.

Microorganisms have been shown not able to survive in highly compacted bentonite clay with a swelling pressure exceeding about 2 MPa [21]. The reason for that is not yet fully understood. It could be a combination of several factors where the low water activity, the high mechanical pressure and the very small pore sizes in the clay may contribute.

5.2.7. The environmental envelope

The copper canister will be exposed to many environments on its way from fabrication to final disposal:

- Different atmospheric conditions before encapsulation.
- Different atmospheric conditions after encapsulation.
- The near-field environment will vary with time.
- The initial oxic period.
- Fully saturated conditions.
- The anoxic period.
- Glaciations.
- What else?

5.2.8. View

The most important task from a corrosion perspective is to ascertain a proper near-field environment for the copper canister. The near-field environment will change with time. The initial oxic period is considered the most harmful, in particular when considering the risk of localization of the corrosion attack.

5.3. Corrosion during the oxic period

Copper coupons are exposed in the LOT test parcels in order to determine the nature and extent of copper corrosion during oxic conditions [9]. Exposure of coupons gives information about average corrosion rates, type of corrosion attack and corrosion products. From a life-time engineering point of view they are however of limited value.

Information obtained from the so far retrieved copper coupons is given below together with some comments about local corrosion of copper.

5.3.1. Corrosion rates

Average corrosion rates in the range from <0.5 μm/year (LOT test parcel A2 exposed six years) to 3 μm/year have been obtained. (For real-time corrosion rates in LOT test parcel A2 see below.)

5.3.2. Type of corrosion attack

A tendency to localization of the corrosion attack has been observed on coupons; the general corrosion is unevenly distributed on the copper surface, however, any signs of active pits have not been found [9].

Similar observations have been done in the Canadian R&D programme where the type of attack has been named 'under-deposit corrosion' [22].

5.3.3. Corrosion products

The corrosion products that have been identified on coupons from the retrieved LOT test parcels and on the canister from the 'Canister Retrieval Test' are cuprite, Cu_2O, and paratacamite, $Cu_2(OH)_3Cl$ [9b]. These are expected corrosion products [23]. The paratacamite appeared as blue-green corrosion products here and there on top of the brownish cuprite layer.

5.3.4. Proposed corrosion mechanism

The corrosion behaviour of copper in chloride media has been extensively treated in two recent reviews [13,24].

Even if available oxygen controls the extent of corrosion during the oxic period, the rate of corrosion is not necessarily governed by oxygen [13a]. Experimental findings are in fact not consistent with an oxygen mass-transport controlled corrosion reaction. The proposed mechanism for corrosion of copper in a bentonite/saline groundwater system during oxic conditions encompasses the following steps: (i) Cu dissolves reversibly as $CuCl_2^-$ which diffuses away from the copper surface (the rate-controlling step), (ii) part of the Cu(I) is precipitated as Cu_2O on the copper surface, (iii) part of the Cu(I) is irreversibly oxidized to Cu(II) by oxygen – $4Cu(I) + O_2 + 2H_2O \rightarrow 4Cu(II) + 4OH^-$, (iv) Cu(II) species are removed from the solution by adsorption and precipitation, and (v) part of the Cu(II) is reduced to $CuCl_2^-$ on the copper surface.

5.3.5. Comments on the tendency to pitting

Copper can suffer from pitting in aqueous environments. Pitting of copper tubing is known to be a generic problem in at least some potable water systems (treated shallow groundwater). The water chemistry is known to be crucial [25].

Even if a tendency to localization of the corrosion attack has been observed on copper coupons exposed in LOT test parcels, any obvious signs of pitting cannot be claimed. Neither have any findings of pitting on copper exposed to deep saline groundwater environments been reported in the literature [13]. Exposure of copper samples with deliberate surface defects in the form of drilled holes in either a synthetic groundwater/bentonite slurry or a bentonite equilibrated groundwater has not resulted in pitting [26].

Severe pitting of the copper canister seems unlikely.

5.3.6. Comments on the likelihood for stress corrosion cracking

Stress corrosion cracking (SCC) of pure copper is known to occur in certain environments [13,27]. It is not a very sensational circumstance that copper can be sensitive to SCC considering today's knowledge, and does not in any way disqualify it as a material for the canister. Most materials, if not all, show susceptibility under some circumstances. The objective is to assure that these circumstances do not appear in the intended application. For instance, while SCC was easily obtained when testing in a sodium nitrite solution, it was not observed when testing with the very same method in a bentonite equilibrated synthetic groundwater [27].

Since SCC is such a treacherous phenomenon, every precaution should be taken to assure that harmful circumstances do not appear in the final repository. Excessive residual tensile stresses on the outer surface of the canister should be avoided. Thus, friction stir welding is a very attractive welding method, since it is a thermo mechanical solid-state process that only introduces low residual stresses, which are of the same magnitude as the stresses from the swelling of bentonite. The propensity for SCC in the welds is thought not to be increased compared to the rest of the canister.

Further efforts will be made to gain a better insight into the conditions for SCC of pure copper.

5.4. Real-time corrosion monitoring at Äspö

Real-time monitoring of copper corrosion in a repository environment is of interest (i) to verify that we have a proper near-field environment and (ii) to learn more about the corrosion behaviour of copper and improve our understanding of the corrosion mechanism.

5.4.1. Real-time corrosion monitoring techniques

A number of electrochemical, electric resistance probe and quartz crystal microbalance techniques are available for real-time corrosion monitoring. The latter has an outstanding resolution, but can unfortunately not be applied in bentonite.

The electrochemical techniques that have been applied in the present work comprise polarization resistance, harmonic distortion analysis, electrode impedance spectroscopy, and electrochemical noise techniques. For the real-time corrosion monitoring at Äspö a commercially available SmartCET® corrosion monitoring system using a three-electrode set-up has been used [28]. The polarization resistance and harmonic distortion analysis techniques are used to derive information regarding the general corrosion rate. A voltage perturbation with a frequency of 0.01 Hz and 50 mV peak-to-peak amplitude is applied and the current response is measured and analyzed synchronously with the perturbing sine wave. The harmonic distortion analysis involves the measurement of the higher harmonic content at 0.02 and 0.03 Hz, which then allows for estimates of the anodic and cathodic Tafel slopes and the Stern–Geary coefficient.

These measurements are supported with back-up experiments. Electric resistance probes are used in one of them.

5.4.2. Copper electrodes in LOT test parcel A2

Cylindrical copper electrodes were installed in bentonite ring 36 belonging to LOT test parcel A2 that was emplaced in October 1999. Fig. 7 shows the experimental set-up. The real-time corrosion monitoring was initiated in May 2001 [28a]. The test parcel was retrieved in January 2006. A typical groundwater composition from the Äspö Hard Rock Laboratory is found in Table 3c.

5.4.3. Copper electrodes in the prototype repository

Cylindrical copper electrodes were also installed in the prototype repository: in the second upper bentonite block in deposition hole 1 and in the upper block in deposition hole 5. At times real-time corrosion monitoring has also been performed on these electrodes with the very same instrumentation as mentioned above.

5.4.4. Back-up experiments

After retrieval of LOT test parcel A2 in January 2006, a bentonite test package containing the cylindrical copper electrodes in bentonite ring 36 was placed in a plastic container, equipped with reference electrodes, and sealed with a thick layer of paraffin on all sides to maintain a similar environment (Fig. 8). Later on new copper and platinum electrodes and finally also electric resistance probes were installed in the test package [28].

Measurements with a SmartCET® corrosion monitoring system are performed on both the 'old' pre-exposed electrodes and new copper electrodes, and combined with corrosion potential, electrode impedance, electrochemical noise, and electric resistance probe measurements. Recorded data from the 'old' electrodes immediately before and just after retrieval of LOT test parcel A2 and from the new copper electrodes are shown in Figs. 9 and 10, respectively.

Back-up experiments have also been performed in synthetic bentonite equilibrated groundwater.

5.4.5. Findings

The following observations have been made: (i) very low instantaneous corrosion rates have been recorded [28,30]; recorded corrosion rates for the copper electrodes in LOT test parcel A2 (before retrieval) and in the prototype repository fall in the range 0.1–2.4 μm/year [30], (ii) even so the electrochemical techniques seem to overestimate the corrosion rate [30], (iii) the pre-exposed copper electrodes were greatly disturbed during retrieval of the LOT test parcel [29], see Fig. 9, (iv) quite a few months elapsed until the pre-exposed and the new copper electrodes after

Table 3c

A typical groundwater composition from the Äspö Hard Rock Laboratory

Ion	mM	mg/dm^3
Na^+	91	2100
K^+	0.2	8
Ca^{2+}	47	1890
Mg^{2+}	1.8	42
Cl^-	181	6410
HCO_3^-	0.2	10
SO_4^{2-}	5.8	560
HS^-	0.005	0.15
pH 7.7	E_{redox} −308 mV SHE	

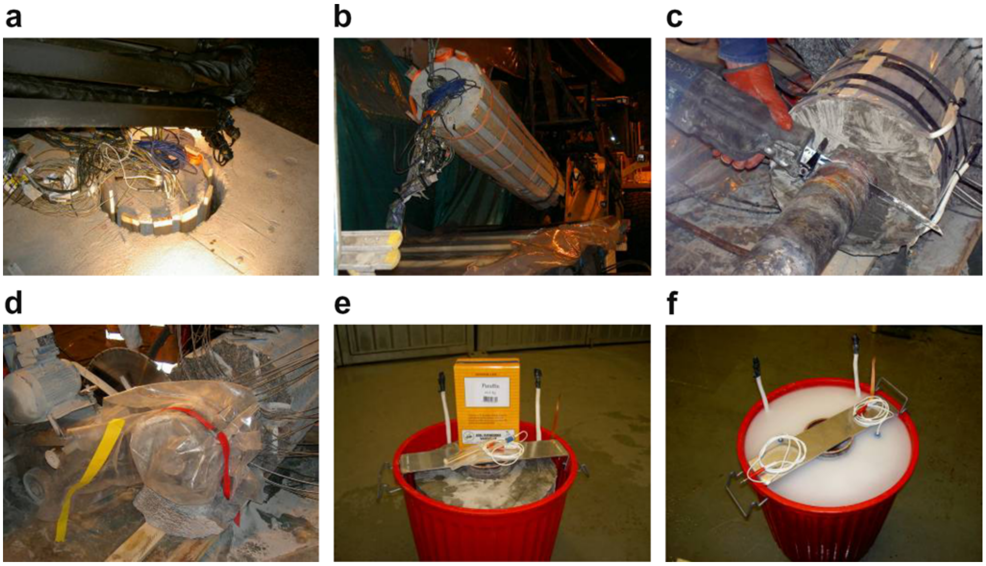


Fig. 8. Retrieval of the pre-exposed copper electrodes in January 2006. (a–b) Lift-up of the test parcel with surrounding rock, (c–d) cutting off the bentonite test package after removal of surrounding rock, and (e–f) moulding the bentonite test package in paraffin.

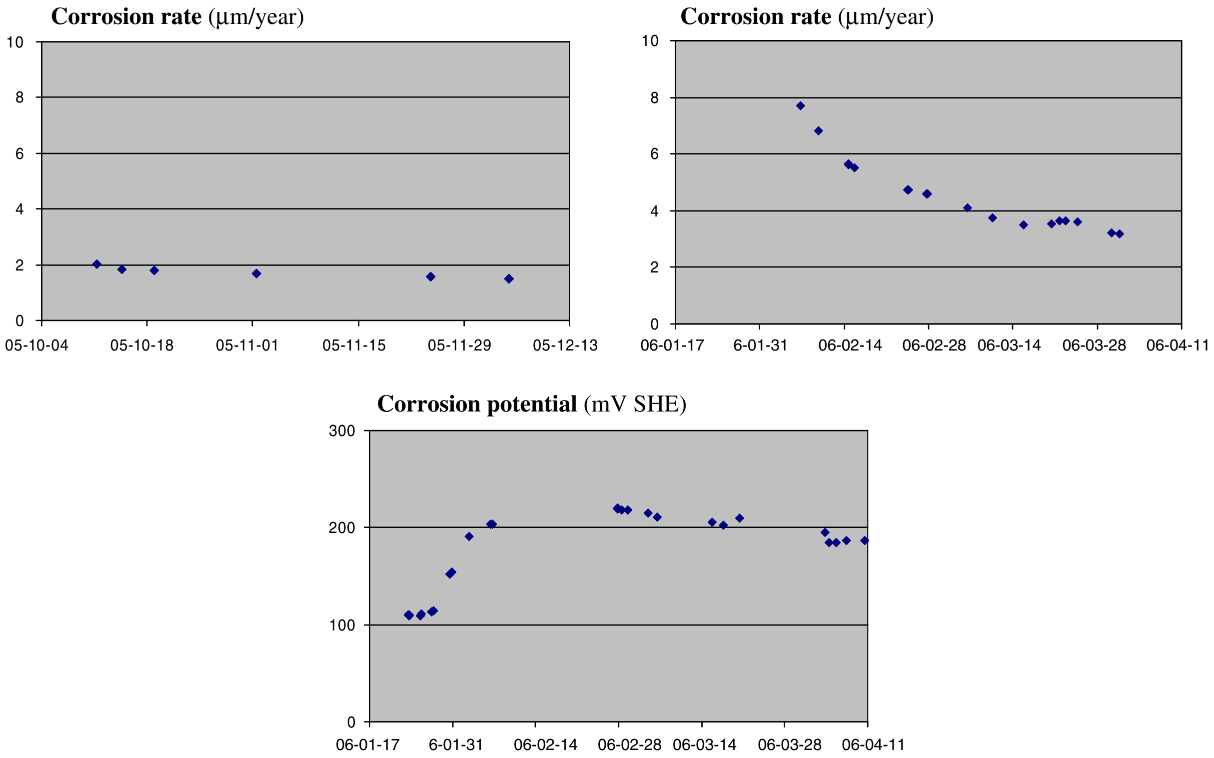


Fig. 9. The recorded corrosion rate (top left) just before retrieval and (top right) after retrieval, and the corrosion potential of one of the pre-exposed copper electrodes after retrieval. Time on the *x*-axis is given as dates (yy-mm-dd) and the retrieval date is 06-01-17.

their respective retrieval and installation returned to low steady-state corrosion rates (Figs. 9 and 10), and (v) the recorded corrosion rates are somewhat higher even long after retrieval; it is reasonable to believe that the bentonite and its swelling pressure contribute favourably to the corrosion resistance of copper in the bentonite/saline groundwater environment by means of improving the adherence of the cuprite layer, and maybe even decreasing the porosity of the outer cuprite layer on the copper surface.

The rationale of the overestimated corrosion rates: the overall 'electrochemical activity' is measured and a redox reaction shields the actual corrosion rate [30]. Alternatively, both the anodic and cathodic reactions are under charge-transfer control, and the corrosion rate is merely overestimated by not using a sufficiently low measuring frequency (0.01 Hz) to obtain the true polarization resistance. The results from the measurements with the electric resistance probes are supposed to clarify this.

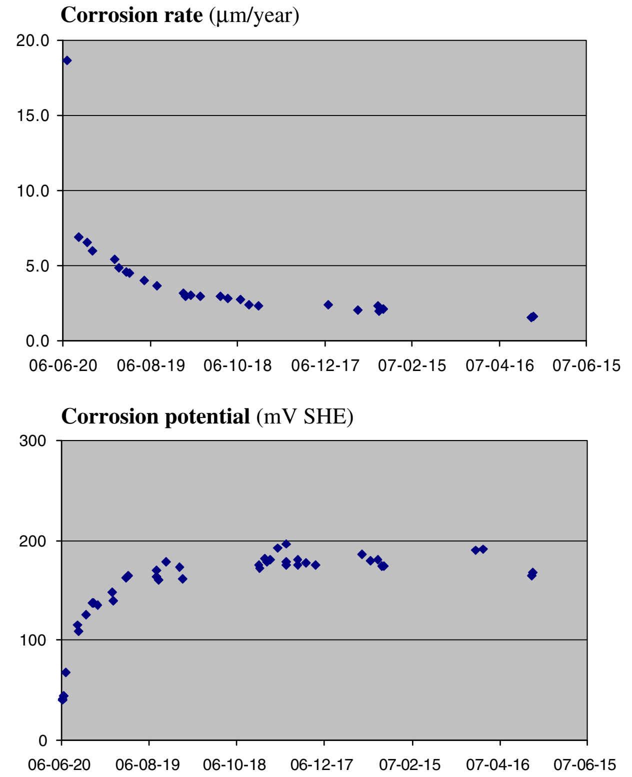


Fig. 10. The recorded corrosion rate (top) and the corrosion potential of one of the new copper electrodes after installation. Time on the *x*-axis is given as dates (yy-mm-dd).

6. Present view about the corrosion behaviour of copper

General corrosion will not be an engineering problem in a KBS-3 repository, neither from a structural integrity point of view nor from any risk to impair the properties of the bentonite. The inventory of oxidants is not enough.

Localization of the corrosion attack is of concern. However, severe pitting of copper in deep saline groundwater has neither been observed in the SKB R&D programme nor has it been reported in the literature and it seems unlikely.

The likelihood for SCC is considered low, but further efforts will be made to gain a better insight into the conditions for SCC of pure copper in bentonite/saline groundwater environments.

7. Summary

SKB has been conducting R&D on methods for safe disposal of nuclear waste for about 30 years.

The final repository – The method SKB has developed (named KBS-3) entails placing the waste in copper canisters and embedding the canisters in bentonite clay. The final repository will be built at a depth of about 500 m in the rock. Site investigations have been performed in the municipalities of Oskarshamn and Östhammar (Forsmark). A preliminary safety assessment based on data from both sites shows that good prospects exist for building a safe final repository in both municipalities. SKB plans to submit an application at the end of 2009 for a permit to build the final repository in one of these municipalities.

The SKB approach – Nature shows the way and research refines and verifies.

The lifetime engineering issue – The starting-point and answer to the seemingly overwhelming challenge stated by politicians to arrange a final storage for the nuclear waste ‘in an absolutely safe way’ with a life of a hundred thousand to a million years is: Nature shows the way. For excellent reasons we know that copper will last if proper environmental conditions are established and maintained. The key issue is then to ascertain a proper near-field environment for the copper canister.

Research refines and verifies – Besides rock movements, the biggest threat to the canister in the repository is corrosion. The initial oxic period is considered the most harmful, in particular when considering the risk of localization of the corrosion attack. The Äspö Hard Rock Laboratory offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository. Here electrically heated full-size canisters are presently exposed in the prototype repository and exposure of copper coupons is performed within the LOT experiment. Also real-time monitoring of copper corrosion are performed and combined with back-up studies for better understanding and evaluation.

While general corrosion will not be an engineering problem, localization of the corrosion attack is of concern. A tendency to localization of the corrosion attack has been observed on copper coupons, however, any signs of active pits have not been found.

Open issues are if low ionic strength water from a melting glacier may push down to the repository level for such a length of time and in such quantities that substantial bentonite erosion will occur and the possibility of SCC, which seems unlikely. Further efforts to better understand these issues will be made.

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