CHEMICAL DURABILITY OF COPPER CANISTERS UNDER CRYSTALLINE BEDROCK REPOSITORY CONDITIONS

ROLF SJÖBLOM*, HANS-PETER HERMANSSON** AND ÖRJAN AMCOFF***
*Swedish Nuclear Power Inspectorate, Box 27 106, S-102 52 Stockholm, Sweden
**Studsvik Material AB, S-611 82 Nyköping, Sweden
***University of Uppsala, Institute of Geology, Department of Mineralogy and Petrology, Box 555, S-751 22 Uppsala, Sweden

ABSTRACT

In the Swedish waste management programme, the copper canister is expected to provide containment of the radionuclides for a very long time, perhaps millions of years. The purpose of the present paper, is to analyse prerequisites for assessments of corrosion lifetimes for copper canisters.

The analysis is based on compilations of literature from the following areas: chemical literature on copper and copper corrosion, mineralogical literature with emphasis on the stability of copper in near surface environments, and chemical and mineralogical literature with emphasis on the stabilities and thermodynamics of species and phases that may exist in a repository environment.

Three main types of situations are identified: (1) under oxidizing and low chloride conditions, passivating oxide type of layers may form on the copper surface; (2) under oxidizing and high chloride conditions, the species formed may all be dissolved; and (3) under reducing conditions, non-passivating sulfide type layers may form on the copper surface.

Considerable variability and uncertainty exists regarding the chemical environment for the canister, especially in certain scenarios. Thus, the mechanisms for corrosion can be expected to differ greatly for different situations. The lifetime of a thick-walled copper canister subjected to general corrosion appears to be long for most reasonable chemistries. (It is assumed that the canister has no defects from manufacturing and that the bentonite buffer is intact). Localized corrosion may appear for types (1) and (3) above but the mechanisms are widely different in character. The penetration caused by localized corrosion can be expected to be very sensitive to details in the chemistry.

INTRODUCTION AND BACKGROUND

The aim of the Swedish programme[1,2] for the development of a system for the direct disposal of spent nuclear fuel is to contain the radionuclides for a very long time. One important strategy to achieve this aim is the application of the *multibarrier principle.*

This principle is applied in the Swedish reference disposal system[1], KBS-3, which is being developed by The Swedish Nuclear Fuel and Waste Management Company (SKB). In this system, the canisters are deposited in holes drilled through floors of tunnels with compacted bentonite clay in between the canisters and the surrounding crystalline basement rock. Barrier functions are provided by the spent fuel itself, by the canister, by the bentonite backfill and by the surrounding rock.

In the Swedish programme[1,2], a great emphasis is put on a long-life canister. The reference canister consists of an inner one made of steel and an outer one made of almost pure copper. The steel canister is intended to provide mechanical support and the copper canister to provide corrosion resistance. Thus, it is essential that assessments - and assurances - can be made regarding the performance of the canisters under repository conditions.

It should be observed, that the long-term performance of the canister must be maintained without any further intervention (e.g. inspection, maintenance or modifications) after the closure of the repository.[2]

Another important prerequisite is that the testing of the canister can only be carried out during times that are much shorter in duration than the intended design life.

Thus, it is essential that all processes relevant to the degradation of the canister should be fully understood and adequately dealt with.[1-4] For the corrosion processes, it is necessary to understand the chemical conditions and reactions in the vicinity of the canister as well as on its surface[2,5,6].

A first prerequisite for the long service life of a canister is that it can be shown to resist *general corrosion* for the required duration. Estimates of lifetimes with regard to general corrosion are usually based on estimates of the availability of reacting species. This availability, in turn, is normally limited by diffusion resistance in the bentonite, possibly in combination with limits on the access of reactive species to the outside of the bentonite.

If the lifetime of a canister is limited by *localized corrosion*, the lifetime will depend on a combination of the availability of reactive species and the mechanism of the attack.

Thus, when the corrosion performance of a copper canister in a repository for spent nuclear fuel is to be evaluated, it is necessary to understand:

- the chemistry of the water contacting the canister
- the reactions that take place at the copper surface
- the properties of the reactants formed
- the migration of reactive species to the canister
- the migration of reactants away from the canister surface.
- the mechanism(s) for the corrosion process(es).

These aspects have been analysed[6-14] as a part of a performance assessment project[6], SITE 94, which is presently being carried out by the Swedish Nuclear Power Inspectorate (SKI). As a part of this project, the general corrosion of a copper canister has been simulated.[13-14] Simulations are also underway for localized corrosion, although this is a more complex task and also subject to greater uncertainties.

The safety to be assessed is that of the entire repository. It is necessary that the safety analysis should be comprehensive, integrated and transparent. It should be based on a thorough understanding of all pertinent phenomena as well as the interrelations between the different parts of the process system.

In SITE 94, a scenario analysis is being carried out as a special sub-project[6]. The purpose of the scenario analysis is to establish a structure for the analysis and to visualize that structure.

Three types of external conditions that may affect canister stability have been identified in SITE 94: mechanical load, manufacturing deficiencies, and the future chemical composition of the groundwater.

The present paper deals with the chemical durability of the copper canisters under crystalline bedrock repository conditions. The purpose of the paper is to compile relevant background knowledge and to analyse and discuss corrosion processes that may determine the lifetime of a copper canister in a repository for spent nuclear fuel.

Issues relating to mechanical loads are beyond the scope of the present paper. This includes synergetic effects involving tensile stresses in combination with chemical attacks - so-called *stress corrosion.*

CHEMICAL ENVIRONMENT

The reactions that might take place at the copper surface depend i.a. on the composition of the surrounding groundwater and of the bentonite clay[6].

The composition of the groundwater is strongly dependent on the composition of the fracture minerals and also on that of the surrounding host rock. The composition of the groundwater can vary considerably, even within a limited rock volume. In particular, the composition varies with depth[6]. Considerable variations can also be expected to appear with time.[6] In addition, there are large uncertainties regarding the future evolution of the groundwater.[6]

Table I. *Content of certain species in three groundwaters at the Äspö site. Concentrations in mg/ℓ.*

bore hole depth	KAS02 530-535 m	KLX02 1631-1681m	HLX01 0-50m
Na	2100	8200	32.5
Ca	1890	18500	37.8
Fe	0.244		4.22
Mn	0.29		
Cl	6410	47200	18
HCO_3	10	14.1	115
SO_4	560	905	47.8

In Table I compositions are given for three selected typical groundwaters at the Äspö Hard Rock Laboratory site in southeast Sweden.[6] The listing includes only dominating species or species of interest for copper corrosion purposes.

The water contacting the canister will be somewhat different from the groundwater in the surrounding rock. The main reasons for these differences are interactions with the bentonite clay and the presence of residual air from the operational phase.

In particular, it can be expected that the redox potential, the iron(II) content and the reduced sulfur content be modified through interactions between the groundwater and the iron sulfide in the bentonite.

During the operational phase, and for some time after closure of the repository, oxygen originating from air may be present in the water contacting the canister[15]. The availability of such residual oxygen for canister corrosion depends on a number of factors, amongst others:

- the initial degree of water saturation in the backfill as well as the manner in which the bentonite takes up water
- the rate and the distribution of the inflow of groundwater to the bentonite
- the rate and the mechanism for oxidation of the iron sulfide in the bentonite
- the pattern of diffusion of the dissolved oxygen

It is also conceivable that surface water containing oxygen might reach repository depth.[6]

Moreover, neither of the concentrations of chloride, sulfide, sulfate and iron(II) ions can be expected to be simple functions of time.

Under reducing conditions, the groundwater will typically contain reduced sulfur species. These will consist of sulfide, hydrogen sulfide, and polysulfide ions. The relative composition will depend on the pH and Eh. The conversion between sulfide and polysulfide ions has been observed to be kinetically hindered[10]. Under mildly oxidizing conditions, sulfur in the iron sulfide might oxidize to form polysulfides.

No example has been found[1] where sulfate ions are reduced under groundwater conditions without the action of microorganisms. The direct reduction of sulfate ions by copper is not thermodynamically possible[1]. Sulfidation of copper by sulfate is, however, thermodynamically possible if iron-II is present[1]. It has been found[16] that even deep fracture systems in crystalline bedrock may host significant microbiological activity (including sulfur-reducing bacteria).

COPPER CHEMISTRY

Copper and copper alloys have been known to man for thousands of years[10]. They are well-known for their resistance to corrosion in near surface environments as has been observed on archaeological artifacts and occurrences of native copper.

This resistance to corrosion can be explained in part by the fact that copper is thermodynamically stable in *pure* oxygen free water[1,7]. However, dissolved species in e.g. groundwater can oxidize copper to form solid phases or dissolved species. At high electrochemical potentials, the solid phases formed are expected to be oxides and oxide-related phases. At low potentials, the solid phases formed are expected to be sulfides and sulfide-related phases.

In the presence of oxygen, and in neutral to moderately alkaline water solutions, copper is oxidized to copper(II)oxide. When present, hydroxide, chloride, sulfate and carbonate ions might be incorporated into the copper(II)oxide type of solids.[9] Different phases will form, depending on the details in the chemistry of the water contacting the canister.[9] The candidate phases include[9]: tenorite (CuO), connellite ($Cu_{37}Cl_8(SO_4)_2(OH)_{62}*8H_2O$), paratacamite ($Cu_2(OH)_3Cl$), brochantite ($Cu_4SO_4(OH)_6$), malachite ($Cu_2CO_3(OH)_2$), and azurite ($Cu_3(CO_3)_2(OH)_2$).

If access to oxygen is limited, copper(I)oxide, cuprite (Cu_2O), is formed instead. Copper(I) is stabilized by chloride ions through the formation of copper chloride complexes. Most of these complexes are charged and appear in solution. Thus, under such conditions, it is possible that no solid phase will form on the copper surface.

Copper reacts swiftly with reduced sulfur species to produce copper sulfide and hydrogen. A simplified Pourbaix diagram showing the stability and metastability fields of copper and reduced sulfur is given in Figure 1.[9,17] As is explained in the figure legend, the stability and metastability fields encountered are very different depending on whether the change is from oxidizing to reducing conditions, or vice versa.[9,17]

Cations present in the groundwater - especially transition metals with a low charge - may, in many cases, readily be incorporated into copper sulfide type phases. This chemistry is even more

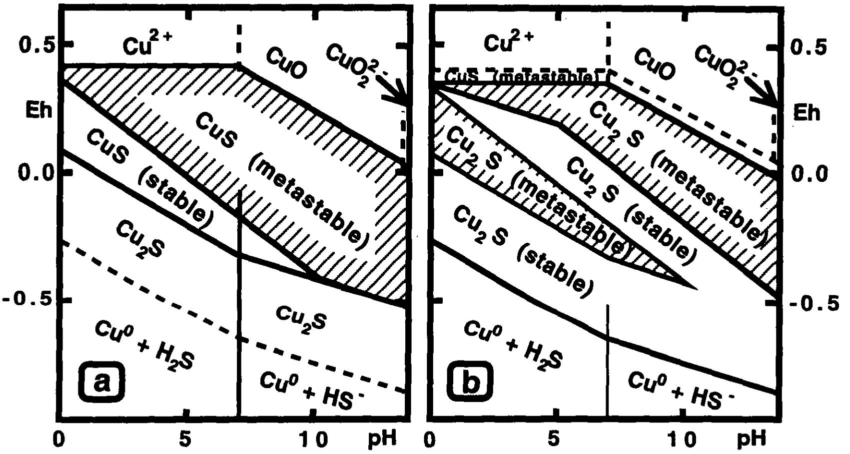


Figure 1. *Persistency fields of (a) copper(II) sulfide and (b) copper(I) sulfide. Several phases of intermediate composition exist; they have been neglected for simplicity. Reduction reactions can be expected to correspond relatively well with equilibrium processes (the lower persistency boundaries in the diagrams), while the oxidation reactions are typically path-controlled (more sulfur-rich phases are formed). Note that in a real repository situation other transition elements will probably also be present in any sulfides formed. See Reference [9] for details.*

complex[9]. The compositions are typically variable, there are many phases and hysterisis effects are legio (kinetic factors play a prominent role). Conversions between phases typically involve redox reactions as well as metastabilities[9]. A typical example of this behaviour can be found in the copper - iron - sulfur system which is described in Reference [9]. This system is of particular interest since iron(II) is present in the groundwater and since the bentonite clay contains iron sulfide.

Much of the explanation of the behaviour of copper under reducing conditions can be found in the fundamental chemistries of copper and sulfur[8,9,10,18]. In sulfides, copper has never been observed to have any other oxidation number than +1.[18] This situation is very different as compared to that for oxides where copper may have oxidation numbers +2 or +1, as mentioned above. The explanation of this behaviour is that sulfur - contrary to oxygen - is not sufficiently electronegative to remove more than one electron from the copper atom. Instead, sulfur has a valence that varies between -1/2 and -2.

Moreover, in most - or perhaps all - copper sulfides, some of the valence electrons are delocalized and give rise to a high electric conductivity. Typically, there are many vacant sites in the structures and a consequent high mobility of cations[9,18].

The fundamental differences that exist between the copper oxide and the copper sulfide chemistries imply that the character of a corrosion attack on a copper canister can be very different depending on the circumstances.

COPPER CORROSION

Under oxidizing, low chloride conditions and at intermediate pH values, copper(I) and copper(II) oxide type layers can be expected to form on copper surfaces. Typically, a copper(I) oxide layer is formed between the copper surface and the copper(II) oxide type layer. Such layers are poor electrical conductors, have a (relatively) fixed composition and show a low mobility of charged species. Thus, the layers can be expected to be protective, i.e. once formed, they will inhibit any further attack on a general corrosion basis.

This situation is a comparatively favourable one from the point of view of canister longevity. The oxygen available only reacts slowly with the canister, thus providing time for reactions with other species that can be oxidized e.g. the iron sulfide in the bentonite. Moreover, since the attack is even, a considerable amount of oxygen will have to diffuse to the canister surface and react before any penetration can take place.

The protective layers on the copper surface are protective in the sense that they hinder reactions that would otherwise take place. Under certain circumstances, local chemistries, different from those in the bulk of the groundwater, may develop in the close vicinity of and on isolated parts of the copper surface. The microchemistry at the copper surface may be separated into anodic and cathodic areas perhaps related to faults in the passive film. At such localized parts, pits can form and, once initiated, they might propagate since the chemical conditions in a pit will inhibit restoration of the local protective film. The mechanism is illustrated in Figure 2.

The possibilities for pit formation as well as the pitting factor can be expected to depend strongly on the details of the chemical environment. (The pitting factor is the ratio between the depth of the deepest pit and the depth of the average corrosion). No records have been found in literature on experimental investigations of pitting corrosion on copper under conditions that resemble those in a nuclear waste repository.[16]

Pitting has, however, been observed on many metals. In cases where the metal surface is passivated by an oxide layer, certain general patterns can be identified. Thus, at low electrochemical potentials, a metal typically shows immunity towards corrosion. At high electrochemical potentials in combination with acidic conditions, no protective layer is formed and a rapid general corrosion can be observed. At high electrochemical potentials, together with moderate to high pH-values, "perfect" passivation might occur (with associated slow uniform corrosion). In between the latter two areas, and above a minimum electrochemical potential (the protective potential[19]), pitting might take place. The location of the pitting area in the Pourbaix diagram is typically heavily dependent on details in the chemistry, e.g. the chloride concentration. The pits are typically shallow on the acidic side and deep on the alkaline side.

Under ordinary conditions, pitting corrosion is rarely observed on copper. This is due to the nobel character of copper itself in combination with the good passivating properties of copper oxides, extending to very high electrochemical potentials. Normally this implies that high potentials are required to initiate a pitting process, potentials that are encountered when the system is in contact with air. However, the situation might be quite different if the chemistry of the water is unfavourable.

Under oxidizing and high chloride conditions, the oxidized copper may form charged chloride complexes that appear in solution. Under such conditions, it is possible that no solid phases will form on the copper surface, and the corrosion can be expected to be uniform.

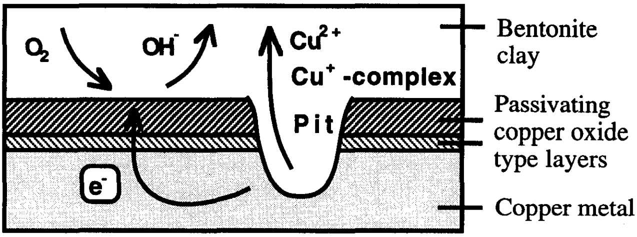
However, a real situation could be more complex[20]. Copper(I) complexes formed at the copper surface may diffuse away from the surface and then react with oxygen to form copper(II) which, in turn, may or may not form dissolved species depending on the specific chemistry. If dissolved species are formed, some of them will diffuse away from the copper surface while others may diffuse to the vicinity of the copper surface. In the latter case, copper(II) and copper(0) may react to form copper(I).

Nonetheless, the copper surface might be clean and the corrosion uniform. (Another possibility is that a slow access of oxygen gives rise to a mild oxidation of iron sulfide in the bentonite. In such a case, polysulfides may form, diffuse to the copper surface and participate as reducible species in corrosion processes).

Under reducing conditions and in the presence of dissolved reduced sulfur species, sulfide layers may form on the copper surface. These layers can not be expected to be protective since they are (at least for the most part) good conductors of electrons as well as of copper cations[9,18]. Consequently, no mechanism for the formation of normal corrosion pits has been identified.

Figure 2.

Mechanism for pitting corrosion of copper



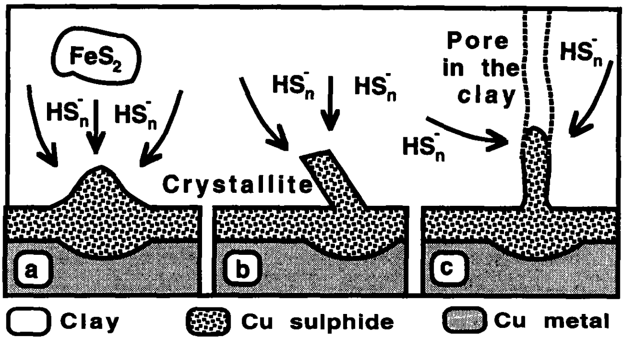


Figure 3.

Proposed mechanism for localized corrosion under reducing conditions

It might therefore be tempting to conclude that such corrosion must be uniform. Localized corrosion is still conceivable, however. It should be realized that while reduced sulfide species can migrate (diffuse) through the groundwater, copper can also be expected to be quite mobile in the copper sulfides formed. Copper might actually transfer more rapidly through the solid sulfide phase formed than reduced sulfur transfers through the groundwater. In such a case, the growth of sulfide on the copper canister might take place at specific locations to form outgrowths of a "whisker"-type using copper from underneath the whisker base. A second possibility is growth of sulfide crystallites in preferred directions and a third possibility is formation of sulfide phase preferentially in voids in the bentonite. In such processes, pits will form although the mechanism for pitting is entirely different from the one described above for oxidizing conditions. The mechanisms are illustrated in Figures 3a-c.

CANISTER PERFORMANCE

The chemical durability of a canister depends on the availability of reactive species and the mechanism of the attack. Evaluations of the availability of reactive species can usually be converted in a relatively straightforward manner to general corrosion lifetimes. They are also necessary when localized corrosion is to be evaluated.

Several calculations of general corrosion have been reported[1,6,13,14] for KBS-3 type of repositories. In most cases, it has been assumed or presumed that residual oxygen will react within a short time, at most a few hundred years. Consequently, previous work concentrated on general corrosion under reducing conditions.

Recently, as a part of the SITE 94 work at SKI, calculations of general corrosion have been carried out for three cases:[13,14]

- diffusive mass-transport of sulfide through the bentonite to the canister surface under reducing conditions (the sulfide originates from the groundwater as well as from the iron sulfide in the bentonite)
- diffusive mass-transport of oxygen from the surrounding groundwater to the canister surface
- diffusive mass-transport of copper chloride species away from the canister surface under comparatively highly oxidizing conditions

In most of the cases analysed, the calculations result in general corrosion canister lifetimes of several hundred thousand years, and longer.

Such results from calculations should, however, not be accepted as likely containment times without a careful analysis of e.g. assumptions and uncertainties. Some topics for such caution may be the following:

- the process for resaturation of the repository with groundwater after closure
- the attack on the canister by uniform corrosion can be expected to take place at different rates on different parts of the surface due e.g. to differences in access to oxygen
- if large pores of unfavourable shapes are present in the canister (e.g. defects from manufacturing), the effective thickness might be significantly reduced
- changes in the groundwater with time
  - * intrusion of oxygenated water (e.g. in connection with a glaciation)

  - * cyclic variations
- changes in the properties of the bentonite with time, including possibilities of channeling
- reduction of sulfate ions through the action of microorganisms (such calculations have actually been performed[13,14])

One interesting feature of general corrosion calculations is that they indicate the significance of intact bentonite barriers and the importance of understanding phenomena that might be detrimental to the barrier functions.

In order to evaluate canister durability with respect to localised corrosion, it is necessary to describe the local character of the attack (in addition to knowing the concentrations of reactive species and their time dependencies).

In previous work[1,13,14] on localized corrosion, the local character of the attack has been taken into consideration by the utilization of a pitting factor. Such an approach has the advantage of simplicity and might be useful for illustrations of the significance of localized corrosion.

It was discussed in the previous section how at high electrochemical potentials, the conditions for pitting corrosion - as well as the shapes of the pits - change with chemistry. It can be expected, that the degree of local character of the corrosion (determined e.g. as the pitting factor) is very sensitive to details in the chemistry. For moderate changes, the system might shift between passivation, pitting and rapid general corrosion.

It should be remembered, especially when localized corrosion is being considered, that the canisters will have to be manufactured, and that different deficiencies may be introduced in the manufacturing processes. Thus, a real canister may have pores and fissures of different sizes and shapes that may promote crevice corrosion. (Crevice corrosion is similar in nature to pitting corrosion). Moreover, matter may segregate in the weld and this could also give rise to localized corrosion if parts of the weld become more susceptible to chemical attack. Segregation of matter could also take place through excessive grain growth which, in turn, could also lead to localized corrosion.

CONCLUDING REMARKS

In the present paper, results from previous and ongoing work[6-14] within the SITE 94 safety analysis project have been presented. The main conclusions so far are as follows:

- Considerable variability and uncertainty exist regarding the chemical environment for the canister, especially in certain scenarios.
- The mechanisms for corrosion can be expected to differ greatly for different repository environments.
- The lifetime of a thick-walled copper canister subjected to general corrosion appears to be long for most reasonable chemistries. (It is assumed that the canister has no defects from manufacturing and that the bentonite buffer is intact.)
- Localized corrosion appears to be possible under reducing as well as oxidizing conditions. The mechanisms are widely different, however.
- The penetration caused by localized corrosion can be expected to be very sensitive to details in the chemistry.

At present, work is underway to determine the actual compositions, redox potentials and pH-conditions under which pitting corrosion can take place as well as the local character of the attack. Other activities are aimed at determining the significance of different factors for localized corrosion under reducing conditions.

REFERENCES

1. RD&D Programme 92, Treatment and final disposal of nuclear waste. Programme for research, development and demonstration and other measures. SKB, Stockholm, September 1992. The reference also includes background reports on siting, detailed R&D Programme and Äspö Hard Rock Laboratory.

2. SKI's Evaluation of SKB's RD&D Programme 92, Summary and conclusions. SKI Technical Report 93:24, Stockholm, May 1993. The reference also includes the review report, SKI Technical Report 93:30, Stockholm, June 1993

3. R. Sjöblom, J. Andersson and S. Norrby. The review of the Swedish R&D Programme 92 for handling and final disposal of nuclear waste. Safewaste 93, International Conference on Safe Waste Management and Disposal of Nuclear Waste, Avignon, France, June 14-18, 1993.

4. R. Sjöblom, B. Dverstorp and S. Wingefors. Objectives and limitations of scientific studies with reference to the Swedish RD&D Programme 1992 for handling and disposal of nuclear waste. Scientific Basis for Nuclear Waste Management XVII, edited by A. Barkatt and R. A. Konynenburg, Materials Research Society, Pittsburgh, 1994, pp. 209-216.

5. R. Sjöblom. Corrosion aspects of copper in a crystalline bedrock environment - with regard to life prediction of a container in a nuclear waste repository. Application of Accelerated Corrosion Tests to Service Life Prediction of Materials, ASTM STP 1194, Gustavo Cragnolino, and Narasi Sridhar, Eds., American Society for Testing and Materials, Philadelphia, 1993.

6. The SKI performance assessment project SITE 94. Main report. SKI Report, in preparation.

7. K. Möller. Copper corrosion in pure oxygen-free water (in Swedish), SKI Technical Report, in print.

8. Ö. Amcoff and K. Holényi. Stability of metallic copper in the near surface environment. SKN Report 57, Stockholm, March 1992. ISBN 91-38-12740-7.

9. Ö. Amcoff and K. Holényi. Mineral formation on metallic copper in a future repository site environment. SKI Technical Report, in print.

10. U. Engman and H-P Hermansson. Corrosion of copper materials for encapsulation of radioactive waste - a literature study (in Swedish). SKI Report 94-6, Stockholm April 1994.

11. B. Beverskog. Copper species in the S - Cl - C environment (in Swedish). SKI Technical Report, to be published.

12. B. Beverskog. Corrosion behaviour of the copper - iron canister (in Swedish). SKI Technical Report, to be published.

13. K. J. Worgan and M. J. Apted. CAMEO: A model of mass-transport limited general corrosion of copper canisters under simulated repository conditions. SKI Technical Report, in print.

14. K. J. Worgan, M. J. Apted and R. Sjöblom. Performance analysis of copper canister corrosion under oxidizing or reducing conditions. Scientific Basis for Nuclear Waste Management XVIII, edited by R.C. Ewing and T. Murakami, Materials Research Society, Pittsburgh, in press.

15. P. Wersin, K Spahiu and J Bruno. Time evolution of dissolved oxygen and redox conditions in a HLW repository. SKB Technical Report 94-02, Stockholm, February 1994.

16. K. Pedersen. The deep subterranean biosphere. Earth-Science Reviews, **34**, 243 (1993).

17. M Sato. Persistency-field Eh-pH diagrams for sulfides and their application to supergens oxidation and enrichment of sulfide ore bodies. Geochimica et Cosmochimica Acta **56**, 3133 (1992).

18. R. Berger, Inst. of Chemistry, University of Uppsala, Sweden. Private communication.

19. M. Pourbaix. Significance of Protection Potential in Pitting and Intergranular Corrosion. Corrosion **26**(10), 431(1970).

20. F. King, D.M. LeNeveu and D. J. Jobe. Modelling the effects of evolving redox conditions on the corrosion of copper containers. Scientific Basis for Nuclear Waste Management XVII, edited by A. Barkatt and R. A. Konynenburg, Materials Research Society, Pittsburgh, 1994, pp. 901-908.