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Corrosion of the Copper Canister in the Repository Environment

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Abstract

The present report accounts for studies on copper corrosion performed at Studsvik Material AB during 1997-1999 on commission by SKI. The work has been focused on localised corrosion and electrochemistry of copper in the repository environment.

The current theory of localised copper corrosion is not consistent with recent practical experiences. It is therefore desired to complete and develop the theory based on knowledge about the repository environment and evaluations of previous as well as recent experimental and field results.

The work has therefore comprised a thorough compilation and up-date of literature on copper corrosion and on the repository environment. A selection of a “working environment”, defining the chemical parameters and their ranges of variation has been made and is used as a fundament for the experimental part of the work. Experiments have then been performed on the long-range electrochemical behaviour of copper in selected environments simulating the repository.

Another part of the work has been to further develop knowledge about the thermodynamic limits for corrosion in the repository environment. Some of the thermodynamic work is integrated here. Especially thermodynamics for the system Cu-Cl-H-O up to 150 °C and high chloride concentrations are outlined. However, there is also a rough overview of the whole system Cu-Fe-Cl-S-C-H-O as a fundament for the discussion. Data are normally accounted as Pourbaix diagrams.

Some of the conclusions are that general corrosion on copper will probably not be of significant importance in the repository as far as transportation rates are low. However, if such rates were high, general corrosion could be disastrous, as there is no passivation of copper in the highly saline environment.

The claim on knowledge of different kinds of localised corrosion and pitting is high, as pitting damages can shorten the lifetime of a canister dramatically. Normal pitting can happen in oxidising environment, but there is probably a chloride induced passivation mechanism slowing down such pitting in the long run. A mechanism for this is proposed here.

A special family of local attacks, based on the growth of sulphide, oxide/hydroxide and even carbonate/malachite whiskers, could also happen in the repository. It has been demonstrated in the experimental part of this work that whiskers can grow on copper in repository related environments containing sulphide. The chemical composition of such whiskers and their growth mechanism is treated in the present work. The integrity related consequences for the copper substrate on which they grow still remains, however, to be investigated.

Reviewed by Approved by

Sammanfattning

I föreliggande rapport redogöres för studier av kopparkorrosion som utförts vid Studsvik Material AB under tiden 1997-1999 på SKIs uppdrag. Arbetet har koncentrerats på lokal korrosion och elektrokemi hos koppar i slutförvarsmiljö.

Den teori som för närvarande beskriver kopparkorrosion stämmer inte överens med experimentella resultat som framkommit på sistone. Av den anledningen är det önskvärt att komplettera och utveckla teorin på basis av kunskap om förvarsmiljön, utvärderingar av nya och gamla experiment och av fältobservationer. Det främsta målet för föreliggande arbete är att vidareutveckla kunskapen om lokal korrosion i förvarsmiljön och att selektera kritiska experiment som kan hjälpa till att vidareutveckla teorin.

Arbetet utgör en omfattande redovisning och en genomgripande uppdatering av litteraturen om kopparkorrosion och om förvarsmiljön. Ett urval av "arbetsmiljöer" har gjorts för vilka kemiparametrar och deras variationsområden definierats. Dessa parametrar har varit fundament för planeringen av den experimentella delen av arbetet. Experiment har sedan utförts med fokus på långsiktigt elektrokemiskt beteende hos koppar i några valda miljöer som simulerar möjliga slutförvarssituationer.

En annan del av arbetet har varit att vidareutveckla kunskapen om de termodynamiska gränserna för kopparkorrosion i slutförvarsmiljön. En del av de termodynamiska beräkningarna inkluderas här. Speciellt beskrivs termodynamiken för systemet Cu-Cl-H-O upp till 150 °C och höga kloridhalter. Det redovisas också en grov genomgång av hela systemet Cu-Fe-Cl-S-C-H-O som ett fundament för diskussionen. Redovisningen sker i form av Pourbaix diagram.

Allmän korrosion kommer förmodligen att sakna betydelse i förvarsmiljön så länge som transporthastigheter är låga. Om högre transporthastigheter skulle inträffa under något skede skulle allmänkorrosion dock kunna vara katastrofal. Detta beror på att höga kloridhalter förhindrar utbildningen av en effektiv passivfilm samtidigt som koppars immunitetsgräns sänks.

Kraven på kunskap om lokal korrosion och gropfrätning är stor eftersom gropfrätning kan förkorta kapslarnas livstid dramatiskt. Normal gropfrätning kan inträffa i oxiderande miljö. Troligtvis finns dock en kloridbaserad inhiberingsmekanism som minskar angreppshastigheten på sikt. Mekanismen diskuteras här.

En speciell familj av lokal attack, baserad på tillväxt av sulfid, oxid/hydroxid och även karbonat/malakit whiskers kan uppträda i förvarsmiljön. Det har visats inom den experimentella delen av detta arbete att whiskers kan växa på koppar i en förvarsrelaterad miljö som innehåller sulfid. Den kemiska sammansättningen och tillväxtmekanismen hos sådana whiskers har belysts. Konsekvenserna för kopparkapselns integritet återstår dock att utreda närmare.

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1 Introduction

According to SKB, the purpose of the waste canister is to provide safety during handling and emplacement of the waste in the repository and also to ensure complete isolation of the waste for a desired period of time. For this time period, 500 to 1000 years is generally considered as the absolute minimum, as the most important fission products have decayed thereafter. This is also the time period during which the heat generation in the waste due to decay is still of importance.

After this introductory period it is required that most canisters still keep their isolating capacity for a very long time. Virtually all times up to several 100 000 years are necessary in order to bring the activity levels down to that of natural uranium. In order to fulfil these requirements, several materials have been considered for the canister as titanium and titanium alloys, carbon steel and copper. Due to its stability in water, copper was presented as reference canister material for the Swedish program.

In a previous research plan from SKB [1] a decrease of the importance of the multi-barrier principle was implied as only a small emphasis is put on geology. Therefore the engineered barriers and especially the canister is rendered a much larger importance for the system integrity. This implies that it is reasonable to put much higher emphasis on all functions of the canister. The proof burden of the canister lifetime thereby increases strongly and the accumulation of knowledge should therefore increase. Because of this general requirement it is motivated to perform a thorough discussion about canister integrity and corrosion focused on eliminating the risks before they manifest themselves in the repository. An appropriate way to do this is by an interaction between experiments and modelling.

An important phenomenon to model for the copper canister is pitting corrosion as this phenomenon to a large extent can shorten the lifetime of the canister. Studies of pitting corrosion and other types of local attack on copper in repository environment are therefore an important part of the SKI commissioned work accounted for here.

The task includes a compilation of results from previous projects performed on commission by SKI. Moreover, existing data have been completed; i.a. with data from an extended literature search specifically on pitting corrosion and local attack on copper and also concerning the repository environment.

The present report is therefore founded both on an extended literature study, thermodynamic calculations and on experimental work on pitting corrosion. The focus is on localised corrosion in the repository environment. The growth of sulphide induced whiskers is also an important part of the study.

The current theory of copper corrosion is not consistent with recent practical experience [2]. It was therefore desired to complete and develop the theory of copper corrosion based on knowledge about the repository environment and evaluations of previous as well as recent experimental and field results. It is very important to emphasise localised corrosion in the repository environment and to point out critical experiments that would help to enlighten the status of the theory. A thorough literature review of copper corrosion was performed to generate a firm basis for subsequent work.

A review of the environment conditions was also made in order to formulate the basis for development of the theory. Much work concerning the environment has already been performed and the objective here is not again to formulate an environmental matrix for the repository. However, there is a need of complementary work especially related to knowledge of critical combinations of parameters related to localised copper corrosion. One example of work that should be performed is to determine possible maximum and minimum limits of critical concentrations, i.a. of chloride, to be used in subsequent discussions of consequences.

One important part of the present work is a thermodynamic evaluation of copper stability in the repository environment. The work has resulted in a systematic description of copper thermodynamics (system Cu-Cl-H-O) at high chloride concentrations up to 150 °C. The present work completes a couple of previous accounts [3]. This is of importance as chloride could prevent the formation of a passive film especially in a case when saline water intrudes the repository. The chemical environment of the repository is, however, more complicated and a corresponding study for the copper system simultaneously containing iron, sulphur, chloride and also other elements should be performed in a systematic way. Some preliminary calculations of such complexity is presented here in order to support the discussion.

It has been demonstrated both theoretically and by experiments that whiskers can form on copper at certain combinations of the chemical parameters of the environment. Especially the presence of sulphide is important. If whisker growth proceeds by local consumption of copper, the formation of whiskers could result in similar consequences for the physical integrity of the copper canister as normal pitting would do in an oxidising environment. This means that a kind of pitting mechanism, however very different from the normal type, could appear and cause a break through of the copper wall of the canister. However, whisker growth on copper is demonstrated, such a degradation mechanism remains to be fully investigated.

It is important to clarify the nature of the whiskers and the chemical limits for their formation. At least as far as this is possible by indicating the critical intervals of the environmental parameters as potential, pH and concentrations of chemical components. It is especially important to penetrate the growth conditions in oxidising as well as reducing environments. The present report contains an account and discussion of results from both theoretical and practical work on whisker growth. Results from long term electrochemical studies with the objective to clarify conditions for whisker formation on copper are also accounted.

Electrochemical experiments on copper have been performed in environments similar to those in the repository. The chemical parameters judged to be of critical importance for copper behaviour in the theoretical parts of this work have been specifically tested in long-range experiments.

The ultimate goal for the present work is to formulate a better theory for localised corrosion on copper in the repository environment. This report accounts for several steps on the path to get there but the very final step still remains to be taken.

2 Literature search on copper corrosion and repository environment

2.1 Copper corrosion in literature

2.1.1 About the search

A literature search was performed on copper corrosion and mechanisms using the INIS database for the period 1975 – 1997/09. A similar search was performed for the repository environment. In the following, the results are accounted briefly in chronological order under a set of subheadings. Hermansson, Sjöblom, Engman and Amcoff [4, 5] made a search that complemented previously performed searches. The account here is an integration of information from the different literature studies.

As there is a need to complete the knowledge about critical combinations of chemical parameters related to copper corrosion there is a try in this survey to find such combinations. One example of work that should be performed is to determine possible maximum and minimum limits of critical concentrations, i.a. of chloride to be used in subsequent discussions of consequences.

2.1.2 R&D reviews

Hermansson [6] evaluated some properties of copper and selected heavy metal sulphides. The interest was focused on crystal structure, electrical properties, atom mobility, solubility in water, mechanisms of sulphidation and selected thermodynamical data. Bowyer and Hermansson [7, 8] commented on the SKB FUD-programs 95 and 98 [9, 10] and focused on canister integrity and corrosion.

It was concluded for the 95- and 98-programs [9, 10] that the interpretation of information already available is overoptimistic. The authors do not believe that all the difficulties have been recognised. It is disagreed that the long-time durability is ascertained. I.a. it is easy to find corrosion mechanisms for the canister system that have to be demonstrated not to be harmful. It is concluded that there are many areas, which need further evaluation.

It is agreed, however, that the materials choices for both the inner and outer canisters are appropriate. It is believed that it should be possible to develop a satisfactory canister for disposal of high level nuclear waste according to the general method proposed by SKB.

There are many areas, which need further evaluation, i.a. effects of non-uniform loading and creep, welding, quality control, effects of radiolysis, corrosion properties, etc. Work should be carried out to determine the nature, size and location of defects, which may be tolerated.

The largest emphasis is placed on the canister to isolate the waste in the final repository. Therefore also a heavy proof burden exists to demonstrate the ability of the canister to fulfil the isolation function at virtually all times up to several 100000 years. The complex mechanical and chemical environment with high pressures varying in time and location and with oxygen, chloride, sulphur and carbon bearing compounds present will cause different types of attacks that are going to prevail during different time periods. There is no guarantee that oxidising conditions will not return at a later stage, for example during glaciation.

At glaciation the pressure fields would be strongly inhomogeneous, which could cause surprising directions of ground water flow to occur, resulting in intrusion of oxygenated water into the repository. During reducing periods SKB consider all corrosion processes coming to a halt. The reviewers think that possible mechanisms for sulphide based localised attacks should be considered during such periods.

A combination of a mechanical fault, materials stress and localised corrosion in an oxidising environment would be especially dangerous and is not at all just hypothetical.

2.1.3 Thermodynamical calculations

Rummery and MacDonald et al [11, 12, 13] predicted corrosion product stability in high-temperature aqueous systems by thermodynamical calculations. Especially copper is treated in [12, 13]. Cubicciotti [14] derived Pourbaix diagrams for mixed metal oxides. Potential-pH diagrams (Pourbaix diagrams) for the Cu-H_2O, Fe-H_2O and Fe-Cu-H_2O systems are presented and the solubilities of copper and iron oxides (including mixed copper-iron oxide) are evaluated. Beverskog and Puigdomenech [3] revised Pourbaix diagrams for Copper at 5-150 °C. The calculated diagrams are used as a basis for the discussion of the corrosion behaviour of the copper canisters in the Swedish radioactive waste management program.

Mohr and McNeil [15] calculated modified log-activity diagrams as a tool for modelling corrosion of nuclear waste container materials, with particular reference to copper. The latter type of diagram, restricted to the standard state of pressure and temperature, serves as a complement to Pourbaix diagrams for the study of equilibria appropriate to solid phases and aqueous ionic species of copper in chloride-bearing waters. Modified log-activity diagrams may be used to model localised corrosion of copper and are potentially useful for the analysis and prediction of failure mechanisms i.a. in high level waste packages.

2.1.4 Mechanisms and kinetics

Kish et al [16] used tracer techniques and measured absorbed oxygen quantities for the continuous determination of copper corrosion rate. The results confirm a catalytic mechanism of copper corrosion. Kish et al also studied copper corrosion by oxygen consumption and by a radiochemical method. They found that copper corrosion is due to oxygen depolarisation in perchloric acid and sulphuric acid media. Proofs of an autocatalytic mechanism of copper corrosion were found. Rubim et al [17] studied copper corrosion kinetics by pulse polarography, especially the influence of corrosion inhibitors.

King et al [18] focused on the corrosion behaviour of copper under simulated nuclear waste repository conditions. The corrosion performance of copper was evaluated in saline groundwaters. In de-aerated solutions the long-term corrosion rate was generally less than 10 μm/yr. and some pitting was observed. In aerated solutions a rate of 70 μm/yr. was observed. These results suggest that copper would have sufficient corrosion resistance for usage as container material. However, further investigation would be required to quantify pitting kinetics.

Rapp [19] made a survey of the high temperature oxidation of metals forming cation-diffusing scales. He found that, in particular at intermediate temperatures, parabolic oxidation rates are higher and activation energies are lower than those values extrapolated from higher temperatures where lattice-diffusion-limited growth occurs. Short-circuit cation diffusion via scale grain boundaries and dislocations supports oxidation in the intermediate temperature regime, and scale growth at the scale/gas interface takes place at edges provided by screw dislocations intersecting the metal.

In situ observations [19] in a hot-stage environmental scanning electron microscope provided insight into scale growth mechanisms and the formation of non-planar oxidation products as whiskers, pyramids, and pits. Specific reference is made to the evolution of oxidation product morphologies for copper, nickel, iron, and chromium.

King [20] developed a technique to investigate the mechanism of uniform corrosion in the presence of a semi-permeable membrane. It was found that for both the anodic and catodic half-reaction, three possible rate-determining steps can be considered. Those are transport of species through the bulk solution diffusion layer, transport of species through the membrane and the electrochemical reaction itself. The technique was based on the measurement of the corrosion potential of a rotating disc electrode under steady-state conditions.

King and Litke [21 – 25] studied the electrochemical behaviour of copper in aerated NaCl solutions at room temperature. The mechanism of the oxygen reduction reaction was studied over a wide range of applied potentials. At potentials close to the corrosion potential, the mechanism is complicated and not fully understood. It is possible that in this potential region, oxygen is reduced to peroxide. At more negative applied potentials, between -0.50 and -0.90 V_{SCE}, the predominant process is the 4-electron reduction of oxygen to hydroxide. In this potential region, the rate is controlled jointly by the interfacial reaction and the rate of supply of oxygen to the electrode surface. At an applied potential of about -1.0 V_{SCE}, the rate of reduction is almost totally controlled by the rate of transportation of oxygen. Values of the kinetic parameters for the 4-electron reaction have been determined. The data found, along with the results on the anodic dissolution of copper, is used to explain the behaviour of copper under freely corroding conditions.

Shoesmith et al [26] developed a mechanistic basis for modelling fuel dissolution and container failures under waste vault conditions. Since the processes are considered to be driven by oxidants in the vault, it is natural to study them by electrochemical techniques. Holmes and Surman [27] used XPS and Auger investigations to study the mechanisms affecting corrosion inhibition of metals. A major interest (in atmospheric corrosion) is in the mechanism by which the initial corrosion initiated and propagated. The initial phase involves the attack of the very outer surface layers; hence it is difficult to observe with conventional techniques such as SEM/EDX.

King et al [28] made a mechanistic study of the uniform corrosion of copper in compacted Na-Montmorillonite/sand mixtures. Under the experimental conditions used, the rate of corrosion is limited by the diffusion of copper through the compacted clay-sand buffer material that will surround the nuclear waste containers. Litke et al [29] made a mechanistic study of the uniform corrosion of copper in compacted clay-sand soil. Evidence is given that suggests that the rate-controlling process is the transport of copper corrosion products away from the corroding surface.

2.1.5 Environment

In [30] there is an account of KBS work on the corrosion resistance of copper canisters for final disposal of spent nuclear fuel. The thermodynamic possibilities for various corrosion reactions on copper under the prevailing conditions were studied, also with regard to bacterial influence. Oxygen entrapped in the buffer material at the time of closing the storage was found to be the oxidant of major importance for the corrosion. Sulphide in the ground water was found to be another reactant of importance. In [31] there is a state of the art estimation by KBS of the corrosion resistance of materials intended for enclosure of nuclear fuel waste. The need of complementary investigations, e.g. on variations in ground water composition at a depth of 500 m, especially the content of oxygen, chloride, nitrite, sulphate and organic matter was underlined.

Copper/bentonite interactions were studied by Pusch [32]. The physical state of the bentonite surrounding the canisters and the chemical interaction between copper and bentonite are considered to be important at canister corrosion. A slow Cu migration and Cu exchanging originally adsorbed cat-ions is suggested.

Ahn et al [33] performed a corrosion study of HLW container materials. Tests were performed for the uniform and crevice corrosion of copper and titanium in brine at 150 °C. Franey [34] studied atmospheric corrosion effects on copper. Studies were performed on the naturally formed patina on various copper samples. It was demonstrated that there are distinct layering effects. This means that the copper base material shows separate oxide and basic sulphate layers on all samples, indicating that patina is not a homogeneous mixture of oxides and basic sulphates.

Fiaud and Guinement [35] studied the effect of nitrogen dioxide and chlorine on the tarnishing of copper and silver in the presence of hydrogen sulphide. Nitrogen dioxide shows oxidative properties against both metals and may accelerate the processes. A similar acceleration of the sulphidation is observed with chlorine on copper and silver. Copper chloride is always obtained, whereas the formation of silver chloride depends on the pressure ratios of the gases. Aaltonen et al [36] studied the stress corrosion of pure OFHC-copper in simulated ground water conditions. Three different types of environmental effects on the fracture mode of pure OFHC-copper were observed.

Glass [37] studied corrosion processes of austenitic stainless steels and copper-based materials in gamma-irradiated aqueous environments. He found that the radiolytic production of such species as hydrogen peroxide and nitric acid exert an influence on corrosion mechanisms and kinetics.

Eriksen et al [38] evaluated corrosion of copper in pure water. They found contrary to Hultquist [39] that no hydrogen evolution was observed during an exposure period of 61 days using a gas-chromatographic technique. Cu_2O was the only corrosion product detected by means of ESCA and catodic reduction. The corrosion rates obtained for two different qualities are much lower than the corrosion rate measured in the study by Hultquist and is ascribed to the reaction between the copper foils and residual oxygen initially present in the water. In conclusion Eriksen´s investigation confirmed well established thermodynamics. This means that oxidation of copper by pure deoxygenated water under the formation of hydrogen as proposed by Hultquist is not thermodynamically feasible.

Smyrl et al [40, 41] studied copper corrosion in irradiated environments. Monitoring the cuprous ions revealed that there was a complex set of events taking place at the copper surface, including film formation and the appearance of cupric ions.

Lutton et al [42] studied the general corrosion of candidate container materials for the basalt waste isolation project. Weight loss and surface analysis data from two short-term tests were reported. In these, the effect of weldings in static groundwater, and that of packing material in an air/steam environment were studied. Early results from long-term testing are also included.

In [43] an assessment of the corrosion resistance of the high-level waste containers proposed by Nagra is presented. The only significant contributions to the corrosion of copper are supposed to come from residual oxygen trapped in the bentonite used as backfill material and from sulphate, if it is assumed that the latter can be reduced to sulphide by microbial activity. The conclusion is that the maximum penetration by corrosion will not exceed 40 mm in 1000 years.

Scholer and Euteneuer [44] studied the corrosion of copper by de-ionised cooling water. The by far dominant influence is the amount of oxygen and carbon dioxide in the cooling water. By this corrosion can be enhanced by a factor of 200 and more. The absolute carry off of copper is about 0.05 mm/year under bad conditions.

Garisto [45], Lam [46], and King and Litke [47] accounted for Ontario Hydro studies on copper corrosion under waste disposal conditions. It was found that the corrosion rate of copper is generally greater in aerated solutions containing sulphide. Also, in the presence of sulphide there is the fear that pitting may occur.

Aaltonen [48] studied the corrosion of pure OFHC-copper in simulated repository conditions. The aim was to evaluate the effects of groundwater composition, bentonite and temperature on the equilibrium and possible corrosion reactions between pure copper and the simulated repository environment.

Akkaya et al [49] performed electrochemical corrosion studies on copper-base waste package container materials in non-irradiated 0.1 N $NaNO_3$ at 95 °C. Anodic polarisation experiments were conducted to determine the passive current densities, pitting potentials, and other parameters. Cyclic Current Reversal Voltammetry tests were also performed to evaluate the stability and protectiveness of the passive oxides formed. X-ray diffraction and Auger Electron Spectroscopy were used for identification of the corrosion products as well as Scanning Electron Microscopy for the surface morphology studies.

Maiya [50] made a review of degradation behaviour of container materials for disposal of high-level nuclear waste in tuff and alternative repository environments. The studies included the effects on corrosion of various environmental factors (such as pH, temperature, and electrochemical potentials), as well as alloying elements and other micro-structural parameters. The modifications of the environment induced by gamma radiation and the stability of the microstructure under gamma irradiation were also described.

Imai et al [51] studied the effects of anionic species on the polarisation behaviour of copper for waste package material in artificial ground water. The effects of HCO_3^-, Cl^-, and SO_4^{2-} on copper were studied at 303 K in dissolved oxygen controlled ground-water, simulating aqueous solutions by using a cyclic polarisation curve method. Two types of polarisation curves were determined: Type A in which free corrosion proceeds in the active dissolution mode, and Type P in which passivation takes place in a potential domain characterised by a potential that corresponds to E_b, the potential at which the passivated film is broken.

Ryan and King [52] studied adsorption of Cu(II) on sodium bentonite in a synthetic saline groundwater. They found that for loose clays, the adsorption behaviour follows a Langmuir isotherm. The maximum adsorbate surface coverage increases with temperature, and exceeds the cation exchange capacity for Cu^{2+} at temperatures of 50 °C and 95 °C. For compacted clays, the data follow a Freundlich-type of isotherm, and exhibit no apparent temperature dependence. King also accounts for environmental influences in [18].

Ahonen [53] reported on the stability of metallic copper and its possible corrosion reactions in the conditions of deep bedrock. McGarvey et al [54] studied the interactions between iron oxides and copper oxides under hydrothermal conditions. They found that magnetite and hematite undergo interconversion reactions, the extent of which is controlled in part by the presence of copper oxides. In oxygenated water, the degree to which magnetite was oxidised to hematite was found to be dependent on the presence of CuO or Cu_2O. When these materials were absent, the dissolved oxygen limited the oxidation of magnetite in the aqueous system.

Pedersen [55] et al treated the conditions for survival of bacteria in nuclear waste buffer materials. The background is that there is a major concern for the performance of the canisters that sulphate-reducing bacteria (SRB) may be present in the clay and induce corrosion by production of hydrogen sulphide.

Möller [56] studied copper corrosion in pure oxygen-free water. The study was initiated following reports on corrosion of Copper in water in absence of Oxygen. The following conclusions could be drawn: No difference in colour was observed for the Pd and Pt seals except in one case for the Copper wire, where only a slight difference was noticed. No significant difference in oxidation between the plates with Pd or Pt seals in quartz glass tubes was observed. No oxide growth was observed during the last year.

King et al [57] studied the effects of dissolved oxygen concentration and mass-transport conditions on the dissolution behaviour of copper nuclear waste containers. The potentials at which copper dissolves directly as Cu(I) and Cu(II) were measured in Cl^-, SO_4^{2-} mixed Cl^-/SO_4^{2-} solutions using rotating ring-disc and rotating splitting disc electrodes. By comparison to corrosion potentials measured in O_2-containing solution, it is shown that copper dissolves as Cu(I) in Cl^--containing solutions, in the form of the $CuCl_2^-$ species. Subsequent precipitation of Cu(II) solids is a consequence of homogeneous oxidation of Cu(I) by O_2. Corrosion potentials measured with a clay-covered copper electrode are approx. 0.1 V more positive than those measured in bulk solution of the same chloride and O_2 concentration. The extent of formation of Cu(II) depends on the relative rates of diffusion and oxidation of Cu(I). The rate of Cu(I) oxidation by O_2 in compacted clay may be lower than that in bulk solution because of spatial restrictions in the compacted medium.

Sjöblom et al [5] evaluated the chemical durability of copper canisters under crystalline bedrock repository conditions. The purpose was to analyse prerequisites for assessments of corrosion lifetimes for copper canisters. Three main types of situations were identified. (1) Under oxidising and low chloride conditions, passivating oxide type of layers may form on the copper surface. (2) Under oxidising and high chloride conditions, the species formed may all be dissolved. (3) Under reducing conditions, non-passivating sulphide 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 penetration caused by localised corrosion can be expected to be very sensitive to details in the chemistry.

Ahonen and Vieno [58] evaluated the effects of glacial melt water on corrosion of copper canisters. The study is concluded with an evaluation of the potential effects of oxygenated melt water on the corrosion of copper canisters.

Werme [59] evaluated the corrosion aspects of copper canisters for nuclear high level waste disposal. The analysis showed that there are no rapid mechanisms that may lead to canister failure. The anticipated corrosion service life of the canister was found to be several million years. If further analysis of the copper canister topic is considered, it should concentrate on identifying and evaluating processes other than corrosion, which may have a potential for leading to canister failure.

Aaltonen and Varis [60] performed long term corrosion tests of OFHC-coppers in simulated repository conditions. The program was planned to provide an experimental evaluation with respect to the theoretical calculations and forecasts made for the corrosion behaviour of OFHC-coppers in bentonite ground water environments at temperatures between 20-80 ^{0}C.

2.1.6 Natural analogues

Hallberg et al [61] evaluated the inferences from a corrosion study of a bronze cannon on high level nuclear waste disposal. The cannon had been embedded in clay sediments in the Baltic Sea since 1676. The corrosion products are cuprite and malachite, mainly derived from transformation of tenorite inclusions of the bronze alloy. The bronze matrix exhibits little corrosion and a conservative estimate for the maximum corrosion of Cu is < 10 mm in 100,000 years.

Chapman and Smellie [62] looked at the potential of natural analogues in assessing the processes, which will lead to the breakdown of engineered barriers and the geological systems. The principal value is the opportunity to examine processes occurring over geological time scales, hence allowing more confident extrapolation of short time scales experimental data. Nine specific processes are identified as being most significant in migration models, based on available sensitivity analyses.

Werme and Papp [63] used natural and archaeological analogues in performance assessment of the KBS-3 copper canister. Wouters et al [64] applied SIMS in patina studies on Bronze Age copper alloys. It was shown that the combined use of metallography, electron probe microanalysis and ion microscopy can obtain very useful information concerning fabrication technology and corrosion mechanisms of ancient metals. Marcos [65] used the Hyrkkölä native copper mineralization as a natural analogue for copper canisters. The author claims that the mineralization is of highest relevance in improving models of anoxic corrosion of copper canisters.

2.1.7 Surface treatment

Morris et al [66] studied the influence of ion implantation on the thermal oxidation of copper. A simple model was proposed whereby the observed behaviour is ascribed to the creation of an n type region in the predominantly p type oxide such that inward hole diffusion is inhibited during oxide growth. Tomlinson [67] studied the surface chemistry of metals and their oxides in high temperature water. He used a broad spectrum of techniques to bring understanding of corrosion product movement in primary coolant circuits.

Preece and Kaufmann [68] studied the effect of boron implantation on the cavitation erosion resistance of copper and nickel. It was found that the composition, structure and state of stress in the surface significantly influence the cavitation erosion. Consequently, the implantation of foreign ions, which introduces a composition change, structural defects and, generally, a compressive stress in the surface, has the potential of markedly affecting the erosion resistance. Implantation improves the erosion resistance of both metals but has a greater effect in nickel than in copper.

Kammlott et al [69] demonstrated that copper sulphidation was inhibited in moist air by boron implantation. The rate of growth of a sulphide film on the boron-implanted copper is lower than on pure copper by at least a factor of four after 18 h under the exposure conditions (H_2S = 3.0 ppm, T = 22.5 °C, RH = 85%). The resistance of the implanted copper to sulphide corrosion is ascribed to inhibition of copper diffusion through the surface oxide layer. Svendsen [70] made a comparison of the corrosion protection of copper by ion implantation of Al and Cr at temperatures below 320 °C.

Ratcliffe and Collins evaluated the influence of ion implantation on the thermal oxidation of copper [71]. The effect of 31 species of ion implanted impurities on the thermal oxidation of polycrystalline copper, and nine implanted species on the oxidation of single crystal (110) copper was studied. The majority of these increased the oxidation resistance of copper. An increase in the degree of oxidation was found with increasing ionic radius of the implanted species. The results generally support a model based on the formation of a p-n junction in the implanted oxide.

Oshe et al [72] studied ion-stimulated passivation of Cu implanted by argon ions. Wright et al [73] studied the effect of ion implantation on the passivation behaviour of pure copper. It was found that the tested ion implantations produced no significant effects on the passivation behaviour of copper in the tested environment. It was concluded that the ion implantation process itself does not affect passivation. Jimenez-Morales et al [74] studied the corrosion behaviour of copper surfaces modified by nitrogen ion implantation by using electrochemical methods. The results obtained indicate that nitrogen ion implantation in copper forms a protective surface layer, which improves the corrosion resistance of the pristine material.

2.1.8 Classification of materials

Mattson [75] evaluated the corrosion resistance of candidate canister materials by corrosion tests and by thermodynamic and mass transport calculations. He found that he principal candidate canister materials are titanium, copper, and high purity alumina. Mattson [76] also reported studies on corrosion resistance of canisters for final disposal of spent nuclear fuel. He concluded that copper canisters with 200-mm-thick walls would last for hundreds of thousands of years.

Nuttall and Urbanic [77] made an assessment of materials for nuclear fuel immobilisation containers in the Canadian program. A wide range of engineering metals and alloys was assessed for their suitability as container materials for irradiated nuclear fuel intended for permanent disposal in a deep, underground hard-rock vault. Materials were assessed for their physical and mechanical metallurgy, weldability, potential embrittlement mechanisms, and economy. A study of the possible mechanisms of metallic corrosion for the various engineering alloys and the expected range of environmental conditions in the vault showed that localised corrosion and delayed fracture processes are the most likely to limit container lifetime. Thus such processes either must be absent or proceed at an insignificant rate. Three groups of alloys are recommended for further study: AISI 300 series austenitic stainless steels, high nickel-base alloys and very dilute titanium-base alloys. Specific alloys from each group are indicated as having the optimum combination of required properties, including cost. For container designs, where the outer container shell does not independently support the service loads, copper should also be considered. The final material selection will depend primarily on the environmental conditions in the vault.

Hanes [78] studied spent nuclear fuel rods encapsulated in copper. He concluded that capsules of copper should contain radioactive materials safely for hundreds of thousands of years in underground storage.

2.1.9 Localised corrosion

Ahn et al [33] performed a corrosion study of HLW container materials. Tests were performed for the uniform and crevice corrosion of copper and titanium in brine at 150 °C. In [79] a radiographic method to find pitting corrosion in copper pipes was developed. The radiographs indicated that pitting corrosion was widespread in water supplies. King et al [18] evaluated the corrosion performance of copper in saline ground waters. In de-aerated solutions some pitting was observed.

Hermansson and Beverskog [80] evaluated pitting corrosion in relation to a copper canister. They found that normal pitting could occur during oxidising conditions in the repository. It was also concluded that a new theory for pitting corrosion has to be developed, as the present theory is not in accordance with all practical and experimental observations. A special variant of pitting, based on the growth of sulphide whiskers, was suggested to occur during reducing conditions.

Taxén [81] evaluated pitting of copper under moderately oxidising conditions. A mathematical model of a corrosion pit on copper under moderately oxidising conditions was developed. At 25 °C and at potentials only slightly higher than that at which pitting may initiate, the propagation rate is very low. A calculation for 100 °C shows that corrosion pits with a much higher propagation rate may develop. The potential has a strong influence on the predicted maximum propagation rate.

In some early literature surveys on copper corrosion performed on commission by SKN and SKI, accounted i.a. in [4], different types of literature material have been found. Part of the literature data is directly related to the repository and has often been performed within special programs that are currently running in Europe, USA and Canada. Moreover literature data from other types of programs but directly useful for the description of copper performance in the repository has been found. There is also data accounted with peripheral importance but that could be of a general background interest for the work.

Some literature, i.a. [82 - 84] treats the different types of pitting corrosion that arise in tubes for potable water. This type of data has been reported frequently as case studies in literature. It is roughly demonstrated that pitting corrosion "type I" mostly occurs in the UK, USA, Belgium and Holland. Initiation of type I requires that the copper tubes are in contact with stagnant or relatively stationary water under certain time periods, but a row of other factors influence too. As an example of this the redox potential in the water has a clear influence on the appearance of pitting. Pitting corrosion does not in general appear under 50 mV while potentials clearly above 100 mV seem to promote.

In [85] a relatively detailed account is made of pitting corrosion in potable water tubes. At a detailed analysis of the development of a pit on copper in contact with potable cold water in Brussels, a set of mechanistic steps was noted. The copper surface has a rather low potential (about -30 à -10 mV_{SCE}) during about ten days. After this time of incubation the potential increases and thereafter oscillates about 50 mV_{SCE} for a month. During the time of incubation, when the potential is increasing, a passive film is formed as Cu_2O is covered by malachite, $CuCO_3 \cdot Cu(OH)_2$. Simultaneously, an increasing greenish colouring of the surface can be observed. In later parts of the process pitting was observed and then always in connection with a potential increase above 100 mV_{SCE}. The mechanism seems to be connected to the formation of a layer of malachite on top of the original Cu_2O layer. The malachite will absorb chloride from the water in an inhomogeneous manner (for example in grain boundaries). CuCl can be formed as a result. As long as the potential is moderately high malachite and CuCl are stable. By lowering the potential (stationary water) Cu_2O becomes the thermodynamic stable copper specie. Both the malachite and the inhomogeniously distributed copper chloride will start their transformation into Cu_2O. In the case of CuCl this will happen through hydrolysis and HCl will be formed beside Cu_2O. When the potential again increases, the acidified areas will again be covered with malachite. Thereby the local attack is initiated and can propagate.

In [86] the protective potential on copper is given (experimentally conditioned potential at which the pitting attack is re-passivated) to be about +350 mV_{SHE}. The immunity potential (inside the pit) is given as about +160 mV_{SHE}. The requirements on the protective potential of course will depend on the chemical environment, for example on chloride concentration. In [86], Pourbaix diagrams are accounted that show the pitting conditions on copper at a couple of different chloride concentrations.

In [1], SKB-FUD 92, with complements, a general summary of the status of the art in -92 as SKB sees it is given. In KBS-3 [87] the original copper investigation was made. Therefore much of "presently valid data" for copper corrosion can be found in [87] and its references. In [88] and [76] original overviews for KBS-3 of work on copper are accounted.

In [89] and [90] copper minerals and solubility of copper in geological environments is discussed. In [91] the system Cu-O-H-Cl is discussed, which is of central importance for the corrosion of the copper canister in its chloride-containing environment. An overview of copper corrosion is accounted in [92].

The literature contains many investigations of specific damage cases in potable water tubes in different environments. The accounts also sometimes contain discussions of mechanisms and can therefore be of a central value for modelling.

In [93-97] a series of mainly Japanese work about pitting in potable water tubes of copper is accounted. The water environment has contained chloride, hydrocarbonate and sulphate. The critical electrode potential for pitting (critical potential

= pitting potential at infinite time) on copper is given in these environments to be 115 - 150 mV_{SCE}. In [98] an investigation of pitting in archaeological objects is accounted in which also the pitting factor is established as a concept.

Field observations of pitting corrosion on copper have induced experiments to reproduce the phenomenon in a laboratory environment in order to find explanations and countermeasures.

In [99] experimental investigations of pitting on copper were performed in an environment at 25 °C containing low chloride- and sulphate concentrations but relatively high hydrogen carbonate concentrations. The results indicate that the following mechanism for the propagation of the pit can be sketched. Chloride is adsorbed by the passive film on the copper surface and causes a deterioration of the film. Copper is dissolved on the metal surface at formation of Cu^+ and Cu^{2+}. Cu^+ thereafter forms CuCl with chloride. Caused by the electrodynamic conditions, Cu^{2+} will migrate out from the pit and Cl^- will migrate into it. CuCl will simultaneously be hydrolysed and form Cu_2O and HCl.

The latter step implies that the environment in the pit is rapidly acidified, This fact in combination with the increased chloride concentration makes the rate of attack to increase strongly. Cu^{2+} diffusing outwards will form malachite together with hydrogen carbonate. This implies that the pit will be covered by a not passivating, but mechanically stable crust of malachite which is supported by the process.

An important factor in connection with pitting is of course the external water environment that the copper surface sees. A number of articles focus on different components in the water. I. a. the influence on pitting on copper by silicate and polyphosphate [100], by hydrogen carbonate, sulphate and chloride [101], by "phytic acid" ($C_6H_6(OPO(OH)_2)_6$, meso-inositol hexaphosphoric acid) as discussed in [102]. In [103] the influence of oxidants is treated. A general discussion of the importance of water composition is performed in [104].

Other environmental factors are also discussed, for example in [105] - [107] the influence of soldering and of the metal quality (composition). In [108] the influence of light and water quality is discussed, in [109], [110] and [111] the influence of chloride.

In [95] the morphology of pitting type I on copper is discussed and in [112] the relation between development of morphology with time and coupling to pitting mechanism. An interesting general description of the processes is given by Shalaby et al in [112].

The objective for the practically focused investigations of damages has of course been to try to find countermeasures against the observed pitting in those cases.

In [113] countermeasures against pitting in tubes of copper by adding polyphosphates to the water is discussed. In [114] inhibition by dosage of bicarbonate, in [115] by control of the redox potential and in [116] inhibition by certain types of complexing agents is discussed. A general discussion of countermeasures is performed in [117].

In [118-125] a number of mechanisms related studies of pitting on copper are presented. In [118] the temperature dependence, in [119] and [120] a general summary about mechanisms are given together with the specific conditions that must be fulfilled for pitting to occur. In [121] the time of incubation till the pit appears is considered and in [122] the importance of the protection potential. In [126] Pourbaix gives a summary of the electrochemical prerequisites for pitting on a number of metals. In [127] the influence of carbon deposits on the copper surface was investigated with ESCA. In [128] Pourbaix discusses the connection between thermodynamics and kinetics.

In [129] and [130] the kinetics for pitting on copper is discussed for borate buffered sodium chloride solutions as well as for alkaline perchlorate solutions. In both articles rate laws and mechanistic reaction steps are accounted. In [131] a kinetic model for the interaction between container and bentonite in the repository is accounted. In [132] -[134] some kinetic data valid for sulphidation reactions are given. Causes and countermeasure are generally discussed in [135] and [117].

2.1.10 Models

Walton and Sagar [136] performed mathematical modelling of copper container corrosion. A conceptual model was defined for bounding of general corrosion rates of copper when used for containment of high level nuclear waste. The model was implemented in a general, two-dimensional finite different code and can be used for estimating performance implications of different design options. Jensen [137] performed geochemical modelling of copper degradation. Here a few of the theoretical aspects of copper stability based on thermodynamic considerations are presented.

King and Litke [138] development a container failure function for copper. They found that short-term failures due to fabrication defects must be taken into account. The model allows for short-term sorption of copper by the clay buffer material, and assumes a steady-state condition for uniform corrosion. Using worst-case assumptions, a container penetration time of 3300 years can be predicted. Garisto [139, 140] also studied container failure models. He discusses the modelling aspects in vault chemistry. King and Kolar [141] developed a numerical model for the corrosion of copper nuclear fuel waste containers. It is based on a kinetic description of the processes involved in the uniform corrosion of Cu in a conceptual Canadian disposal vault. The 1-dimensional, multi-layer model accounts for mass-transport, electrochemical and chemical processes and predicts the spatial and temporal variations of the concentrations of various dissolved, precipitated and adsorbed species, as well as the time dependence of the corrosion rate and the corrosion potential (E_{CORR}). The variation of [O_2], [Cu(II)] and E_{CORR} with time can also be used to predict the maximum period over which localised corrosion processes, such as pitting or stress corrosion, may occur. Predictions from the model suggest that 25-mm-thick Cu containers will not fail due to uniform corrosion or pitting in periods < 10^6 yr. Kolar and King [142] modelled the consumption of oxygen by container corrosion and reaction with Fe(II). The most important reactions leading to the consumption of O_2 for Cu containers in a conceptual Canadian disposal vault are container corrosion, the oxidation of dissolved Cu(I) and the oxidation of organics and other impurities in the clay. Consumption of O_2 by the oxidation of dissolved Fe(II) from biotite is significant in backfill materials containing crushed granite, and in the rock itself. The O_2 initially trapped in the disposal vault is predicted to be consumed in between 50 and 670 yr. King et al [143] modelled the effects of evolving redox conditions on the corrosion of copper containers. For copper containers, uniform corrosion and, possibly, pitting will occur during the initial aggressive phase, to be replaced by slow uniform corrosion during the long-term anoxic period.

Wersin et al [144] made kinetic modelling of bentonite-canister interaction and made long-term predictions of copper canister corrosion under oxic and anoxic conditions. From these predictions it is suggested that copper canister corrosion does not constitute a problem for repository safety, although certain factors such as temperature and radiolysis have not been explicitly included. The possible effect of bacterial processes on corrosion should be further investigated as it might enhance locally the described redox process. Wersin et al [145] also made kinetic modelling of bentonite - canister interaction. From the kinetic information obtained by experimental and archaeological data, long-term corrosion rates were assessed. The model is applied to the corrosion of Cu under anoxic conditions and upper and lower limits of corrosion rates are derived.

Worgan et al [146] made a performance analysis of copper canister corrosion under oxidising or reducing conditions using the finite-difference CAMEO code for modelling general corrosion of copper canisters. King et al [147] modelled the effects of porous and semi-permeable layers on corrosion processes. They found that porous layers might affect the rate of corrosion by affecting the rate of mass transport of reactants and products to and from the corroding surface. Semi-permeable layers can further affect the corrosion process by reacting with products and/or reactants. Reactions in semi-permeable layers include redox processes involving electron transfer, adsorption, ion exchange and complexation reactions as well as precipitation/dissolution processes.

2.2 Short summary of literature on copper corrosion in the repository environment

King [20] found that for both the anodic and catodic half-reactions involved, three possible rate-determining steps can be considered: transport of species through the bulk solution diffusion layer, transport of species through a membrane and the electrochemical reaction itself. Kish et al [16], also found proofs of an autocatalytic mechanism.

King and Litke [21 - 25] also found that at potentials close to the corrosion potential, the mechanism is complicated and not fully understood. It is possible that oxygen is reduced to peroxide in this potential region. At more negative applied potentials, between -0.50 and -0.90 V_{SCE}, the predominant process is the 4-electron reduction of oxygen to hydroxide. In this potential region, the rate is controlled jointly by the interfacial reaction and the rate of supply of oxygen to the electrode surface. At an applied potential of about -1.0 V_{SCE}, the rate of reduction is almost totally controlled by the rate of transportation of oxygen. A transportation-controlled mechanism was found in compacted Na-Montmorillonite/sand mixtures [28, 29]. For copper containers, uniform corrosion and, possibly, pitting will occur during the initial aggressive phase. These mechanisms will be replaced by slow uniform corrosion during the long-term anoxic period [144].

Oxygen entrapped in the buffer material at the closing of the storage is suggested to be the oxidant of major importance for the corrosion. Sulphide in the ground water was found to be another reactant of importance [30]. The need for complementary investigations, e.g. on variations in ground water composition at a depth of 500 m, especially the content of oxygen, chloride, nitrite, sulphate, sulphide and organic matter is underlined in [31].

Fiaud and Guinement [35] found that chloride accelerated the sulphidation of copper. Also Glass et al [37] found that the radiolytic production of such species as hydrogen peroxide and nitric acid exert a general influence on corrosion mechanisms and kinetics and not only in a sulphide environment. In general influences in varying degree are reported of pH, potential, temperature, HCO_3^-, Cl^-, SO_4^2, iron oxides and also by radiation.

It is indicated that (1) under oxidising and low chloride conditions, passivating oxide type of layers may form on the copper surface. (2) Under oxidising and high chloride conditions, the species formed may all be dissolved, leaving a naked copper surface; and (3) under reducing conditions, non-passivating sulphide type layers may form on the copper surface.

King et al [147] also found that porous layers may affect the rate of corrosion by affecting the rate of mass transport of reactants and products to and from the corroding surface. Semi-permeable layers can further affect the corrosion process by reacting with products and/or reactants. Reactions in semi-permeable layers include redox processes involving electron transfer, adsorption, ion exchange and complexation reactions and precipitation/dissolution processes.

As also stated in [18] many workers agree that copper would have sufficient corrosion resistance for use as a container material. However, further investigation is required to quantify pitting kinetics. There exist a row of different studies of pitting on copper, among others appearing in failure analyses of water pipes.

A part of the work includes countermeasures against pitting in copper by different means of additions. As examples are mentioned changes of alloy composition, addition of polysulphate, addition of carbonate, dosage of iron (II) and an increase of pH. These actions are founded on the suggestions of mechanisms, which have been proposed for the described types of corrosion.

However the mechanisms for corrosion can be expected to differ greatly for different situations, the general conclusion of the repository oriented literature data is that copper is an excellent canister material. It is foreseen to have a very long lifetime in the intended environment. There are, however, uncertainties in the estimation of the lifetime, as the pitting mechanisms are not yet fully evaluated. Localised corrosion of copper is expected to be very sensitive to details in the chemistry. Also radiolysis and the presence of bacteria should be further investigated [131, 144].

2.3 Repository environment in literature

2.3.1 Background

As there is a need to complete the knowledge about critical combinations of chemical parameters as related to copper corrosion this survey is partly devoted on finding such combinations. One example of work that should be performed is to determine possible max and min limits of critical concentrations, i.a. of chloride to be used in subsequent discussions of consequences. Another part is to use the information to briefly discuss possible influences on copper corrosion.

2.3.2 General description

The layout of the planned Swedish repository for spent nuclear fuel is described in general terms in several older and recent sources [87, 148, 149]. The general features of the nearest field are demonstrated in Figure 1, modified from [88].

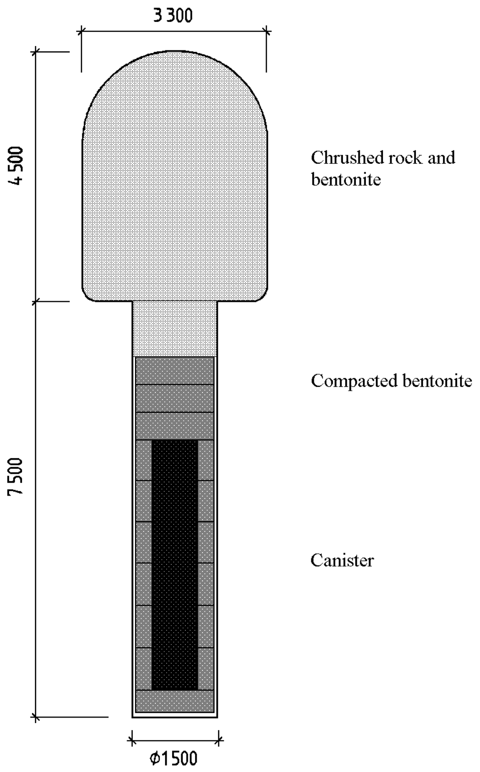


Figure 1 Deposition cavity with canister, buffer and backfill, modified from [88]. Measures in mm.

As seen from Figure 1, there is a tunnel in the crystalline, granitic bedrock in which copper canisters containing the spent nuclear fuel are placed into holes drilled in the tunnel floor. After loading a tunnel with canisters it is filled with blocks of compacted bentonite around the canisters. Non-compacted bentonite and crushed rock is filled into the tunnel. After closing the facility, ground water has access to the whole system and there will be a ground water flow through the repository. The flow rate and composition of the water is determined by the surrounding conditions as well as by the repository conditions.

In SITE-94 [150] the geosphere, the engineered barriers and the processes for radionuclide release and transport are treated as an integrated, interdependent system. The groundwater chemistry is evaluated and a model, fairly consistent with a flow model, for the origin of the different waters is developed. Several phenomena of relevance for copper corrosion in a repository environment are also discussed.

The main parameters of the groundwater composition as given in KBS 3 [87] are accounted in Table 1.

Table 1. Typical compositions of the groundwater in the near field. Estimates are made on the basis of extensive field investigations and bentonite water interaction tests.

pH		6.5 - 9.0
E_h {V}		-0.5 - 0
HCO_3^-	mg/dm^3	40 - 500
SO_4^{2-}	“	40 - 60
HS^-	“	0.1 - 1
HPO_4^{2-}	“	0.1 - 0.2
PO_4^{3-}	“	0.01 - 1
NO_3^-	“	0.01 - 0.6
NO_2^-	“	0.01 - 0.1
Cl^-	“	1 - 17000
F^-	“	0.2 - 10
Ca^{2+}	“	5 - 3200
Mg^{2+}	“	1 - 50
Fe^{2+}	“	0.1 - 3
Fe^{3+}	“	<0.1
Mn^{2+}	“	0.2 - 0.5
K^+	“	1 - 25
Na^+	“	10 - 4000
Al^{3+}	“	0.01 - 0.2
SiO_2	“	2 - 20
TOC	“	1 - 8

2.3.3 Repository model sites

There are several areas in Sweden that have been investigated as models for the final repository site. The most intensely investigated is the Äspö HRL in Oskarshamn. A majority of data used in the present work is taken from investigations performed at Äspö and is therefore mentioned here. In Figure 2 [151] there is an overview of the Äspö facility in which the different kinds of waters found are indicated.

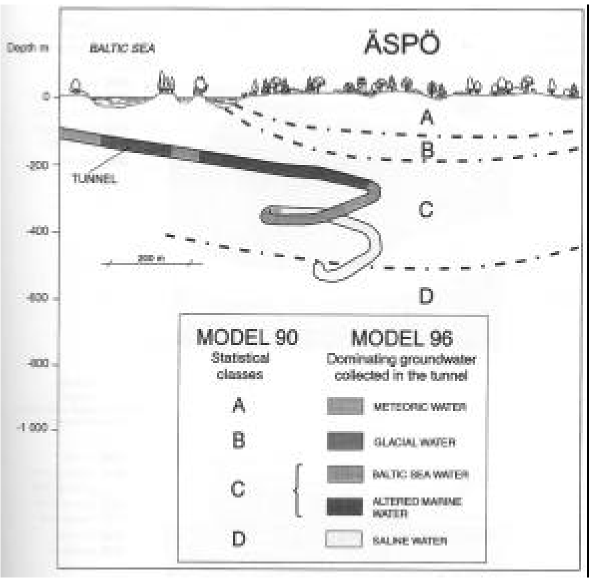


Figure 2 The Äspö facility. Different types of waters present are indicated [151].

In [152, 153, 154] there are accounts of the pre-investigations for the Äspö HRL. Those were started in 1986 and involved extensive field measurements, aimed at characterising the rock formations with regard to geology, hydrogeology, hydrochemistry and rock mechanics.

In [154] three sites, arbitrarily named Aberg, Beberg and Ceberg, are compared, based on previous SKB site characterisation programs conducted in Sweden. The report is a compilation of existing data and descriptions for use in the hydrogeologic modelling of these hypothetical sites.

Hydrogeological and chemical data are found in [152, 153, 154]. In [155] there are comparisons between computer model simulations i. a. of salinities and measured values. Examples from different boreholes are given in table 2 [155].

Table 2 Comparisons of calculated and measured salinity [156].

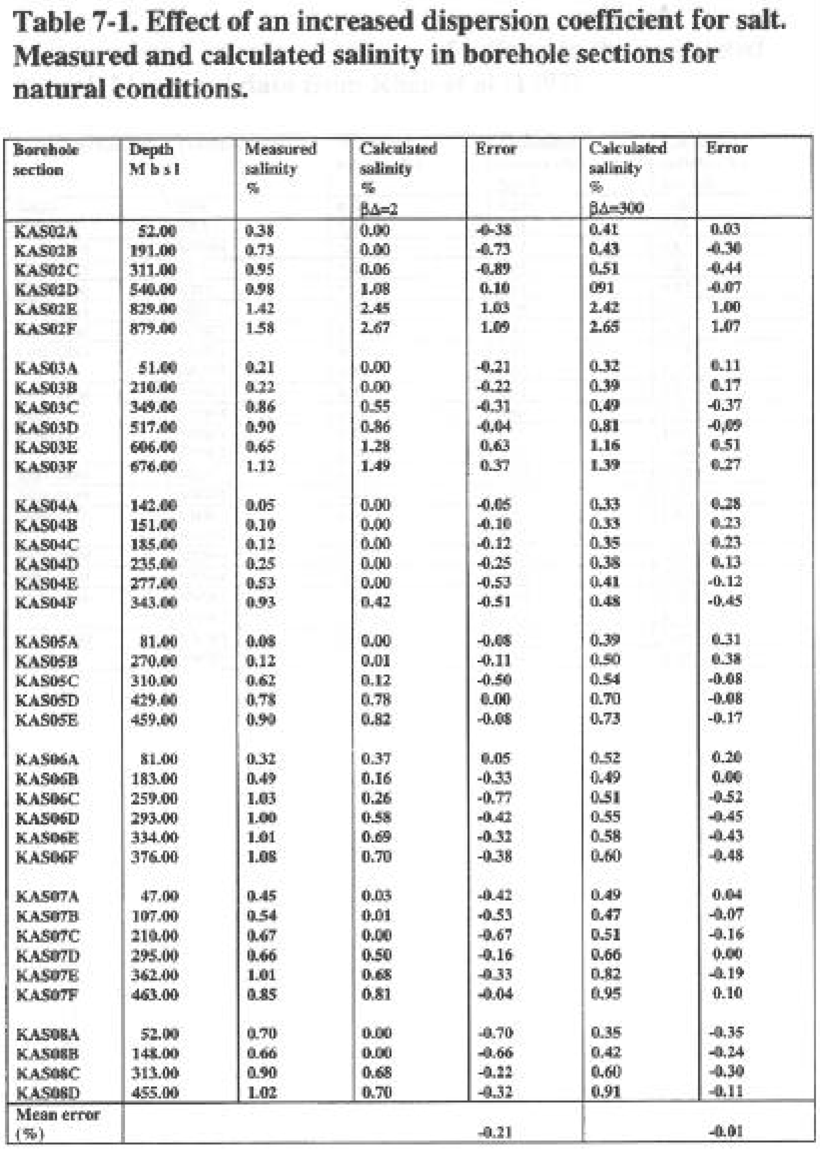


Table 7-1. Effect of an increased dispersion coefficient for salt. Measured and calculated salinity in borehole sections for natural conditions.

Borehole section	Depth M b s l	Measured salinity %	Calculated salinity % βΔ=2	Error	Calculated salinity % βΔ=300	Error
KAS02A	52.00	0.38	0.00	-0-38	0.41	0.03
KAS02B	191.00	0.73	0.00	-0.73	0.43	-0.30
KAS02C	311.00	0.95	0.06	-0.89	0.51	-0.44
KAS02D	540.00	0.98	1.08	0.10	091	-0.07
KAS02E	829.00	1.42	2.45	1.03	2.42	1.00
KAS02F	879.00	1.58	2.67	1.09	2.65	1.07
KAS03A	51.00	0.21	0.00	-0.21	0.32	0.11
KAS03B	210.00	0.22	0.00	-0.22	0.39	0.17
KAS03C	349.00	0.86	0.55	-0.31	0.49	-0.37
KAS03D	517.00	0.90	0.86	-0.04	0.81	-0,09
KAS03E	606.00	0.65	1.28	0.63	1.16	0.51
KAS03F	676.00	1.12	1.49	0.37	1.39	0.27
KAS04A	142.00	0.05	0.00	-0.05	0.33	0.28
KAS04B	151.00	0.10	0.00	-0.10	0.33	0.23
KAS04C	185.00	0.12	0.00	-0.12	0.35	0.23
KAS04D	235.00	0.25	0.00	-0.25	0.38	0.13
KAS04E	277.00	0.53	0.00	-0.53	0.41	-0.12
KAS04F	343.00	0.93	0.42	-0.51	0.48	-0.45
KAS05A	81.00	0.08	0.00	-0.08	0.39	0.31
KAS05B	270.00	0.12	0.01	-0.11	0.50	0.38
KAS05C	310.00	0.62	0.12	-0.50	0.54	-0.08
KAS05D	429.00	0.78	0.78	0.00	0.70	-0.08
KAS05E	459.00	0.90	0.82	-0.08	0.73	-0.17
KAS06A	81.00	0.32	0.37	0.05	0.52	0.20
KAS06B	183.00	0.49	0.16	-0.33	0.49	0.00
KAS06C	259.00	1.03	0.26	-0.77	0.51	-0.52
KAS06D	293.00	1.00	0.58	-0.42	0.55	-0.45
KAS06E	334.00	1.01	0.69	-0.32	0.58	-0.43
KAS06F	376.00	1.08	0.70	-0.38	0.60	-0.48
KAS07A	47.00	0.45	0.03	-0.42	0.49	0.04
KAS07B	107.00	0.54	0.01	-0.53	0.47	-0.07
KAS07C	210.00	0.67	0.00	-0.67	0.51	-0.16
KAS07D	295.00	0.66	0.50	-0.16	0.66	0.00
KAS07E	362.00	1.01	0.68	-0.33	0.82	-0.19
KAS07F	463.00	0.85	0.81	-0.04	0.95	0.10
KAS08A	52.00	0.70	0.00	-0.70	0.35	-0.35
KAS08B	148.00	0.66	0.00	-0.66	0.42	-0.24
KAS08C	313.00	0.90	0.68	-0.22	0.60	-0.30
KAS08D	455.00	1.02	0.70	-0.32	0.91	-0.11
Mean error (%)				-0.21		-0.01

In [156] the geochemistry of deep groundwaters as found in the Klipperås site is described. There is a representative presentation made of major ion compositions, originally taken from [157], see table 3. In [156] there are also examples given on the composition of some acidified waters and estimated composition of atmospheric water (rain/snow).

Table 3 Major ion compositions [157].

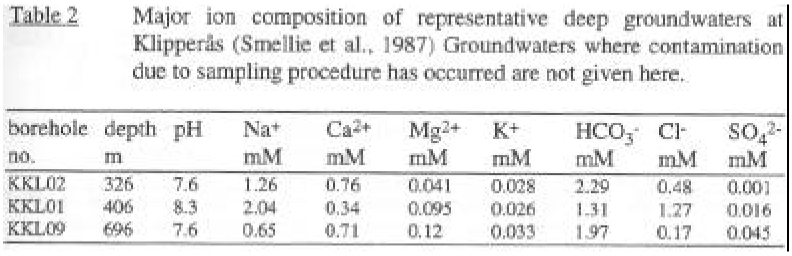


Table 2 Major ion composition of representative deep groundwaters at Klipperås (Smellie et al., 1987) Groundwaters where contamination due to sampling procedure has occurred are not given here.

borehole no.	depth m	pH	Na^+ mM	Ca^{2+} mM	Mg^{2+} mM	K^+ mM	HCO_3^- mM	Cl^- mM	SO_4^{2-} mM
KKL02	326	7.6	1.26	0.76	0.041	0.028	2.29	0.48	0.001
KKL01	406	8.3	2.04	0.34	0.095	0.026	1.31	1.27	0.016
KKL09	696	7.6	0.65	0.71	0.12	0.033	1.97	0.17	0.045

In table 4, also from [156], there is a comparison between the measured and calculated compositions of deep ground waters (KKL01, KKL02, and KKL09).

Table 4 Comparison between the measured and calculated compositions of some deep ground waters [156].

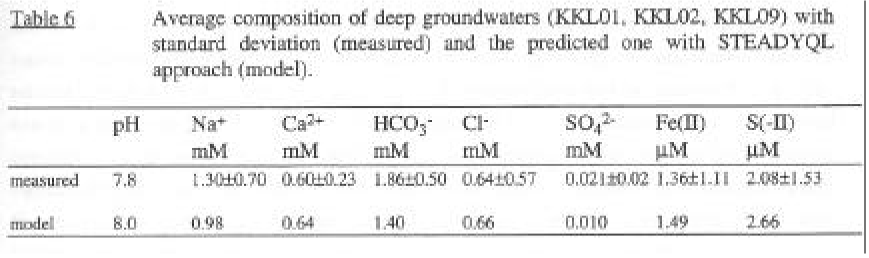


Table 6 Average composition of deep groundwaters (KKL01, KKL02, KKL09) with standard deviation (measured) and the predicted one with STEADYQL approach (model).

	pH	Na^+ mM	Ca^{2+} mM	HCO_3^- mM	Cl^- mM	SO_4^{2-} mM	Fe(II) µM	S(-II) µM
measured	7.8	1.30±0.70	0.60±0.23	1.86±0.50	0.64±0.57	0.021±0.02	1.36±1.11	2.08±1.53
model	8.0	0.98	0.64	1.40	0.66	0.010	1.49	2.66

Detailed data on groundwater sampling and chemical characterisation is given in [158] concerning the Laxemar deep bore hole, KLX02 (1705 m depth), located close to the Äspö Hard Rock Laboratory (HRL). Groundwater sampling was conducted on two occasions and using different methods. The first sampling was taken in the open borehole using the so-called tube sampler; the second sampling used the SKB-packer equipment to isolate pre-determined borehole sections.

Groundwater compositions consist of two distinct groupings; one shallow to intermediate sodium-bicarbonate type (Na(Ca,K):$HCO_3Cl(SO_4)$) to a depth of 1000 m, and the other of deep origin, a calcium-chloride type (Ca-Na(K):Cl-SO_4(Br)), occurring below 1000 m. The deep brines contain up to 46000 mg of Cl^- per litre. The influence of bore hole activities are seen in tritium data which record significant tritium levels down to 1000 m, and even to 1420 m. The upper 800 m of bedrock at Laxemar lies within a groundwater recharge area. The sub-vertical to moderate angled fracture zones facilitate groundwater circulation to considerable depths, at least to 800 m, thus accounting for some of the low saline brackish groundwaters in these conducting fracture zones. Below 1000 m the system is hydraulically and geochemically "closed" in such a way that highly saline brines exist in a near-stagnant environment.

In figure 3 [158], some main features of the groundwater at Laxemar are shown.

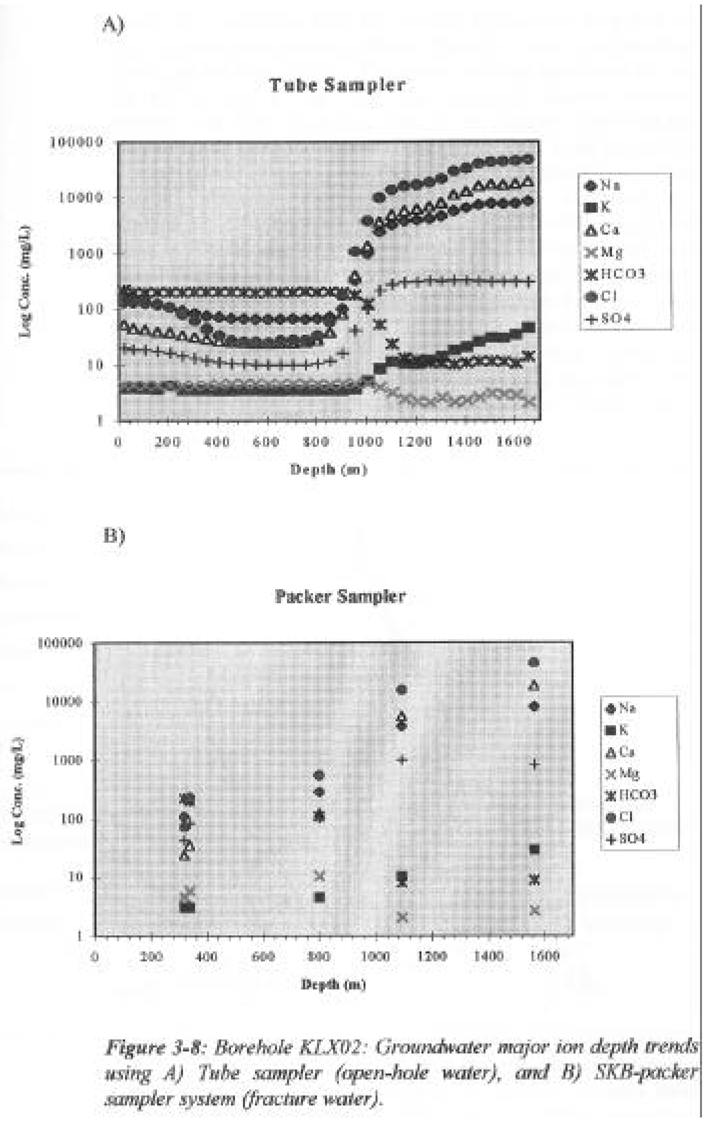
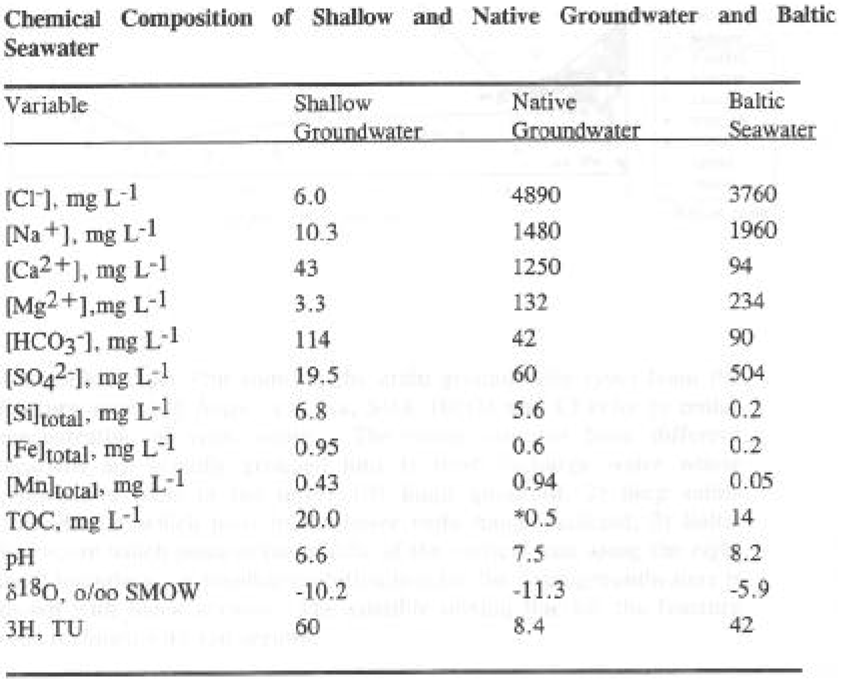


Figure 3-8: Borehole KLX02: Groundwater major ion depth trends using A) Tube sampler (open-hole water), and B) SKB-packer sampler system (fracture water).

Figure 3 Groundwater major ion concentration trends in Laxemar [158].

In [159], the chemical composition of shallow and native groundwater and Baltic seawater are compared, see table 5.

Table 5 Chemical composition of shallow and native groundwater and Baltic seawater, from [159].



Chemical Composition of Shallow and Native Groundwater and Baltic Seawater

Variable	Shallow Groundwater	Native Groundwater	Baltic Seawater
$[Cl^-]$, mg L^{-1}	6.0	4890	3760
$[Na^+]$, mg L^{-1}	10.3	1480	1960
$[Ca^{2+}]$, mg L^{-1}	43	1250	94
$[Mg^{2+}]$,mg L^{-1}	3.3	132	234
$[HCO_3^-]$, mg L^{-1}	114	42	90
$[SO_4^{2-}]$, mg L^{-1}	19.5	60	504
$[Si]_{total}$, mg L^{-1}	6.8	5.6	0.2
$[Fe]_{total}$, mg L^{-1}	0.95	0.6	0.2
$[Mn]_{total}$, mg L^{-1}	0.43	0.94	0.05
TOC, mg L^{-1}	20.0	*0.5	14
pH	6.6	7.5	8.2
$\delta^{18}O$, o/oo SMOW	-10.2	-11.3	-5.9
3H, TU	60	8.4	42

In [158] the chloride concentration dependence on depth for the boreholes KLX01 and KLX02 are accounted.

2.3.4 Bentonite environment

Colloids behaviour related to the bentonite environment is described in [160]. The processes, parameters and data used to evaluate the potential of nuclide transport (could also transport corrosion products!) by a colloid facilitated mechanism are reviewed and discussed in the report. Both steady-state (present situation) and possible future non-steady-state hydro-geochemistry in the geosphere are covered. In the steady-state scenario, the colloid (clay, silica, iron(III)hydroxide) concentration is around 20-45 micrograms/l which is considered to be a low value. The low colloid concentration is justified by the large attachment factor to the rock, which reduces the stability of the colloids in the aquifer. Both reversible and irreversible sorption processes are reviewed. In the non-steady-state scenario, changes of hydro-geochemical properties may induce larger colloid concentrations. The increase of concentration is however limited and relaxation is always observed after any change. Emphasis is placed on the glaciation-deglaciation scenario. A change in salinity could cause peptisation of colloids (synergistic effect for corrosion processes). In Figure 4 a relation between salinity concentration and colloid concentration (peptisation) is given.

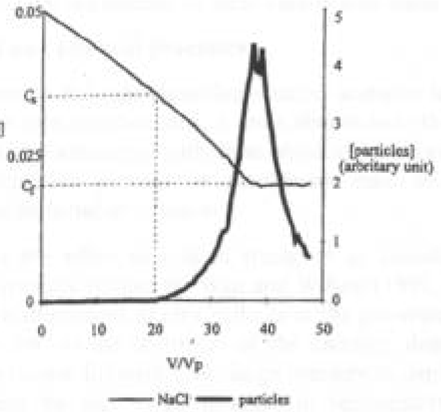


Figure 3-2: Influence of salinity concentration on colloid concentration. Conditions: elution of clay colloids through column with Na solution gradient (Faure et al., 1994).

Figure 4 Influence of salinity concentration on colloid concentration [160].

In [161] a surface chemical model of the bentonite water interface is discussed in relation to the near field chemistry in the repository. There are accounts of the Äspö ground water composition, see Table 6 and of its pH as a function of the number of exchange cycles, see Figure 5.

Table 6 Äspö ground water, [161].

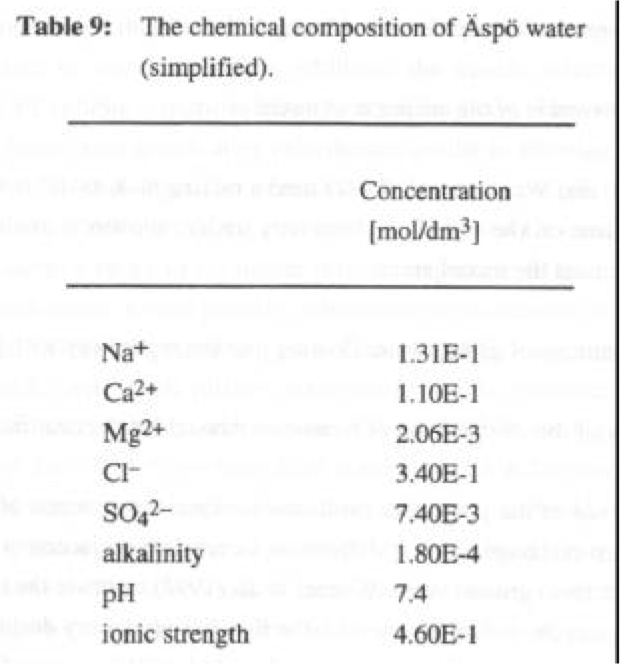


Table 9: The chemical composition of Äspö water (simplified).

	Concentration [mol/dm^3]
Na^+	1.31E-1
Ca^{2+}	1.10E-1
Mg^{2+}	2.06E-3
Cl^-	3.40E-1
SO_4^{2-}	7.40E-3
alkalinity	1.80E-4
pH	7.4
ionic strength	4.60E-1

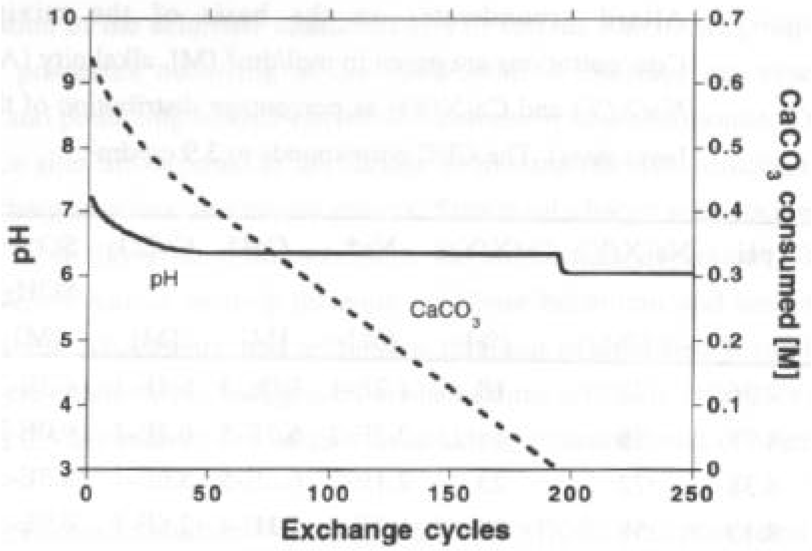


Figure 5 pH as a function of the number of exchange cycles for Äspö ground water [161].

The bentonite composition is discussed i.a. in KBS 3 [87]. The composition varies but the main components are clay minerals (>80) like smektites (>70 %). Montmorillonite is a common representative. The chemical main components are Si and Al and lesser concentrations of Na, Mg, Fe, K and Ca. The concentration of sulphides and organic material should be below 200 mg/kg. The most common sulphide phase is pyrite, FeS_2.

2.3.5 Bacteria and microbial influence

In [162] there is a discussion of microbial influences on repository environment. Different types of compacted bentonite clay, or mixtures with sand, will be placed as a buffer around the waste canisters. A major concern for the performance of the canisters is that sulphate-reducing bacteria (SRB) may be present in the clay and induce corrosion by production of hydrogen sulphide. The report presents data on viable counts of SRB in the bedrock of Äspö HRL. A theoretical background on the concept water activity is given, together with basic information about SRB. Some results on microbial populations from a full scale buffer test in Canada is also presented. The results suggest water activity to be a strong limiting factor for survival of bacteria in compacted bentonite. As a consequence, experiments were set up to investigate the effect of water activity on survival of SRB in bentonite. It is shown that survival of SRB in bentonite depends on the availability of water and that compacting a high quality bentonite to a density of 2.0 g/cm^3, corresponding to a water activity (a_w) of 0.96, prevents SRB from surviving in the clay.

There is also a presentation of a broad and thorough investigation on how micro-organisms may influence safety of repositories for radioactive waste. First, an overview of the Swedish concepts for disposal is given, including a discussion of the geological, chemical and hydrological conditions in repositories. Then the limiting and stimulating factors for life of micro-organisms are reviewed, such as relations to oxygen, temperature, pH, radiation, pressure, water and nutrients availability. Bacteria in the cycles of carbon, nitrogen, sulphur, iron, manganese and hydrogen are also discussed. A literature review of subterranean bacteria is given. Investigations of micro-organisms in repository-like environments, and microbial corrosion and redox processes relevant for materials in the repository and for the mobility of radionuclides are discussed. Possibilities to predict the activity and presence of micro-organisms through mathematical models are discussed.

In [163] there is a presentation of Canadian work on microbial influences on the buffer/container environment. The buffer/container experiment was carried out during 2.5 years to examine the in-situ performance of compacted buffer material in a single emplacement borehole under vault-relevant conditions. During decommissioning of this experiment, numerous samples were taken for microbial analysis to determine if the naturally present microbial population in buffer material survived to conditions and to determine which groups of micro-organisms would be dominant in such a simulated vault environment. Microbial analyses were initiated within 24 hour of sampling for all types of samples taken. The culture results showed an almost universal disappearance of viable micro-organisms in the samples taken from near the installed heater surface. The microbial activity measurements confirmed the lack of viable organisms with very weak or no activity measured in most of the samples. Generally, aerobic heterotrophic culture conditions gave the highest mean colony-forming units (CFU) values at both 25 and 50 °C. Under anaerobic conditions, and especially at 50 °C, lower mean CFU values were obtained. In all samples analysed, the numbers of sulphate reducing bacteria were less than 1000 CFU/g dry material. Methanogens were either not present or were found in very low numbers. Anaerobic sulphur oxidising bacteria were found in higher numbers in most sample types with sufficient moisture. The statistical evaluation of the culture data demonstrated clearly that the water content was the variable limiting the viability of the bacteria present, and not the temperature.

In [164] evidence and indications of sulphate reduction based on geological, hydro geological, groundwater, isotope and microbial data gathered in and around the Äspö HRL tunnel have been evaluated. This integrated investigation showed that sulphate reduction had taken place in the past but is most likely also an ongoing process. Anaerobic sulphate-reducing bacteria can live in marine sediments, in the tunnel sections under the sea and in deep groundwaters, since there is no access to oxygen. The sulphate-reducing bacteria seem to thrive when the Cl^- - concentration of the groundwater is 4000-6000 mg/l. Sulphate reduction is an in situ process but the resulting hydrogen-sulphide rich water can be transported to other locations. A more vigorous sulphate reduction takes place when the organic content in the groundwater is high (>10 mg/l DOC), which is the case in the sediments and in the groundwaters under the sea.

Some bacteria use hydrogen as an electron donor instead of organic carbon and can therefore live in deep environments where access to organic material is limited. The sulphate-reducing bacteria seem to adapt to changing flow situations caused by the tunnel construction relatively fast. Sulphate reduction seems to have occurred and will probably occur where conditions are favourable for the sulphate reducing bacteria such as anaerobic brackish groundwater with dissolved sulphate and organic carbon or hydrogen.

Some main conclusions for microbial influences are that microbes need water for their existence and their ability to act is highly influenced by the presence of water. Furthermore they normally need surfaces to bind to in order to function properly.

2.3.6 Ranges of chemical parameters

The following chemical parameters, see table 7, are selected as a fundament for calculations and discussions. They are in accordance with the findings from different sources accounted above. Only data in accordance with storage in crystalline bedrock, filled with bentonite as in KBS 3 [87] is considered. The maximum concentration range that should be considered in modelling of canister corrosion is also accounted in the table.

Table 7 Selected chemical parameter ranges from various sources. The ionic concentrations are selected from referred data to represent a ground water on 500 m depth.

Param.	Dim.	Selected value	Min value	Max value
pH		8		9
E_h	V	-0.5		0.7
HCO_3^-	mg/l	100	100	300
SO_4^{2-}	mg/l	8	5	500
Cl^-	mg/l	200	170	6500(50000)
HS^-	mg/l	0.1		0.5
Ca^{2+}	mg/l	80	40	2000
Na^+	mg/l	100	60	2000
Fe^{2+}	mg/l	0.1		1
K^+	mg/l	5	5	20
Mg^{2+}	mg/l	9	20	130
$\mathrm{Log}p_{O2}$	(bar)	-2.8		-2.8
$(O_2$	mg/l			8)
S^{2-}	mg/l	0.1		0.5

Compositions of synthetic groundwaters selected for electrochemical experiments are accounted in table 8 of section 5.2.2.

2.4 Short summary of literature on repository environment

In this section some important findings from literature on repository environment are accounted. There is an abundance of information available. The selection was guided by the need to complete the knowledge about critical combinations of environmentally influenced chemical parameters related to copper corrosion. One example of work that should be performed is to determine possible max and min limits and also mean values of critical concentrations, i.a. of chloride to be used in subsequent discussions of consequences. Another part is to use the information to briefly discuss possible influences on copper corrosion.

There are extensive sets of information available for the planned Swedish repository for spent nuclear fuel. The fundamental pieces of information are found in KBS 3 [87], in which also older information is summarised.

In the KBS 3 concept there is a tunnel in crystalline, granitic bedrock in which copper canisters containing the spent nuclear fuel are placed into holes drilled in the tunnel floor. After loading a tunnel with canisters it is filled with blocks of compacted bentonite around the canisters. Non-compacted bentonite is filled into the tunnel. After closing the facility, ground water has access to the whole system and there will be a ground water flow through the repository, the flow rate and composition of which is determined by the surrounding conditions as well as by the repository conditions.

There are several areas in Sweden that have been investigated as models for the final repository site. The most intensely investigated is the Äspö HRL in Oskarshamn. A majority of data used in the present work is taken from investigations performed at Äspö.

In [152, 153, 154] there are accounts of the pre investigations for the Äspö HRL. Those were started in 1986 and involved extensive field measurements, aimed at characterising the rock formations with regard to geology, hydrogeology, hydrochemistry and rock mechanics.

One of the important aspects of the Äspö works has been to compare predictions with later actual findings. As an example of such work, relations between prediction model results and the actually measured values for chloride concentration as a function of tunnel phase position can be found in [151].

Representative presentations of major ion compositions in the ground water can be found [157]. In [156] there are also examples given on the composition of some acidified waters and estimated composition of atmospheric water (rain/snow) and relations between P_{CO2}, pH and [$CaCO_3$] to illustrate the variation of data.

Groundwater compositions at Äspö consist of two distinct groupings; one shallow to intermediate sodium-bicarbonate type ($Na(Ca,K):HCO_3Cl(SO_4)$) to a depth of 1000 m. The other is of deep origin, a calcium-chloride type (Ca-Na(K):Cl-

$SO_4(Br)$), occurring below 1000 m. The deep brines contain up to 46000 mg of Cl^- per litre. Below 1000 m the system is hydraulically and geochemically "closed" in such a way that highly saline brines exist in a near-stagnant environment.

In the non-steady-state scenario, like glaciation, changes of hydro-geochemical properties may also induce large colloid concentrations. A change in salinity could cause peptisation of colloids. (Synergistic effect for corrosion processes).

The composition of the KBS 3 bentonite varies but the main components are clay minerals (>80) like smektites (>70 %). Montmorillonite is a common representative. The chemical main components are Si and Al and lesser concentrations of Na, Mg, Fe, K and Ca. The concentration of sulphides and organic material should decrease 200 mg/kg. The most common sulphide phase is pyrite, FeS_2.

A major concern for the performance of the canisters is that sulphate-reducing bacteria (SRB) may be present in the clay and induce corrosion by production of hydrogen sulphide. It has been shown that survival of SRB in bentonite depends on the availability of water and that compacting a high quality bentonite to a density of 2.0 g/cm^3, corresponding to a water activity (a_w) of 0.96, prevents SRB from surviving in the clay.

However, it is also shown that anaerobic sulphate-reducing bacteria can live in marine sediments. The sulphate-reducing bacteria seem to thrive when the Cl^- -concentration of the groundwater is 4000-6000 mg/l. Sulphate reduction is an in situ process but the resulting hydrogen-sulphide rich water can be transported to other locations. A more vigorous sulphate reduction takes place when the organic content in the groundwater is high (>10 mg/l DOC) which is the case in the sediments and in the groundwaters under the sea. Some bacteria use hydrogen as an electron donor instead of organic carbon and can therefore live in deep environments where access to organic material is limited. Sulphate reduction seems to have occurred and will probably occur where conditions are favourable for the sulphate-reducing bacteria such as anaerobic brackish groundwater with dissolved sulphate and organic carbon or hydrogen.

The choice of conditions for the electrochemical experiments as demonstrated in tables 7 and 8 has been governed by the findings in the literature search. The choice of parameters and the variation of data is done in relation to this background.

3 Copper thermodynamics

3.1 General

There are several chemical environments around and also inside the canister that can be foreseen. It is also well known that chemical components like copper, iron, chloride, sulphide and carbonate are present at varying concentrations. Beside those there is of course a residual probability of important chemical components appearing that either cannot be foreseen at present or are misjudged as being unimportant. In all cases the environment is framed by the presence of the surrounding rock and of the bentonite that could be inhomogeniously composed, wetted, heated and mechanically loaded by an an-isotropic pressure field. The conclusion is that the total system is very complex and could therefore not be described in a simple way. A thermodynamic description therefore has to be simplified and will cover only the most important parameters.

The first type of chemical environment prevailing during excavation and filling of the repository with canisters is oxidising and containing varying concentrations of chloride, determined by the surrounding groundwater. This environment is also going to dominate the scene a shorter or longer time after sealing of the repository. The second type is probably reducing, still containing chloride but also possibly sulphide by action of bacteria and/or presence of pyrite. Oxidising and reducing environments are foreseen to replace each other during specific periods of time like glaciation. Both types of chemical environment will also contain other species like sulphate, carbonate, and matter with an organic origin and also anthropogenic substances. Iron would also be present, either as pyrite, FeS_2 or as iron metal in the inner canister of cast iron. In an environment like this, concentrations of dissolved species would in some cases vary within wide limits depending on position and time. Concentrations of other species could be more stable. In table 7 a set of probable species and their concentrations are given. These concentration levels are used in the present calculations also considering the probable variation i.a. for chloride. The global pH value is dominated by the bentonite and will be in the range 8-9. Local deviations will occur.

The thermodynamics of copper specifically in saline environments form a fundamental part of this work. It gives the framework for subsequent modelling discussions. It should be described in relation to as many environmental parameters as possible of those mentioned above. As seen in previous parts of this work, thermodynamic data is available from many sources and in many shapes. We have found that it is a very convenient way to present data as Pourbaix diagrams, calculated for a given set of conditions. The chemical system discussed here is limited to Cu-Fe-Cl-S-C-H-O and its subsystems.

The following account is started by a presentation of some previous work specifically on copper performed by Beverskog, Puigdomenech [3] and Hermansson [165]. The overview is followed by an account of calculations performed within the present project. Our calculations try to complete the picture of the system Cu-Fe-Cl-S-C-H-O by including iron, sulphide and carbonate as well as performing calculations for very high salinities. Calculations are also performed at an elevated temperature of 150 °C for the subsystem Cu-Cl-H-O.

It should be underlined that all the calculations performed within the present work have been done using Puighdomenech´s set of programs and also in part his database, appearing on his web page at the Royal Institute of Technology, KTH. Our calculations performed on the system Cu-Cl-H-O to higher salinities and temperatures (150 °C) were, however, done using data published in [3].

3.2 Closely related previous thermodynamic calculations

3.2.1 The subsystem Cu-Cl-H-O

In [3] three different total concentrations (10^{-4}, 10^{-6}, and 10^{-8} molal) for dissolved copper were used for the calculations.

It was found in [3] that copper is a noble metal, but corrodes with hydrogen evolution at low pH, both at a concentration level of 10^{-6} m at $T \geq 125$ °C, and at a concentration of 10^{-8} m from $T \geq 50$ °C. The oxides (Cu_2O (cr) and CuO (cr)) are stable at all temperatures and concentration levels $\geq 10^{-8}$ m, with the exception of 10^{-8} m at $T \geq 100$ °C where the oxides are not stable. The copper (II) hydroxide, $Cu(OH)_2$(cr), is not thermodynamically stable in the interval investigated. Cu^+ predominates at $T > 80$ °C at all concentrations levels. CuOH (aq) appears in the Pourbaix diagrams only at the lowest concentrations, and in the predominance diagram for dissolved species at 125 and 150 °C. $Cu(OH)_2^-$ predominates at all temperatures and concentrations investigated.

At acidic pH, an increasing temperature decreases the immunity area, and therefore the risk for corrosion of copper increases. At alkaline pH-values corrosion also increases with temperature due to decrease of both the passivity and immunity areas.

3.2.2 The subsystem Cu-Fe-H-O

Hermansson calculated Pourbaix diagrams for part of the system Cu-Fe-H-O [165]. In this work a short theoretical study on the thermodynamic stability of steam generator S/G secondary side sludges in PWR was performed. The technical background was the stability at shut down conditions of the sludge pile. The S/G sludge is supposed to primarily contain magnetite and copper at 60 °C. A couple of shutdown conditions were investigated containing humid air (100 % humidity), hydrazine water (100 ppm) and air saturated water. Humid air conditions were also evaluated at 22 °C.

Two bi-metallic oxides were found in the system, i.e. delafossite, $CuFeO_2$ and cuprospinel, $CuFe_2O_4$. Only delafossite was found to be stable at 60 and 22 °C. Cuprospinel was not stable. Beside delafossite and the pure metals, hematite and magnetite were also stable. Delafossite and hematite are stable in humid air and air saturated water. Magnetite is stable in the hydrazine environment. Metallic copper is also stable in the hydrazine environment but not in humid air and air saturated water. The solubility of copper ranges between 10^{-7} m and 10^{-5} m, depending on environment.

3.3 Thermodynamic calculations performed within the present project

3.3.1 Subsystems to Cu-Fe-Cl-S-C-H-O

Calculations were performed on the total system Cu-Fe-Cl-S-C-H-O and some of the subsystems. In all calculations, programs (PREDOM, PREDOM 2, MEDUSA and HYDRA) by I Puigdomenech were used. In some instances the database in HYDRA was used and in some other the database found in [3]. The latter is the case especially for diagrams on the subsystem Cu-Cl-H-O accounted for in appendices 1 and 2.

An example of a Pourbaix diagram calculated within the present project for the subsystem Cu-Cl-O-H at 25 °C and $[Cl]_{tot}=1.5$ is shown in figure 6. See also figure A1:8.

It is interesting to see that calculations demonstrate, as also mentioned in [3], that there is no protecting, passivating layer on copper in highly saline media. If the diagram in figure 6, which is calculated for 25 °C, is compared with those for higher temperatures presented in [3] and those in appendices 1 and 2, it can be seen that the immunity limit for copper descends as a function of temperature at high chloride concentrations. This means a risk that copper could be neither noble, nor passive at elevated temperatures in the repository environment, containing large concentrations of chloride.

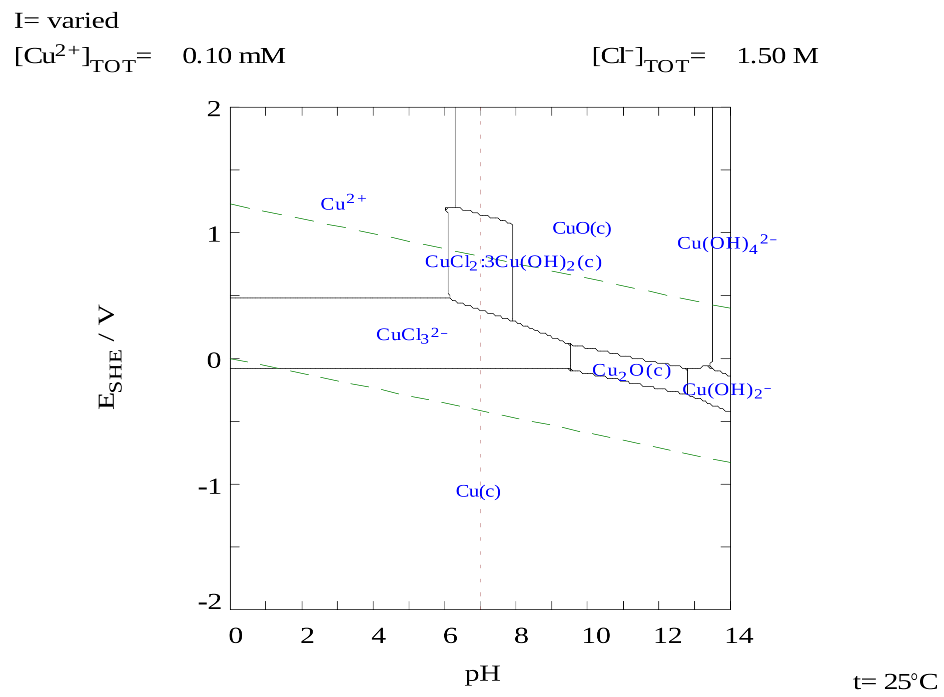


Figure 6 Pourbaix diagram for the system Cu-Cl-H-O at indicated conditions.

In certain types of environment sulphide and also iron would have an influence on copper stability. Sulphide is important at low potentials. Iron is important if there would be a break through of the copper, exposing the cast iron insert for galvanic corrosion. An example of a Pourbaix diagram calculated for the system Cu-Fe-S-Cl-O-H at 25 °C and $[Cl]_{tot}$=1.5 is shown in figure 7.

One important feature that can be observed in figure 7 is that the immunity limit of copper is further lowered in the S-Cl containing system compared with systems not containing sulphur. This could have consequences for copper corrosion in a reducing environment as a formed sulphide film probably would have a disputable passivating ability.

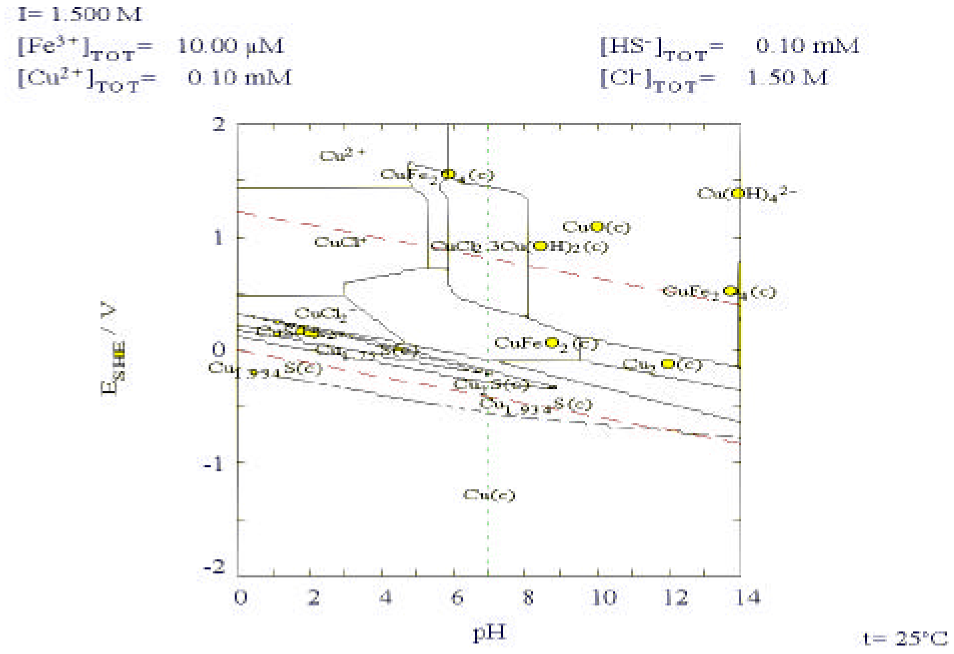


Figure 7 Pourbaix diagram for the system Cu-Fe-Cl-S-H-O at indicated conditions.

In figure 8 the system Cu-Cl-C-H-O is shown for indicated conditions at chlorine and carbonate concentrations precisely at which copper species containing those components are starting to appear. It is found that the first chlorine containing specie to appear is $CuCl_2^-$ at a total chlorine concentration slightly above 1 mM. The first carbonate containing specie is $CuCO_3$, appearing at a total carbonate concentration of 0.5 mM.

The same system is demonstrated in figure 9 at the total concentrations chosen for the repository model system as shown in table 7. It can be seen that at those slightly higher concentrations of chlorine (2 mM) and carbonate (6 mM), $CuCl_2^-$ is still the predominating copper specie containing chloride. Among copper carbonates, malachite ($Cu_2CO_3(OH)_2$) appears beside the simple copper carbonate $CuCO_3$.

In figure 10, the same conditions as in figure 8 are used for the calculation. The difference is a higher total copper concentration. It can be seen that malachite is the first carbonate phase appearing in the diagram instead of simple copper carbonate at the lower copper concentration and that the predominance area for CuO is extending to higher pH values.

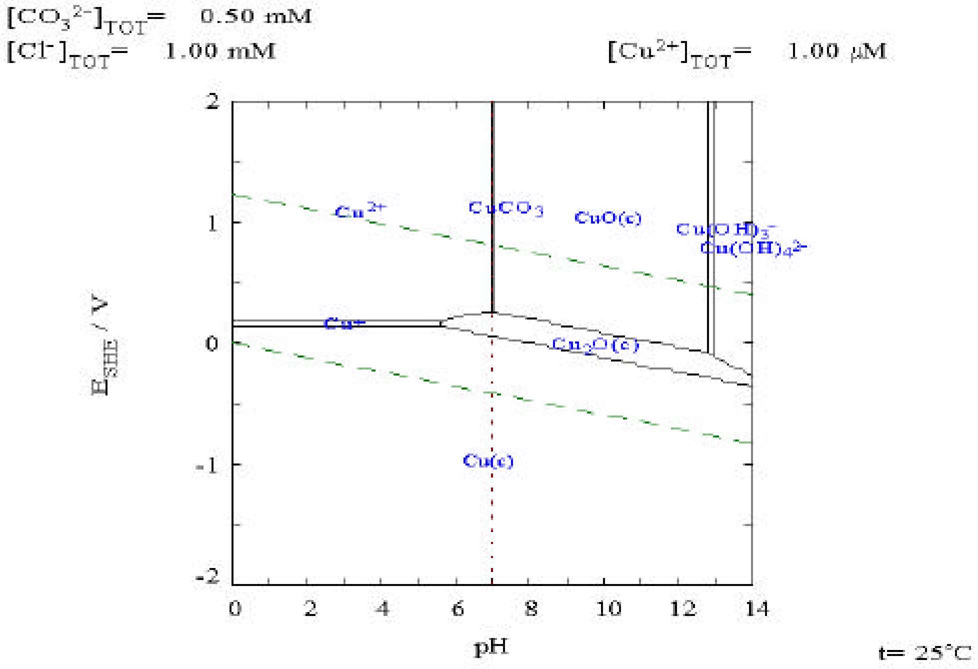


Figure 8 Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

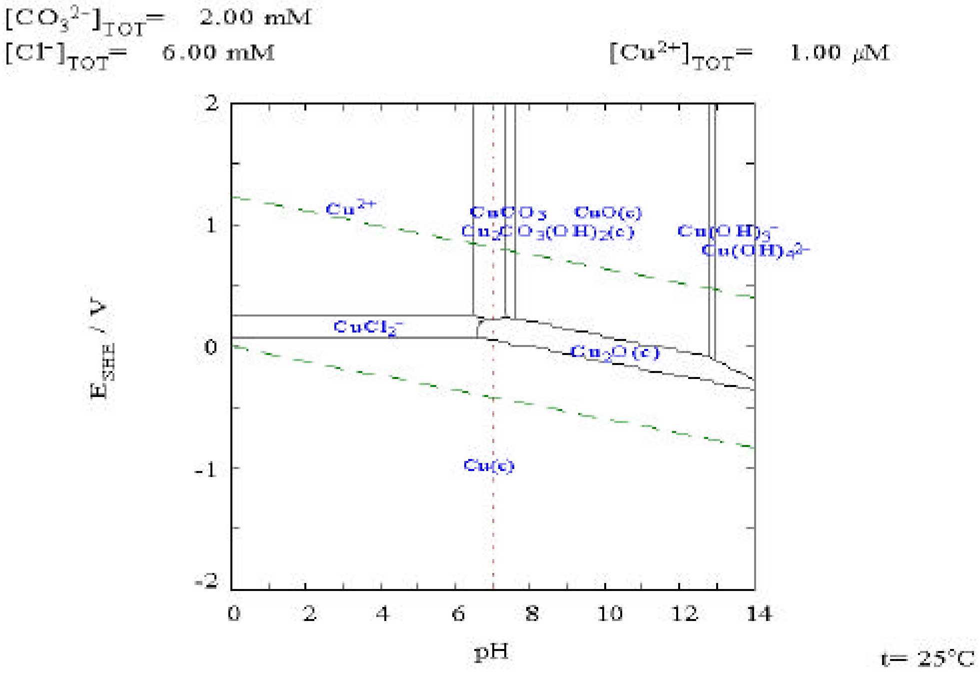


Figure 9 Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

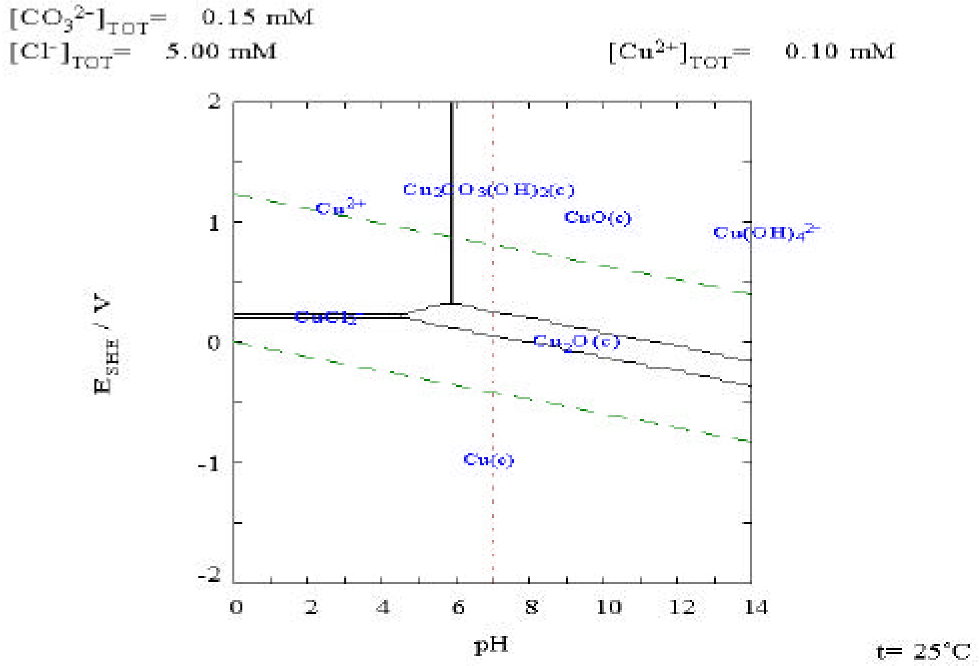


Figure 10 Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

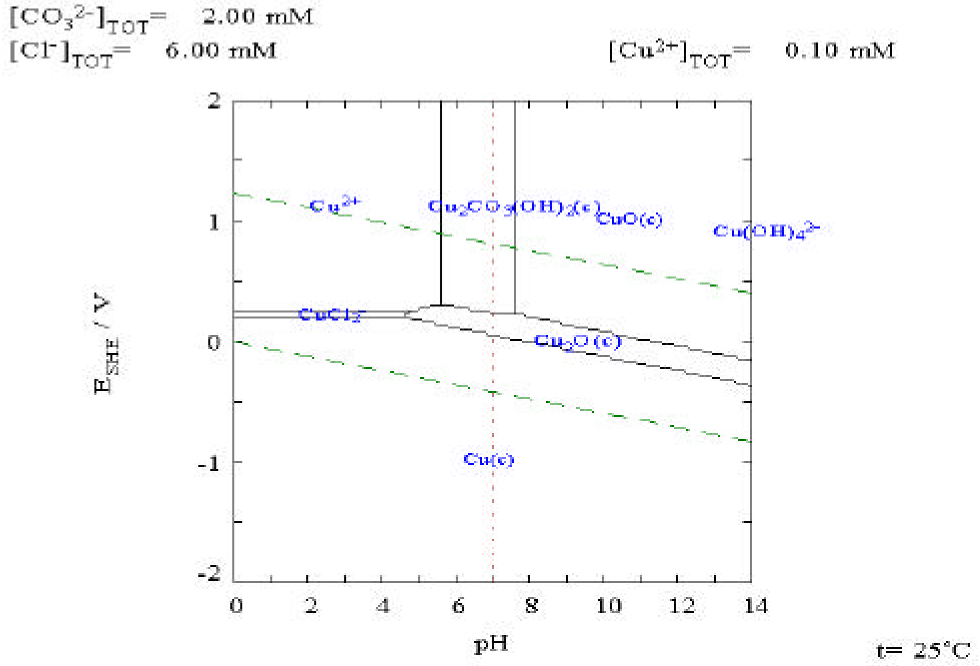


Figure 11 Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

In figure 11 the system is shown under the same conditions as in figure 9 but with the higher total copper concentration. It can be seen that the only copper carbonate present is now malachite and that CuO has an extended stability area in figure 11.

3.3.2 The specific subsystem Cu-Cl-S-C-H-O

In figures 12-14 a set of diagrams for the subsystem Cu-Cl-S-C-H-O is accounted for 25 °C at a couple of indicated conditions of interest for the modelling. Those are the most generalised diagrams accounted here for the repository system as far as iron is not present. They demonstrate the calculated equilibrium state for the system at a set of different component concentrations. A full account would require many more diagrams. However, already in figures 12-14 it could be seen (very roughly) that sulphides predominate at low potentials, chloride at intermediate and carbonates at high. Sulphide is clearly decreasing the immunity area of the metal in a way that seems independent of the total sulphide concentration within the calculated range. Increased chloride concentrations don't influence the sulphide predominance very much.

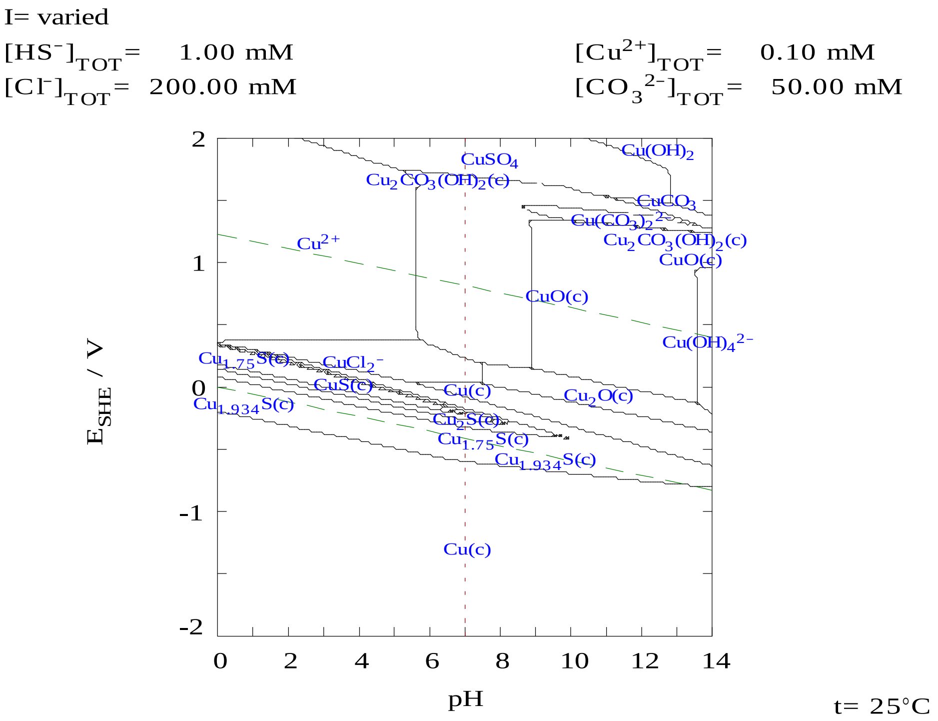


Figure 12 Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions.

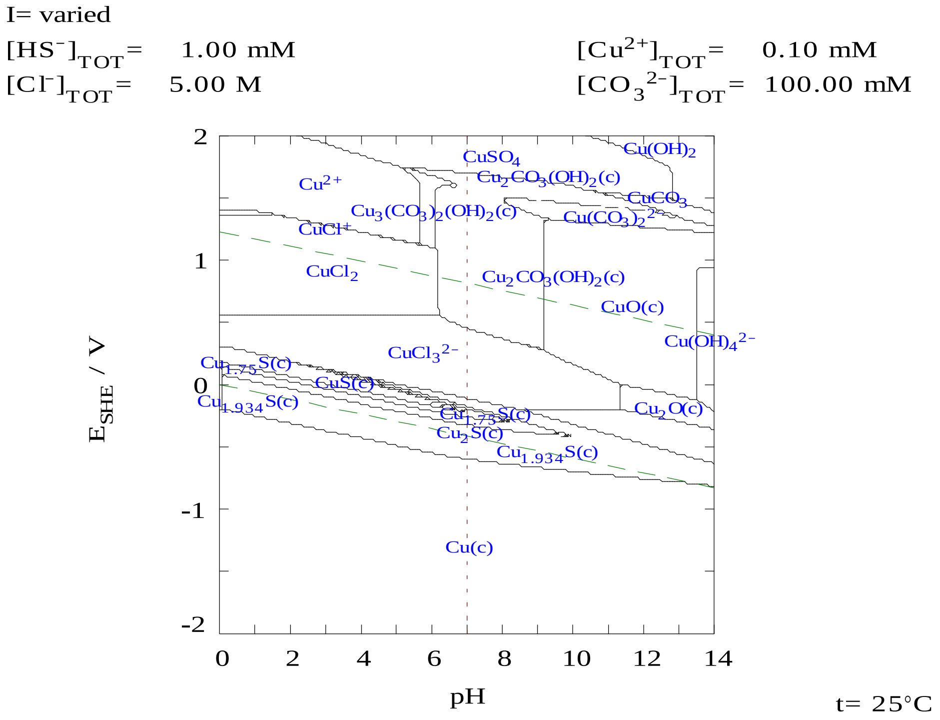


Figure 13 Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions.

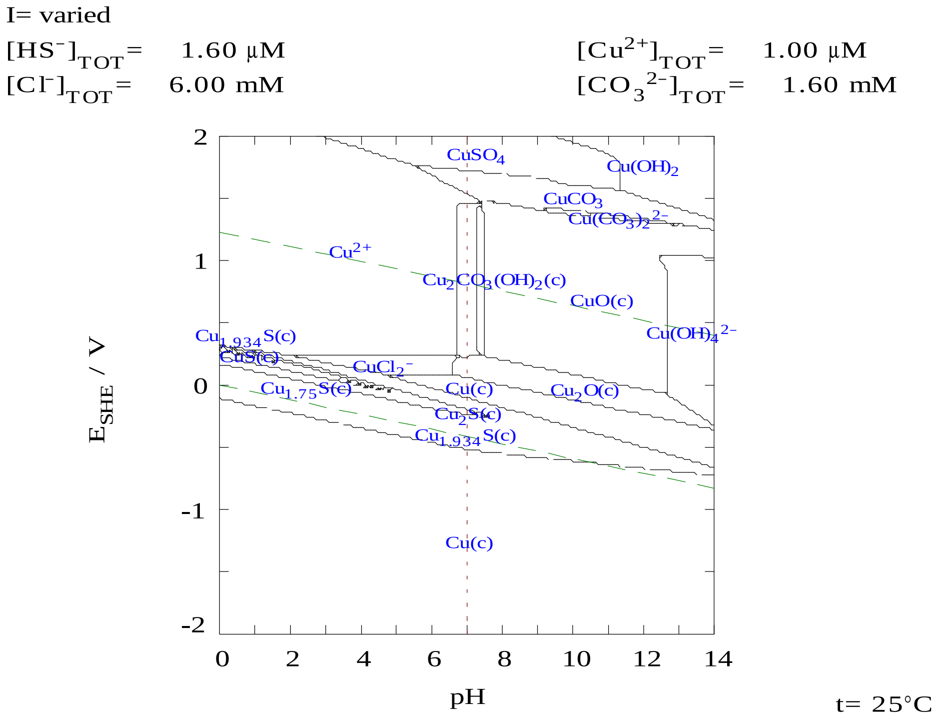


Figure 14 Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions.

3.3.3 The subsystem Cu-Cl-H-O at very high salinity up to 150 °C

One part of this work was to perform thermodynamic calculations specifically on the subsystem Cu-Cl-H-O in a systematic way. The primary objective of the calculations performed within the present work was an extension to 150 °C and to a total chloride concentration of 5M. Calculations were performed for temperatures 25, 100 and 150 °C at total concentrations of dissolved copper of 10^{-8}, 10^{-6} and 10^{-4} M and of chlorine 0.02, 1.5 and 5 M. The results are accounted in appendices 1 and 2. Pourbaix diagrams are shown in figures A1:1-27. The corresponding diagrams for dissolved species only are given in figures A2:1-27. Some of these diagrams are the same as in [3] but recalculated here for the purpose of checking and inter calibration. The agreement between calculations is good.

The production of diagrams accounted in appendices 1 and 2 were performed in the same manner, using the same data and program package as in [3]. The present calculation was, however, extended to 150 °C and up to a chlorine total concentration of 5M. Thermochemical data and estimations of heat capacity temperature dependence as given in [3] were made to calculate log k values at 150 °C. The quality of our estimates could be checked. This was done by comparing our calculations at 150 °C with those for the sub-system Cu-H-O as given in [3]. The agreement is good. Puighdomenech´s program automatically calculates activity factors at actual ionic strengths, which is important for the high chloride concentrations.

The diagrams in appendices 1 and 2 have not been calculated with exactly the same requirements on quality assurance as in [3]. However, we judge the information in the diagrams as being good enough to form a basis for the modelling of localised corrosion on copper in a highly saline environment.

The main impressions of this series of diagrams are:

1. There will be no passive film on copper at lower potentials in a highly saline system.
2. The immunity of copper metal decreases with increasing chlorine concentration.
3. The effects mentioned in points 1 and 2 are steadily increased with increasing temperature.
4. The step from a solution with 1.5 M chlorine to 5 M is a question of degree. There are no fundamental changes taking place.
5. The increased temperature from 100 to 150 °C is also essentially a question of degree. There are no fundamental changes taking place.

3.3.4 The total system Cu-Fe-Cl-S-C-H-O

In figure 15 a diagram for the full system of Cu-Fe-Cl-S-C-H-O is accounted for 25 °C at the conditions given in table 7. In figure 16 the same system is shown at a higher chloride concentration of 5 M. These are the most generalised diagrams for the repository system when also iron is present. However, to calculate the diagrams it has been necessary to reduce the number of species participating in the calculation. The way of selecting species to be included in calculations can of course be debated. We have tried to cancel out species with a low probability to appear within the environmental envelope of the repository.

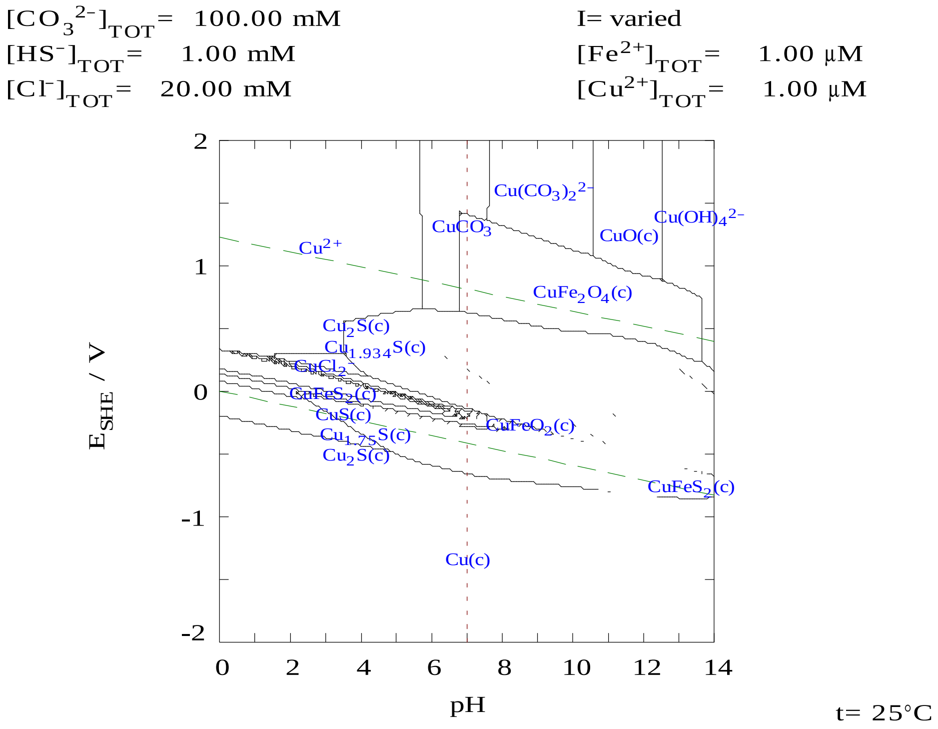


Figure 15 Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions. Low salinity.

Figure 15 demonstrates that copper sulphides dominate at low chloride concentrations in the central parts of the diagram. There are also indications in the diagram that the program cannot properly select the predominating specie in every location. The information should therefore be used with caution.

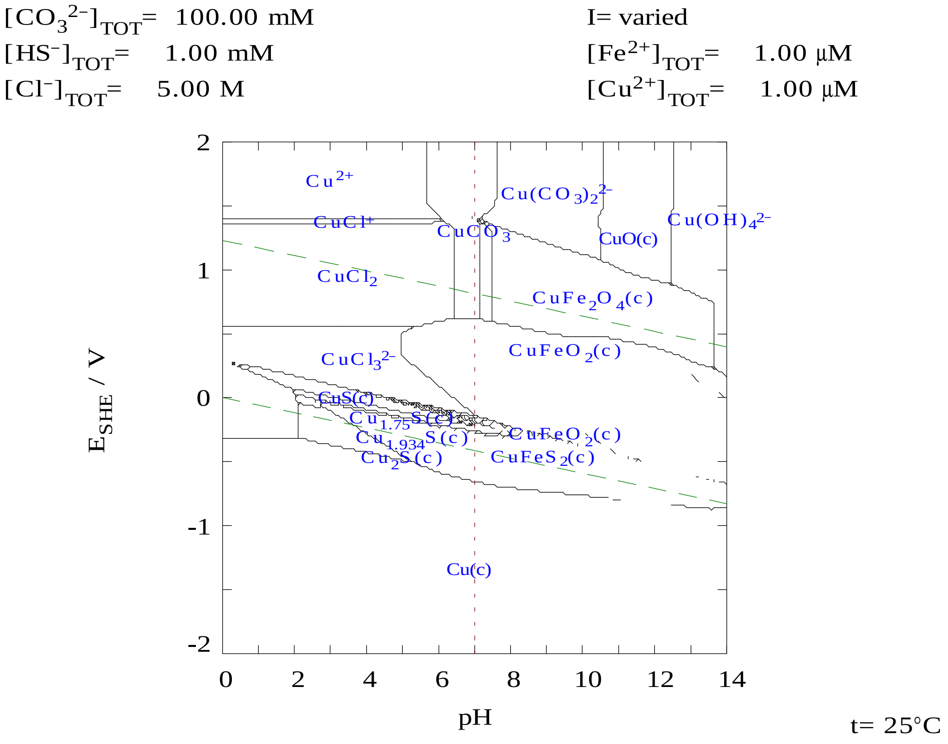


Figure 16 Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions. High salinity.

Figure 16 demonstrates that copper sulphides still dominate in central parts of the diagram at high chloride concentrations but only at low potentials. At intermediate potentials $CuFeO_2$ predominates. The program had obvious difficulties to converge at this calculation and the information should be used with caution.

4 Copper corrosion in the repository environment

4.1 A selected repository environment and variations

In this work a design of the repository as described in KBS-3 with later modifications is anticipated [87]. According to this concept the repository is placed on 500 m depth in granitic bedrock. The main parts of the repository is the rock with its environment of aquatic (and perhaps gas-) flows, the repository itself with a tunnel system where composite canisters according to [10] (copper/cast iron, encasing the fuel) is deposited in cylindrical holes in the floor of the tunnel system. The whole system is filled with bentonite and crushed rock, and sealed, i. a. with concrete. The composite canister is supposed to serve as a protection during handling at production and burial and as a barrier against effluent of radionuclides from the fuel both during the handling and during the long storage period. See also figure 1 for a schematic overview.

The canister is considered to be the most important barrier for a long time and geology is considered to supply retardation effects on leaking radio nuclei. The aim of the research according to resent research plans [1, 9, 10] implies a weakening of the multi/barrier principle, since the importance of the geological barrier is strongly diminished. By doing this, SKB places a much larger emphasis on the canister itself as a barrier. Thereby the demands on both mechanical and corrosion resistance of the canister is going to increase substantially.

In order to achieve a high corrosion resistance in the repository environment the canister is designed according to the composite principle as an inner mechanically supporting canister of cast iron and an external corrosion resistant lining of copper.

In the repository the canister is surrounded by compacted bentonite in its deposition hole. The tunnel system is filled with a mixture of bentonite and crushed rock. The surrounding crystalline bedrock is more or less rich of fractures. The ground water is therefore going to flow through the repository with a velocity and composition, which can depend on a set of outer factors varying from one time to another. An example of such a variation is the glaciation cycle. Another is if heavy environmental changes caused by man were to occur.

Mechanical and chemical processes and combinations of them can influence the canister and its integrity. An example of the latter is stress corrosion. Mechanical influences could happen by deformation and pressure build up as well as by movements in the bedrock. The chemical stability of the canister has been evaluated earlier [31, 87].

The chemical environment in the repository is complicated and varies as a function of time as both inner and external processes are going to influence. As an example of inner processes, heat induced transportation in the repository can be mentioned.

Examples of external processes are changes of the ground water flow direction, velocity and composition.

Main parameters of the chemical environment are pressure, temperature and groundwater flow. Furthermore there are variable concentrations of different transportable chemical components in the groundwater, bentonite and presumably in gas. pH and Eh will depend on these. Kinetic factors will play a very important role for the chemical processes.

The limits of possible pressures in the repository are 5 MPa (no glaciation) and 35 MPa (glaciation) and 14 MPa is used by SKB as a design pressure. The pressure influences mechanical and chemical systems but also ground water flow and thereby transportation patterns.

The temperature in the repository will roughly vary with time in a manner, which could give a maximum close to a canister of about 85 °C a short time after the sealing. Thereafter the temperature decreases and will after some time adopt the surrounding rock temperature, about 15 °C. Lower temperatures can appear in connection with glaciation.

The ground water flows slowly through the repository and its composition can vary with time from different reasons, for example in connection with glaciation and as a function of other climate and environmental changes. The water is supposed to contain i a chloride, carbonate and sulphide/sulphate in concentrations and relations that could vary. Furthermore there will exist very low concentrations of reducible species, for example Mn(III, IV) and Fe(III), bound as complexes together with i a chloride and organic complexing agents. The latter species can exist in the organic material in the bentonite. The species are supposed to have a large influence on the prerequisites for corrosion.

It is also of interest for corrosion processes which kind of water will fill the repository after the sealing. Would it be fresh surface water or chloride containing deep water? In [10] there is also a discussion to use salt water or brine for hydro-dynamical retrieval of canisters. This is an example of anthropogenic actions that could add to the risk of corrosion.

At sealing, the repository environment will be oxidising. It is of course of importance to estimate how long oxidising conditions can prevail. In a shorter perspective just after the sealing, free oxygen will decide the redox potential. It is probably going to be relatively high. The total amount of free oxygen in the aerated repository consists of oxygen left in pockets of air and oxygen dissolved in water, for example in the bentonite pore water. The bentonite has also an open porosity, which is filled with air. The air and thereby the oxygen can have entered into the bentonite pore water and porosity during the relatively lengthy and extensive handling period in connection with excavation, transportation and storage of the bentonite.

As an example of calculation, it could be supposed that the bentonite pore water would be oxygen saturated (8 mg/l at normal pressure and temperature). Then the bentonite in a canister pit (about 12 m^3 of bentonite) is going to contain about 10 g oxygen dissolved in water if the bentonite moisture content is about 10 vol. %. If only this oxygen were consumed in some mechanism of attack, it would correspond to a dissolution of about 70 g of copper metal. It should simultaneously be pointed out that the amount of oxygen, which is found initially in the open pores of the bentonite, is much bigger than what is dissolved. SKB have from certain laboratory experiments and considerations estimated the oxidising time in the repository to be about 100 years. The uncertainty is judged to be large. Perhaps oxidising conditions can prevail under considerably shorter or longer periods of time. As long as porosity in the bentonite is open and not filled with water, oxygen can still reach the canister hole from the tunnel refill, which would extend the oxidative period.

After the oxidising period relatively large amounts of reducible species are still present in the masses of bentonite. Those can serve as electron sinks in combination with other processes, for example formation of copper sulphide.

The repository pH is supposed to be buffered by the bentonite, which implies a pH of about 8-9. The bentonite itself consists of clay minerals as Montmorillonite and can be supposed to vary in composition. It can also contain many of the elements in the periodic table as impurities. For example pyrite ($\approx FeS_2$) will occur and also residuals of organic materials.

The repository will probably be exposed to events, which implies penetration by water with high salt- and/or oxygen concentrations. There can also be events, which result in crack formation in the bentonite. Such events can, if they would happen, be supposed to strongly influence the chemical environment of the repository. Furthermore, it shall be pointed out that if the rock fracture system is not already biologically contaminated, the very opening and construction of the repository will imply a biological contamination. Therefore it is probable that microbes will exist in the repository after the sealing.

Human incursion in the repository can be supposed to happen in a multitude of ways and will, if it would happen, probably influence the chemical and the physical environment very strongly. Acidification, deposition of chemical waste in the proximity of the repository, and climate changes are all examples of anthropogenic events that can be considered to influence water chemistry. Different types of alien material will probably unwittingly be left at the sealing of the repository. The alien material can thereafter influence in several ways. For example it could sustain biological processes and thereby contribute to sulphate reduction, formation of sulphide and in the prolongation of copper corrosion. Furthermore the alien substances themselves can have chemical and mechanical properties which directly would influence corrosion and transportation processes.

As a summary it can be said that the global pH in the repository will be in the range of 8-9, buffered by the bentonite. The redox potential will probably run through an initial period of oxidising conditions and gradually turn into a reducing. Oxidising and reducing conditions can alternate i a during glaciation periods. A very rough estimation based on figures 6 and 7 and also other information indicates that the redox potential would vary in the interval $-0.5 < E_h$ (V) < 0.7. The global concentrations of Cl^- can rise to the order of 1.5 m, O_2 to $3*10^{-4}$ m. The same conditions will prevail initially on the canister surface. However, the change with time on micro sites on the surfaces can differ slightly from position to position and from the global environment in the rest of the repository. One example of this is the higher temperature (and the temperature distribution) during the first, hot time after the sealing at the canister. This could cause transportation effects not occurring in other parts of the repository. Components could by the temperature gradient be concentrated on the canister surface or in the proximity of the canister and cause a chemistry that differs strongly from the repository in general. For example chloride and other water borne components can be suspected to concentrate all the way to saturation and precipitation in such a process, at least within certain zones of vicinity of the canister. Circulation in the immediate proximity of the canister through convection is, however, less probable. If it still occurs, it can imply that the local environment close to the canister have access to a supply of considerably more oxygen than foreseen from global environmental data. This implies that the redox potential can decrease more slowly on the surface of the canister than foreseen from pure diffusion data.

Mechanical and chemical inhomogeneities in the adjacent bentonite as well as on the copper surface itself can also be foreseen. Such inhomogeneities can be present from the beginning, but also be created by the described circulation process or by external events. For example the canister will initially have an oxide layer which could be locally disturbed and made unstable by high chloride concentrations. This could happen through the influence of the handling equipment and by the fact that the oxide layer locally can be exchanged for a sulphide layer or by local concentration effects. Further, defects in the copper material can be present from the production process, for example pores as well as welding and handling faults.

4.2 Chemical entities in the repository related to copper corrosion

The most important chemical entities related to copper corrosion in the repository would be:

Metals: Cu and Fe
Simple anions: Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, and HS^-
Simple cations: Na^+, Ca^{2+}, Mg^{2+}, Cu^+, Cu^{2+}, Fe^{2+}, and Fe^{3+}
Complexes: $CuCl_n^{1-n}$, $CuCl_n^{2-n}$, $FeCl_n^{2-n}$, $FeCl_n^{3-n}$, $Cu(OH)_n^{1-n}$, $Cu(OH)_n^{2-n}$, $Fe(OH)_n^{2-n}$, $Fe(OH)_n^{3-n}$, $Cu(CO_3)_n^{1-n}$, $Cu(CO_3)_n^{2-n}$, $Fe(CO_3)_n^{2-n}$, $Fe(CO_3)_n^{3-n}$, $Cu(HCO_3)_n^{1-n}$, $Cu(HCO_3)_n^{2-n}$, $Fe(HCO_3)_n^{2-n}$, and $Fe(HCO_3)_n^{3-n}$
Solids: CuO, CuO_2, Fe_2O_3, Fe_3O_4, $CuFe_2O_4$, $CuFeO_2$, $CuCl_2{:}3Cu(OH)_2$, $CuCO_3$, $Cu_2CO_3(OH)_2$, Cu_2S, $Cu_{1.75}S$, $Cu_{1.93}S$, CuS, and $\approx FeS_2$
Colloids
Organic matter, for example humic and fulvic acids
Surfaces of *bentonite minerals*
Dissolved O_2 and other chemical components that at proper pressure and other circumstances might generate gas ("*geogas*").

Concentrations for some of the above species and total concentrations of their systems can be found i.a. in table 7.

4.3 General copper corrosion in an oxidising environment

In [1] it is concluded that the canister, disregarded from the short initial phase of presence of oxygen, will be exposed only for corrosion during anaerobic conditions. As a result of this the lifetime of the canister is estimated to be more than 1 million years.

Both general and localised corrosion can be active simultaneously on the canister. Already a simple structuring of the different parts of a corrosion process gives a complicated impression. In the present situation work is focused on one of the components, which most rapidly can cause problems, namely localised corrosion, and pitting. However, thereby general corrosion is not discarded as of no interest, since high concentrations of chloride can cause a general breakdown of the passive film. This is clearly demonstrated in figures 12 and 13, where $CuCl_2^-$ or $CuCl_3^-$ are shown to predominate at repository conditions with a high chloride concentration. However, for this phenomenon to have an influence of the same severity as pitting, a much larger transportation capacity to and from the total canister surface is required. This situation is potentially dangerous but will probably not appear as long as the transportation capacity is low.

It is interesting to see that calculations demonstrate [3], [app. 1,2] that there is no protecting, passivating layer on copper in highly saline media over a range of potentials at 50-150 °C. If the diagram in figure 6, which was calculated for 25 °C, is compared with those for higher temperatures presented in [3], [app. 1,2] it can be seen that the immunity limit for copper descends as a function of temperature at high chloride concentrations. This means a risk that copper is neither noble, nor passive in a repository environment containing large concentrations of chloride. It should thus again be pointed out that copper in such an environment is protected from serious general corrosion only by keeping transportation rates of reacting species very low.

There is an obvious need to evaluate the risk for high transportation rates to appear during those periods and also to evaluate the resulting corrosion.

4.4 Localised copper corrosion in an oxidising environment

4.4.1 General

As already pointed out both general and localised corrosion can be active simultaneously on the canister. The latter can in turn be of different characters, namely pitting corrosion, crevice corrosion and if there exist mechanical stresses, also stress corrosion. Localised corrosion can give damages of type pits or cracks and there is a much lower need of total dissolution capacity than at general corrosion to cause serious damage. A localised corrosion process can also be much more rapid than general corrosion and cause serious damage in a very short time.

Pitting is a local type of corrosion, characterised by an extremely localised attack, which can result in a through hole in the metal. Pitting is one of the most destructive and dangerous forms of corrosion. It can cause that a construction fails due to perforation of the material. The weight loss, which is caused by pitting, is normally only a very small, negligible part of the total mass of the construction. The consequences of the perforation can, however, cause very serious events, i.e. it shows for the first time when it is too late and the breakthrough is a fact.

The pits are often difficult to detect due to their smallness and that the pits are often hidden by a cover of corrosion products. Simultaneously, it is difficult to quantitatively measure and compare the degree of pitting corrosion due to varying depth and number of pits, which can appear under identical conditions. Pitting is also difficult to study through laboratory experiments. Sometimes the pits need some time at experiments, up to months or a year, before they show themselves.

The following is given as an example of calculation. A penetrating pit through the copper lining down to the cast iron insert with a diameter of 1 mm in 5 cm thick copper (never really observed) only needs (theoretically) an oxidation capacity corresponding to 600 ml air of NTP (120 ml oxygen of NTP). A deposition hole for one canister would contain a maximum of 10 g of oxygen or 7000 ml at NTP. This amount of oxygen would theoretically allow the formation of about 60 such pits. Later it will be described how other mechanisms can be thought of to take over the role of oxygen as an electron sink in combination with another driving force at localised corrosion.

A complication in resent programs compared with the KBS-3 concept is the introduction of an inner canister, which entails that a postulated pit through the external copper canister could be followed by electrochemically induced dissolution of the cast iron insert. At a complete dissolution of the steel canister during evolution of hydrogen, an amount of gas corresponding to about 2000 normal cubic meters is formed. It is not probable from several reasons that such an amount would be released. It must, however, be pointed out that if this were the case there would be obvious consequences for the transportation mechanisms in the system.

4.4.2 Influences of system components

The theory of pitting corrosion on copper emphasises chloride (Cl^-) as the ion, which initiates and propagates the pitting. Chloride was considered as a prerequisite for initiation and propagation of pitting on copper. Sulphate (SO_4^{2-}) is, according to the theory considered to be inert and not influencing pitting corrosion on copper. Influence of pH is not explained by the theory.

The theory is to a large part founded on short time experiments and electrolytes with a high ionic strength. Literature is filled with investigations about pitting on copper, but only a small number of studies have been performed at pH values and concentrations of dissolved oxygen which is typical for natural waters. However, the theory about pitting of copper shows a significant discrepancy compared with practical experience i.a. regarding frequency of pitting as a function of water quality and also in long time experiments [166-170]. This is not surprising since the theory is founded on short time experiments and electrolytes with high ionic strengths. Edwards et al [168] examined pitting on copper at ion concentrations that are found in natural waters at different pH values (5.5, 7.0, 8.5, and 10.6). Anions as chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), hydrogen carbonate (HCO_3^-) and perchlorate (ClO_4^-) were studied with concentrations that occur in natural tap waters. Perchlorate, which indeed is not an anion that occurs in natural waters, was included still since it does not form complexes with neither monovalent nor divalent copper. The perchlorate solution was used in order to examine pitting of copper in an "inert" electrolyte.

New as well as aged copper surfaces were used in the investigation. The temperature was 8.5°C (cold water corrosion), but it is still interesting what was concluded. Edwards et al [167, 168] found that the influence of different inorganic anions was different at short and long time, respectively. For example at pH 8.5 and 8.5°C in aerated solution the following applied: The chloride ion has a distinct time dependent performance. Systems containing chloride had a distinct trend to increase pitting initially, but gave the best passivating layers (lowest anodic current) at the end of the experiment (72 hours). The coating of copper chloride was an obvious protective layer; i.e. the surface was passivated. Thus the chloride ion had a negative short time but a positive long time effect. The results contradict present theory.

The chloride ion has earlier been considered as the key to the theory on pitting on copper. In practice [167], it appeared to reduce the probability and the degree of pitting corrosion. Sulphate turned out not at all to be an inert electrolyte. It correlated strongly to the frequency of pitting and did not cause passivation at any pH. This was demonstrated by an increasing corrosion current.

Carbonate is generally considered to form passivating layers on copper at all pH. Here the anodic current is significantly diminished only at pH 10. Nitrate reduced the corrosion current with 25% but the surface was still active. Only at pH 10 did nitrate cause passivation. Perchlorate, which can be considered as a nearly ideal anion, increased the anodic current at its presence. Perchlorate caused passivation only at pH 10. Morphology of the formed coatings was considered partly to be responsible for the observed differences between the various an ions. Porous crystalline films caused pitting while non-porous films were resistant to pitting corrosion. It was concluded that as well sulphate ion as nitrate ion initiate pitting on copper.

According to investigations by Edwards et al [167, 168] copper seems to be predestined for pitting at the pH and oxygen concentrations which occur in natural waters at low temperatures (8.5°C). The question is whether this also applies for high temperatures. In order to understand the behaviour of copper in natural water systems probably the interaction between Cl^{-}-SO_4^{2-}-HCO_3^{-} and copper needs to be investigated at relevant conditions.

The above information clearly shows the need for a new theory for pitting on copper. This has to explain the effect of the different anions, differences between short and long term effects and the influences of a set of system parameters.

Another factor, which has been supposed to increase the frequency of pitting on copper, is the presence of a contaminating surface film of carbon from the production. Such a film is supposed to form a galvanic couple with copper [168-171]. Carbon films are supposed to be cathodic in relation to the copper material and would thereby increase the frequency of pitting. Once it was considered that all incidents with pitting was caused by carbon films. However, later evidence has clarified that they are not important for the phenomenon [172, 173]. It should be pointed out that the pitting potential is also dependent on previous surface treatment of the metal. However the surface history is of importance, its corrosion properties would be dominated by the immediate repository conditions.

Passivating metals are covered in certain environments by a layer which often is called a passive layer and which more or less efficiently hinders a continued attack or corrosion. This is because transportation processes through the layer are more or less slowed down and therefore more or less efficiently hinder a continuation of the attack. However, the layer is passivating in various degrees depending on the circumstances.

An example of the more extreme passive layers is Al_2O_3 on Al, which in a very efficient manner prevents corrosion of aluminium. The same system for passivation also constitutes an elegant example of what happens if the passive layer by one or other reason is deteriorated locally. If this happens on aluminium a very strong pitting can appear, which during unfavourable conditions quickly penetrates a thin layer of the metal. Metals that are nobler in character than aluminium, for example copper, can be protected efficiently already by passive layers, which not at all are as protecting as Al_2O_3. A breakthrough of copper is however still possible if the right environment and large enough time periods are available.

Consequently various metals have widely different properties as applied to pitting attack, even if the fundamental phenomenon is very similar. If a pit shall arise it is required that there is a passive film with local weakness zones enabling a local breakdown of the protective ability of the passive film. Furthermore, it is required that the potential exceeds a certain value for the phenomenon to appear. This potential is in general called the pitting potential. In order to achieve a guaranteed protection from pitting attack the potential must be less than a certain value, which is called the protection potential. The zone in between the two potentials constitutes a "grey zone" where attack can happen but most often does not. The values of the mentioned potentials vary depending both on the metal and its chemical environment.

4.4.3 Mechanism

Applied to copper in an oxidising, chloride and carbonate bearing environment the following mechanism for pitting could be sketched [123, 174]. From the beginning the copper is supposed to be covered with a layer of Cu_2O. At contact with carbonate a malachite layer could be formed on top of the copper oxide layer. Malachite is probably inhomogeneous and can take up chloride in certain places from the local environment.

Under the prerequisite that chloride penetrates into the malachite, CuCl will be formed and as long as the potential is moderately high, malachite and CuCl will be stable. At a lower potential Cu_2O will be the thermodynamically stable solid copper specie. Both the malachite and the inhomogeniously distributed copper chloride will start its transformation for Cu_2O at falling potential. In the case of CuCl this happens through hydrolysis and beside Cu_2O, HCl is also formed in the process. If the potential again increases, the acidified areas are covered again with malachite. Cu_2O is dissolved by the locally falling pH value below the protective layer of malachite and metallic copper is subsequently uncovered. Thereby the local attack is initiated and can then propagate as long as the potential of the surrounding malachite is high enough.

An example of a pit on copper according to the sketched mechanism is shown in figure 17. It should be pointed out that there are obvious deviations between this mechanism and resent observation. I.a CuCl is probably not formed. According to [3], and as can also be seen in figure 6, $CuCl_2{:}3Cu(OH)_2$ would be formed instead of CuCl beside malachite, $Cu_2CO_3(OH)_2$ at higher potentials. At low potentials neither solid copper chloride nor malachite would be stable, but instead copper metal and $CuCl_2^-$.

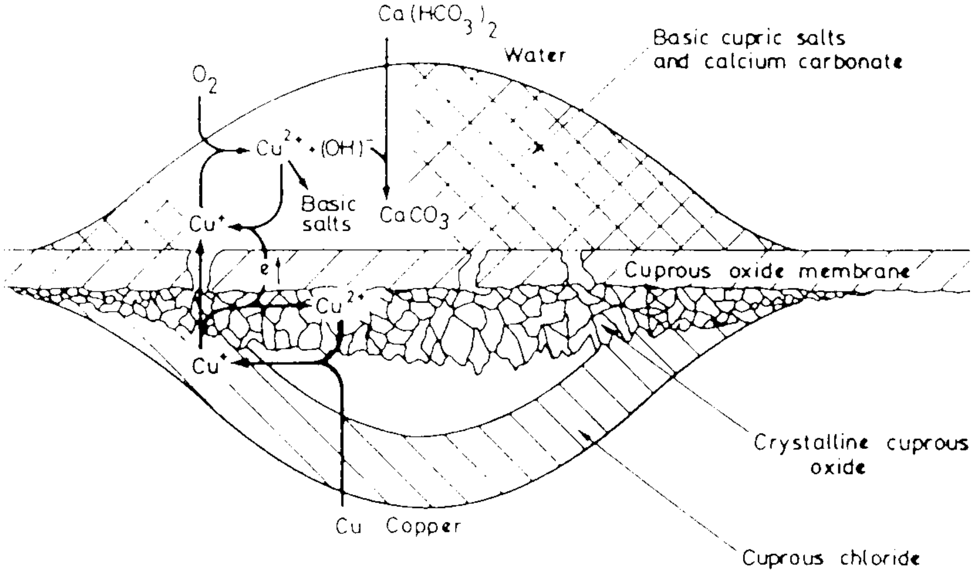


Figure 17 Example of pit on copper under oxidising conditions according to [123, 174].

The various steps in the mechanism (according to [123, 174]), which drives the attack after the initiation can roughly be sketched according to the following. See figure 17.

1. On the large un-destroyed *cathodic* surface of Cu_2O/unaffected malachite electrons are consumed, for example through the following reactions:

   $Cu^{2+} + e^- \rightarrow Cu^+$
   eqv. 1

   $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ eqv. 2

   $H^+ + e^- \rightarrow \frac{1}{2}H_2(g)$ eqv. 3

   $S^{2-} + 2e^- \rightarrow S$ eqv. 4

2. The *anodic* reaction implies dissolution of copper metal and can happen in several steps, for example:

   $Cu^+ \rightarrow Cu^{2+} + e^-$ eqv. 5

   $Cu(s) + Cu^{2+} \rightarrow 2Cu^+$ eqv. 6

3. Electrons move through metal and passive layer from the anodic inner part of the pit to the external cathode and are consumed there. Because of metal oxidation and electron migration a positive charge surplus arises inside the pit, which the following transportation mechanisms strive to neutralise:

4. Cl^-(outside) → Cl^-(inside) eqv. 7

5. The following reactions can thereafter occur in the pit:

   Cl^-(inside) + Cu^+ → CuCl(s) eqv. 8

   2CuCl(s) + H_2O → Cu_2O(s) + 2HCl eqv. 9

   Cl^-(inside) + CuCl(s) → $CuCl_2^-$ eqv. 10

   $Cu^{2+} + Cl^- \rightarrow CuCl^+$ eqv. 11

6. The following outward transportation can occur:

   Cu^+(inside) → Cu^+(outside) eqv. 12

   Cu^{2+}(inside) → Cu^{2+}(outside) eqv. 13

   $CuCl^+$(inside) → $CuCl^+$(outside) eqv. 14

   $CuCl_2^-$(inside) → $CuCl_2^-$(outside) eqv. 15

   The transportation according to eqv.15 happens if the concentration gradient becomes large enough.

7. On the outer surface of the destroyed passive layer of the pit, the following reactions can happen:

   $2Cu^+ + 1/2O_2 + HCO_3^- + OH^- \rightarrow CuCO_3{*}Cu(OH)_2(s)$ eqv. 16

   $2Cu^{2+} + HCO_3^- + 3OH^- \rightarrow CuCO_3{*}Cu(OH)_2(s) + H_2O$ eqv. 17

   $2CuCl^+ + HCO_3^- + 3OH^- \rightarrow$
   $CuCO_3{*}Cu(OH)_2(s) + H_2O + 2Cl^-$ eqv. 18

   $2CuCl_2^- + 1/2O_2 + HCO_3^- + OH^- \rightarrow$
   $CuCO_3{*}Cu(OH)_2(s) + 4Cl^-$ eqv. 19

Some of these reactions are more important than others and equations 1 - 19 say in brevity that the continuation in the pit means an inward transportation of chloride followed by acidification of the pit environment through hydrolysis of CuCl. In the acidic, chloride containing environment copper is dissolved followed by outward transportation perhaps mainly of copper - chlorine complexes, and finally a precipitation of malachite outside the pit. Electrons are consumed on the cathodic surfaces in the proximity of the pit through reaction with oxygen.

Already moderate concentrations of chloride can consequently be thought of to contribute to the deepening of the pits by formation of soluble complexes with copper that continuously diffuse away from the pit.

The presence of a pit means that the oxide layer in the proximity of the pit is protected and also reinforced. This means that the distribution of pits can be supposed to depend not only of the initiation of pits but also of "competition" between pits. The competition means that a slightly larger pit can passivate (i.e. generate a protective passive layer) a slightly smaller pit in its proximity, and thus acquire improved growth opportunities on the account of the passivated smaller pit. The time factor can here turn out to be very important. A slow inward diffusion to the corroding metal of oxygen and a long time can imply fewer and deeper pits. A long exposure time is thus in favour for a fewer number of pits, which penetrate to a larger depth. This means that the pitting ratio (biggest pit depth divided by the mean depth of the attack) can be supposed to increase with increased exposure time if the chemistry is the same.

In the mechanistic chart above a number of steps have been indicated for the pitting, eqv. 1 - 19. For all reactions, rate constants can be roughly estimated beside constants for transportation of reacting species to and from the metal surface. This gives a possibility to determine (very roughly) a rate-determining step, which can then be used to evaluate rates of attack and to calculate very rough times to breakthrough. This will not be attempted here.

Pitting on copper in an oxidising environment could be summarised as follows. Present theory emphasises the importance of Cl^- for initiation and propagation. It states that sulphate has no influence and that other anions are more or less inert. The theory is verified for short times but deviates for long as chloride passivates in the long run and sulphate (supposed to be inert) has a long time influence at all pH values. Carbonate, nitrate and also perchlorate passivates, but only at pH>10. Recent calculations of Pourbaix diagrams indicate that mechanisms for pitting in the Cu-Cl-C-H-O system would be different from those earlier suggested. Therefore, there is a need to formulate a new theory for pitting on copper in an oxidising environment.

4.5 General copper corrosion in a reducing environment

In the repository, there will certainly be an introductory period with an oxidising environment followed by a reducing. There is, however, no guarantee that the oxidising conditions will not return at later stages, for example during glaciation events. At such events the pressure field will have a complex gradient, which could cause surprising directions and velocities of the ground water flow, resulting in intrusion of oxygenated water into the repository and subsequent replenishment of the oxidising conditions. During such periods, oxygen will provide the driving force for the corrosion processes. Different mechanisms can prevail during different sub periods of time but also simultaneously in different geometrical parts of the non-homogeneous pressure, heat and chemistry fields that could form in the repository. Unfortunately a non-homogeneous environment is a good starting point for corrosion.

There will probably be long reducing periods between oxidising, during which corrosion processes are generally considered to come to a halt. However, several mechanisms for i.a. sulphide based attacks should be considered during reducing conditions.

The reducing environment will still contain chloride and carbonate as well as the oxidising but also sulphide by action of bacteria and/or via the presence of pyrite. There will also be other chemical species present like sulphate, and matter with an organic origin. Also anthropogenic substances are likely as remains from the construction and operative parts of the repository life but also as a result of later human actions.

Copper sulphides are formed on the copper surface at lower potentials in environments containing sulphide and also high chloride concentrations, see figure 7. The sulphide film formed could be of a rather complex nature consisting of several phases. The local micro-composition of the sulphide could under such circumstances depend very much on local micro-conditions in the bentonite close to the metal surface. For example would variations in pyrite concentration probably have an influence on the local copper sulphide composition. A slight variation in the potential over the copper surface would also have a high influence on the composition of the copper sulphide film. Calculations as those accounted for in figures 6, 7 and app. 1, 2 also show that the immunity of copper decreases as the chloride and sulphide concentrations increase. This results in a dangerous situation with low immunity of copper and a complex copper sulphide film of variable and disputable ability to passivate.

Such a system would probably not cause any general corrosion problems during a period of stable reducing conditions due to slow transportation and low concentrations of sulphide. However, a transfer from reducing conditions with a bad copper sulphide film into oxidising, in combination with increased water flow, would probably cause immediate corrosion problems. This could all happen during a glaciation period.

4.6 Whisker growth

4.6.1 General

It has been demonstrated both theoretically and by experiments that whiskers can form on copper metal at certain combinations of the chemical parameters of the environment. This is not to be looked upon as localised corrosion in the normal sense. However, the formation of whiskers could result in similar serious consequences, as whisker growth might proceed by local consumption of copper. This means that a kind of pitting mechanism, consuming copper metal, could appear also in a reducing or low potential environment and cause a break through of the copper wall.

Whisker growth has been demonstrated on copper. It remains, however, to clarify the nature, growth mechanism and the chemical limits for whisker formation. It is especially important to know if they are formed using copper from the local vicinity of their place of growth, or if copper is taken from a larger area on the copper surface.

It was concluded earlier that the potential must lie above a certain value if a pit of the normal type will be able to propagate. Furthermore oxygen or any other suitable oxidant must be present. If the potential drops under the protection potential the attack will come to a halt.

However, pitting on copper cannot be excluded at a low potential. It is certainly a completely different type of attack compared with the case appearing during oxidising conditions. In a reducing environment with sulphide present copper sulphides are stable and can come to dominate the film on the copper surface. Sulphide for formation of copper sulphide is found in the proximity of the canister, for example in original pyrite beads in the bentonite or as a result of previous or present microbial activity at the time of attack.

It must be clarified that significant differences in several respects exist between copper oxides and copper sulphides. There are many copper sulphides, all with varying composition. Some of them are shown in figure 7. Copper always has the valance (I) and never (II) in copper sulphide [175]. Also a number of meta stable phases exist in the copper - sulphur system. Iron (II) reacts willingly with those, and it is probable that the surface of the copper in reality can be covered by a mixed sulphide at reducing conditions. The copper sulphides are in contrast to the oxides good electron conductors. Moreover copper (I) ions migrate very easily in most copper sulphides. This is a substantial and noteworthy difference from copper oxides where the mobility of copper is very much lower.

At a low redox potential and reasonable access to hydrogen sulphide ions in solution a sulphide layer can be formed. The attack on the copper becomes approximately uniform over the whole surface (general corrosion) and access to and the diffusion rate in the environment of hydrogen sulphide ions guide the reaction rate. According to this model of general corrosion the copper canister is going to remain intact over a very long time.

It should, however, be observed that the process in any manner assumes that the sulphide growth becomes evenly distributed during general corrosion. Three prerequisites exist for this:

The in-diffusion of sulphide ions happens relatively uniformly. The chemical potential for copper in the sulphide is higher on the surface of the thinner parts of the sulphide layer. The sulphide crystals have no (enough) favoured directions of growth.

At comparatively high diffusion flows of sulphide through the bentonite buffer, a higher chemical potential is developed for copper on the surface of the sulphide layer where this is as thinnest. This can then govern the reaction to such areas whereafter the sulphide layer is stabilised and becomes evenly thick. Eventual thin areas therefore become self-healing. At low diffusion flows of sulphide in solution, diffusion of copper ions in the sulphide layer can happen to such extent that the chemical potential for copper is approximately the same over the whole of the sulphide layer surface. In this case the sulphidation happens primarily where the diffusion distance for hydrogen sulphide ions is least and on the crystal surface or in a screw dislocation, where the growth is most favourable.

4.6.2 Mechanism

A conceivable process, which describes the situation at low redox potential and low access to hydrogen sulphide ions, is shown in figure 18. It should be observed that even if a pit can to be formed in the copper also in this case, it is not pitting in the usual sense.

The sulphide - and chloride systems can here exist relatively independently of each other. High concentrations of chloride can cause concentrations of complex ions of copper and chloride, which can participate in transportation processes. (The chemical potential for copper is supposed to still be approximately the same everywhere in the sulphide phase on the copper surface).

Transformations and reactions with pyrite in the bentonite are also probable in a reducing environment. Copper, which has been dissolved in low concentration, can be thought of to move to the pyrite beads and be incorporated into the pyrite structure. Inversely the pyrite beads can be thought of to release sulphide in a very low concentration to the solution, whereupon the ions can move to the copper sulphide and react there. Also the iron, which is divalent in pyrite, can be thought of to transfer to the water phase in low concentration and to move to the copper sulphide and be incorporated there.

Beside a general corrosion on the basis of a sulphide, also local attacks can be thought of according to the mechanism demonstrated in figure 18.

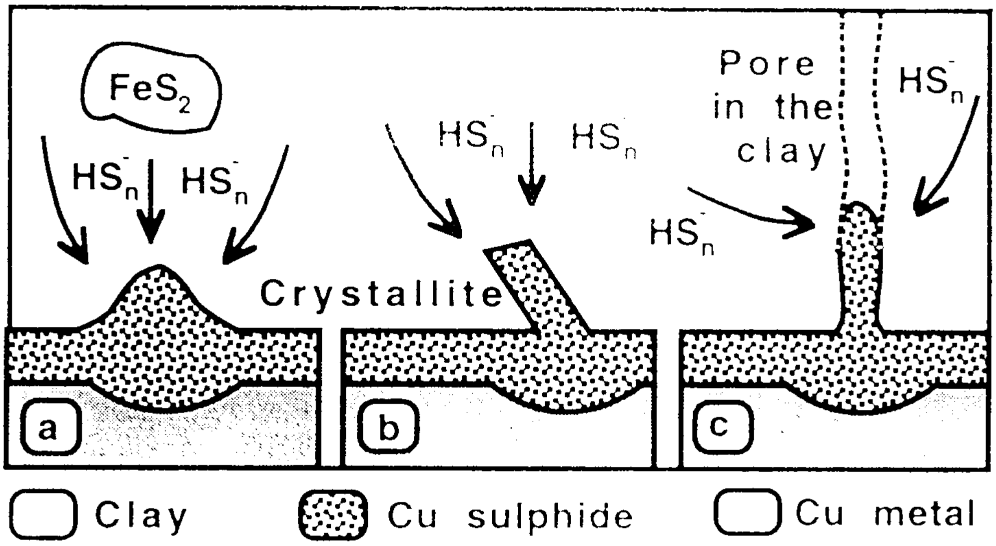


Figure 18 Mechanism for local, sulphide based corrosion on copper [176].

Copper has a very large affinity to sulphur and sulphide. The affinity of silver is sometimes even larger. This is important to remember when silver alloyed copper is considered as a canister material in order to improve the creep properties. Sulphur is found in the bentonite, as sulphide but also as sulphate. The latter can be transformed into sulphide if the repository has been infected by sulphate reducing bacteria and living conditions are reasonable for them. As sketched above it is therefore not ruled out that the copper canister can be covered with a layer of copper sulphide instead of an oxide layer after some time of exposure in the repository environment. At least it is probable that "islands" of copper sulphide will form on the surface in a reducing situation.

As already mentioned copper sulphide has very different properties from copper oxide. Copper diffusion in solid sulphide phase is opened as a possible path of transportation for the metal out from the canister. This can imply that the formed sulphide crystals will grow as copper ions will easily migrate out from the canister via dendrite crystals ("whiskers") into the areas in the surrounding bentonite, where sulphide can be found. See figure 18. The reaction between sulphide and copper ions then proceeds on the site where the sulphide was originally found. This means that sulphide transportation in liquid phase only needs to happen over comparatively short distances. The electrons which are formed at dissolution of the copper metal migrate in metal and copper sulphide (the latter is also an excellent semiconductor). They are taken care of through reduction by oxygen as long as it remains, or by Fe(III) and/or by poly sulphide in combination with precipitation/ growth of Cu_2S (or another copper sulphide phase) as a driving force. A proposal of a mechanism is sketched below for 25°C. In reality the situation is more complicated and should be evaluated more closely.

A primary copper sulphide (embryo crystal) is established on the copper metal surface. It can be initiated in several ways, for example mechanically in connection with depositing of the canister in the repository.

A. Dissolution of copper metal happens

$Cu(s) = Cu^{+} + e^{-}$ $e_0(A) = 0.552$ V

The formed copper ions and electrons migrate in metal and sulphide to the place where they can react and find the locus of lowest energy. The copper transportation happens with ease in a copper sulphide crystal, where sulphur atoms form the stable crystal gitter and copper (I) ions are relatively easily moved.

B. Copper ions find and react with sulphide ions, which have been adsorbed on the growing surface of the copper sulphide in the area where sulphide is available. Probably the growth proceeds in a screw dislocation.

$Cu_2S(s) = 2Cu^{+} + S^{2-}$ $K_S(B) = 10^{-45}$

C. Electrons find Fe (III) and together they form Fe (II).

$Fe^{3+} + e^{-} = Fe^{2+}$ $e_0(C) = 0.770$ V

The details of the reaction C, and thereby $e_0(C)$ - value, of course depend on in which form Fe(III) and Fe(II) exist. The suggested half reaction with its $e_0(C)$ - value is only to be regarded as an example. As mentioned the details in this mechanism should be studied more closely.

D. The total reaction is

$2Cu(s) + 2Fe^{3+} + S^{2-} = Cu_2S(s) + 2Fe^{2+}$ $k(D) = 2.5 \cdot 10^{52}$

The k value is calculated from $e_0(A)$, $K_S(B)$ and $e_0(C)$. Consequently the reaction is, at the given prerequisites, very strongly displaced to the right, with the resulting formation of $Cu_2S(s)$. The formation of Cu_2S from Cu^{+} and S^{2-} is the principal driving force. A prerequisite is that copper ions and electrons move easily in the copper sulphide, which will serve as a solid electrolyte with a low inner resistance. The copper sulphide will in that case grow as a "whisker" into the areas where there is access to sulphide. Therefore it is not necessary for the sulphide containing specie to be transported long distances to the copper surface via water based, slow transportation processes.

The performance of iron is foreseen to be more complex than what is indicated in the mechanism sketch above. The reaction "C" above could be replaced by others as reduction of polysulphides.

Consequently the result can be dendritic copper sulphide crystals or whiskers, which grow out from the canister surface. Their starting point could be where sulphide sprouts have been formed initially. Thereafter they grow further on into the surrounding bentonite, following paths with a comparably high sulphide concentration, see figure 18. Under the sulphide dendrites the copper metal could be consumed, which would be equal in effect to a situation where a pit forms and propagates. However, the mechanism is quite different.

In the mechanistic chart above a number of steps have been indicated for the sulphide based "pitting". For all reactions diffusion and rate constants can be roughly estimated, which gives a possibility to determine, still very roughly, a rate-determining step. This can then be used in order to do evaluations of rates of attack and to calculate time to breakthrough of the 5 cm thick copper layer of the canister. This will not be attempted here.

The whisker phenomenon has been discussed earlier, i.a. in [177]. Resent experiments demonstrate that it is possible to grow whiskers on copper. However growth of whiskers in non-oxidising environments has been observed, further investigations are necessary to judge the importance of such a mechanism. For example it should be investigated if whisker growth really gives local attacks causing pits in the general sense. The high mobility of copper in sulphides would for example indicate that the metal could be taken from a larger surface area than locally below the growing whisker.

Other types of whiskers are also possible as demonstrated by the following experimental results.

5 Long time studies of copper corrosion in the repository environment

5.1 Introduction

In polarisation experiments done on copper in synthetic groundwater it was found that the formation of a passive film was either very slow or totally inhibited in chloride-rich solutions. It was also found that sulphide changed the corrosion behaviour of the copper surface drastically [178]. However it was not possible to draw any far going conclusions about the long time behaviour of copper in deep rock groundwaters. Such information is vital for the planning of a repository for nuclear waste disposal in copper canisters.

A long time experiment (>6 months) where copper is exposed to synthetic groundwaters in a closed system is reported here.

5.2 Experimental

Here is a description of the equipment, the experimental techniques and the procedures used for sample preparation, during the long time studies and for evaluation of the results after the experiments.

5.2.1 Sample preparation and equipment

The sample preparation procedure was similar to what was used in earlier copper corrosion studies. The samples (figure 19) where polished with 1000 mesh paper and ultrasonically cleaned in water, acetone and ethanol, 5 min. in each. After cleaning the samples where stored in a dessicator until they where immersed in the investigated groundwater.

The long time studies of copper corrosion where carried out in glass flasks with a volume of 0,5 L. Before immersion of the samples into the solution, most of the resolved oxygen was removed by bubbling of nitrogen through the solution. After immersing of the samples the flasks where rapidly sealed off and kept sealed throughout the experiments to minimise the influx of oxygen to a minimum. A small amount of oxygen was present at the start of the experiment, and diffusion of a very small amount of oxygen during the experiment cannot be ruled out.

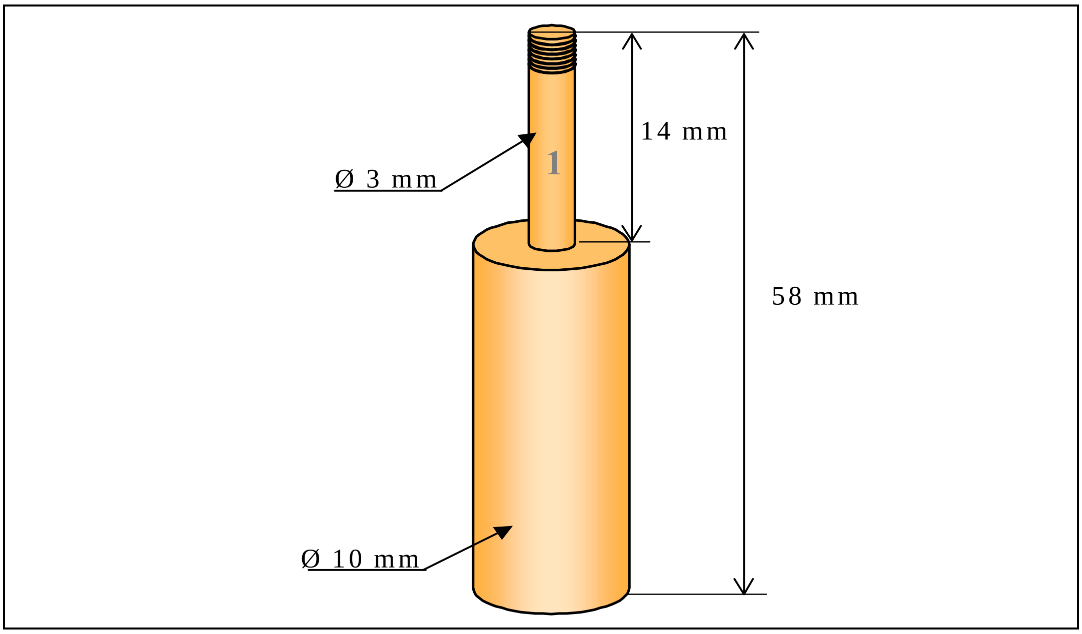


Figure 19 The size of the samples

5.2.2 Investigated environments

For the long time tests there has been a matrix of experimental conditions that is based on the results in earlier studies of localised corrosion on copper in waste disposal environment. It was found in earlier studies that the salt content (mainly chloride) of the ground water is of importance for the formation of a protective film on the copper surface. For this reason groundwaters with three different concentrations of salt has been used.

It was further found that sulphide (HS^-) and carbonate (HCO_3^-) ions were species in the groundwater that under certain conditions could be expected to give pitting corrosion on copper. Therefore these species have been added to higher concentration in some of the groundwaters. When synthetic groundwater with a large range of salts in varying concentrations where compared to water with only chloride added to the same ionic strength there was no significant difference in the polarisation curves of copper. Based on this finding the synthetic groundwaters for these experiments where simplified by removing salts present in small amounts in natural groundwaters, as long as they where not expected to be of special importance for pitting corrosion on copper.

The synthetic groundwaters were made with three different levels of total salt concentration, a high level, a medium level and a low level. The waters were deaerated before the start of the experiment and the vessels were sealed. The temperature was held close to 20 °C throughout the experiment and the starting pH was close to 8.5. A detailed list of the used groundwaters can be found in table 8.

The electrochemical equipment used in the experiments consisted of a zero resistance ampere meter to measure the corrosion current, an electrometer to measure the potential, the electrochemical cell with the copper sample and a computer to control the equipment. It is schematically drawn in Figure 20.

Table 8 Synthetic groundwaters used in the long-time experiments

GW 1 High salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	10000	Na^+	4000	Cl^-	6000
$CaCl_2$	3000	Ca^+	1075	Cl^-	1925
Na_2SO_4	500	Na^+	160	SO_4^{2-}	340
$MgCl_2*6H_2O$	668	Mg^{2+}	80	Cl^-	114

GW 2 Low salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	100	Na^+	40	Cl^-	60
$CaCl_2$	30	Na^+	10,8	SO_4^{2-}	19,2
Na_2SO_4	5	Ca^+	1,6	Cl^-	3,4
$MgCl_2*6H_2O$	7	Mg^{2+}	0,8	Cl^-	1,2

GW 3 Medium salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	1000	Na^+	400	Cl^-	600
$CaCl_2$	300	Na^+	108	SO_4^{2-}	192
Na_2SO_4	50	Ca^+	16	Cl^-	34
$MgCl_2*6H_2O$	67	Mg^{2+}	8	Cl^-	11,4

GW 4 Carbonate / low salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	100	Na^+	40	Cl^-	60
$CaCl_2$	30	Na^+	10,8	SO_4^{2-}	19,2
Na_2SO_4	2,5	Ca^+	1,6	Cl^-	3,4
$MgCl_2*6H_2O$	7	Mg^{2+}	0,8	Cl^-	1,2
$NaHCO_3$	500	Na^+	138	HCO_3^-	362

GW 5 Sulphide / low salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	100	Na^+	40	Cl^-	60
$CaCl_2$	30	Na^+	10,8	SO_4^{2-}	19,2
Na_2SO_4	2,5	Ca^+	1,6	Cl^-	3,4
$MgCl_2*6H_2O$	7	Mg^{2+}	0,8	Cl^-	1,2
Na_2S	100	Na^+	59	S^{2-}	41

GW 6 Carbonate / high salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	10000	Na^+	4000	Cl^-	6000
$CaCl_2$	3000	Ca^+	1075	Cl^-	1925
Na_2SO_4	500	Na^+	160	SO_4^{2-}	340
$MgCl_2*6H_2O$	668	Mg^{2+}	80	Cl^-	114
$NaHCO_3$	500	Na^+	138	HCO_3^-	362

GW 7 Sulphide / high salt…(1 ppm = 1 mg/*l*)……

SALT ADDED /ppm		**CATION** /ppm		**ANION** /ppm	
NaCl	10000	Na^+	4000	Cl^-	6000
$CaCl_2$	3000	Ca^+	1075	Cl^-	1925
Na_2SO_4	500	Na^+	160	SO_4^{2-}	340
$MgCl_2*6H_2O$	668	Mg^{2+}	80	Cl^-	114
Na_2S	100	Na^+	59	S^{2-}	41

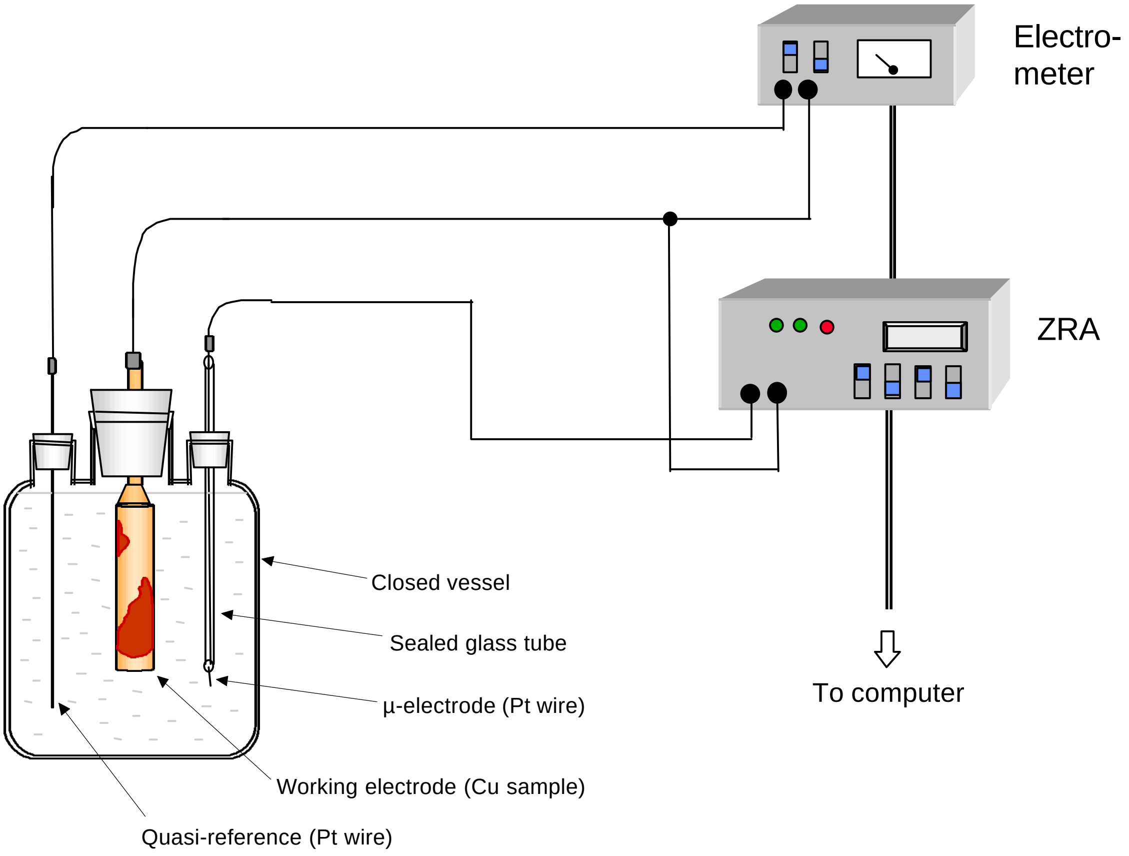


Figure 20 The electrochemical equipment

5.2.3 Analysis

After the long time tests the surfaces of the copper samples were investigated for signs of pitting corrosion. The investigations consisted of visual inspection of the samples and for some surfaces also an investigation in SEM. An analysis of the composition of the surface or surface film was made in SEM.

For the groundwaters containing sulphide an analysis of the sulphide concentration after the long time tests was performed in order to determine if the sulphide was consumed and thus limiting the growth of whiskers or surface films containing sulphide.

The whiskers and a surface film formed in sulphide-containing waters were also analysed with X-ray diffraction.

5.3 Results

In this section the results of the long time tests and the following analysis is reviewed.

5.3.1 Electrochemical noise

The electrochemical noise consists of the small variations in current between two identical working electrodes, and the small variations in potential between a working electrode and a reference electrode or a third identical electrode [179-185]. A variation in the electrochemical noise technique using asymmetric electrodes was developed by Chen and Bogaerts [186]. Here one of the identical electrodes is replaced by a microelectrode with a surface area much smaller than the surface of the investigated electrode. The microelectrode's contribution to the electrochemical noise is then negligible and the mathematical treatment and the interpretation of the noise data is simplified considerably.

The cause of the current and potential variations in electrochemical noise is often corrosion processes taking place on the surface of the working electrode. The noise variations take place on a rather short time-scale, usually in the order of a few seconds. In this work the variations that had a time-scale from about a second to a minute were monitored.

Analysing the electrochemical noise can give vital information on the surface processes causing the noise, such as general or localised corrosion. In this work the emphasis has been on detecting localised corrosion on copper in synthetic groundwater. However, no clear case of localised corrosion has been detected in the investigated groundwaters. In most cases the levels of the electrochemical noise has been very low and the signals do not give any clear indication of any specific type of corrosion (figure 21).

The most logic interpretation of the result of the noise measurements as well as from other observations is that the copper surface slowly passivates and then stays passivated with very little electrochemical activity on the surface.

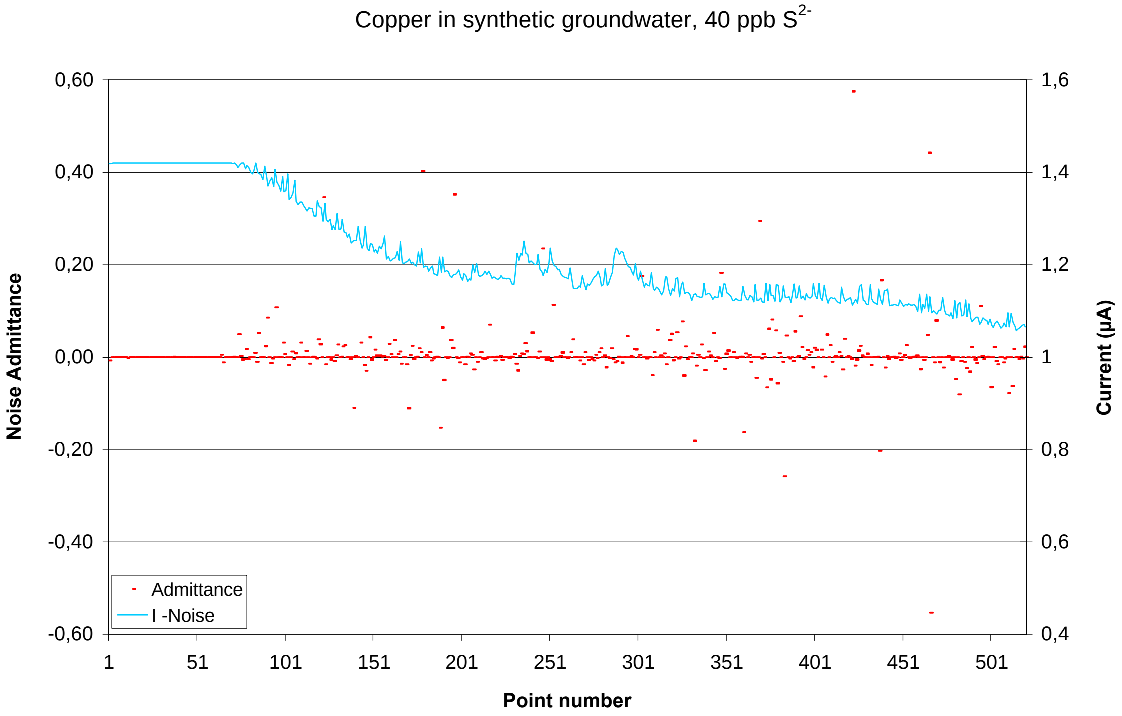


Figure 21 Typical electrochemical noise signals.

5.3.2 Corrosion potential

As a part of the electrochemical testing the corrosion potential was recorded as a function of time. Variations in the corrosion potential gives an indication on the changes taking place in the corrosion properties of the surface, such as formation of a passivating film, pitting corrosion etc. As there is a clear difference in the corrosion potentials in the beginning and in the end of each electrochemical noise scan, potentials have been recorded both in the beginning and in the end.

In the groundwaters not containing sulphide the change of corrosion potential on copper with time was small and the rate of change was slow. When the water contained sulphide there was a clear change of corrosion potential with time (table 9 and figure 22). The potential is low to start with but rises quickly in the first few hours. After about ten hours it goes down a little for another ten hours and after that the potential slowly goes up again. And in the same time the difference between the corrosion potential taken in the beginning and in the end of each scan gradually disappears.

Table 9

<u>Corrosion potential of copper in groundwater with sulphide</u>:

Time (h from start)	Beginning of scan (point no. 1 /mV)	End of scan (point no. 520 /mV)
0	-217	-117
2	-151	-37
6	-140	-36
10	-109	-21
15	-130	-48
20	-142	-50
50	-71	-40
80	+27	+24

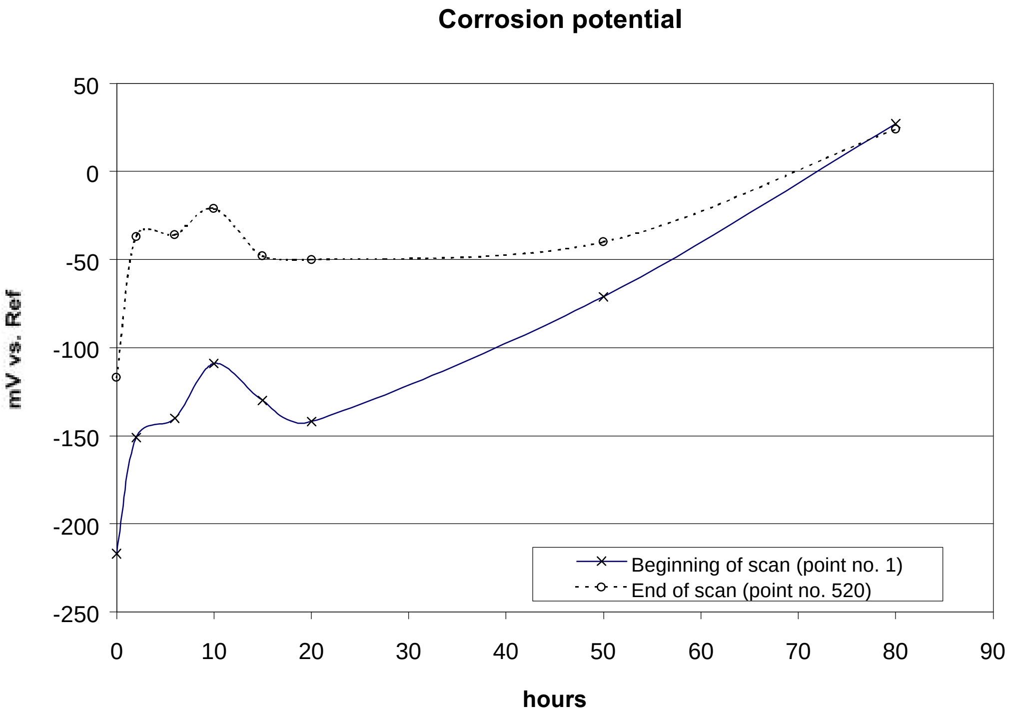


Figure 22 Corrosion potential variations in groundwater with sulphide

The change of corrosion potential on the copper surface when sulphide is present seams to be linked with the changes that can be visually seen on the surface. There is a rapid change of potential in the beginning when the surface is rapidly darkening, the change then slows down and the potential reaches a peak after about 10 days. At about the same time the first rapid change in the surface appearance also stops.

After ten days the potential starts dropping again and falls to about -150 mV after another ten days. During this time there is no visible change in the surface appearance. After twenty days the potential starts rising again and about the same time the formation of visible whiskers is seen. The exact time of whisker initiation is not known, but it is somewhere between 15 and 25 days. Sometime after 40 days the whiskers stop growing, and some whiskers fall off from the surface.

5.3.3 Visual appearance

There were large differences on the visual appearance of the copper surfaces after some time in the synthetic groundwater depending on the groundwater composition. The largest difference was between groundwaters containing sulphide and groundwaters without sulphide. In water containing sulphide there is an almost immediate change of the copper surface appearance on contact with the water.

When the water is without sulphide there are no visible changes during the first days after exposure, but after several weeks all tested environments have caused a film formation to take place on the copper surface or at least parts of the surface. The appearance is depending on the amount of chloride in the groundwater.

In waters with high chloride concentration (8000 ppm Cl^-), there is a brown-red surface film slowly forming. It appears on parts of the surface after several weeks of exposure. Some green amorphous growth is seen close to the water surface. After several months the entire surface is covered with film but the film is of uneven thickness. The water becomes turbid.

In waters with medium chloride concentration (800 ppm Cl^-), there is a dark red surface film slowly forming. It appears on the entire surface after several weeks of exposure. Even after several months of exposure there are no large changes of the surface film. The water remains clear.

In waters with low chloride concentration (80 ppm Cl^-) the film formation on the copper surface from exposure to the water is very slow. Only after long time of exposure (several months) is there a visible change in the surface appearance. There is a slight darkening of the surface but no other changes can be observed. The water remains clear.

In waters with high chloride concentration (8000 ppm Cl^-) and carbonate (360 ppm Cl^-) there is a red surface film slowly forming on the entire surface. Some green amorphous growth is seen close to the water surface. The water becomes strongly turbid.

5.3.4 SEM inspection of whiskers

The sample with whiskers was investigated in SEM and EDS. This was done in order to take a closer look at the structure of the whiskers and to make a first analysis of the whisker composition. It was also performed to see if any local attack could be detected on the copper surface below the whiskers. A complication in this investigation was that most of the whiskers fell off into the water when the sample was lifted out of the solution. This indicates that the whiskers were very fragile.

The sample that had been in water with sulphide without forming whiskers was also investigated in SEM as a reference sample and to see if there were any differences in composition between the whiskers and the covering surface film. Some caution must be taken in interpreting the composition analysis in the SEM, as the electrons used for the EDS spectra only penetrates a few atom layers in the surface. It is thus only the composition close to the surface that can be determined from the electron spectra. The composition deeper down in a thick surface film or the bulk composition of an analysed material may differ from the composition at the surface.

The surface films and the whiskers are clearly visible in the SEM pictures (figure 23). Areas with surface films of different morphology ranging from clearly crystalline (figure 23 c) to mostly irregularly shaped morphology (figure 23 d) is seen. Some very distinct crystalline sulphur-rich flakes can be seen in some areas of the surface (figure 23 b).

It was unexpectedly found that very little sulphur was present in most of the surface films and it was also less than expected in the whisker material. Copper and oxygen are the elements dominating in all film and whisker surfaces (Table 10). In some places there is also plenty of carbon present. Only on some isolated crystals and in the cracked amorphous surface film are significant amounts of sulphur found. The origin of carbon is not clear, but it probably comes from the small amount of dissolved air, and thus also a small amount of carbonate, that is present at the start of the experiment.

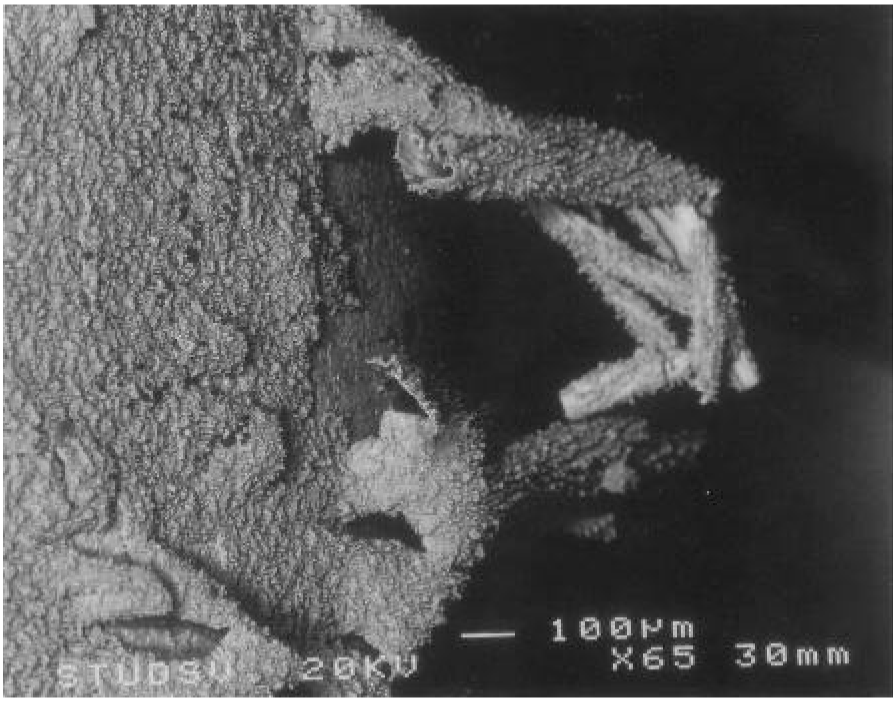


Figure 23 a) Whisker

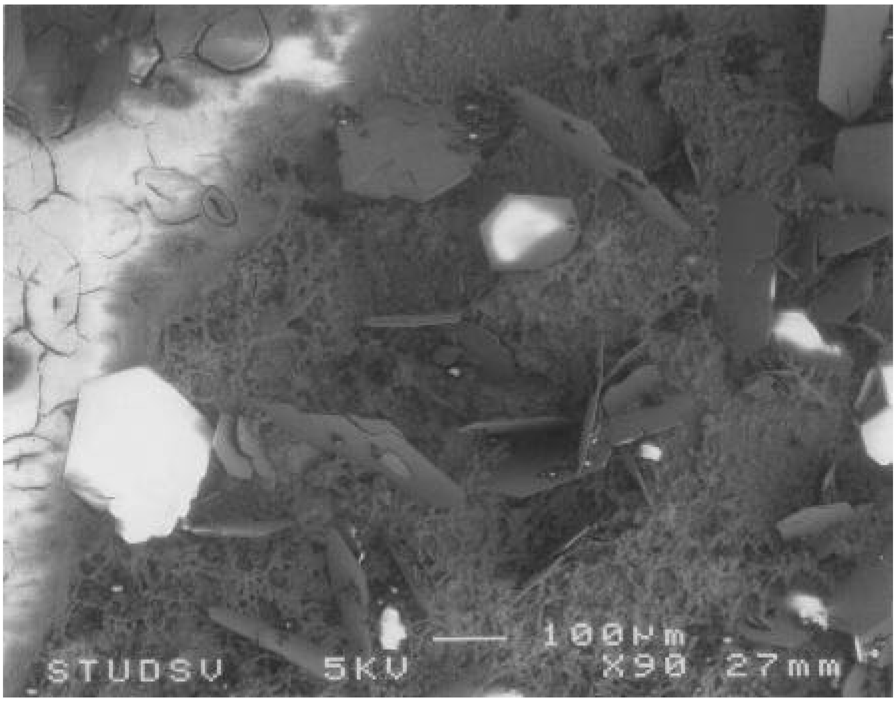


Figure 23 b) Sulphide-rich crystals

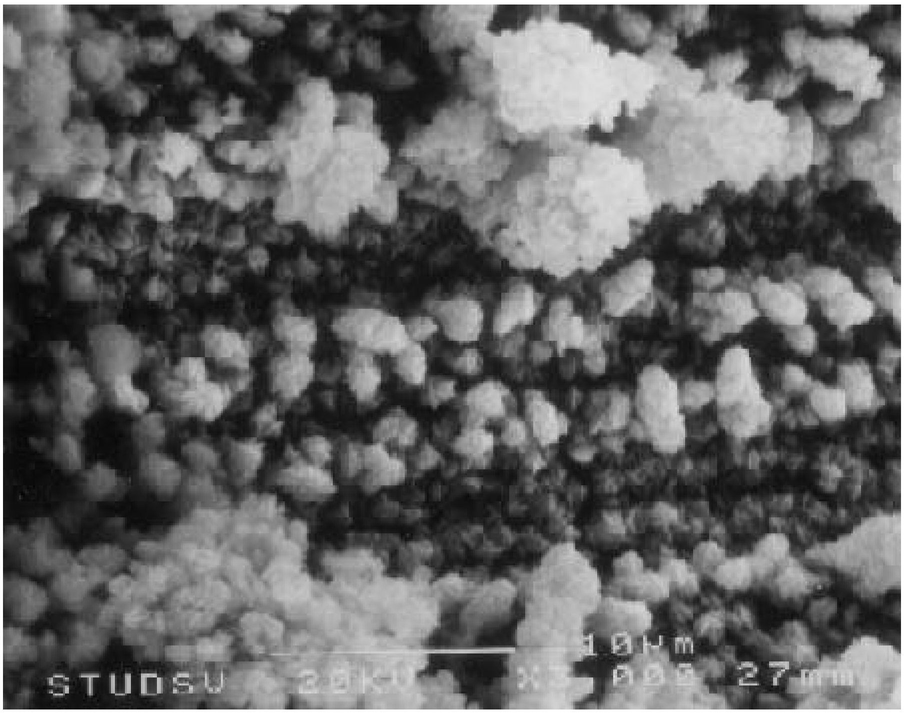


Figure 23 c) Surface film particles with a crystalline appearance

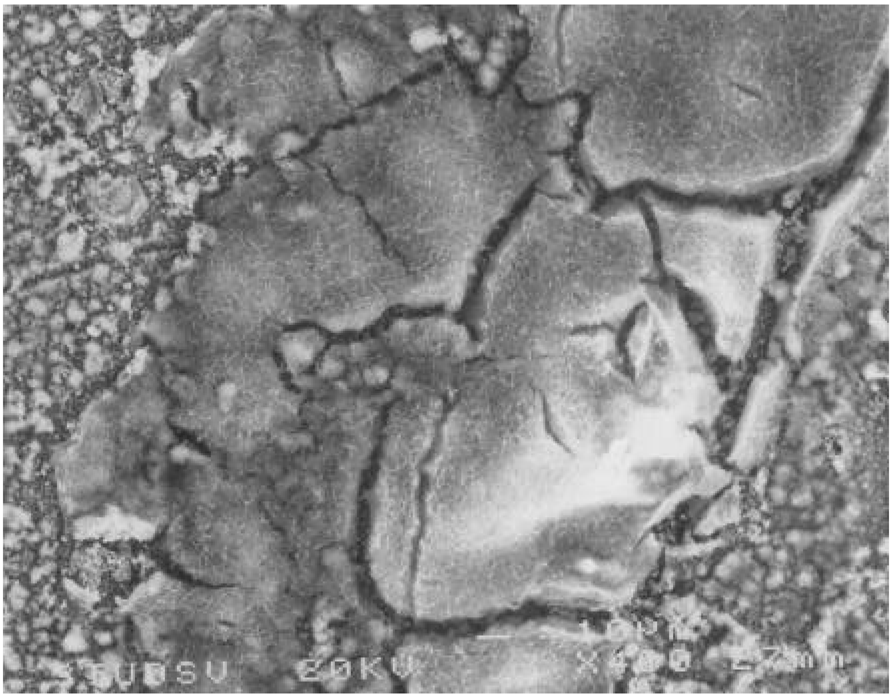


Figure 23 d) Cracks in surface film

Table 10

EDS relative intensities for copper surface films and whiskers:
(largest peak set to 100)

Feature	**Cu**	**O**	**C**	**S**	**Other**
A	100 54, 7	26	2	1	Si (4) Cl (1)
B	100 55, 14	25	17	2	Si (5) Zn (5)
C	100 61, 9	59	2	*17*	Cl (4)
D	100 33, 4	1			Cl (7)
E	100 46, 9	70		*46*	
F	Due to the shape of the whiskers the EDS results are a little uncertain and not given as numbers, but copper and oxygen dominates and no or very little sulphur is seen				

The features are the following:

A Bright particle (figure 23c)
B Film formed close to water surface
C Crack in film surface (figure 23d)
D Copper surface where film is pealed off
E Flat dark crystal (figure 23b)
F Whisker (figure 23a)

5.3.5 X-ray diffraction of whiskers

To further determine the composition and to get some information on the structure of the material in the surface film and of the whiskers, x-ray diffraction analysis was done on some whisker material and pieces of the surface film formed in groundwater with sulphide. The somewhat unexpected result is that no crystals with sulphide are found in the whiskers and in the surface film.

The diffraction lines consist of some sharp lines and some more diffuse lines. The lines match crystals of copper(I)oxide, copper(II)oxide, and copperhydroxide (Tables 11 and 12). All observed lines can be explained with these three phases. Sulphide could possibly be present if crystals are extremely small or the material is amorphous and therefore does not diffract the X-rays.

Table 11
X-ray diffraction lines; d-values and intensities for the black surface film. Listed d-values and intensities for $Cu(OH)_2$, Cu_2O and CuO taken from the database "JCPDS-ICDD, International Centre for Diffraction Data"

Surface film			
Observed d-values (I)*	**$Cu(OH)_2$ d (I)** JCPDS 35-0505	**Cu_2O d (I)** JCPDS 5-0667	**CuO d (I)** JCPDS 5-0661
5.30 (3)	5.29 (80)		
3.72 (2)	3.73 (90)		
3.020 (4)		3.02 (9)	
2.75 (3)			2.751 (12)
2.72 (1)			
2.60 (3)	2.63 (100)		
2.53-2.51 (46)	2.50 (60)		2.530 (49) 2.523 (100)
2.465 (100)		2.465 (100)	
2.39 (1)	2.36 (50)		
2.336-2.308 (49)			2.323 (96) 2.312 (30)
2.274 (2)	2.266 (70)		
2.210 (<1)			
2.135 (26)		2.135 (37)	
1.873 (3)			1.866 (25)
1.711 (2)	1.718 (70)		1.714 (8)
1.509 (20)		1.510 (27)	1.505 (20)
1.410-1.404 (5)			1.418 (12) 1.410 (15)
1.377 (2)			1.375 (19)
1.288 (9)		1.287 (17)	
1.231 (3)		1.233 (4)	

* When an interval is given for the d-value it means the diffraction line is broad and diffuse. The intensity value is then the integrated d-values across the line. Intensities are relative with the largest peak set to 100.

Table 12
X-ray diffraction lines; d-values and intensities for the whisker material. Listed d-values and intensities for $Cu(OH)_2$, Cu_2O and CuO taken from the database "JCPDS-ICDD, International Centre for Diffraction Data"

Whisker			
Observed d-values (I)*	**$Cu(OH)_2$ d (I)** JCPDS 35-0505	**Cu_2O d (I)** JCPDS 5-0667	**CuO d (I)** JCPDS 5-0661
5.31 (5)	5.29 (80)		
3.72 (5)	3.73 (90)		
2.75 (5)			2.751 (12)
2.61 (4)	2.63 (100)		
2.53-2.50 (55)	2.50 (60)		2.530 (49) 2.523 (100)
2.35-2.29 (100)			2.323 (96) 2.312 (30)
2.274(2)	2.266 (70)		
1.885-1.886 (9)			1.886 (25)
1.719-1.704 (5)	1.718 (70)		1.714 (8)
1.414-1.405 (9)			1.418 (12) 1.410 (15)
1.379-1.374 (5)			1.375 (19)

5.3.6 Solution analysis

It is of interest, at least in the groundwaters containing sulphide, to know to what extent the reacting species in the solution are consumed. Is it because the reactants are consumed or for some other reason the formation of whiskers appears to slow down and stop after some time? Analysing the solutions after 6 months of exposure shows that there is very little left of sulphide in the groundwaters that contained sulphide in the beginning. The sulphide is either all consumed or some sulphide has evaporated out of the solution (through the mechanism: $HS^- + H_2O \rightarrow H_2S(g) + OH^-$). It is thus reasonable to believe that the formation of whiskers is slowed down and stopped due to lack of sulphide in the solution.

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6 Discussion

6.1 Requirements

Copper can be exposed for both general and different kinds of localised corrosion in the repository. The complex mechanical, chemical and microbial environment with high pressures varying in time and location and with oxygen, chloride, sulphur and carbon bearing compounds present will cause different types of attacks that are going to prevail during different time periods. The procedures of production, handling and treatment of the canister throughout the processes of filling, transportation and deposition are crucial for its later, corrosion-related integrity throughout the storage period in the repository. There is also a risk that due to systematically induced faults, many canisters may have later corrosion related problems of the same kind.

There will certainly be an introductory period with an oxidising environment followed by a reducing. There is, however, no guarantee that the oxidising conditions will not return at later stages, for example during glaciation events. At such events the pressure field could have a complex gradient, which would cause surprising directions and velocities of the ground water flow, resulting in intrusion of oxygenated water into the repository and subsequent replenishment of the oxidising conditions. During such periods, oxygen will provide the driving force for the corrosion processes. Different mechanisms can prevail during different sub periods of time but also simultaneously in different geometrical parts of the non-homogeneous pressure, heat and chemistry fields that could form in the repository. Unfortunately a non-homogeneous environment is a good starting point for corrosion.

There will probably be long reducing periods between oxidising. During such periods corrosion processes are generally considered to come to a halt. However, several mechanisms for i.a. sulphide based attacks should be considered during reducing conditions.

Different periods of the repository lifetime are going to be exposed to different transportation mechanisms for the groundwater. As a consequence the reacting chemical species transported by the water will be transported with different velocities. This is valid both on a global and a local scale. A couple of mechanisms for such variable transportation mechanisms could be mentioned, but others are probably also possible. Normal ground water flow during normal conditions is a first. Changes of flow gradients due to different pressure gradients during glaciation periods is a second. Anhtropogenically caused changes is a third. Gas evolution due to processes in the repository as well as a flow of substances that at some stage might evolve geogas is a fourth possible mechanism for transportation. A fifth is the presence of temperature gradients.

All procedures of production, filling, transportation and deposition of the canister are crucial for its later integrity throughout the storage period in the repository. There are risks of metallurgical and mechanical faults in the canister due to any of those processes that can influence the corrosion integrity at a later stage. Also buckling of the copper onto the iron insert due to the pressure field of the closed repository and also changes of that field could cause subsequent corrosion related problems.

6.2 General corrosion

As already mentioned there are several chemical environments around and also inside the canister that can be foreseen. During oxidising conditions in a highly concentrated chloride solution, which will prevail for example during the first time after closure of the repository, there will be general corrosion of copper in a situation of rather homogenous environmental conditions. According to thermodynamic calculations copper is not stable in such an environment, see figures in appendix A1. Such a homogeneous attack is, however, not disastrous for copper integrity, as long as transportation rates of reacting matter are low.

The immunity limit for copper descends as a function of temperature at high chloride concentrations. See figures in appendix A1. This means a risk that copper is neither noble, nor passive at least at higher temperatures in the repository environment containing large concentrations of chloride. Thus, in such an environment copper is protected from serious general corrosion only by keeping transportation rates of reacting species very low. Increased transportation rates would, however, be disastrous for copper integrity. It is essential that this situation of general corrosion be addressed for cases of higher transportation rates of reacting species above the immunity limit.

6.3 Localised corrosion

However, different types of localised corrosion that can occur as a result of any inhomogeneity in the system are probably more dangerous than the general corrosion outlined above. The inhomogeneity could be of a chemical nature (concentration gradients), or mechanical (pressure load gradient), as a temperature gradient (different heat conducting conditions from the canister surface) and also as materials faults and inhomogeneities in the copper metal itself caused by inadequate manufacture-, transportation- and handling processes.

All of those cases can be disastrous to canister integrity if they prove to be able to cause a rapid break through of the copper layer. Pitting of copper in an oxidising environment is well known from several applications and environments and could also appear in the repository during the oxidising periods. Localised attacks could be a dangerous reality at the right combination of environment chemistry and material faults as cracks, pores, welding faults etc.

A localised attack could result in exposing the underlying iron insert. In an oxidising environment such an event could be followed by galvanic corrosion as well. The exposed iron insert would then be the dissolving, anodic electrode. An electrochemical cell with a very large copper cathode, short-circuited with a very small iron anode would develop and could rapidly generate an opening to the inner parts of the canister and the fuel. Only retarded transportation of reacting species would hinder such a dangerous situation to develop. This scenario should be better evaluated.

A combination of a mechanical fault, materials stress and localised corrosion in an oxidising environment would be especially dangerous as it could appear simultaneously in many canisters. As already mentioned there could be systematic and undetected mechanical damages on many canisters due to handling procedure faults. It is therefore essential to further evaluate these combined risks and also to extend the QA system to cover all of the chain down to the final closure of the repository.

At lower potentials copper sulphides are formed on the copper surface in environments containing sulphide and also high chloride concentrations, see figure 7. The sulphide film formed could be of a rather complex nature consisting of several phases. The micro-composition of the sulphide could under such circumstances depend very much on local micro-conditions in the bentonite close to the metal surface. For example would variations in pyrite and bacteria+sulphate concentration probably have an influence on the local copper sulphide composition. A slight variation in the potential over the copper surface could also have a dramatic influence on the composition of the copper sulphide film. Calculations as those accounted for in figures 6 and 7 also show that the immunity of copper decreases as the sulphide and chloride concentrations increase. This results in low immunity and a complex copper sulphide film of variable and disputable ability to passivate. Such a system should not be left without further study, i.a. of the protective ability of the copper sulphide passive film within the span of possible repository environments.

Another type of corrosion attack of a localised nature that appears on copper in a sulphide environment is whisker growth. As already pointed out, resent experiments clearly demonstrate that it is possible to grow whiskers on copper. However growth of whiskers in non-oxidising environments has been observed, further investigations are necessary to judge the importance of such a mechanism. For example it should be investigated if whisker growth really gives local attacks causing pits in the general sense. The high mobility of copper in sulphides would indicate that the metal could be taken from a larger surface area than locally below the growing whisker. However, this remains to be demonstrated in order to dismiss whisker growth as a potentially dangerous corrosion mechanism.

Focus should be put on localised corrosion on copper, as the consequences of relatively small attacks could be disastrous. Pitting of copper is demonstrated in an oxidising environment and local attacks in a reducing sulphide-containing environment is possible. The nature of those, however, remains to be investigated.

6.4 The nature of oxidative pitting on copper

Present pitting theory in oxidising environment emphasises on the importance of Cl^- for initiation and propagation. It says that sulphate has no influence and that other anions are more or less inert. The theory is verified for short times but deviates for long times, so there is a need to reconsider the theory.

Some of the observed deviations from the present theory are that chloride passivates in the long run and that sulphate has a long time influence at all pH values. Therefore a distinct warning should be made for extrapolation of short-range results to longer time periods like repository life times.

A description of a currently valid pitting mechanism is given in section 4.4 above. One objection against this mechanism is that CuCl would occur in the pit as a result of Cl^- migration into the pit. However, CuCl never predominates. See figures in A1. In a pit the chloride concentration could be very high, of the order of several moles/l, due to inwards migration of Cl^-. In such an environment $CuCl_2^-$ or $CuCl_3^{2-}$ would predominate together with naked copper metal at the low potential depending on total chloride concentration. There would be no CuCl precipitate, see figures 20 and 21 and also in A1. $CuCl_2^-$ or $CuCl_3^{2-}$ would instead hydrolyse, I a according to:

$$2CuCl_2^- + H_2O \rightarrow Cu_2O + 2HCl + 2Cl^-$$

$$2CuCl_3^{2-} + H_2O \rightarrow Cu_2O + 2HCl + 4Cl^-$$

If these formulas of hydrolysis are compared with the one suggested for the current mechanism,

$$2CuCl(s) + H_2O \rightarrow Cu_2O(s) + 2HCl$$

it can be seen that the Cl^- ion is produced in a surplus at the hydrolysis of the complexes compared with hydrolysis of a supposed CuCl precipitate. If no CuCl precipitate is formed all chloride is going to stay dissolved in the pit. These observations indicate that a mechanism involving the complexes and no CuCl precipitate would be more sensitive (fourth power instead of second) to the increasing total chloride concentration compared with a CuCl precipitate mechanism. At increasing chloride concentration the hydrolysis of complexes, and thus also the acid formation, would slow down and virtually come to an end. As a result the pitting attack would also slow down as the chloride concentration in the pit environment increases, which is observed in field investigations and experiments as long time effects. The suggested high sensitivity of complex hydrolysis on chloride concentration could therefore be part of the explanation of observed deviations from the present theory.

6.5 The nature of localised attack on copper at low potentials

It has been demonstrated both theoretically and by experiments that whiskers can form on copper metal at certain combinations of the chemical parameters of the environment. However, whisker growth has been demonstrated on copper it remains to clarify the nature.

In a reducing environment with sulphide present, copper sulphides are stable and can come to dominate the film on the copper surface, see figure 7. Sulphide for formation of copper sulphide could be found in the proximity of the canister, for example in original pyrite beads in the bentonite or as a result of previous or present microbial activity at the time of attack.

It must be clarified that significant differences in several respects exist between copper oxides and copper sulphides. There are many copper sulphides, all with varying composition. Some of them are shown in figure 7. Copper always has the valance (I) and never (II) in copper sulphide [178]. Also a number of meta stable phases exist in the copper - sulphur system. Iron (II) reacts willingly with those, and it is probable that the surface of the copper in reality can be covered by a mixed sulphide at reducing conditions. The copper sulphides are in contrast to the oxides good electron conductors. Moreover copper (I) ions migrate very easily in most copper sulphides. This is a substantial and noteworthy difference from copper oxides where the mobility of copper is very much lower.

To further determine the composition of the whiskers formed in the present investigation and to get some information on the structure of the material in the whiskers, x-ray diffraction analysis was performed on some whisker material. The somewhat unexpected result of the x-ray diffraction of the whiskers was that they were not made up by any simple copper sulphide. The diffraction lines consist of some sharp and some more diffuse lines. The sharp lines match crystals of copper carbonate and copper chloride, the diffuse lines do not match any simple crystal, but could be some complex sulphide containing compound.

It was also found that the film formed on the copper surface before whisker growth started contained sulphur rich "islands", see figure 23b. Those islands are probably composed of copper sulphide and could form starting points for whisker growth as the supply of copper ions probably is very good in these sites according to the above discussion of copper mobility in copper sulphides.

It is of interest, at least in the groundwaters containing sulphide, to know to what extent the reacting species in the solution are consumed. Is it because the reactants are consumed or for some other reason the formation of whiskers appears to slow down and stop after some time? Analysing the solutions after 6 months of exposure shows that there is very little left of sulphide in the groundwaters that contained sulphide from the beginning. The sulphide is either all consumed or some sulphide has evaporated out of the solution (through the mechanism: $HS^- + H_2O \rightarrow H_2S(g) + OH^-$). It is thus reasonable to believe that the formation of whiskers is slowed down and stopped perhaps due to a shortage of sulphide in the solution.

From the appearance of the surface during and after the long time tests and from the electrochemical data collected, the conclusion drawn must be that no localised corrosion of significance to the copper canister integrity has taken place. Observed corrosion currents and potential changes have always been of low magnitude and the tendency is that the magnitude gets even smaller with time.

If any corrosion process in deep rock groundwaters should be dangerous for the copper canister integrity, it is most likely found in groundwaters containing sulphide, as the surface reactions taking place in sulphide are much faster. Thus the analysis of the results have had their emphasis on groundwaters with sulphide and especially the formation of whiskers.

Considering the results of the analysis on the whiskers, there are a few unanswered questions that arise: What are the limits in the groundwater composition and pH for the formation of the whiskers? What is the mechanism for the whisker formation? Is copper taken from directly below the whisker or from a larger part of the surface?

The X-ray diffraction and EDS analysis of the whiskers and the surface films formed in groundwaters containing sulphide tells us that sulphur is not present or at least at very low concentrations in most of the surface film and in the whiskers. No crystalline phase containing sulphur is found in the whiskers. Still it is obvious that the presence of sulphur as sulphide is essential for the surface film and whisker formation, perhaps by forming original nuclei from which other substances can grow. See below.

6.6 Oxide/hydroxide whisker formation

The continued whisker growth observed in the present experiments is obviously not based on growing copper sulphide as demonstrated in section 6.5. Instead copper oxide (CuO or Cu_2O), copper hydroxide ($Cu(OH)_2$), copper chloride-hydroxide ($CuCl_2 \cdot 3Cu(OH)_2$) or some combination of those phases probably constitutes the growing whisker at the slightly elevated pH, see figures A1:1, 2, 3, 4, 7, etc. It is important, however, to notify that sulphide is observed in SEM-EDS as being distributed over the surface film in isolated small areas and also forming a small part of the whisker itself. Sulphide is therefore probably essential for the whisker growth. As the experimental chemical system has been closed in relation to sulphide, there has been a shortage and no general formation of copper sulphide has been possible in the long run. Copper sulphide has therefore appeared sparse and patch-wise.

There is experimental information available from electrochemical experiments, SEM-EDS investigations and XRD analyses. If those observations were combined with information from the thermodynamic calculations as outlined above it would be possible to suggest the following growth mechanism for oxide/hydroxide whiskers in a sulphide environment:

1. The high chloride concentration decreases the immunity of copper and at the same time hinder the formation of a good passivating oxide. See figures in A1. A non-passivating surface film will, however, form at the low potential with sulphide present. The film consists of copper sulphide islands in a mixture of copper oxide, hydroxide and chloride-hydroxide.

2. The sulphide islands supply areas in the poorly passivating film where copper can be easily transported in solid phase from the metal to the outer surface of the film. The sulphide islands are open windows in the film for outward copper ion transportation. There is an anodic reaction below or in the vicinity of the sulphide islands at which copper(I) ions are formed. Cathodic surfaces are found between sulphide islands.

3. Copper ions react on the sulphide surface with water and form copper oxide or hydroxide. The elevated pH and high chloride concentration govern the formation of these phases in the system and the rate of transportation to the copper sulphide island surface, which is the place of reaction. Copper(I) ions are probably easily available on the surfaces of the sulphide islands.

4. A pile of oxide/hydroxide is formed on top of a sulphide island. The growth zone is on top of sulphide grains. The pile of oxide/hydroxide is pushed away from the growth zone forming the growing whisker. The observed mat of whisker beard on the copper specimen indicates the surface concentration of active sulphide islands, promoting the growth.

5. A trace of sulphide has been observed in the whiskers. Sulphide is therefore gradually removed from the surface. This process will cause the mechanism to come to a halt if fresh sulphide is not introduced.

The whisker growth thus requires high chloride concentrations, an anodic/cathodic couple, and sulphide islands going from the metal to the outer surface of the film covering the copper. The anode is probably situated below the sulphide island. An oxidant driving the cathodic reaction is also necessary for the growth of the whiskers. The absence or shortage of one of these requirements would inhibit the whisker growth.

It is thus probable that there are at least two mechanisms for whisker formation on copper in repository environments. Both cases require the presence of copper sulphide. One mechanism is founded on the growth of "pure" copper sulphide whiskers. This growth can probably operate at very low potentials driven by the very high copper affinity to sulphide. The other mechanism involves growth of oxide/hydroxide whiskers. However, the latter mechanism still requires small amounts of copper sulphide for easy copper supply to a growth zone and also a better supply of an oxidation agent compared with growth of "pure" copper sulphide whiskers.

As already mentioned there could be other possible ways to grow whiskers on copper. In a carbonate environment, as in the repository, carbonate/malachite whiskers could grow, see figure 12. Essentially the same mechanism would work as far as there are copper sulphide islands present as spots of easy supply of copper.

7 Conclusions

The following conclusions regarding copper corrosion in the repository environment have been drawn from the present work:

- A passivating oxide film is formed on copper only at a low chloride concentration in a sulphide free environment.
- High chloride concentrations can prevent formation of a passive film and destabilise a passivating oxide film present from the beginning.
- Copper sulphides can be formed at low potentials. Copper sulphides give poor passivating films.
- Both chloride and sulphide lower copper immunity.
- At high chloride and sulphide concentrations copper could be neither passive nor immune in certain potential/pH intervals. The only protection against dangerous general corrosion would then be a shortage of oxidising agents and low transportation rates of reacting species.
- Pitting in oxidative environments is slowed down by chloride in the long run. An explanation for this is suggested.
- Pitting/localised corrosion at lower potentials can proceed as whisker growth if sulphide is present. There are at least two mechanisms available, depending on circumstances. One pure sulphide whisker growth mechanism and another oxide/hydroxide whisker growth mechanism.
- Other whisker growth mechanisms in the repository environment like carbonate/malachite growth could also be possible.
- The film formation on the copper surface in groundwater is a slow process taking weeks or months.
- The chloride concentration affects the rate of film formation and the morphology of the film formed.
- The chloride concentration also affects the formation of whiskers in sulphide containing groundwaters.
- In the presence of sulphide the surface processes are much faster and film formation takes only minutes to hours.
- The whiskers observed here contain very little or no sulphur but sulphide is necessary for their formation. At least small amounts of sulphide seem to be necessary for the whisker mechanisms to work.
- No signs of localised corrosion on copper were detected in the sulphide-free groundwaters.
- The mechanisms for different types of local attacks need to be further investigated. This is especially the case for whisker growth in groundwaters with sulphide in order to know their significance on the integrity of the copper canister in the repository environment.
- Also general corrosion in highly saline environments needs further studies.

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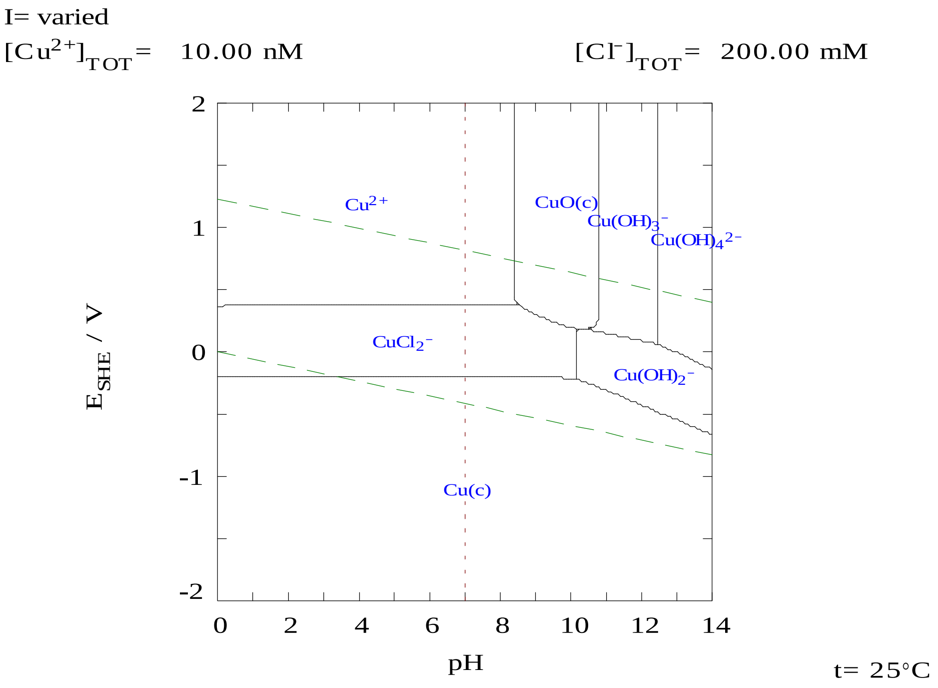
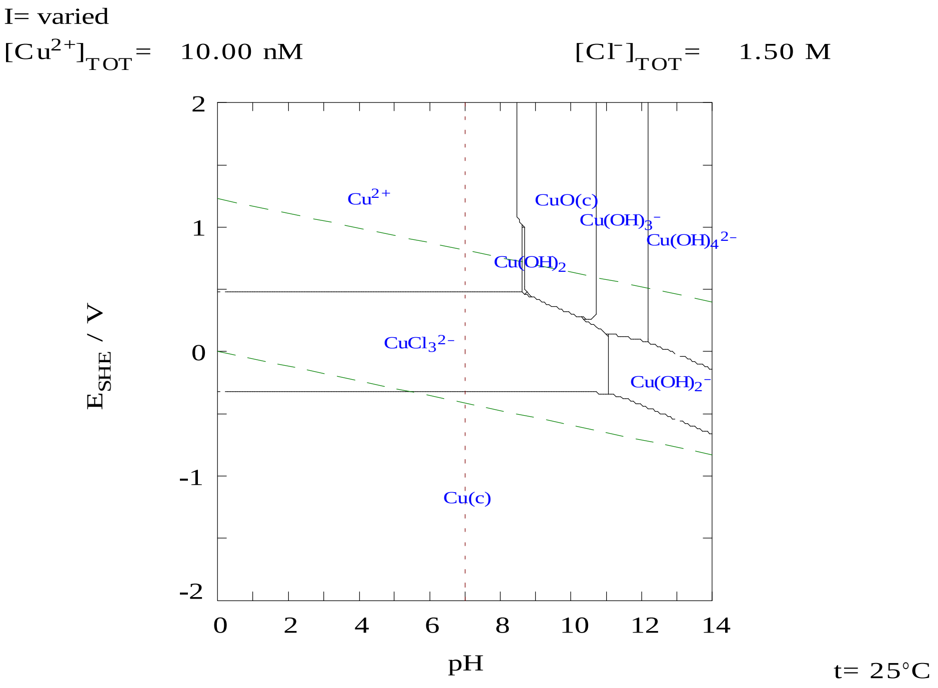
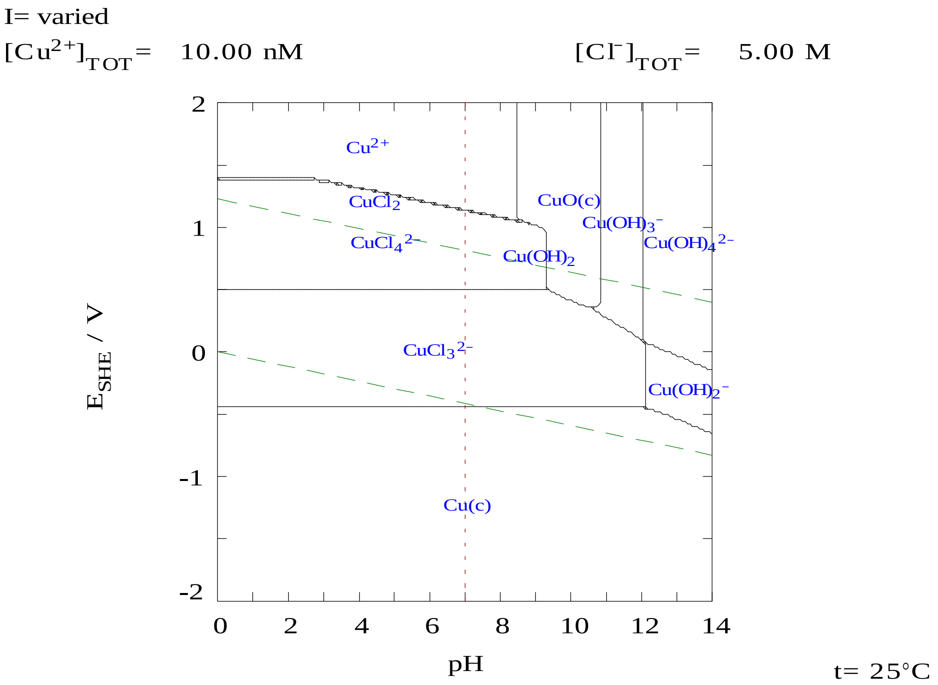
Appendix 1, Figures A1:1-27. Pourbaix diagrams for the system Cu-Cl-H-O in the temperature range 25 - 150 °C at indicated conditions. The diagrams were calculated using I Puigdomenec`s programs and database.



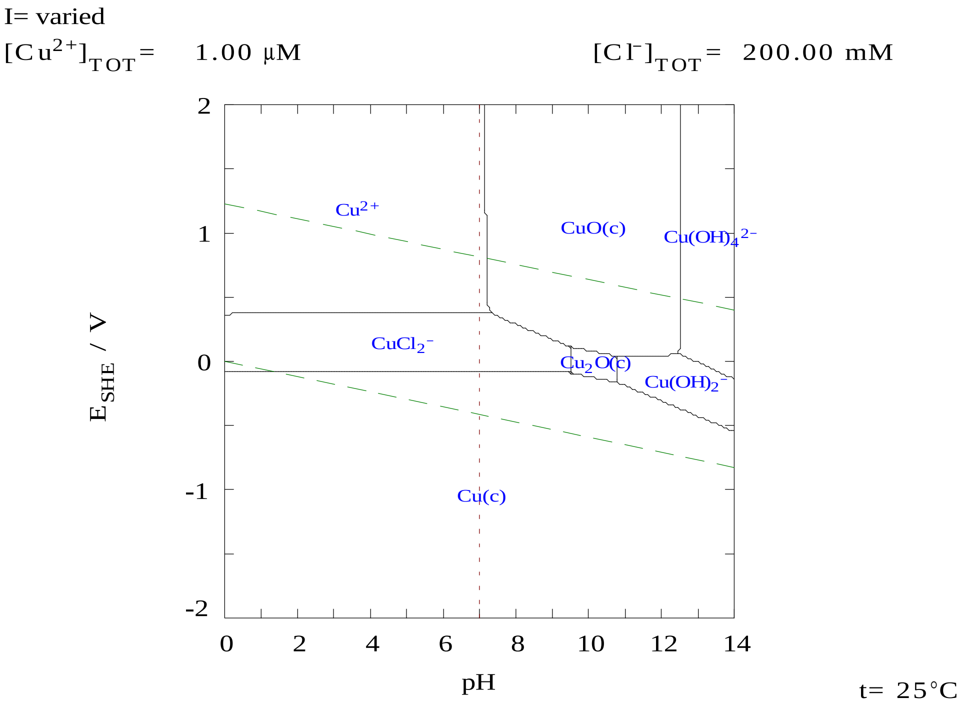
A1:1



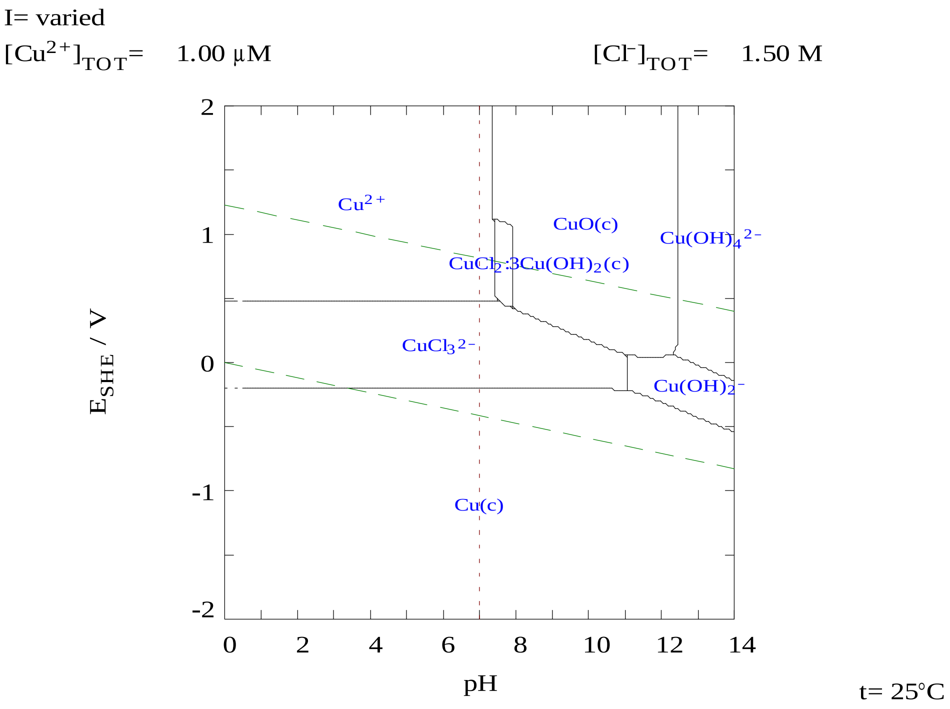
A1:2


I= varied
[Cu^{2+}]$_{TOT}$= 10.00 nM
[Cl$^-$]$_{TOT}$= 5.00 M
Cu^{2+}
CuCl$_2$
CuCl$_4^{2-}$
CuO(c)
Cu(OH)$_3^-$
Cu(OH)$_4^{2-}$
Cu(OH)$_2$
CuCl$_3^{2-}$
Cu(OH)$_2^-$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

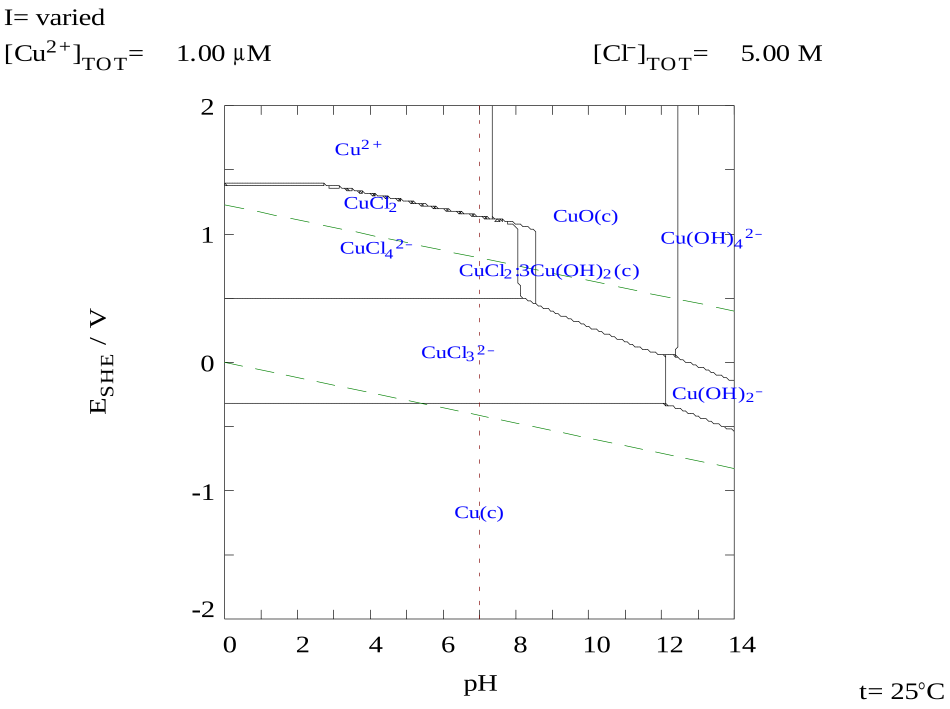
A1:3


I= varied
[Cu^{2+}]$_{TOT}$= 1.00 µM
[Cl$^-$]$_{TOT}$= 200.00 mM
Cu^{2+}
CuO(c)
Cu(OH)$_4^{2-}$
CuCl$_2^-$
Cu$_2$O(c)
Cu(OH)$_2^-$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

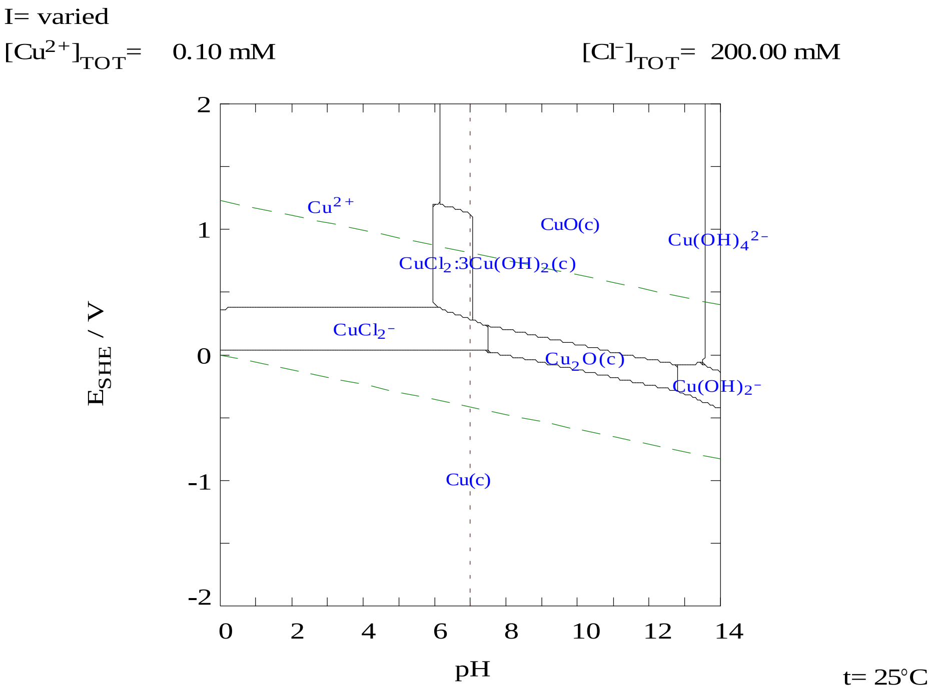
A1:4


I= varied
[Cu2+]TOT= 1.00 µM
[Cl-]TOT= 1.50 M
Cu2+
CuO(c)
Cu(OH)4 2-
CuCl2:3Cu(OH)2(c)
CuCl3 2-
Cu(OH)2 -
Cu(c)
ESHE / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

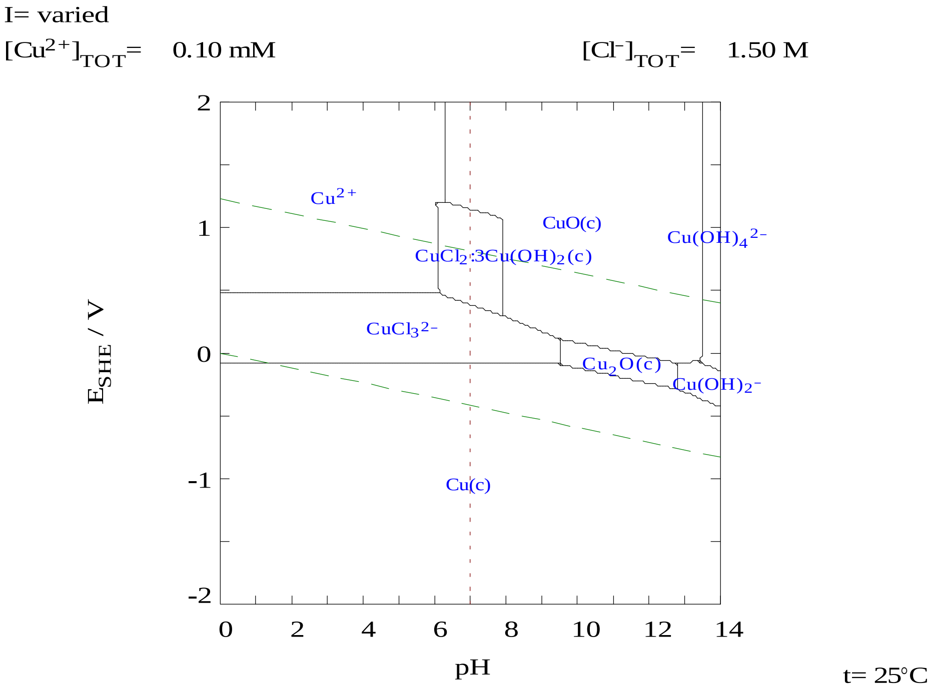
A1:5


I= varied
[Cu2+]TOT= 1.00 µM
[Cl-]TOT= 5.00 M
Cu2+
CuCl2
CuCl4 2-
CuO(c)
Cu(OH)4 2-
CuCl2:3Cu(OH)2(c)
CuCl3 2-
Cu(OH)2 -
Cu(c)
ESHE / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

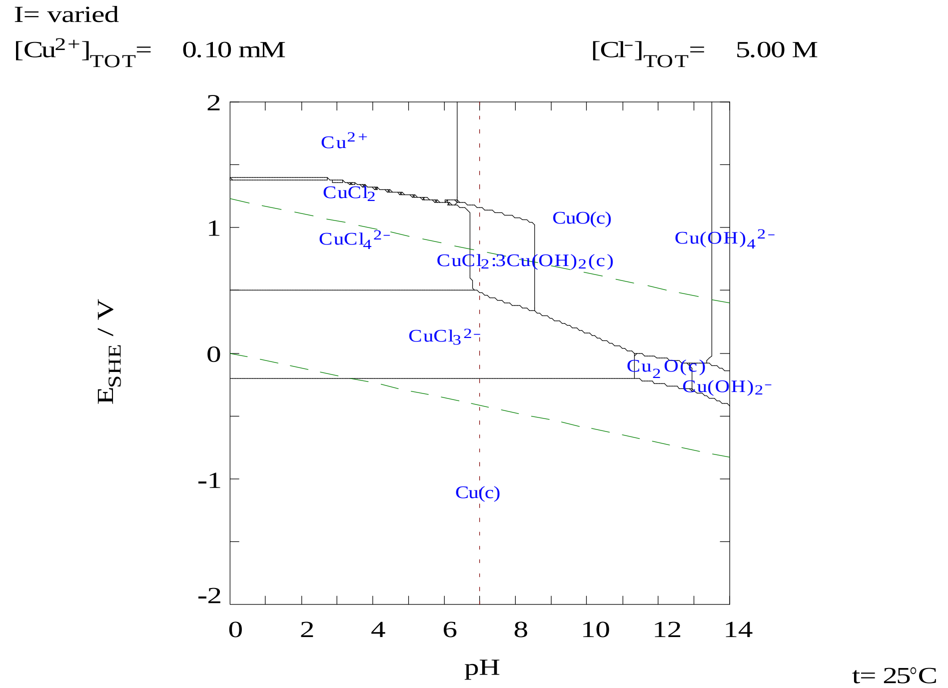
A1:6


I= varied
[Cu2+]TOT= 0.10 mM
[Cl-]TOT= 200.00 mM
2
1
0
-1
-2
ESHE / V
Cu2+
CuO(c)
Cu(OH)42-
CuCl2:3Cu(OH)2(c)
CuCl2-
Cu2O(c)
Cu(OH)2-
Cu(c)
0
2
4
6
8
10
12
14
pH
t= 25°C

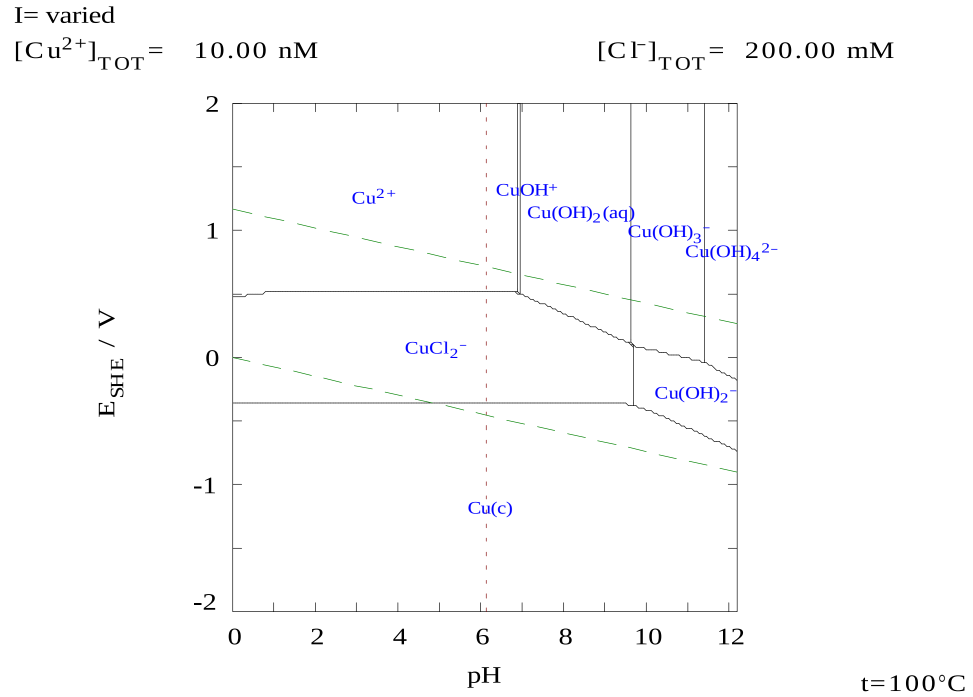
A1:7


I= varied
[Cu2+]TOT= 0.10 mM
[Cl-]TOT= 1.50 M
2
1
0
-1
-2
ESHE / V
Cu2+
CuO(c)
Cu(OH)42-
CuCl2:3Cu(OH)2(c)
CuCl32-
Cu2O(c)
Cu(OH)2-
Cu(c)
0
2
4
6
8
10
12
14
pH
t= 25°C

A1:8


I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl_2$
$CuCl_4^{2-}$
CuO(c)
$Cu(OH)_4^{2-}$
$CuCl_2{:}3Cu(OH)_2(c)$
$CuCl_3^{2-}$
$Cu_2O(c)$
$Cu(OH)_2^{-}$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

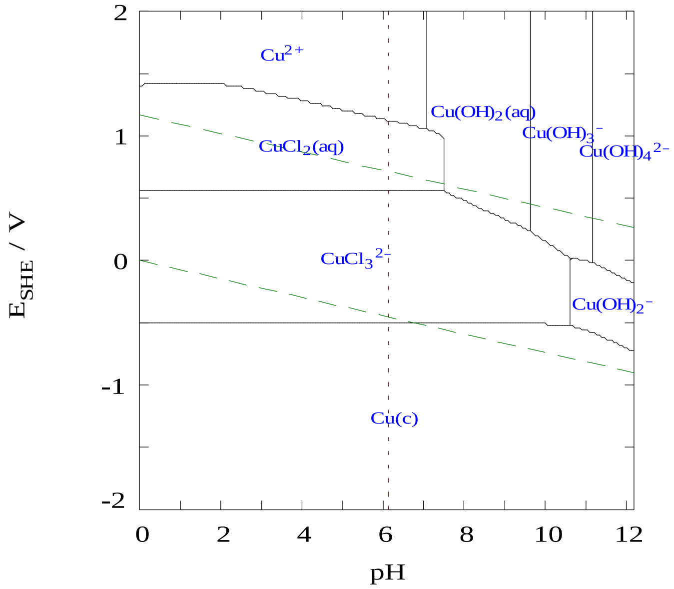
A1:9


I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^{-}]_{TOT}$= 200.00 mM
Cu^{2+}
$CuOH^{+}$
$Cu(OH)_2(aq)$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_2^{-}$
$Cu(OH)_2^{-}$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

A1:10

I= varied

$[Cu^{2+}]_{TOT}=$ 10.00 nM $[Cl^{-}]_{TOT}=$ 1.50 M

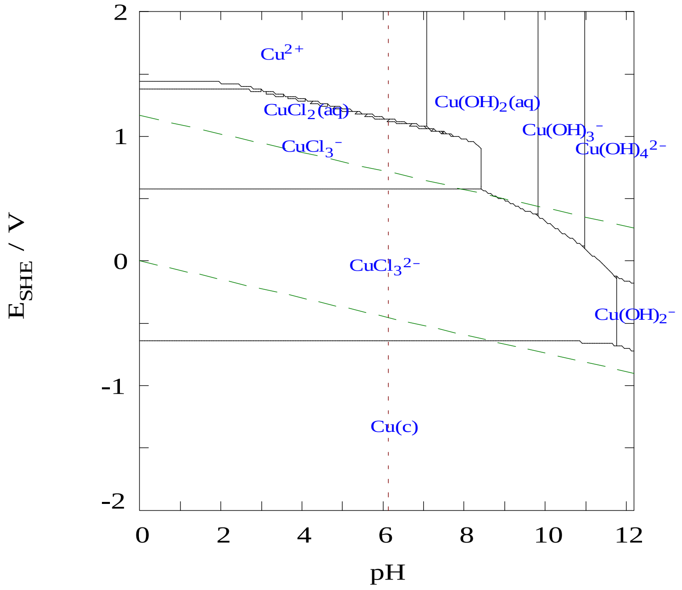


t=100°C

A1:11

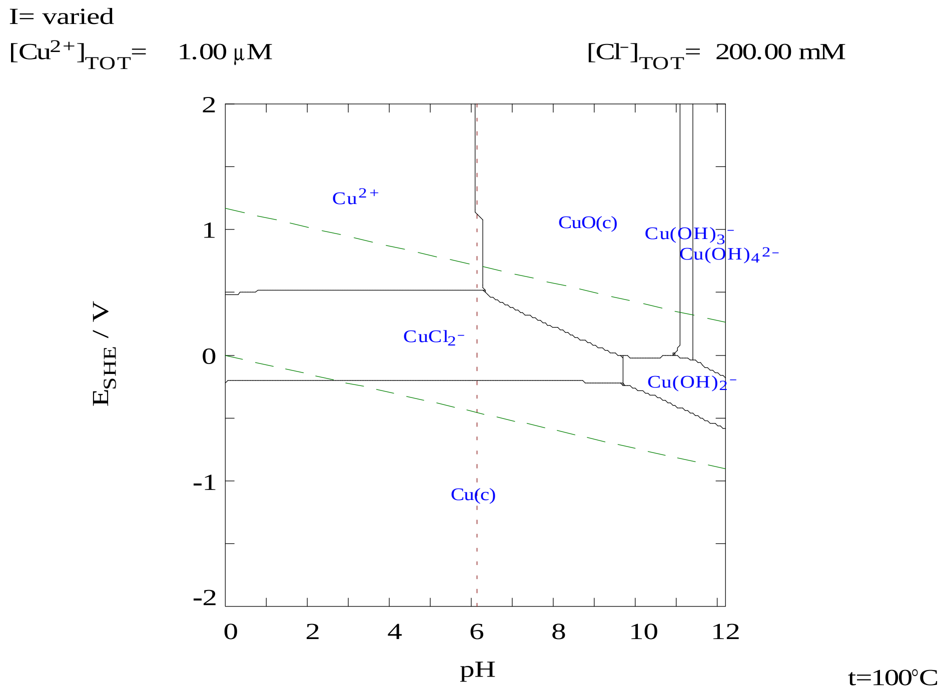
I= varied

$[Cu^{2+}]_{TOT}=$ 10.00 nM $[Cl^{-}]_{TOT}=$ 5.00 M

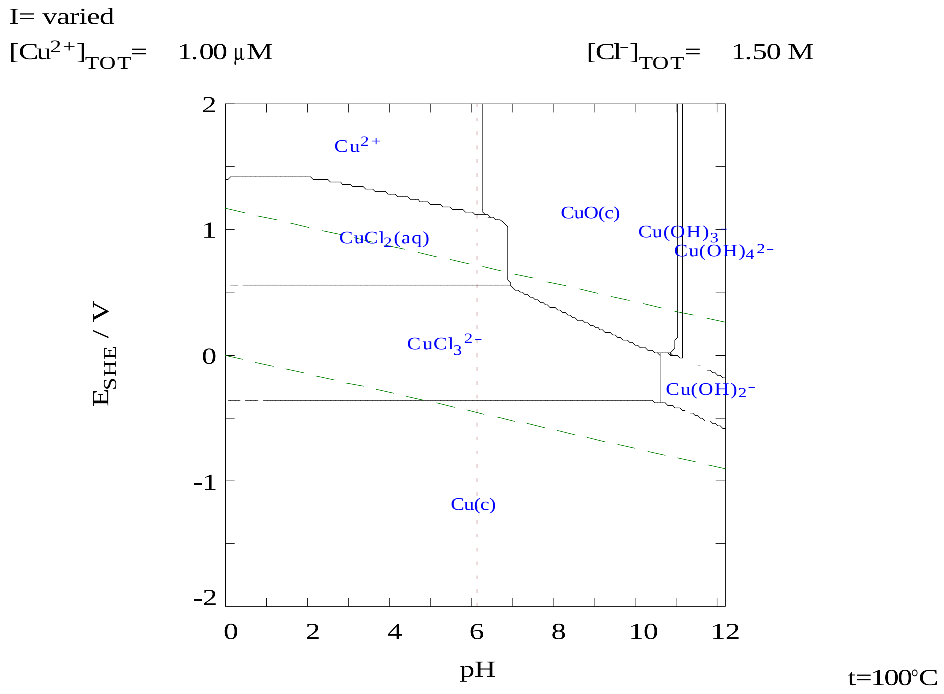


t=100°C

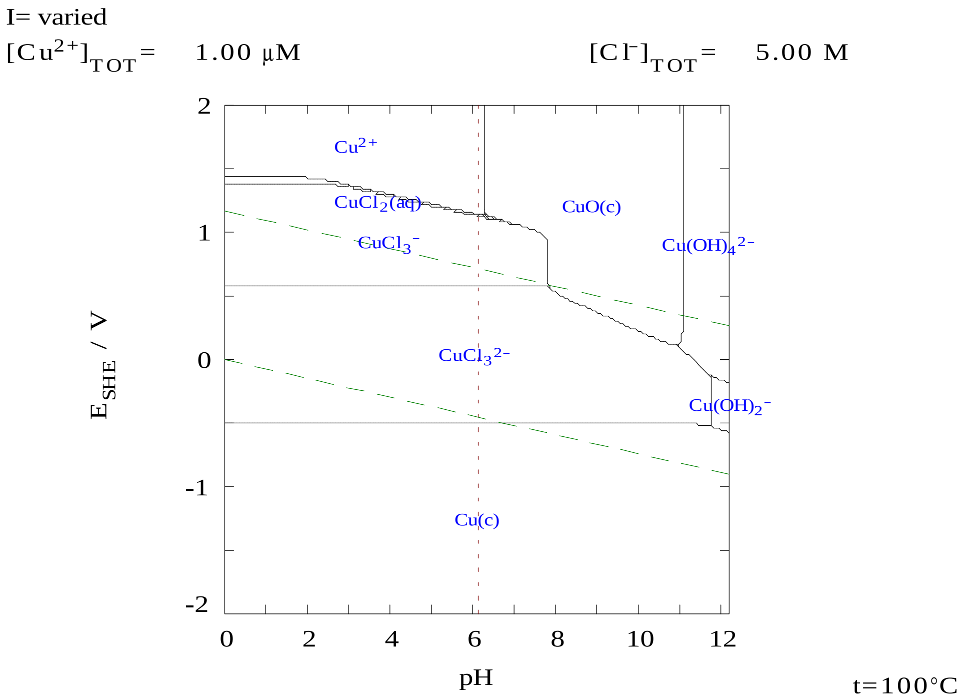
A1:12


I= varied
$[Cu^{2+}]_{TOT}$= 1.00 μM
$[Cl^-]_{TOT}$= 200.00 mM
Cu^{2+}
CuO(c)
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_2^-$
$Cu(OH)_2^-$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

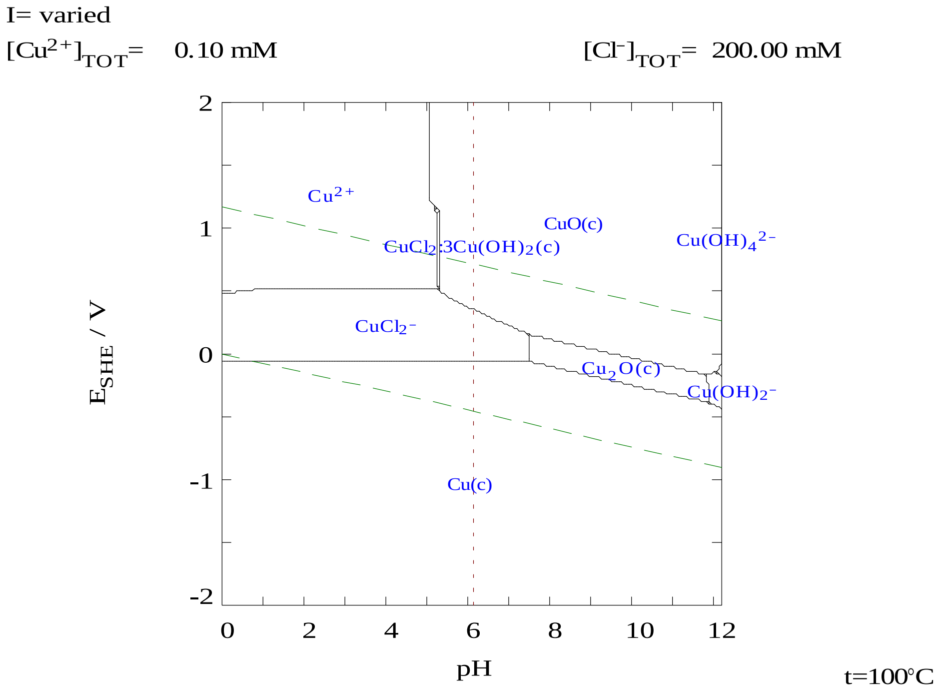
A1:13


I= varied
$[Cu^{2+}]_{TOT}$= 1.00 μM
$[Cl^-]_{TOT}$= 1.50 M
Cu^{2+}
CuO(c)
$CuCl_2(aq)$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

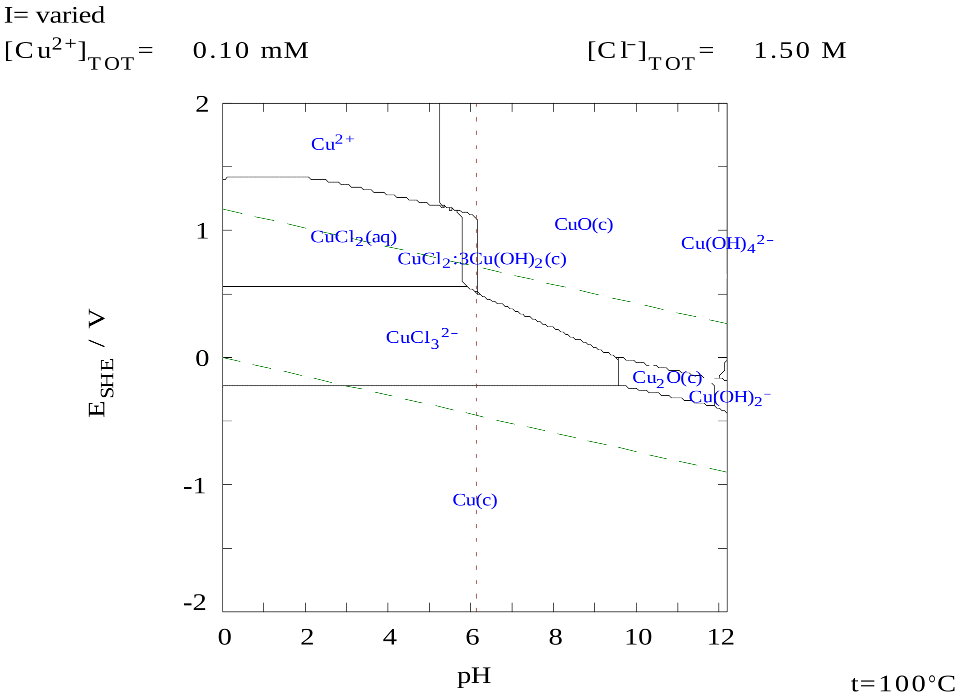
A1:14


I= varied
[Cu2+]TOT= 1.00 µM
[Cl-]TOT= 5.00 M
2
1
0
-1
-2
ESHE / V
0
2
4
6
8
10
12
pH
Cu2+
CuCl2(aq)
CuCl3-
CuO(c)
Cu(OH)42-
CuCl32-
Cu(OH)2-
Cu(c)
t=100°C

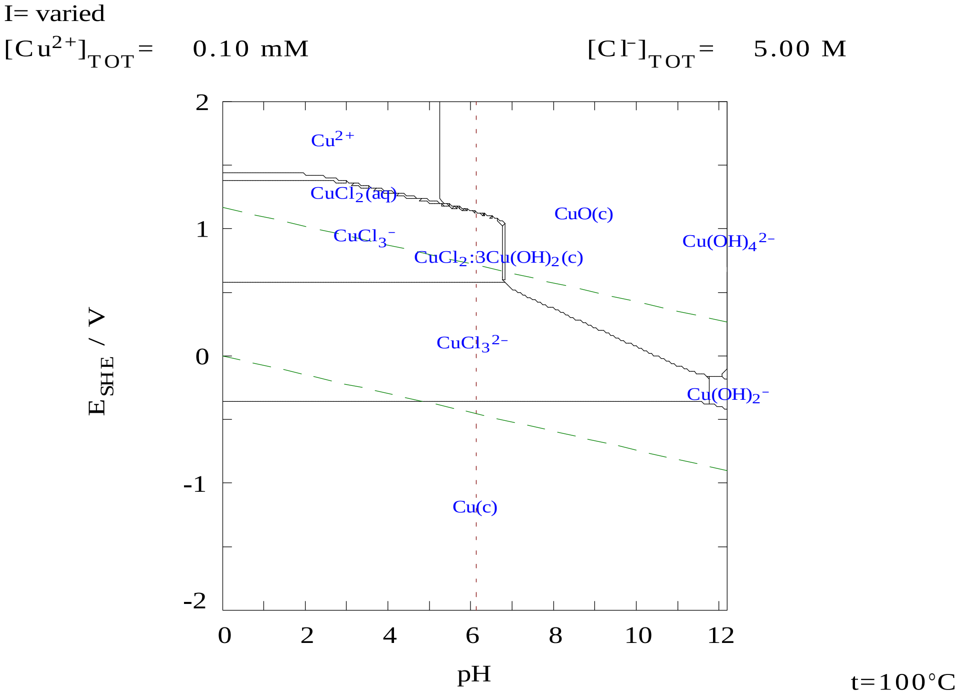
A1:15


I= varied
[Cu2+]TOT= 0.10 mM
[Cl-]TOT= 200.00 mM
2
1
0
-1
-2
ESHE / V
0
2
4
6
8
10
12
pH
Cu2+
CuO(c)
CuCl2:3Cu(OH)2(c)
Cu(OH)42-
CuCl2-
Cu2O(c)
Cu(OH)2-
Cu(c)
t=100°C

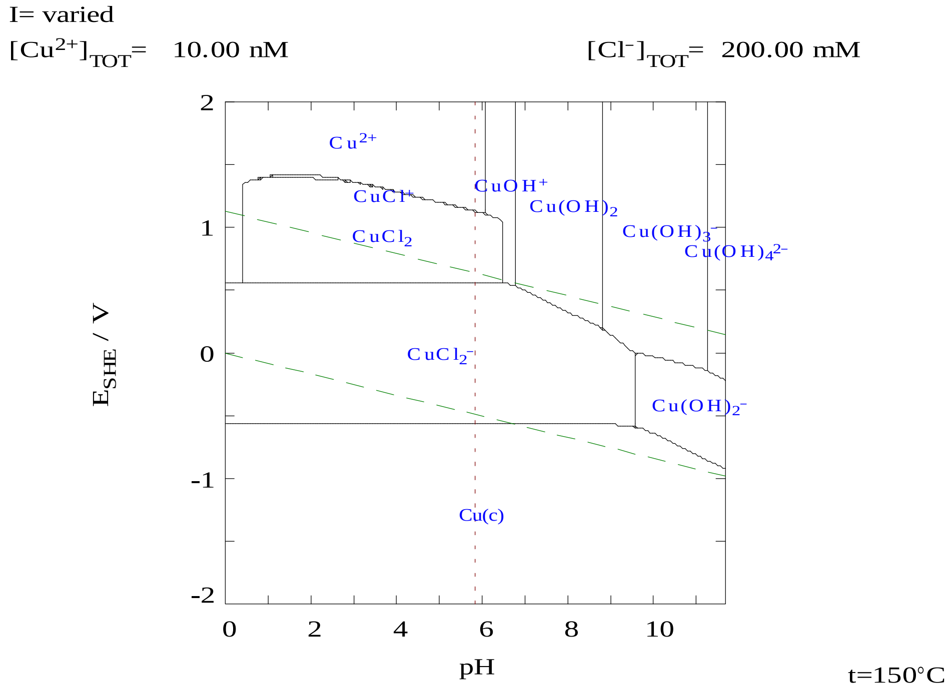
A1:16


I= varied
[Cu^{2+}]$_{TOT}$= 0.10 mM
[Cl$^-$]$_{TOT}$= 1.50 M
Cu^{2+}
CuCl$_2$(aq)
CuCl$_2$:3Cu(OH)$_2$(c)
CuO(c)
Cu(OH)$_4^{2-}$
CuCl$_3^{2-}$
Cu$_2$O(c)
Cu(OH)$_2^-$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

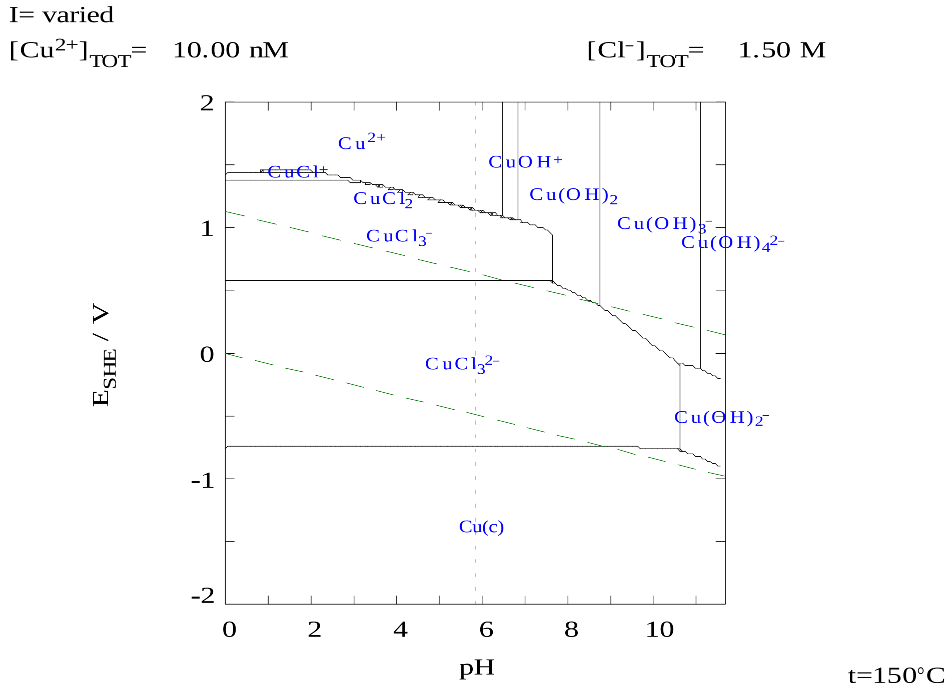
A1:17


I= varied
[Cu^{2+}]$_{TOT}$= 0.10 mM
[Cl$^-$]$_{TOT}$= 5.00 M
Cu^{2+}
CuCl$_2$(aq)
CuCl$_3^-$
CuCl$_2$:3Cu(OH)$_2$(c)
CuO(c)
Cu(OH)$_4^{2-}$
CuCl$_3^{2-}$
Cu(OH)$_2^-$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

A1:18

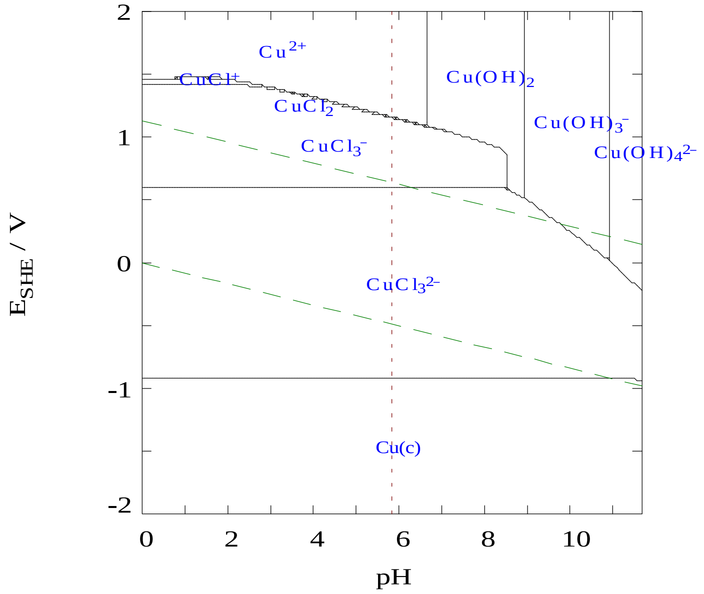

I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^-]_{TOT}$= 200.00 mM
Cu^{2+}
$CuCl^+$
$CuCl_2$
$CuOH^+$
$Cu(OH)_2$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_2^-$
$Cu(OH)_2^-$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A1:19


I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^-]_{TOT}$= 1.50 M
Cu^{2+}
$CuCl^+$
$CuCl_2$
$CuCl_3^-$
$CuOH^+$
$Cu(OH)_2$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A1:20

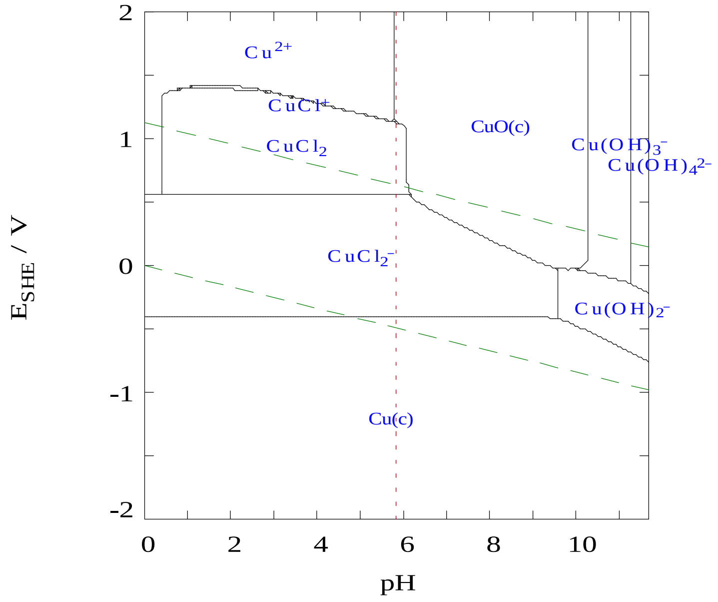
I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM $[Cl^{-}]_{TOT}$= 5.00 M



t=150°C

A1:21

I= varied
$[Cu^{2+}]_{TOT}$= 1.00 μM $[Cl^{-}]_{TOT}$= 200.00 mM

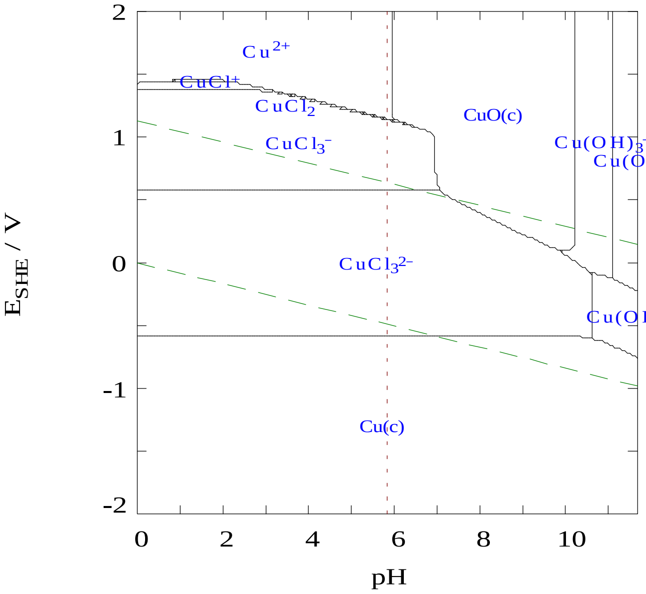


t=150°C

A1:22

I= varied

$[Cu^{2+}]_{TOT}$= 1.00 µM $[Cl^{-}]_{TOT}$= 1.50 M

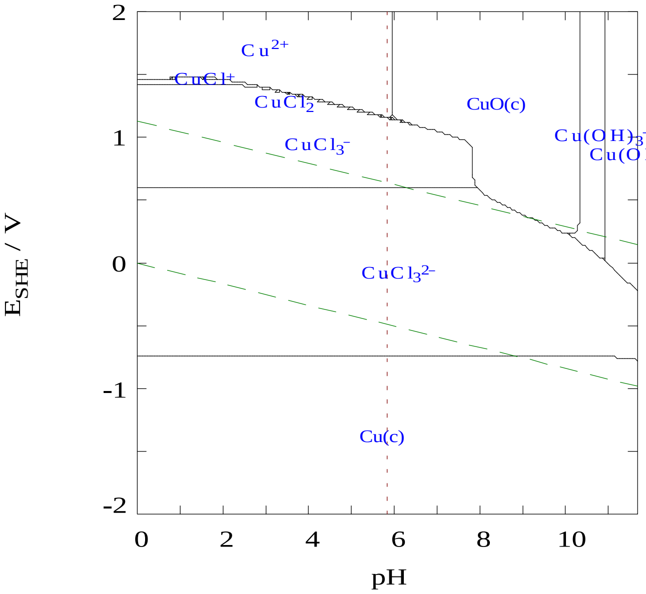


t=150°C

A1:23

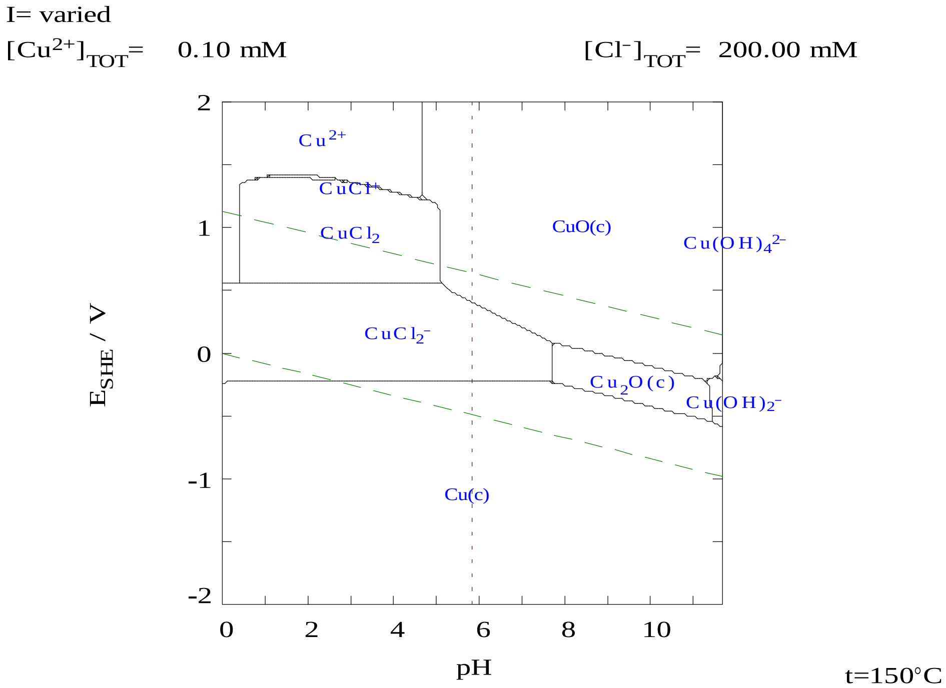
I= varied

$[Cu^{2+}]_{TOT}$= 1.00 µM $[Cl^{-}]_{TOT}$= 5.00 M

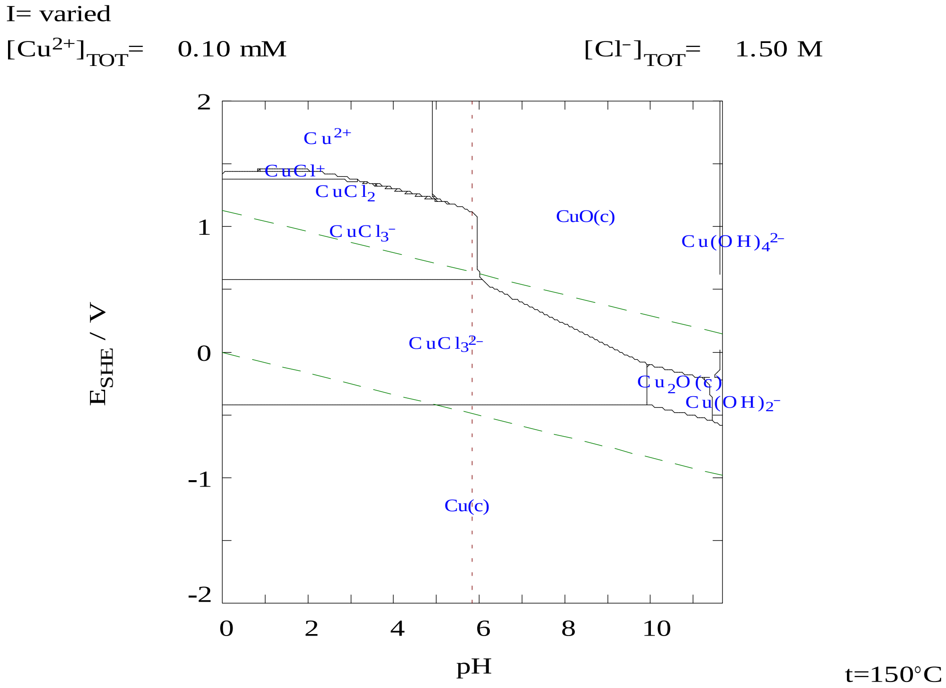


t=150°C

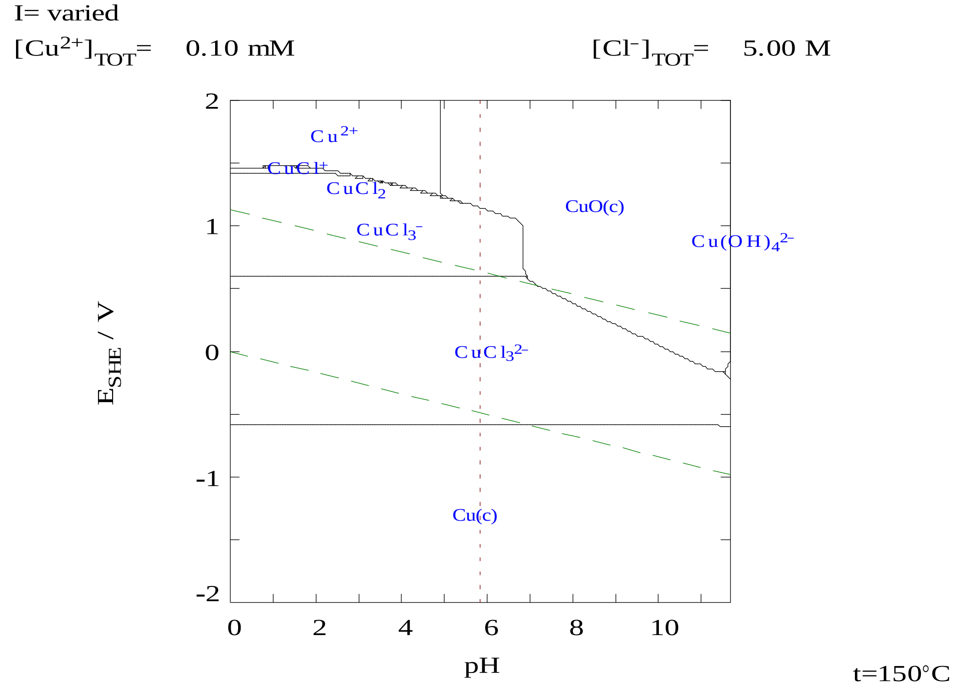
A1:24


I= varied
[Cu^{2+}]$_{TOT}$= 0.10 mM
[Cl^{-}]$_{TOT}$= 200.00 mM
Cu^{2+}
CuCl^{+}
CuCl$_2$
CuO(c)
Cu(OH)$_4^{2-}$
CuCl$_2^{-}$
Cu$_2$O(c)
Cu(OH)$_2^{-}$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A1:25

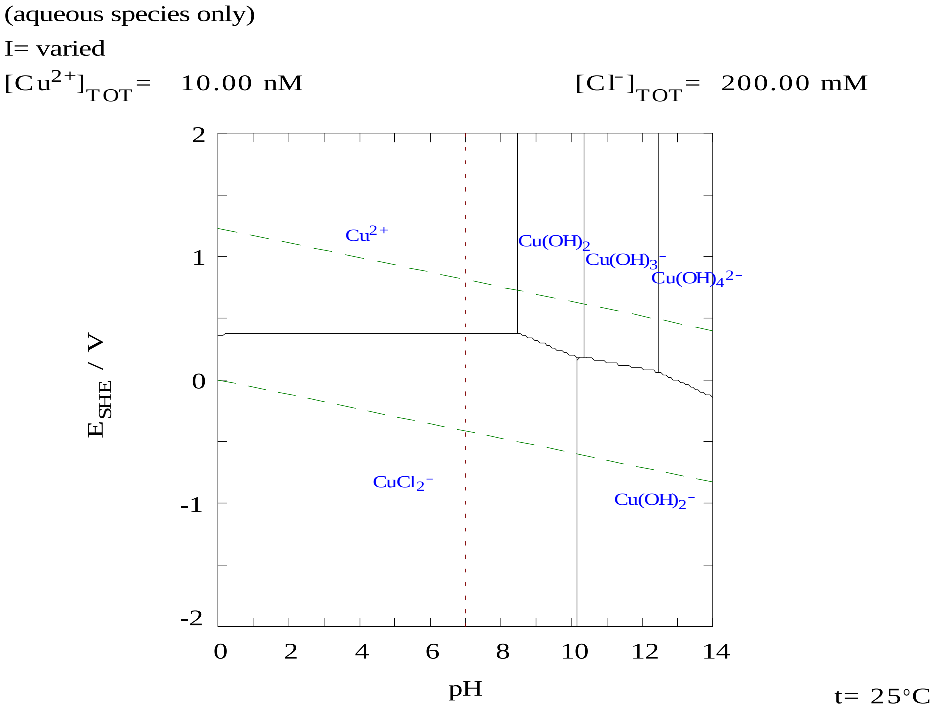

I= varied
[Cu^{2+}]$_{TOT}$= 0.10 mM
[Cl^{-}]$_{TOT}$= 1.50 M
Cu^{2+}
CuCl^{+}
CuCl$_2$
CuCl$_3^{-}$
CuO(c)
Cu(OH)$_4^{2-}$
CuCl$_3^{2-}$
Cu$_2$O(c)
Cu(OH)$_2^{-}$
Cu(c)
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A1:26

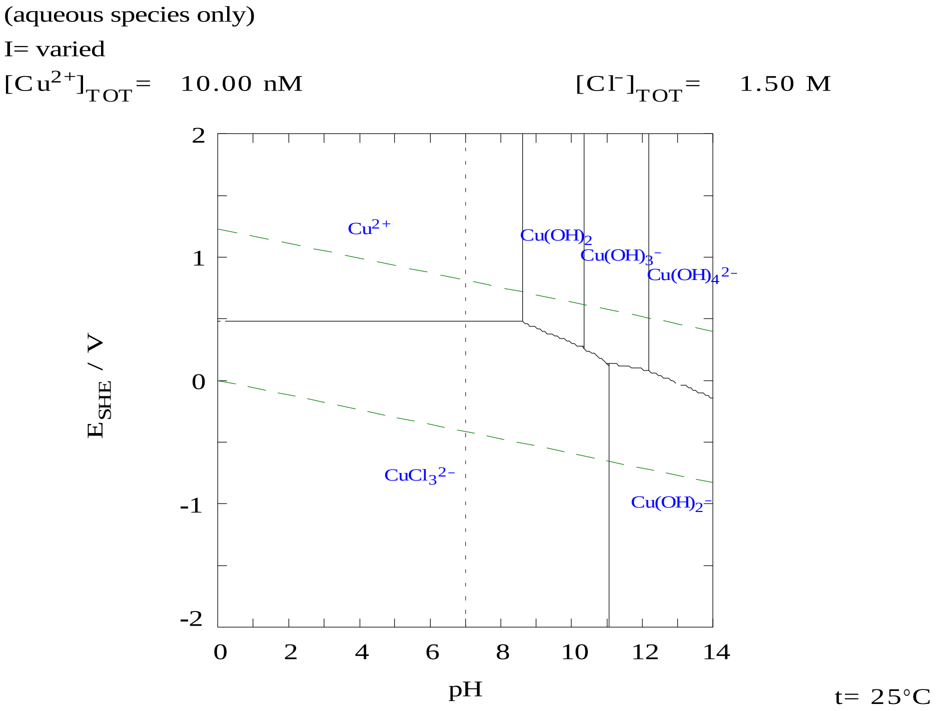

I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl^{+}$
$CuCl_2$
$CuCl_3^{-}$
CuO(c)
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
Cu(c)
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A1:27

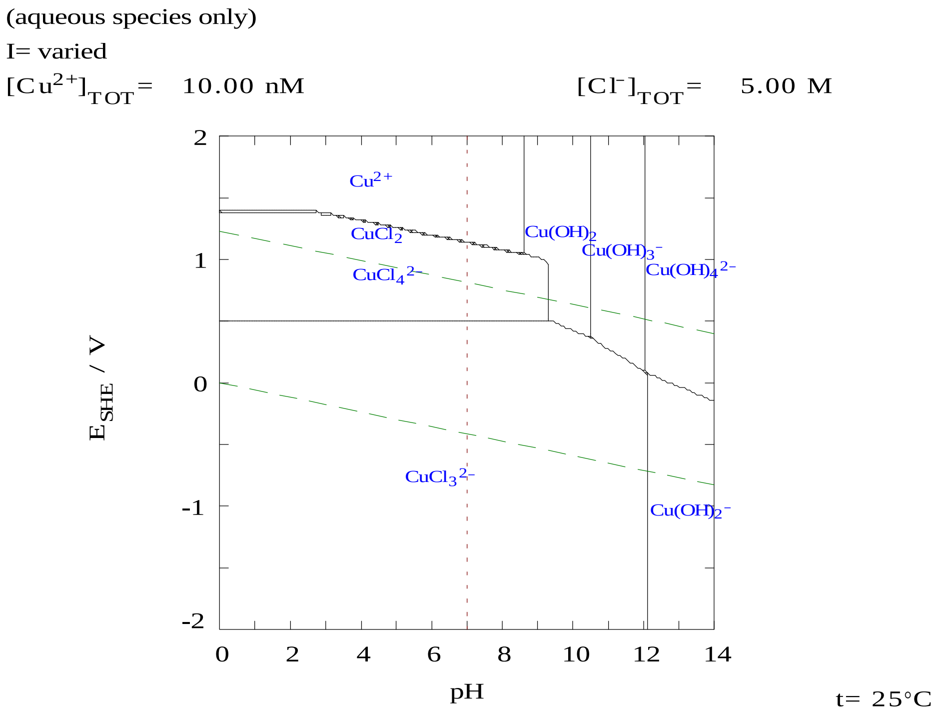
Appendix 2, Figures A2:1-27. Pourbaix diagrams (dissolved species) for the system Cu-Cl-H-O in the temperature range 25 - 150 °C at indicated conditions. The diagrams were calculated using I Puigdomenec`s programs and database.



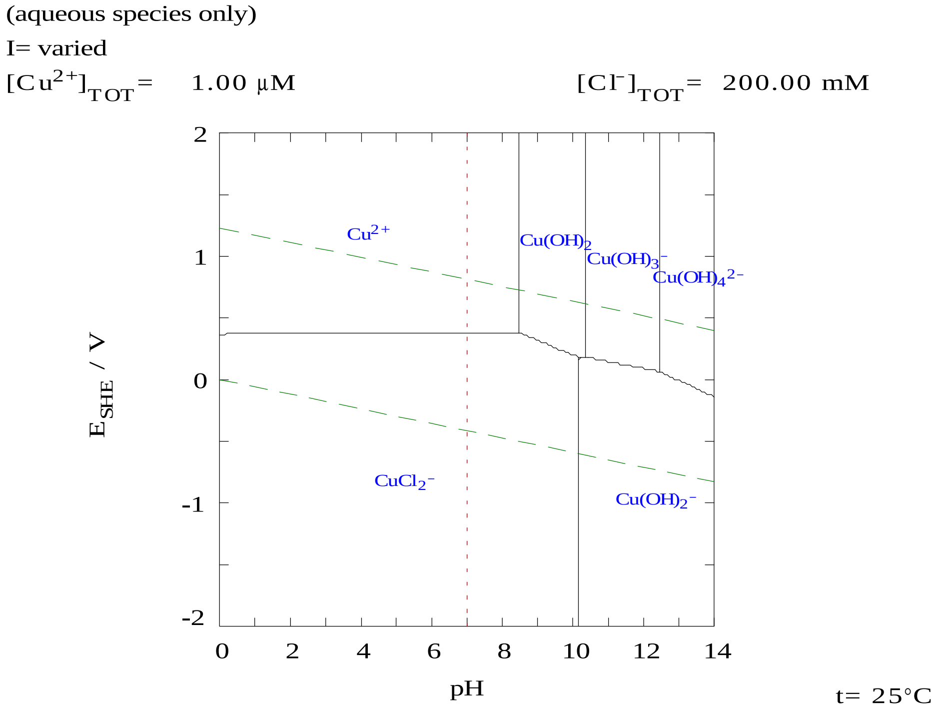
A2:1



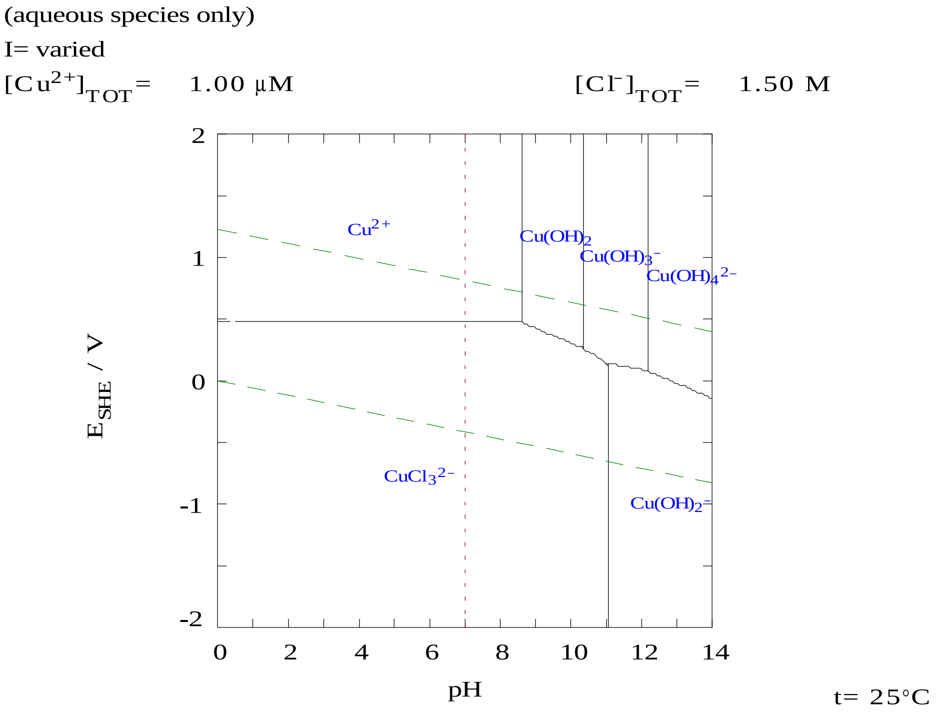
A2:2


(aqueous species only)
I= varied
[Cu^{2+}]$_{TOT}$= 10.00 nM
[Cl$^-$]$_{TOT}$= 5.00 M
Cu^{2+}
CuCl$_2$
CuCl$_4^{2-}$
Cu(OH)$_2$
Cu(OH)$_3^-$
Cu(OH)$_4^{2-}$
CuCl$_3^{2-}$
Cu(OH)$_2^-$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

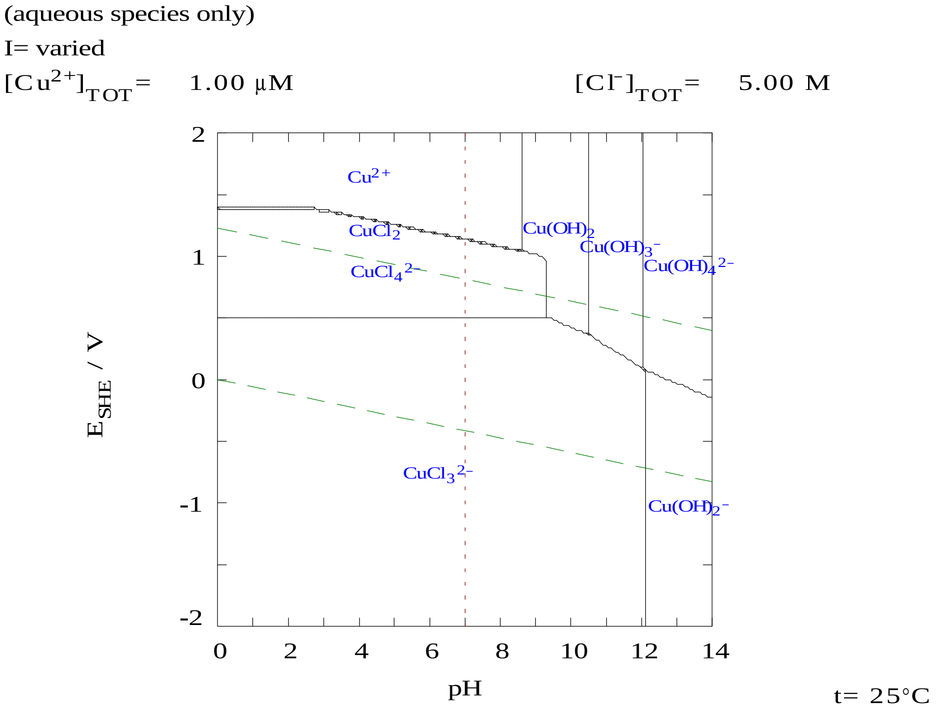
A2:3


(aqueous species only)
I= varied
[Cu^{2+}]$_{TOT}$= 1.00 μM
[Cl$^-$]$_{TOT}$= 200.00 mM
Cu^{2+}
Cu(OH)$_2$
Cu(OH)$_3^-$
Cu(OH)$_4^{2-}$
CuCl$_2^-$
Cu(OH)$_2^-$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

A2:4

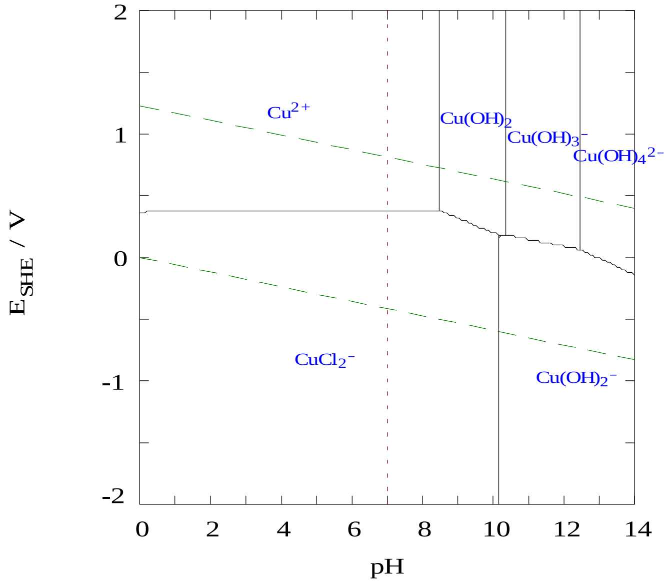

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM
$[Cl^{-}]_{TOT}$= 1.50 M
Cu^{2+}
$Cu(OH)_2$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

A2:5


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl_2$
$CuCl_4^{2-}$
$Cu(OH)_2$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

A2:6

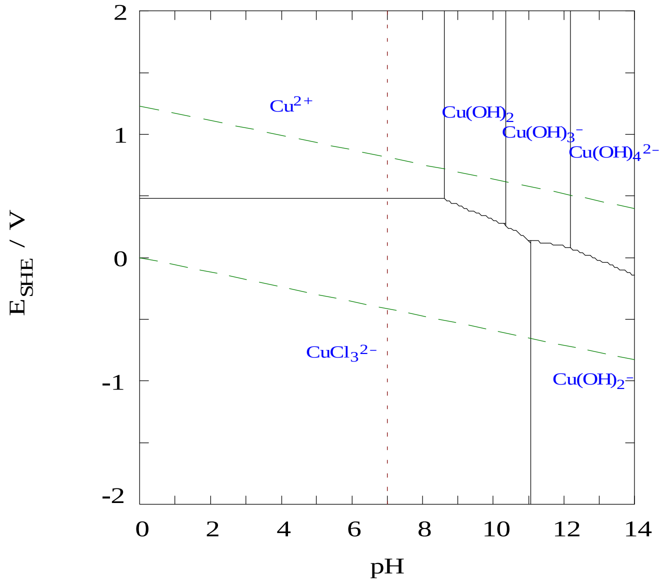
(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}=$ 0.10 mM $[Cl^{-}]_{TOT}=$ 200.00 mM



t= 25°C

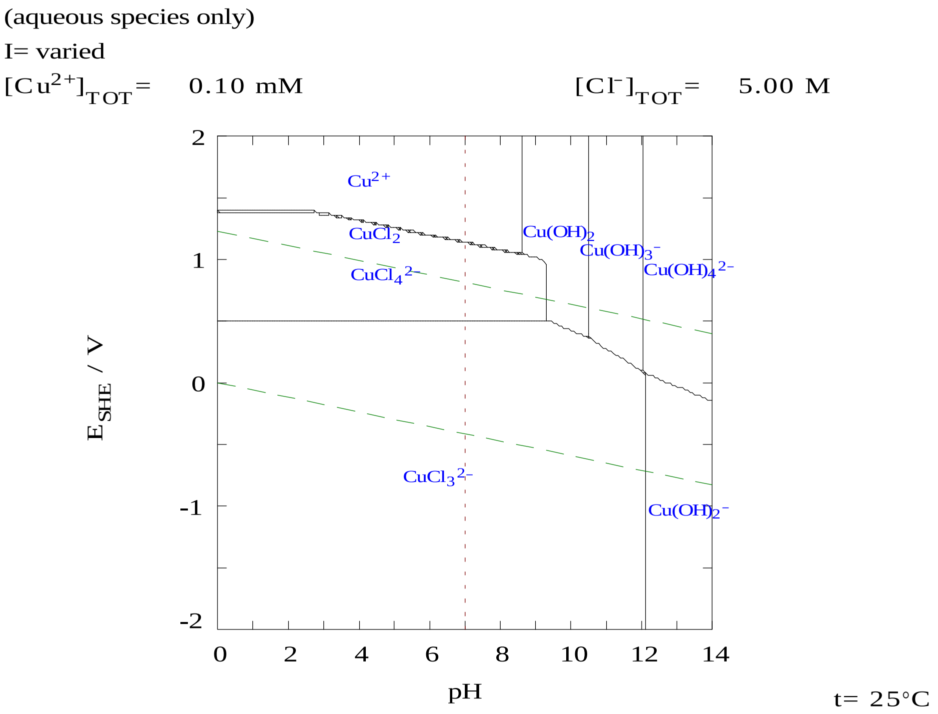
A2:7

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}=$ 0.10 mM $[Cl^{-}]_{TOT}=$ 1.50 M

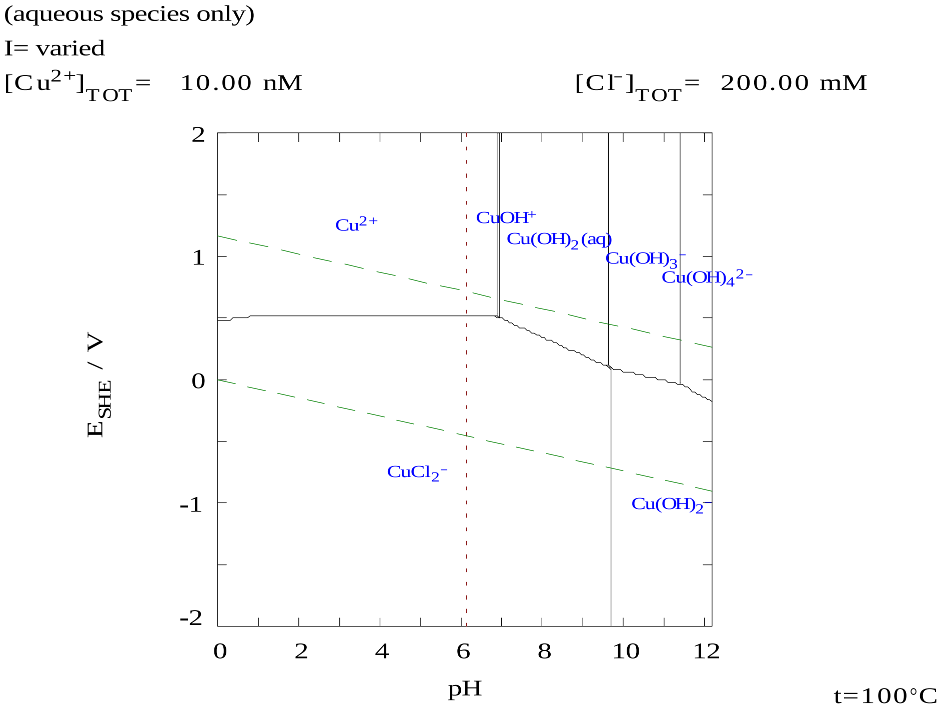


t= 25°C

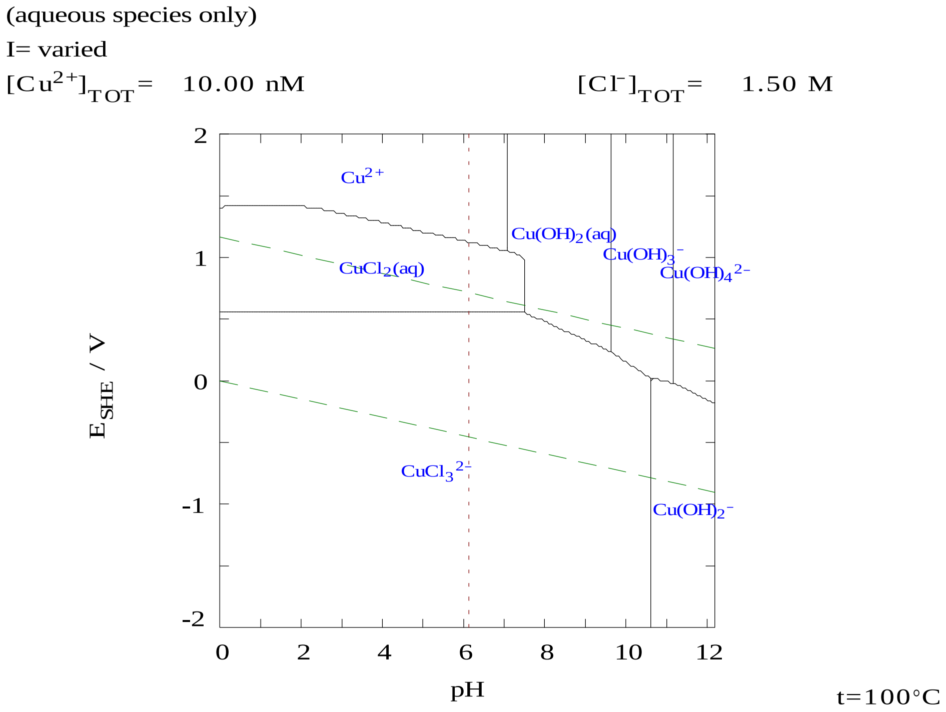
A2:8


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}=$ 0.10 mM
$[Cl^{-}]_{TOT}=$ 5.00 M
Cu^{2+}
$CuCl_2$
$CuCl_4^{2-}$
$Cu(OH)_2$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^{-}$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
14
pH
t= 25°C

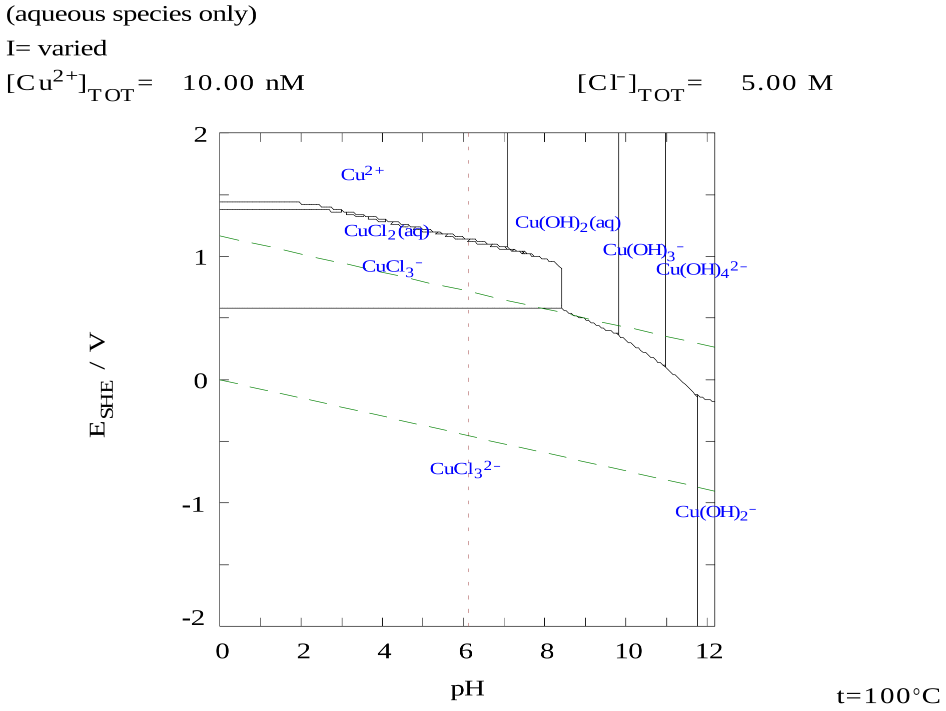
A2:9


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}=$ 10.00 nM
$[Cl^{-}]_{TOT}=$ 200.00 mM
Cu^{2+}
$CuOH^{+}$
$Cu(OH)_2(aq)$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_2^{-}$
$Cu(OH)_2^{-}$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

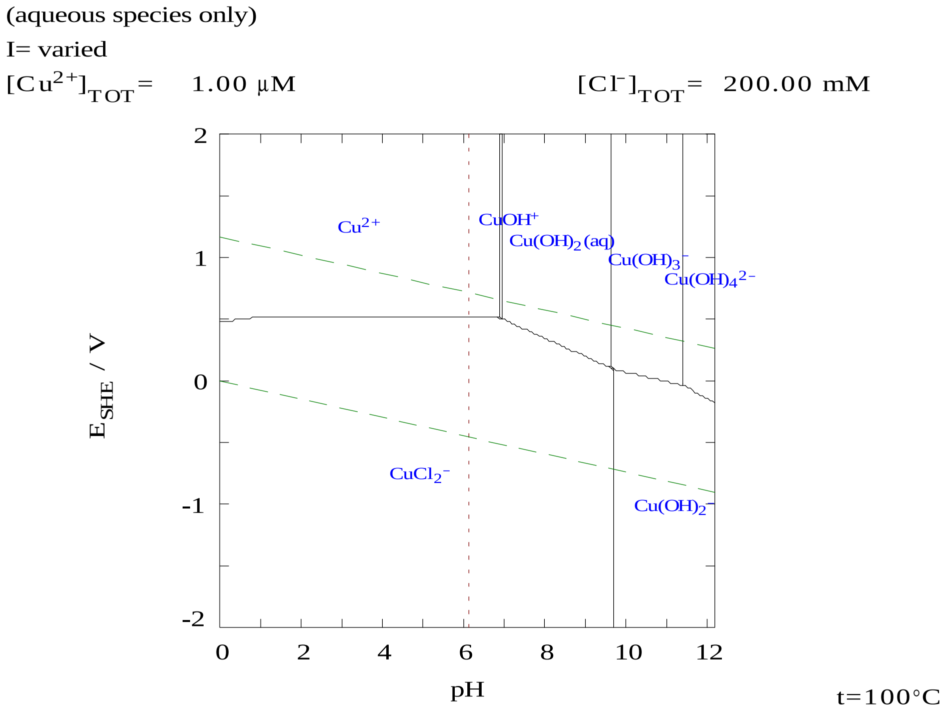
A2:10


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^{-}]_{TOT}$= 1.50 M
Cu^{2+}
$Cu(OH)_2(aq)$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_2(aq)$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

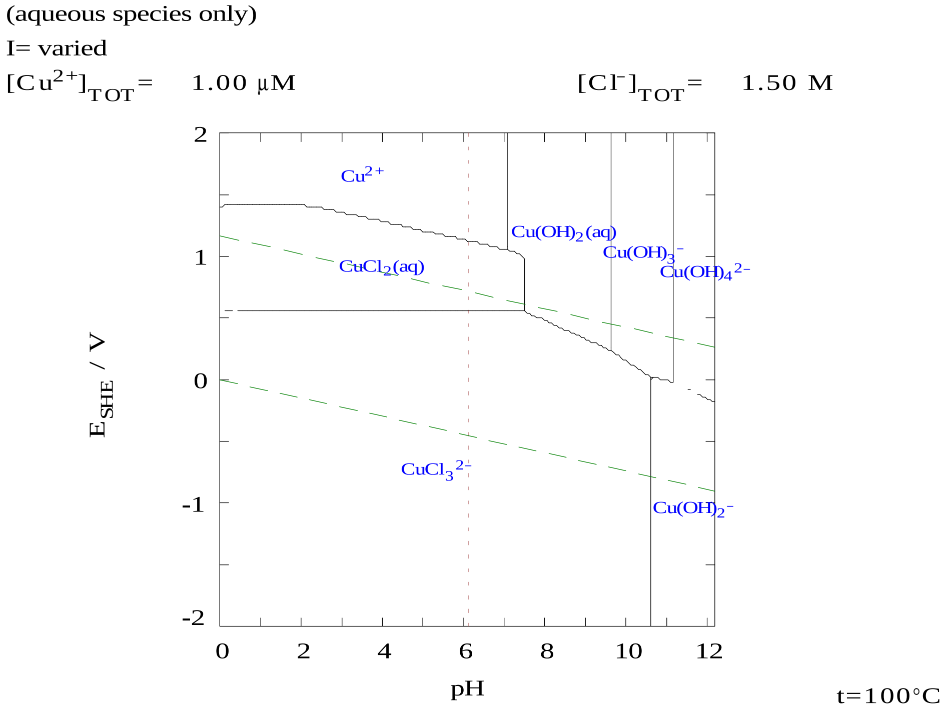
A2:11


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl_2(aq)$
$CuCl_3^-$
$Cu(OH)_2(aq)$
$Cu(OH)_3^-$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^-$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

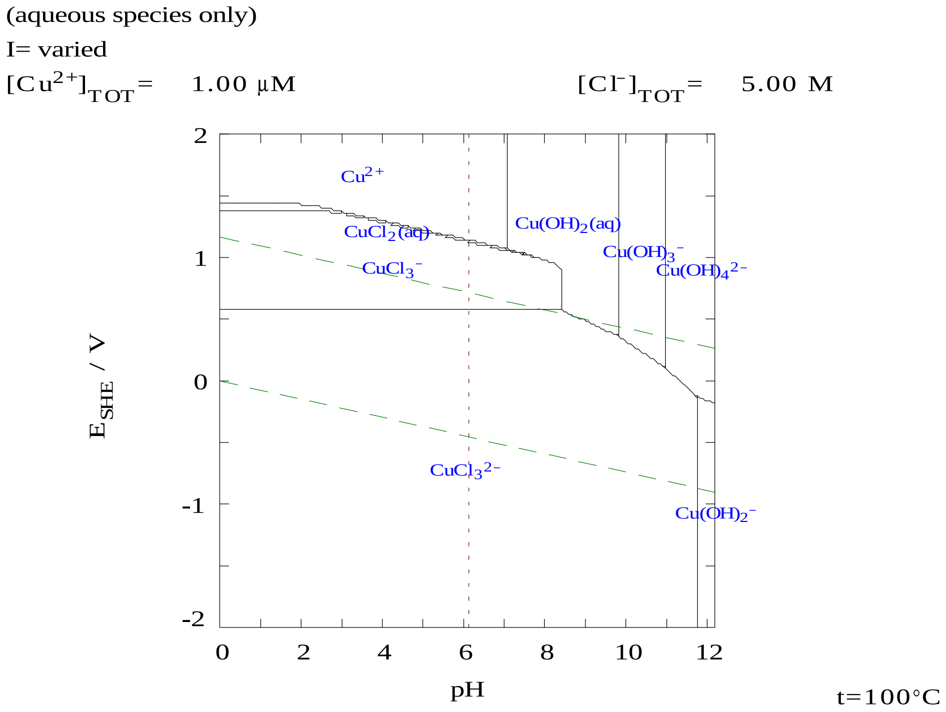
A2:12


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM
$[Cl^{-}]_{TOT}$= 200.00 mM
Cu^{2+}
CuOH^{+}
Cu(OH)$_2$(aq)
Cu(OH)$_3^{-}$
Cu(OH)$_4^{2-}$
CuCl$_2^{-}$
Cu(OH)$_2^{-}$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

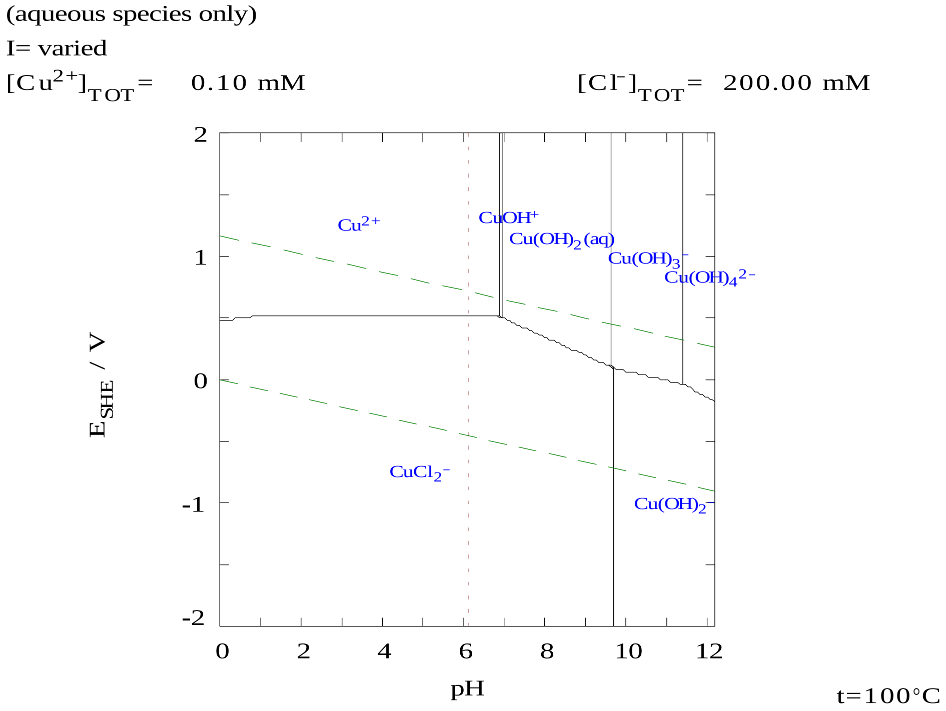
A2:13


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM
$[Cl^{-}]_{TOT}$= 1.50 M
Cu^{2+}
Cu(OH)$_2$(aq)
Cu(OH)$_3^{-}$
Cu(OH)$_4^{2-}$
CuCl$_2$(aq)
CuCl$_3^{2-}$
Cu(OH)$_2^{-}$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

A2:14

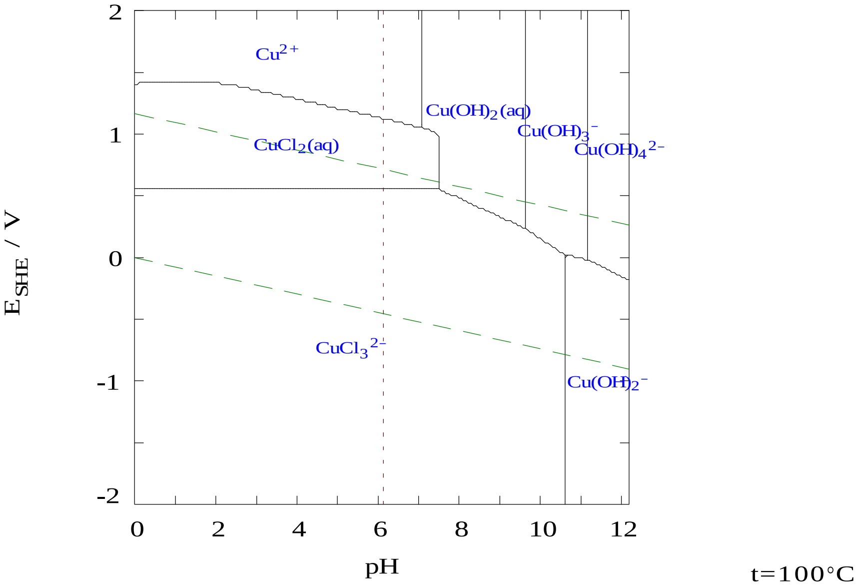

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl_2(aq)$
$CuCl_3^{-}$
$Cu(OH)_2(aq)$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
$Cu(OH)_2^{-}$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

A2:15


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM
$[Cl^{-}]_{TOT}$= 200.00 mM
Cu^{2+}
$CuOH^{+}$
$Cu(OH)_2(aq)$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_2^{-}$
$Cu(OH)_2^{-}$
E_{SHE} / V
2
1
0
-1
-2
0
2
4
6
8
10
12
pH
t=100°C

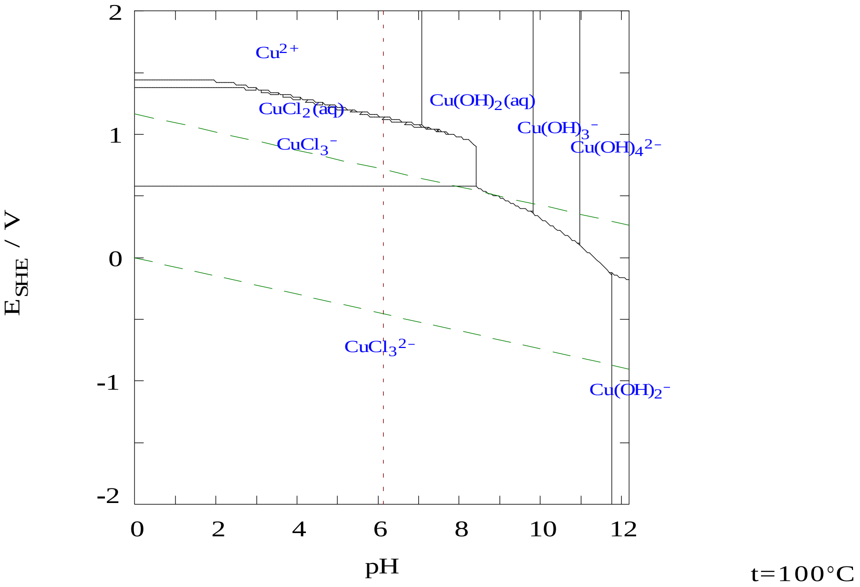
A2:16

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM $[Cl^{-}]_{TOT}$= 1.50 M

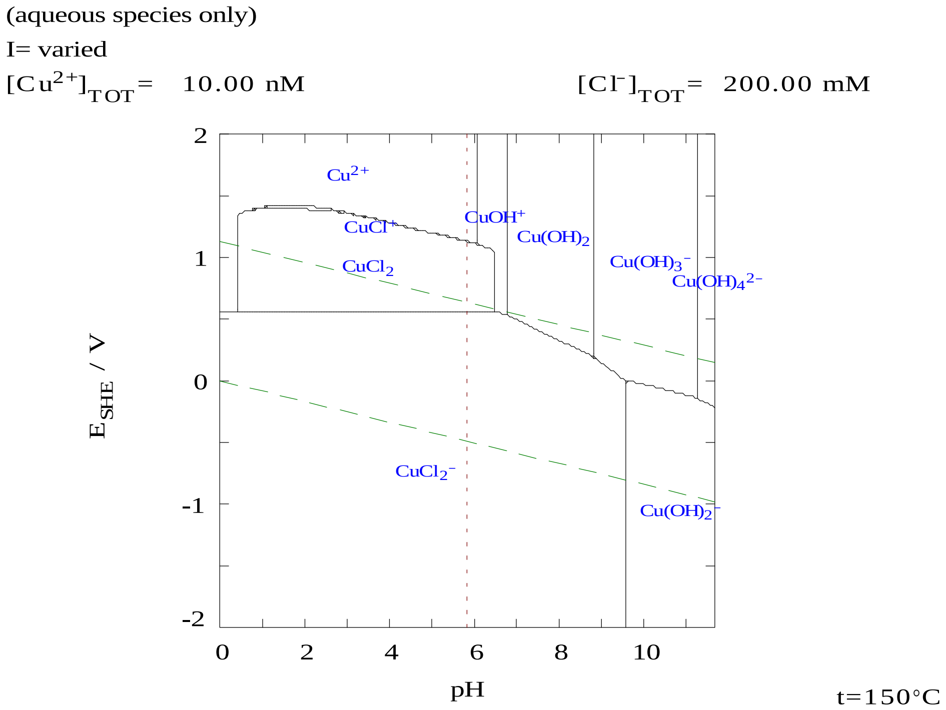


A2:17

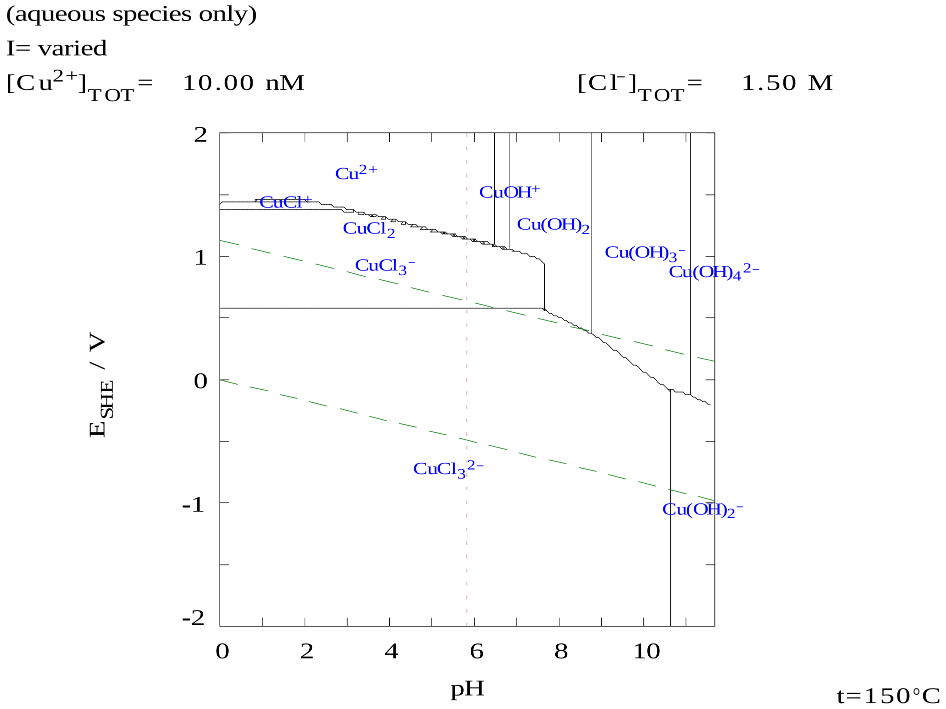
(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM $[Cl^{-}]_{TOT}$= 5.00 M



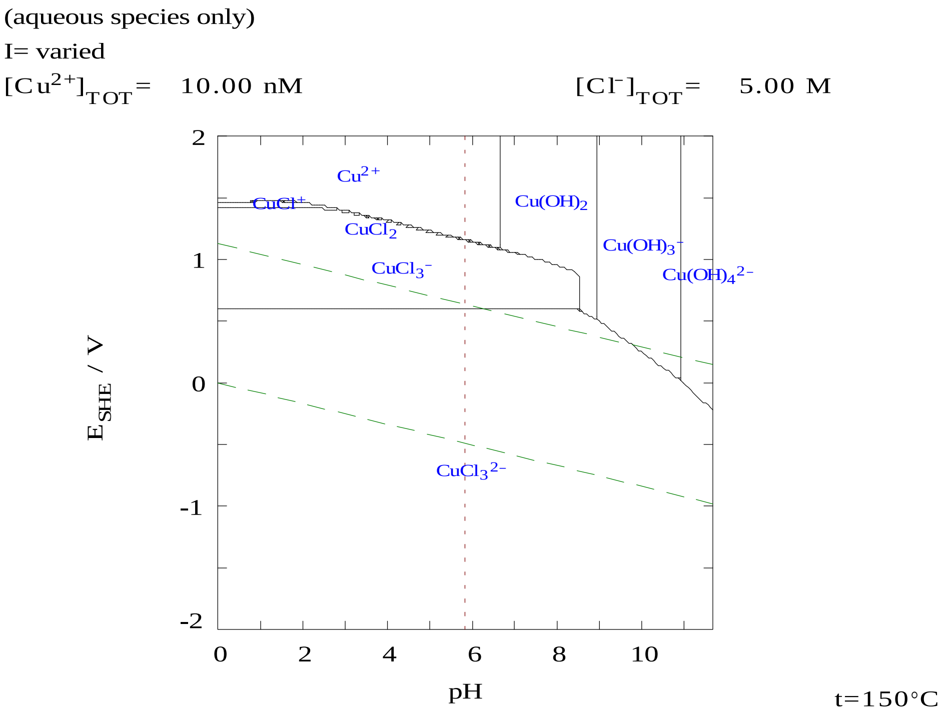
A2:18


(aqueous species only)
I= varied
[Cu^{2+}]$_{TOT}$= 10.00 nM
[Cl^{-}]$_{TOT}$= 200.00 mM
Cu^{2+}
CuCl^{+}
CuCl$_2$
CuOH^{+}
Cu(OH)$_2$
Cu(OH)$_3^{-}$
Cu(OH)$_4^{2-}$
CuCl$_2^{-}$
Cu(OH)$_2^{-}$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

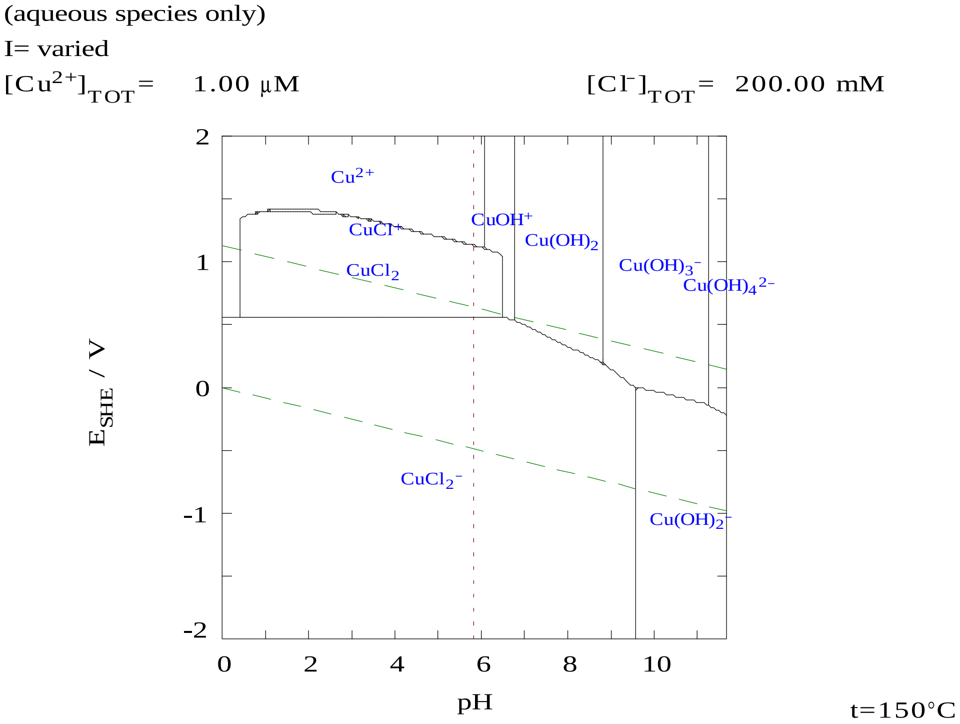
A2:19


(aqueous species only)
I= varied
[Cu^{2+}]$_{TOT}$= 10.00 nM
[Cl^{-}]$_{TOT}$= 1.50 M
Cu^{2+}
CuCl^{+}
CuCl$_2$
CuCl$_3^{-}$
CuOH^{+}
Cu(OH)$_2$
Cu(OH)$_3^{-}$
Cu(OH)$_4^{2-}$
CuCl$_3^{2-}$
Cu(OH)$_2^{-}$
E$_{SHE}$ / V
2
1
0
-1
-2
0
2
4
6
8
10
pH
t=150°C

A2:20

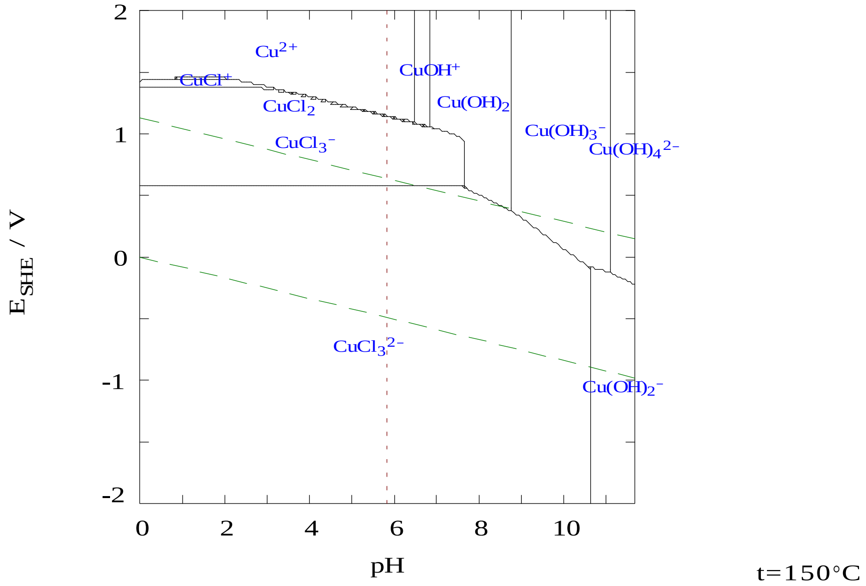

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 10.00 nM
$[Cl^{-}]_{TOT}$= 5.00 M
Cu^{2+}
$CuCl^{+}$
$CuCl_2$
$CuCl_3^{-}$
$Cu(OH)_2$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_3^{2-}$
2
1
0
-1
-2
E_{SHE} / V
0
2
4
6
8
10
pH
t=150°C

A2:21


(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 μM
$[Cl^{-}]_{TOT}$= 200.00 mM
Cu^{2+}
$CuCl^{+}$
$CuOH^{+}$
$Cu(OH)_2$
$CuCl_2$
$Cu(OH)_3^{-}$
$Cu(OH)_4^{2-}$
$CuCl_2^{-}$
$Cu(OH)_2^{-}$
2
1
0
-1
-2
E_{SHE} / V
0
2
4
6
8
10
pH
t=150°C

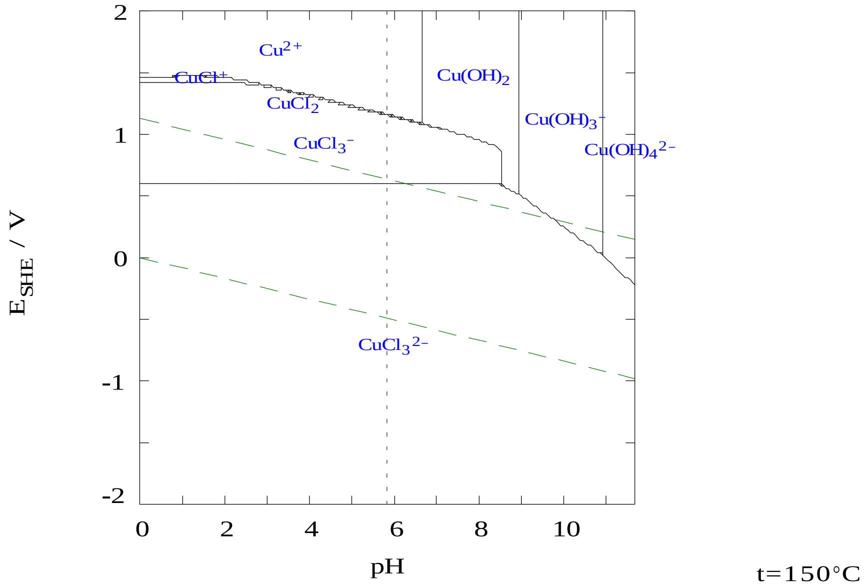
A2:22

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM $[Cl^{-}]_{TOT}$= 1.50 M



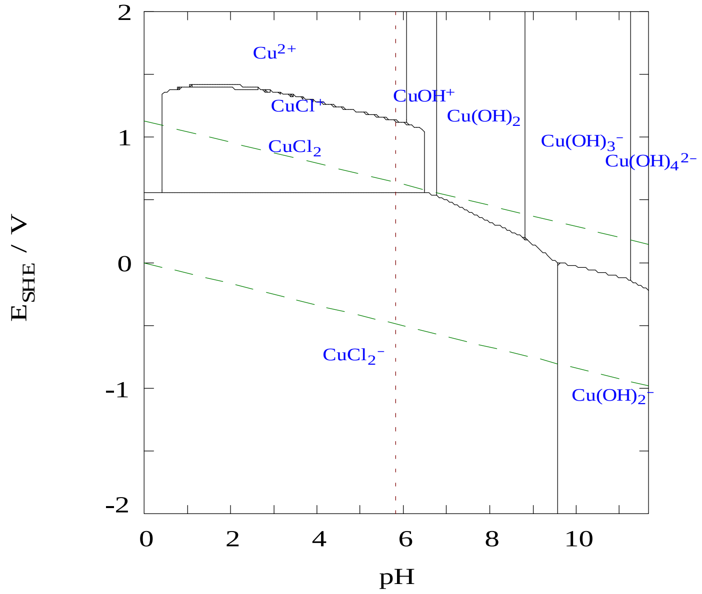
A2:23

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 1.00 µM $[Cl^{-}]_{TOT}$= 5.00 M



A2:24

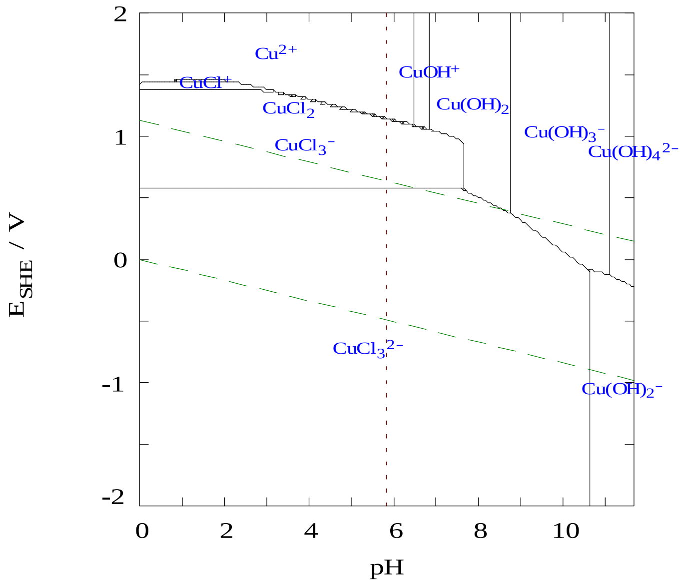
(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM $[Cl^{-}]_{TOT}$= 200.00 mM



t=150°C

A2:25

(aqueous species only)
I= varied
$[Cu^{2+}]_{TOT}$= 0.10 mM $[Cl^{-}]_{TOT}$= 1.50 M



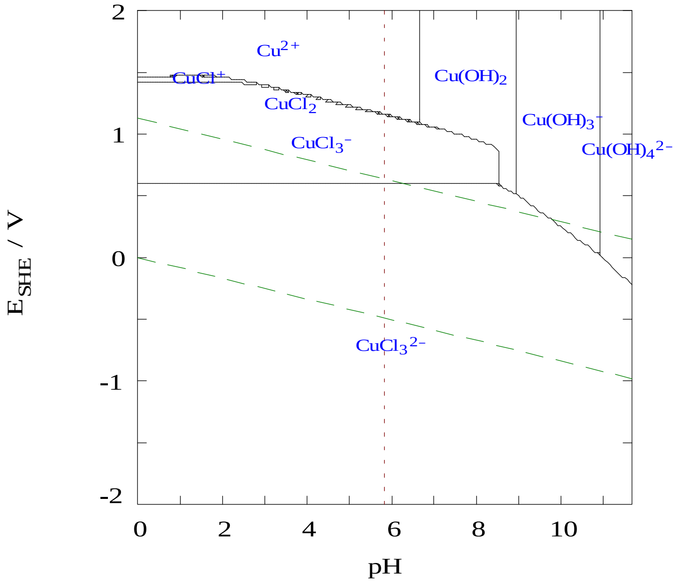
t=150°C

A2:26

(aqueous species only)

I= varied

$[Cu^{2+}]_{TOT}$= 0.10 mM $[Cl^{-}]_{TOT}$= 5.00 M



t=150°C

A2.27