Technical Report

TR-00-13

Thermodynamic data for copper

Implications for the corrosion of copper under repository conditions

I Puigdomenech
Royal Institute of Technology, Stockholm

C Taxén
Swedish Corrosion Institute, Stockholm

August 2000

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

Thermodynamic data for copper

Implications for the corrosion of copper under repository conditions

I Puigdomenech
Royal Institute of Technology, Stockholm

C Taxén
Swedish Corrosion Institute, Stockholm

August 2000

ABSTRACT

The stability of copper canisters has a central role in the safety concept for the planned nuclear spent fuel repository in Sweden. The corrosion of copper canisters will be influenced by the chemical and physical environment in the near-field of the repository, and thermodynamic equilibrium calculations provide the basis for understanding this system.

Thermodynamic data have been selected in this work for solids and aqueous species in the system: Cu - H_2O - H^+ - H_2 - F^- - Cl^- - S^{2-} - SO_4^{2-} - NO_3^- - NO_2^- - NH_4^+ - PO_4^{3-} - CO_3^{2-}. For some reactions and compounds, for which no experimental information on temperature effects was available, entropy and heat capacity values have been estimated. The compiled data were used to calculate thermodynamic equilibria for copper systems up to 100°C.

The stability of copper in contact with granitic groundwaters has been illustrated using chemical equilibrium diagrams, with the following main conclusions:

- Dissolved sulphide and O_2 in groundwater are the most damaging components for copper corrosion. If available, HS^- will react quantitatively with copper to form a variety of sulphides. However, sulphide concentrations in natural waters are usually low, because it forms sparingly soluble solids with transition metals, including Fe(II), which is widespread in reducing environments.
- Chloride can affect negatively copper corrosion. High concentrations (*e.g.*, $[Cl^-]_{TOT} \geq 60$ g/ℓ) may be unfavourable for the general corrosion of copper in combination with in the following circumstances:
    - Low pH ($\lesssim 4$ at 25°C, or $\lesssim 5$ at 100°C).
    - The presence of other oxidants than H^+.

  The negative effects of Cl^- are emphasised at higher temperatures. The chloride-enhancement of general corrosion may be beneficial for localised corrosion: pitting and stress corrosion cracking.

The concept of redox potential, E_H, has been found to be inadequate to describe copper corrosion in a nuclear repository. The available amounts of oxidants/reductants, and the stoichiometry of the corrosion reactions are instead the main parameters in the system.

TABLE OF CONTENTS

1 INTRODUCTION

The SKB concept for disposal of high level nuclear waste includes isolation of spent fuel in copper canisters buried approximately 500 meters deep in granitic bedrock. A critical safety aspect is the chemical stability of the canister.

Repository performance assessment issues related to the chemical stability of the canister material are:

- The presence and fate of molecular oxygen, O_2, which would corrode copper metal.
- Microbial sulphate reduction may produce hydrogen sulphide, HS^-, in the deep environment after the closure of the repository. The presence of sulphide will affect negatively the corrosion properties of the copper canister.
- Chloride concentrations of the groundwaters: high salinities affect both the swelling properties of the bentonite buffer, and the corrosion of copper.

Initial assessments for the corrosion of copper were conducted by the Swedish Corrosion Institute (SCI, 1978; SCI, 1983). These reports established the suitability of copper as a canister material for spent nuclear fuel from the corrosion point of view.

1.1 OBJECTIVES

The main objective of this work is to provide an overview of the thermodynamic constraints on copper corrosion in granitic environments for temperatures up to 100°C. It is therefore intended to be an update of earlier SKB reports (SCI, 1978; SCI, 1983).

An assessment of the thermodynamic data for copper is the basis on which models for copper corrosion can be made. The most important ligands in granitic groundwaters, described in Section 1.2, must be considered. The following components are included in this work: $Cu - H_2O - H^+ - H_2 - F^- - Cl^- - S^{2-} - SO_4^{2-} - NO_3^- - NO_2^- - NH_4^+ - PO_4^{3-} - CO_3^{2-}$.

1.2 HYDROCHEMICAL CONDITIONS FOR THE SWEDISH NUCLEAR WASTE REPOSITORY CONCEPT

SKB has studied the groundwater chemical conditions at repository depth for about 20 years. The studies have shown that the groundwaters can be divided into two distinct groups: fresh waters and saline waters. Table 1 shows compilations of the results obtained that are of importance to the barrier functions of the nuclear fuel, the copper canister, the bentonite buffer and the bedrock (SKB, 1998).

Under the undisturbed conditions in the bedrock at a depth of 500 m the environment is reducing (Grenthe et al., 1992b). Iron and sulphide minerals in the rock will determine the E_H-value of the groundwater. E_H-values between –200 and –400 mV (*versus* the normal hydrogen electrode) have been measured in the Swedish sites investigated by SKB (Grenthe et al., 1992b).

Amounts of dissolved gases vary considerably between location. For instance, the concentration of dissolved molecular hydrogen has been found to vary between 0.1 and 50 μM (Pedersen, 1997). This corresponds to equilibrium partial pressures for $H_2(g)$ of 10^{-4} to 0.07 bar, respectively.

The temperature in the canister surface is expected to be as high as ≈80°C after repository closure, gradually decreasing to typical temperatures of around 15°C.

Characteristic hydraulic pressures at repository depth are ≈45 bar. Under glacial periods larger pressures might prevail, perhaps as large as 250 bar.

1.3 PRACTICAL EXPERIENCE OF THE INFLUENCE OF WATER COMPOSITION ON THE CORROSION OF COPPER

Experience of the corrosion of copper and its alloys comes from several types of investigations:

- Details used under service conditions
- Controlled exposures
- Electrochemical or chemical experiments

The corrosion problems that are discussed in the literature can roughly be grouped into six categories.

- Pitting corrosion with the perspective of damage to the construction (plumbing)
- General corrosion with the perspective of pollution of the corrosive medium (tap water)
- Erosion corrosion - effects of flow rate
- Environmentally assisted cracking

- Atmospheric corrosion or staining
- Corrosion in soil

Table 1. The concentration intervals (in mg/ℓ) for 95 % and 99 % of all observations from locations with fresh and saline groundwaters.

Fresh Groundwaters

Component	95 % of all observations	Median value	99 % of all observations
pH	6.2 - 9.2	8.1	6.1 - 9.3
Cl^-	0.6 - 440	5.8	0.5 - 470
SO_4^{2-}	0.1 - 230	3.0	0.1 - 480
HCO_3^-	9 - 270	120	7 - 300
Ca^{2+}	3 - 110	16	2 - 190
K^+	0.5 - 5	1.8	0.1 - 6.2
Fe (dissolved)	0.007 - 20	0.88	0.004 - 28
HS^-	0.01 - 1.1	0.01	0.01 - 1.2
TOC	1.2 - 40	4.4	0.5 - 6.7

Saline Groundwaters

Component	95 % of all observations	Median value	99 % of all observations
pH	6.3 - 8.4	7.9	6.0 - 8.5
Cl^-	9.6 - 30000	4200	5.7 - 47000
SO_4^{2-}	21 - 930	280	17 - 1100
HCO_3^-	7 - 320	61	6 - 450
Ca^{2+}	15 - 13000	1100	10 - 20000
K^+	1.3 - 30	6.8	1 - 33
Fe (dissolved)	0.02 - 3.2	0.34	0.003 - 4.4
HS^-	0.01 - 2.6	0.41	0.01 - 5.0
TOC	0.5 - 24	5.9	0.1 - 29

Copper metal in water is not stable against oxidation in the presence of dissolved oxygen. Copper(I)oxide is almost invariably found at the metal surface. This oxide is however also unstable with respect to oxidation and with respect to dissolution. A second layer is frequently found on top of the Cu_2O. This layer consists of Cu(II) in the form of CuO or in the form of basic salts, mainly with carbonate but sometimes also basic salts with sulphate, chloride, nitrite or phosphate can be found. Successful application of copper in aerated systems seems to be dependent on the properties of both these more or less protective layers of corrosion products.

Copper in plumbing systems is also affected by organic matter in the water including live bacteria. The effect on corrosion of organic components in the water may depend on the actual substance. One effect found in waters from shallow sources is that the water may contain a naturally occurring organic inhibitor. This inhibitor reduces the rate of the electrochemical oxygen reduction, which is manifested as a decrease in the corrosion potential. Because of the lower corrosion potential, pitting corrosion of copper is seldom observed in natural waters form shallow sources (Cornwell et al., 1973; Cornwell et al., 1976).

Another effect of organic matter is that it can bind copper by complex formation. Increased concentrations of copper in tap waters have been attributed to natural organic matter (Elfström Broo et al., 1998).

Bacteria have a tendency to form colonies at the inner walls of copper plumbing tubes. These colonies form what is called a biofilm by dead and live bacteria and excreta. The role of the biofilm on corrosion is not fully understood but it is sometimes associated with pitting corrosion of copper but also with increased copper concentrations in the water (Wagner et al., 1996).

The literature on the corrosion of copper is rather extensive and sometimes apparently contradictory. Investigated conditions are usually at the border between corrosion and passive behaviour of copper. Thermodynamics is most successful in predicting the border between immunity and possible corrosion. Attempts to apply equilibrium considerations to predict and explain corrosion as opposed to passive behaviour has met with limited success (Edwards et al., 1994a). One reason for these shortcomings may be that thermodynamics can only predict the existence and solubility of a solid phase. How adherent and covering the solid is and what degree of protection is conferred to the underlying metal is not predicted by thermodynamics alone.

A major part of the literature deals with conditions far from that of a copper canister in bentonite. Mass transport limitations can be predicted to play a much more dominating role in the stagnant bentonite system than in copper plumbing systems. The absence of convection around the copper canister in a repository limits the supply of oxygen, which is the main oxidant or electron acceptor, but also affects the rates with which corrosion products are transported away. There is also very little in the literature on such a large construction in such a conducting medium as a copper canister in bentonite. Theoretically, this open geometry could support much higher cathode/anode area ratios than the confined geometry of the internal surface of a copper plumbing tube. A high cathode/anode area ratio could imply few and deep corrosion pits.

The closest analogues to the copper canister in bentonite are perhaps grounding plates for lightning shields. These were usually made of copper and were intentionally buried in high conductivity soil. SKB have therefore had a number of such grounding plates examined with respect to corrosion.

Yet another effect imposed by the compacted bentonite is that mechanical work will have to be exerted by the corrosion process to allow the volume expansion associated with the precipitation of solid corrosion products. The swelling pressure of the bentonite will press the solid corrosion products against the metal surface. This pressure is likely to decrease the porosity of the corrosion products. The resulting, more dense, oxide layer is likely to be more protective. The swelling pressure of the bentonite is therefore predicted to promote passive behaviour rather than corrosion.

With all these reservations as to the applicability of the experience from service and from exposure tests and electrochemical experiments, some conclusions can still be drawn about the likely role of the different anions.

Carbonate stabilises the +II oxidation state of copper. Complex formation is mainly as $CuCO_3(aq)$ but also as $Cu(CO_3)_2^{2-}$. The pH-dependence of the carbonate ion is such that the stabilisation is stronger at the higher pH of the bulk than at a lower pH of a corrosion pit.

The acid-base couple $H_2CO_3(aq)$-HCO_3^- is a major pH-regulating system in many natural waters as well as in tap waters. In a corrosion pit the transport of hydrogen carbonate into the pit and the diffusion of carbonic acid out from the pit has the effect of increasing the transference number for H^+. carbonate thereby favours the processes that release H^+ in a pit.

The process that may ultimately stop a corrosion pit from growing is formation a covering layer of $Cu_2O(s)$ at the metal surface. This process releases protons. High concentrations of carbonate in the water are therefore beneficial against pitting corrosion (Adeloju and Duan, 1994).

Basic carbonate salts of copper are commonly found at corroded copper surfaces. Precipitation of calcium carbonate on copper tube walls is associated with a particular type of corrosion pits where the reduction of oxygen seems to take place at the site of the corrosion pit. Practical experience and laboratory experiments indicate that carbonate is beneficial with respect to pitting corrosion (Adeloju and Duan, 1994; Mattsson and Fredriksson, 1968) but the rate of general corrosion may increase with increasing carbonate concentrations (Edwards et al., 1996; Elfström Broo et al., 1997; Francis et al., 1990; Thomas and Tiller, 1972).

Sulphate stabilises the +II oxidation state of copper. Complex formation is in the form of CuSO4(aq). Because of the higher charge, the sulphate ion has a stronger tendency to accumulate in a corrosion pit than chloride, nitrate and hydrogen carbonate. The stabilisation of the aqueous +II oxidation state is therefore stronger in a corrosion pit than in the bulk solution. High sulphate concentration in the water is detrimental with respect to pitting corrosion (Al-Kharafi et al., 1987; Mattsson and Fredriksson, 1968; Shalaby et al., 1990). Basic sulphate salts of copper(II) is sometimes found at copper surfaces.

Sulphide forms very stable solid compounds with copper. There are however only weak aqueous complexes formed between copper and sulphide. Localised corrosion usually requires a high solubility of the corrosion product. In a system with a moderate excess of sulphide, the solubility of the corrosion products of copper is very low. So, while the presence of sulphide in the system allows corrosion of copper to occur also at low potentials, the minimum potential required for pitting corrosion is probably not lower because of the presence of sulphide.

Nevertheless, the presence of dissolved hydrogen sulphide in the water has been associated with pitting corrosion of copper and copper alloys. The copper sulphide film formed in polluted seawater is more cathodic than the corrosion film developed in clean seawater. If there are breaks in the sulphide film, local attack is stimulated by the large area of active cathode (Schumacher, 1979).

Chloride stabilises the oxidation states +I and +II of copper. Both oxidation states form series of chloride complexes. Apart from sulphide, chloride is the anion that has the greatest influence on the low potential stability limit for copper metal.

The role of chloride in the pitting corrosion of copper is complex. CuCl(cr) is frequently, but not always, found at the bottom of corrosion pits. Aqueous Cu(I) complexes can precipitate as Cu_2O(cr) when the pH is high enough. It seems likely that there are pH gradients not only in corrosion pit but also in a porous oxide film on copper during general corrosion. The lowest pH at the corroding metal is then caused by the fraction of the oxidised copper that forms Cu_2O as the site of corrosion. As higher pH values are encountered more and more of the aqueous chloride complexes of Cu(I) precipitate as Cu_2O. The result is a thick and protective oxide layer on the copper metal (Drogowska et al., 1994). Although chloride in short-term electrochemical experiments causes micro-pits in copper, the long-term seems to be beneficial (Edwards et al., 1994b). A basic chloride salt of copper(II) is sometimes found at corroded copper surfaces.

2 METHODOLOGY

Effects on the corrosion of copper have been estimated by calculating equilibrium chemical compositions, and displaying the results in diagrams. Chemical thermodynamics is the theoretical foundation of such calculations. The methods used are summarised in this section.

2.1 THERMODYNAMIC DATA

Equilibrium constants are calculated from thermodynamic data according to,

$$\ln K^\circ = -\frac{1}{RT}\sum_i \nu_i \;\Delta G^\circ_\mathrm{f}(i)$$

where K° is the standard equilibrium constant, R is the gas constant, T is the absolute temperature, $\Delta G^\circ{}_\mathrm{f}(i)$ is the Gibbs energy of formation for a reactant (or product) "*i*", and ν_i is the corresponding stoichiometric coefficient.

Selected values of $\Delta G^\circ{}_\mathrm{f}(i)$, and the selection criteria are described in Section 7 (Appendix).

Medium effects have been incorporated with the equations described below in Section 2.2, while temperature extrapolation methods are given in Section 2.3.

2.2 IONIC STRENGTH EFFECTS

When equilibrium constants are calculated from thermodynamic data, the values obtained are valid for ideal solutions (standard state, equivalent to zero ionic strength). It is necessary to know, however, the values of the equilibrium constants for the ionic medium of the system being modelled.

For a general equilibrium reaction

$$n\,\mathrm{A} + m\,\mathrm{B} \rightleftharpoons p\,\mathrm{C} + q\,\mathrm{D}$$

the relationship between its standard equilibrium constant and the value for a given ionic medium is

$$\begin{aligned} K^\circ{}_\mathrm{eq} &= a_\mathrm{C}{}^{p}\, a_\mathrm{D}{}^{q}\, a_\mathrm{A}{}^{-n}\, a_\mathrm{B}{}^{-m} \\ &= \gamma_\mathrm{C}{}^{p}\,[\mathrm{C}]^{p}\;\; \gamma_\mathrm{D}{}^{q}\,[\mathrm{D}]^{q}\;\; \gamma_\mathrm{A}{}^{-n}\,[\mathrm{A}]^{-n}\;\; \gamma_\mathrm{B}{}^{-m}\,[\mathrm{B}]^{-m} \\ &= \gamma_\mathrm{C}{}^{p}\,\gamma_\mathrm{D}{}^{q}\,\gamma_\mathrm{A}{}^{-n}\,\gamma_\mathrm{B}{}^{-m}\,K_\mathrm{eq} \end{aligned}$$

where: brackets, [], indicate concentrations; a_i and γ_i are the activity and the activity coefficient of species "*i*" respectively; and $K^\circ{}_\mathrm{eq}$ and K_eq are the equilibrium constant for standard and non-standard conditions, respectively.

For neutral aqueous species it is usually approximated that the activity coefficients are unity at all values of ionic strength and temperature. This has in general negligible effects on calculated equilibrium compositions.

For ionic species several models may be used to describe activity coefficients as a function of the chemical composition of the medium. These models have often limited ranges of applicability (in terms of temperature, pressure and ionic composition).

2.2.1 Activity Coefficients in Calculated Equilibrium Diagrams

In the calculations to create equilibrium diagrams, the activity coefficients, γ_i, have been approximated by a slight modification of the model by Helgeson *et al.*, *cf.* Eqs. 121, 165-167, 297, and 298 in (Helgeson et al., 1981); and Eqs. 22 and 23 in (Oelkers and Helgeson, 1990):

$$\log \gamma_i = -\frac{z_i^2 A \sqrt{I}}{1 + B\mathring{a}\sqrt{I}} - \log(1 + 0.018015 I) + b\, I \qquad (1)$$

For moderate ionic strengths, this model gives results quite similar to those of the Davies expression, Eq.(7) in the Appendix. In the Helgeson model, Eq.(1), I is the ionic strength, A, B, and b are temperature-dependent parameters, z_i is the electrical charge of the species i, and $\mathring{a}$ is a "distance of closest approach", which may be taken to be equal to that of NaCl (3.72×10^{-10} m). The values of A, B, and b as a function of temperatures are:

T / °C	p / bar	A	$B \times 10^{-10}$	b
0	1.000	0.491	0.325	0.041
25	1.000	0.509	0.328	0.064
100	1.013	0.600	0.342	0.076
150	4.76	0.690	0.353	0.065

Eq.(1) offers the advantage of simplicity as compared with the SIT model, Eq.(6) described in the Appendix. For the SIT model several ε-values and their temperature dependence are required, while this is not necessary for the Helgeson model. This makes Eq.(1) appropriate for model simulations where ionic medium effects of moderate accuracy may be sufficient.

2.3 TEMPERATURE EXTRAPOLATIONS

Temperature effects for solids and gaseous compounds have been obtained from the integrals of the heat capacity temperature functions,

$$\Delta G°(T) = \Delta G°(T_0) - (T - T_0)\Delta S°(T_0) + \int_{T_0}^{T} \Delta C_p^\circ \,\mathrm{d}T - T\int_{T_0}^{T} \frac{\Delta C_p^\circ}{T}\,\mathrm{d}T \qquad (2)$$

This procedure is described in many references, for example in (Kubaschewski et al., 1993; Puigdomenech et al., 1997).

For aqueous species the $C_p°$-equations in the revised Helgeson-Kirkham-Flowers (HKF) model have been used (Shock and Helgeson, 1988; Shock et al., 1989; Shock et al., 1992; Tanger and Helgeson, 1988). Some simplifications have been applied to use this model when only the value of $C_p°$ at 25°C is available. For each aqueous species, the values of $C_p°$ and $S°$ at 25°C are used to estimate the parameters in the revised HKF-model: c_1, c_2 and ω, *cf.* Eqs. 29, 31, 35, 45, 56, 57 and 89 in (Shock and Helgeson, 1988), and Eqs. 21, 23, 26, 44 and 45 in (Shock et al., 1989). With this simplifications, the apparent standard partial molar Gibbs free energy of formation, $\Delta G_a°$, for aqueous species participating in a chemical reaction can be calculated at higher temperatures. The equilibrium constants are calculated as a function of T, from the $\Delta G_a°$ values, *cf.* Eqs. 93 and 94 in (Shock and Helgeson, 1988). The complete procedure is also described in (Sverjensky et al., 1997).

However, given the limited temperature range considered here, *i.e.* up to 100°C, the temperature extrapolation method used for aqueous species is not crucial for the calculation results. The uncertainties in the thermodynamic data are as a rule much larger than the problem of selecting an adequate T-extrapolation method for this T-range. This is illustrated with an example in Figure 1.

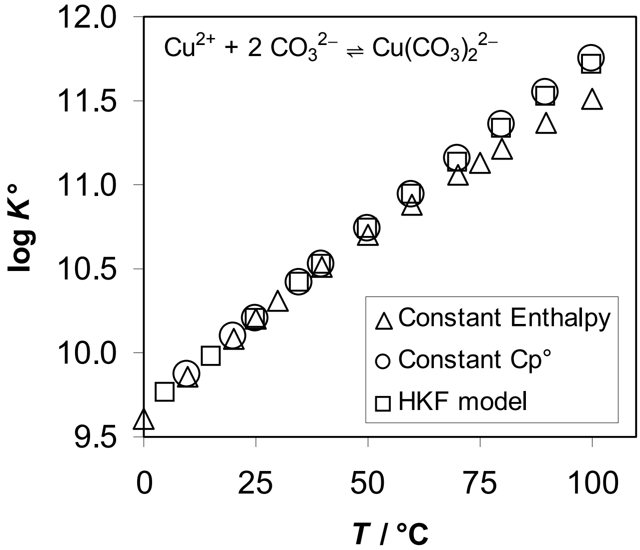


Figure 1. Calculated equilibrium constant for reaction: $Cu^{2+} + 2\ CO_3^{2-} \rightleftharpoons Cu(CO_3)_2^{2-}$ according to data in Table 2 and different temperature extrapolation methods.

2.4 PRESSURE EFFECTS

In the Swedish concept for a spent nuclear fuel repository, the hydrostatic pressure at depth is expected to be at least 45 bar. The swelling pressure of bentonite, must be added to that. Furthermore, during cold climatic conditions, it is anticipated that a thick ice sheet (perhaps 2000 m) will form above the repository. The ice sheet will also increase the hydrostatic pressure at depth. In summary, pressures perhaps up to 0.3 kbar should be expected, at least during some periods of the repository lifetime.

This increased pressure (as compared with the thermodynamic standard of $p° = 1$ bar) is likely to favour the formation of dense phases at the expense of solids with lower density.

2.4.1 Pressure Dependence of Equilibrium Constants

The effect of pressure may be estimated as (Langmuir, 1997; Stumm and Morgan, 1996):

$$\log \frac{K^{\circ}_{p}}{K^{\circ}_{p^{\circ}}} = -\frac{\Delta V^{\circ}_{r}\,(p - p^{\circ})}{\ln(10)\,R\,T}$$

where $p°$ is the standard pressure (1 bar), and $\Delta V°_r$ is the standard molar volume change for the reaction.

Because of lack of molar volume data, especially for aqueous complexes, pressure effects have not been considered in this work. Nevertheless, as will be shown here, pressure effects are not expected to introduce any changes in the conclusions from this work.

It is experimentally found that for dissociation reactions $\Delta V°_r \geq -50$ cm^3/mol, see for example (Langmuir, 1997). Molar volumes for many minerals may be found in (Robie and Hemingway, 1995). The "maximum" value of $\Delta V°_r = -50$ cm^3/mol, corresponds to an increase of 0.26 log-units in the equilibrium constant at 300 bars, which may be compared with the temperature effects shown in Figure 1.

2.4.2 The "Stability Field" of Water in Pourbaix Diagrams

pH/E_{H} predominance diagrams, also called Pourbaix diagrams, are frequently used in corrosion studies. These diagrams usually indicate the stability field of water, which is calculated from the following equilibria:

$$H_2O(l) \rightleftharpoons \tfrac{1}{2}\,O_2(g) + 2\,H^+ + 2\,e^-$$

$$2\,H_2O(l) + 2\,e^- \rightleftharpoons H_2(g) + 2\,OH^-$$

For a given pH, H_2O may be oxidised or reduced with $O_2(g)$ or $H_2(g)$ evolution when the potential falls outside that of the stability field of water. On a Pourbaix diagram these equilibria are indicated with two diagonal dashed lines. These lines indicate the pH/E_H limit at which the pressure of the gas becomes larger than the standard pressure of 1 bar.

Naturally, the stability of water towards oxidation and reduction is dependent on both pressure and temperature, because the equilibrium constants for the corresponding reactions are p- and T-dependent. Furthermore, if the pressure of the system is increased, $O_2(g)$ or $H_2(g)$ evolution can not occur until the system pressure is exceeded and a gas bubble may be formed, and the stability field of water is increased.

2.5 EQUILIBRIUM DIAGRAMS

Equilibrium diagrams have been calculated with computer programs (Puigdomenech, 1983) that use either the SOLGASWATER (Eriksson, 1979) or the HALTAFALL (Ingri et al., 1967) algorithms.

Diagrams have been drawn at 25 and 100°C, a range of temperatures which includes the environment that copper canisters will experience in the proposed Swedish final repository for spent nuclear fuel. To avoid temperature effects in the volume of the aqueous solutions modelled, *molal* concentration units are used (mol/kg of water), and most calculations have been performed at a total concentration of dissolved copper species of 10^{-6} molal.

pH-values are at the specified temperature. The temperature dependence for the ion product of water,

$$H_2O(l) \rightleftharpoons H^+ + OH^-$$

affects the neutral pH value of pure water (neutral pH for aqueous solutions = ½ $pK_{w,T}$).

Electrochemical potentials given in figures, *etc*, are referred to the standard hydrogen electrode (E_{SHE}) at the specified temperature. The standard hydrogen electrode is considered to have zero potential at all temperatures. For brevity, potentials referred to the standard H_2-electrode are often denoted by the symbol E_H (*i.e.*, E_H is equivalent to E_{SHE}).

The *ionic strength* corresponding to each coordinate in the diagrams has been calculated iteratively from the electroneutrality condition: in acid solutions a hypothetical anion has been added to keep the solutions neutral, and on alkaline solutions a cation has been added. The concentration of these hypothetical components has been taken into account when calculating the value of the ionic strength. The electroneutrality condition has a large impact on ionic strength; for example, at pH ≈ 0 electroneutrality implies that $I \geq 1$ mol/kg. *Activity coefficients* have then been calculated with Eq.(1).

3 COPPER CANISTER CORROSION

3.1 GENERAL CONSIDERATIONS

3.1.1 Electron Acceptors

A metal corrodes when it releases electrons:

$$\mathrm{Cu(cr)} \rightleftharpoons \mathrm{Cu}^{2+} + 2\ \mathrm{e}^{-} \qquad (3)$$

these electrons ***must*** be taken up by an oxidant, for example by O_2:

$$\tfrac{1}{2}\ \mathrm{O_2(aq)} + 2\ \mathrm{e}^{-} + 2\ \mathrm{H}^{+} \rightleftharpoons \mathrm{H_2O(l)} \qquad (4)$$

or

$$\tfrac{1}{2}\ \mathrm{O_2(aq)} + 2\ \mathrm{e}^{-} + \mathrm{H_2O(l)} \rightleftharpoons 2\ \mathrm{OH}^{-} \qquad (5)$$

without the presence of an electron acceptor, corrosion is ***not*** possible. Many substances may act as electron acceptors. The main oxidants in groundwater systems are: hydrogen ions, nitrate, sulphate, and iron(III). However, many redox reactions require the “catalytic action” of bacteria, for example the reduction of sulphate

$$\mathrm{SO_4}^{2-} + 9\ \mathrm{H}^{+} + 8\ \mathrm{e}^{-} \rightleftharpoons \mathrm{HS}^{-} + 4\ \mathrm{H_2O}$$

is only achieved bacterially in low temperature environments.

3.1.2 Thermodynamic Considerations

The oxidation-reduction reaction must be thermodynamically possible. If there is no energy gain, no corrosion will occur. For example, hydrogen ions, which are present in pure water, may act as electron acceptors:

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightleftharpoons \tfrac{1}{2}\ \mathrm{H_2(aq)}$$

It is found that energetically H^+ is an adequate electron acceptor for the corrosion of iron metal in pure water:

$$\mathrm{Fe(cr)} + 2\ \mathrm{H}^{+} \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{H_2(aq)}$$

for this reaction $\log K° = 13.0$ (at 25°C) gives $[\mathrm{Fe}^{2+}] = 0.3$ mol/kg at pH = 7. On the other hand, it may be seen that pure water does not contain electron acceptors adequate for the corrosion of copper. The corresponding reactions:

$$\mathrm{Cu(cr)} + \mathrm{H}^{+} \rightleftharpoons \mathrm{Cu}^{+} + \tfrac{1}{2}\ \mathrm{H_2(aq)}$$

$$\mathrm{Cu(cr)} + 2\ \mathrm{H}^{+} \rightleftharpoons \mathrm{Cu}^{2+} + \mathrm{H_2(aq)}$$

$$\mathrm{Cu(cr)} + \mathrm{H_2O} \rightleftharpoons \mathrm{CuO(cr)} + \mathrm{H_2(aq)}$$

are unfavourable energetically, with log $K°$ = −10.1, −14.5 and −22.2 respectively (at 25°C). These equilibrium constants give at pH = 7: $[Cu^+] = 10^{-11.3}$ mol/kg, $[Cu^{2+}] = 10^{-14.3}$ mol/kg , and $[H_2(aq)] = 10^{-22.2}$ mol/kg, respectively. This indicates that copper does not corrode appreciably in pure water.

3.1.2.1 The Corrosion Potential

During corrosion of a metal there are, at least, two processes that strive to control the potential of the metal. One redox potential may be defined by the reduction of the electron acceptor, *e.g.*,

$$\tfrac{1}{2}\,O_2(aq) + 2\,e^- + H_2O(l) \rightleftharpoons 2\,OH^- \qquad (5)$$

and another potential is defined by the oxidation of the electron donor:

$$Cu(cr) \rightleftharpoons Cu^+ + e^-, \qquad \text{or}$$

$$Cu(cr) \rightleftharpoons Cu^{2+} + 2\,e^-$$

Corrosion is possible only when the electron acceptor or oxidant defines a higher redox potential than the donor. The difference between the two redox potentials can be said to be the driving force for corrosion. Because of its good electrical conductivity, a metal has only one electrical potential. A common potential is established as a compromise between the redox potential defined by the electron acceptor and that defined by the electron donor. This potential, the corrosion potential, is always lower than the redox potential of the electron acceptor and higher than that of the electron donor.

3.1.2.2 The Formation of Secondary Products

The formation of stable complexes and insoluble solids will in general favour the corrosion process. For example, in the presence of sulphides copper(I) forms very insoluble solids. In the presence of sulphide, hydrogen ions which are always present in water, act as electron acceptors:

$$2\,Cu(cr) + S^{2-} + 2\,H^+ \rightleftharpoons Cu_2S(cr) + H_2(g)$$

3.1.3 General and Localised Corrosion

Metals are sometimes found to corrode uniformly throughout the surface in contact with a source of electron acceptors.

However, because metals are good electrical conductors, the electrons released through reaction (3) do not need to be taken by the electron acceptor in the same location. Reaction (4) may occur in a part of the metal surface which apparently is not corroding.

In the case of copper, this spatial separation between sites for metal oxidation and oxygen reduction may result in pitting corrosion. Pitting corrosion is a phenomenon observed on copper and many other metals and alloys such as aluminium and iron and stainless steels. A necessary condition for pitting is that electric charge can be transported not only in the metal but also in the corrosive medium. We shall here consider only cases where the medium can be described as an aqueous electrolyte, *i.e.* water with some dissolved salts. Soil or clay can be treated within that description provided that there is an aqueous phase that allows transport of reactants and corrosion products. In aqueous solutions the electric charge is transported by ions.

3.1.3.1 The Composition of the Solution in a Corrosion Pit

In the case of pitting corrosion of copper, the metal is oxidised to Cu^{2+} and Cu^{+} at the bottom of the corrosion pit. Complex formation, mainly with chloride and sulphate, takes place so that the composition of the solution approaches local equilibrium. The concentration gradient causes the aqueous Cu(II) and Cu(I) to diffuse outwards from the site of oxidation. The continuous production of positive charge in the solution at the bottom of the pit causes an electric field to arise. The polarity of this field is such that ions carrying positive charge are driven out of the pit and negative ions are driven into the pit. Thus, there are two phenomena that cause negatively charged ions to enrich in the pit solution. There is a diffusion gradient caused by complex formation with copper ions (this applies also to neutral ligands) and there is an attraction from the electric field.

For non-reacting ions the electric field tends to generate a concentration gradient such that diffusion and migration cancel. If changes in activity coefficients are neglected, the concentration profile can be described by (Shinohara et al., 1997):

$$C_{\text{in}} = C_{\text{out}} \cdot \exp(-\frac{zF\Delta\Phi}{RT})$$

where C_{out} is the bulk concentration, C_{in} is the concentration at a particular location in the pit and $\Delta\Phi$ is the corresponding potential difference. Since both Cl^{-} and SO_4^{2-} form complexes with copper ions, the equation above gives perhaps a poor approximation, but the higher charge of the sulphate ion results in a stronger accumulation than for chloride. Even when SO_4^{2-} is a minor species in the bulk it may become a major anion in the pit (Taxén, 1996).

3.1.3.2 The pH of the Solution in a Corrosion Pit

The pH of the solution in a corrosion pit is generally lower than outside. Several types of reactions may contribute to this local acidification:

- Precipitation of oxides or mixed hydroxides, *e.g.*:

$$2\,Cu^{+} + H_2O \rightleftharpoons Cu_2O(cr) + 2\,H^{+}$$

$$Cu^{2+} + H_2O \rightleftharpoons CuO(cr) + 2\,H^{+}$$

$$4\,Cu^{2+} + 2\,Cl^{-} + 6\,H_2O \rightleftharpoons CuCl_2{\cdot}3Cu(OH)_2(cr) + 6\,H^{+}$$

- Complex formation, *e.g.*:

$$Cu^{2+} + HCO_3^{-} \rightleftharpoons CuCO_3(aq) + H^{+}$$

- Hydrolysis (complex formation with hydroxide), *e. g.*:

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^{+} + H^{+}$$

- Reactions of minor constituents in an alloy. For example, copper is frequently alloyed with small amounts of phosphorous:

$$P(\text{in Cu}) + 4\,H_2O \rightleftharpoons H_2PO_4^{-} + 6\,H^{+} + 5\,e^{-}(\text{in Cu})$$

All of these reactions may take place in one single corrosion pit but at different locations, corresponding to different local pH values. Each reaction has its own region of importance where it may contribute to the local acidification. The reactions listed above are only examples and the equilibrium composition consists of a whole range of products of hydrolysis and complex formation.

Because of the enrichment of negatively charged ions which may act as ligands to Cu^{2+} and Cu^{+}, and because of the decreased pH in the pit, the solution is much more corrosive than the medium when it is unaffected by the corrosion processes. This is of course not only a result of the locally high corrosion rate but also a cause. Pitting corrosion is an autocatalytic process such that the locally higher corrosion rate in the pit creates local conditions that lead to a locally higher corrosion rate.

3.1.4 Stress Corrosion Cracking

A special form of localised corrosion can occur on a metal under mechanical strain. This, so called stress corrosion or stress corrosion cracking (SCC) is usually associated with a particular environment. For copper alloys a typical environment promoting stress corrosion cracking is a solution containing nitrite or ammonia (Beavers, 1992). For copper-zinc alloys the tendency for SCC decreases with decreasing zinc concentration. But also for 99.999 % pure copper there is a tendency to crack under mechanical strain. The time to failure was found to show a minimum at a characteristic concentration. At 70°C the critical concentration NH_4OH was 0.05 mol/ℓ and higher at lower temperatures (Suzuki and Hisamatsu, 1981).

3.1.5 Factors Affecting Corrosion

Corrosion processes are greatly affected by the accessibility of oxidants and by the overall energy gain in the process. Various types of barriers frequently limit the rate of corrosion.

Probably the most important barrier is the oxide layer formed on the metal surface (passivation). Indeed, most of the common construction metals and alloys have so low thermodynamic stability that it is only because the underlying metal is partly protected by this self-repairing oxide barrier that acceptable lifetimes are achieved.

The barrier effect of an oxide layer may be twofold. It may prevent an oxidant from coming in direct contact with the metal and thereby interfere with the electrochemical reduction of the oxidant. It may also protect the underlying metal from direct contact with the corrosive medium. Of these two effects the latter seems to be the most important. Metal oxides can some times behave as electronic conductors and allow the reduction to take place on the oxide surface instead of the metal surface. Moreover, passivity is associated with relatively high corrosion potentials. This indicates that there is no lack of electron acceptors but that the low corrosion rate is a result of that the metal atoms are prevented from reaching a low energy state as ions in the solution or as oxide at the surface. Thus, there are energy aspects also to the effects of mass transport and barriers. The following separation of factors affecting corrosion, into two categories may nevertheless be meaningful:

- Access to electron acceptors:
    - Renewal of the electron acceptors being consumed by transport phenomena, such as diffusion and flow. All processes affecting the transport of chemicals in the system will affect corrosion.
    - Bacterial activity affects the availability of oxidants, for example by facilitating the reduction of sulphate, iron(III) oxides, *etc*.
- Energetic factors:
    - The formation of complex ions in solution or insoluble solid phases with the metal cation will favour corrosion from the thermodynamic standpoint. The presence of ligands like chloride, carbonate, phosphate, *etc*, will in general favour corrosion. However, solid corrosion products may in some cases act as a transport barrier (passive film) that hinders further corrosion. The primary effect of hydroxide is to form oxides that may act as passivating films, but at high concentrations, negatively charged hydroxide complexes may increase the solubility of the oxide and favour corrosion.
    - Sorption and ion-exchange reactions may act as sink for the corrosion products, and will favour corrosion in the same way as complex formation.
    - In localised corrosion (pits, crevices, *etc*) the formation of complexes and secondary solids may favour corrosion, but it will also affect the transport of corrosion products into and out from the corroding cavity. These transport aspects might decrease the corrosion rate, or even stop the corrosion process altogether.
    - Localised corrosion requires more energy in the system than general corrosion. The concentration gradients inevitably associated with localised corrosion must be maintained by energy liberated by the corrosion process. Otherwise the local environment will change towards that of general corrosion. Localised corrosion is, in terms of energy, an inefficient type of corrosion. If there is not

enough energy in the system this will result in a relatively low corrosion potential. Pitting corrosion requires a high corrosion potential and there is a potential range where copper is immune against pitting corrosion although not immune against general corrosion (Taxén, 1996).
- Temperature, ionic strength, and to a lesser extend, pressure, will affect the equilibrium constants and rates that govern all chemical reactions.

The focus of this report is on thermodynamic effects: the formation of complexes and secondary solid phases. Many possible ligands are present simultaneously in natural waters, and this must be taken into account when comparing the effects of the different chemical parameters on the corrosion of copper.

3.2 THE CORROSION OF COPPER IN PURE WATER

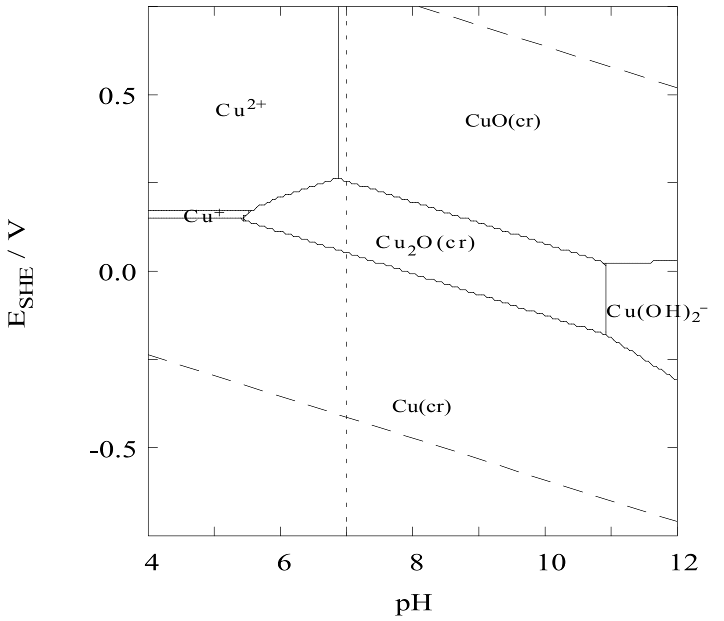
The thermodynamic constraints for the corrosion of copper in pure water have been discussed in (Beverskog and Puigdomenech, 1997a).

Calculated pH/E_H (Pourbaix) diagrams for copper are shown in Figure 2 for 25 and 100°C. The diagrams show that copper does not corrode appreciably in pure water at these temperatures and pH values. The diagrams also show that O_2 reacts with metallic copper to form either soluble ions or oxides.

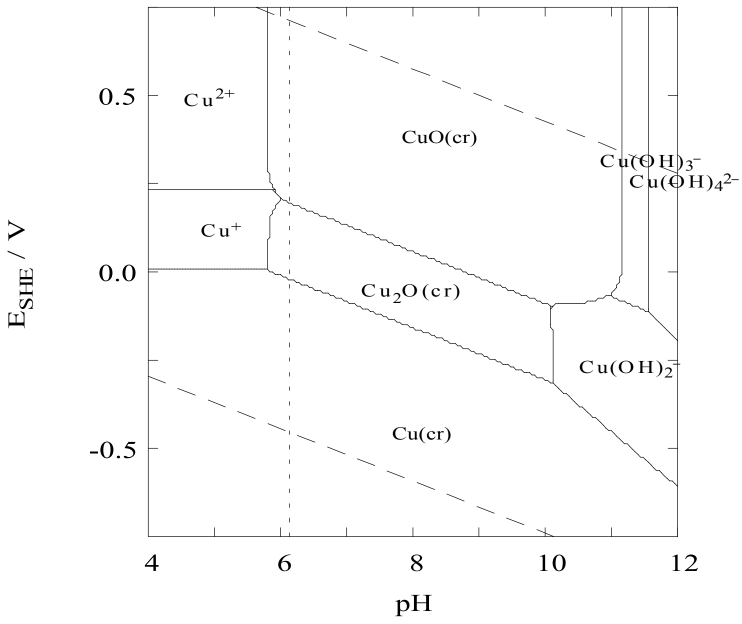
The thermodynamic stability of copper in pure water was questioned by the experiments reported by (Hultquist, 1986; Hultquist et al., 1989) where hydrogen evolution in the copper – pure water system was “demonstrated”. However, this evidence was disproved by later studies (Eriksen et al., 1989; Möller, 1995; Simpson and Schenk, 1987). The calculated partial pressure of $H_2(g)$ for the corrosion of copper in pure water is found from

$$\mathrm{Cu(cr)} + \mathrm{H}^+ \rightleftharpoons \mathrm{Cu}^+ + \tfrac{1}{2}\,\mathrm{H_2(aq)} \qquad \log K° = -10.1$$

which gives $[\mathrm{Cu}^+] = 10^{-11.3}$ mol/kg and $[\mathrm{H_2(aq)}] = 10^{-11.6}$ mol/kg. This corresponds to $P_{\mathrm{H2(g)}} = 10^{-8.5}$ bar.



t= 25°C



t=100°C

Figure 2.a. Pourbaix diagram for copper at 25°C (upper diagram) and 100°C (lower diagram), $[Cu]_{TOT}$ = 1 μmol/kg.

3.3 THE INFLUENCE OF FLUORIDE

Fluoride is commonly found in natural waters. In Swedish groundwaters F^- is a minor component, usually with concentrations below 0.01 mol/dm^3. Its concentration appears to be regulated by the solubility of fluorite, CaF_2(cr), see for example (Nordstrom et al., 1989; Puigdomenech and Nordstrom, 1987).

As described in Section 7.4, only the first Cu(II) complex is formed. The calculated predominance of this complex may be visualised in Figure 3 at $[F^-]_{TOT}$ = 0.01 mol/dm^3, a concentration which is much higher than what may be expected in granitic groundwaters. The influence of fluoride ions in this concentration range on copper corrosion appears to be unimportant.

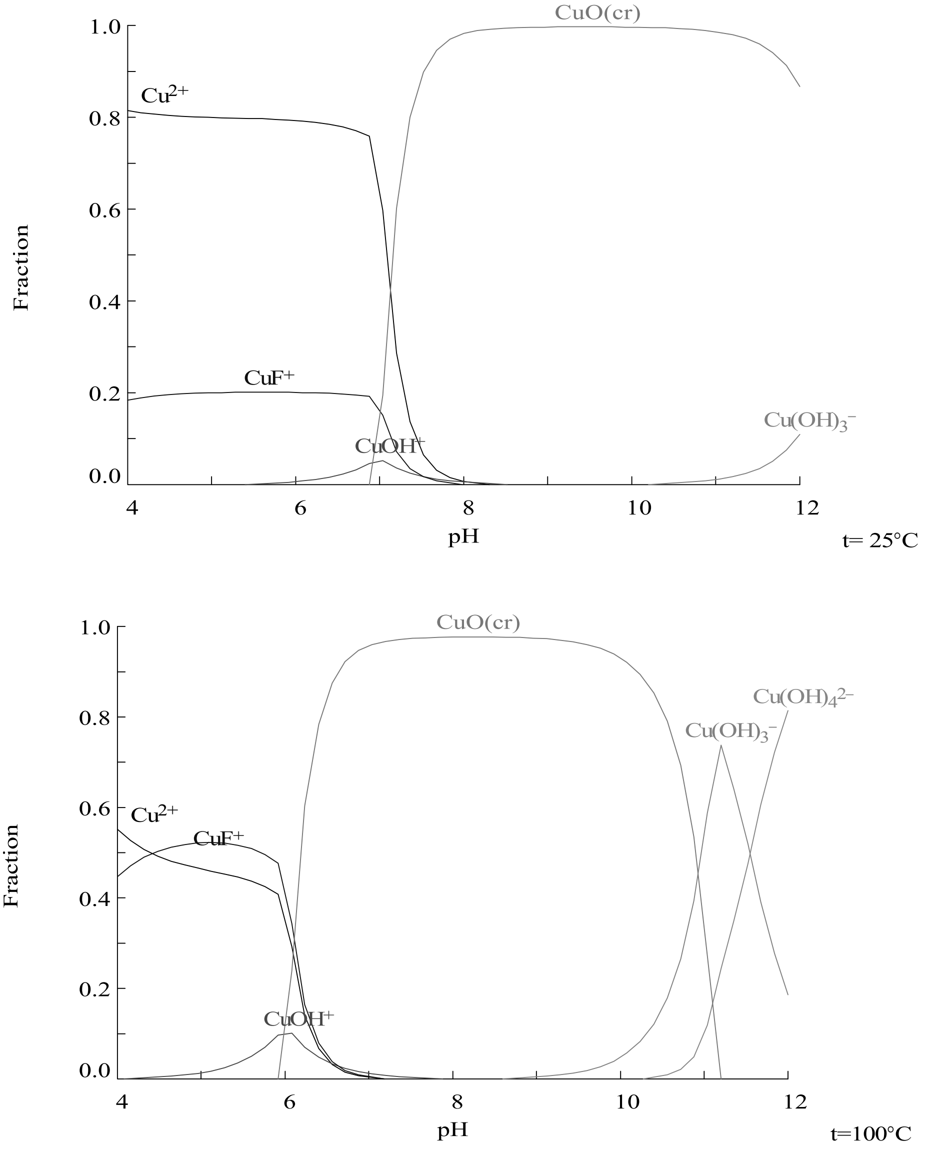


Figure 3. Cu(II)-fraction diagrams in $[F^-]_{TOT}$ = 0.01 mol/kg and $[Cu^{2+}]_{TOT}$ = 1 µmol/kg, at 25 and 100°C (upper and lower diagrams, respectively).

3.4 THE INFLUENCE OF CHLORIDE IONS

Chloride is a common component of natural waters. Most Swedish groundwaters have a Cl^- contents between 10^{-5} and 1.4 mol/dm^3, *cf.* Table 1. Seawater has $[Cl^-]_{TOT} = 0.56$ mol/dm^3. Chloride ions may influence the corrosion of copper by the formation of aqueous complexes and solid phases. The effects of chloride have been previously discussed by (Ahonen, 1995; Ahonen, 1999; Beverskog and Puigdomenech, 1998; SCI, 1983).

3.4.1 Chloride Complexes

The relative stability of the chloride complexes of copper(I) are shown in Figure 4, where it may be seen that the relative stabilities Cu^+ and CuCl(aq) increase substantially at 100°C.

Copper(II) forms weaker chloride complexes, as can be seen by comparing Figure 4 and Figure 5. The effect of temperature on this system is again to increase the stability of the Cu(II)-Cl^- complexes.

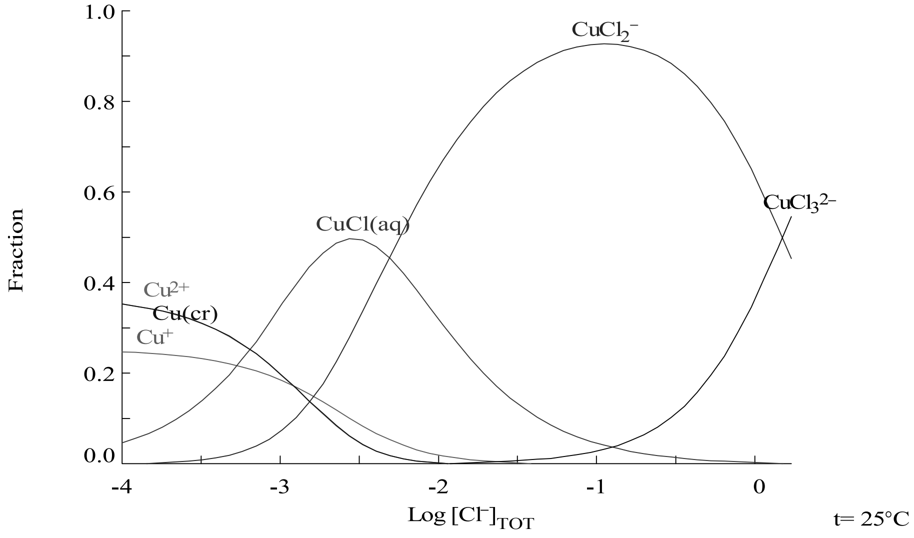


Figure 4.a. Fraction of copper(I) as chloride complexes: 25°C. Diagram calculated for pH = 3, $[Cu]_{TOT} = 10^{-5}$ mol/dm^3, and $[Cl^-]_{TOT}$ between 10^{-4} and 1.7 mol/kg. The diagram shows that at 25°C, Cu^+ does not predominate in the absence of reducing agents: for the given conditions copper(I) disproportionates to copper metal and copper(II) when $[Cl^-] < 0.01$ mol/kg.

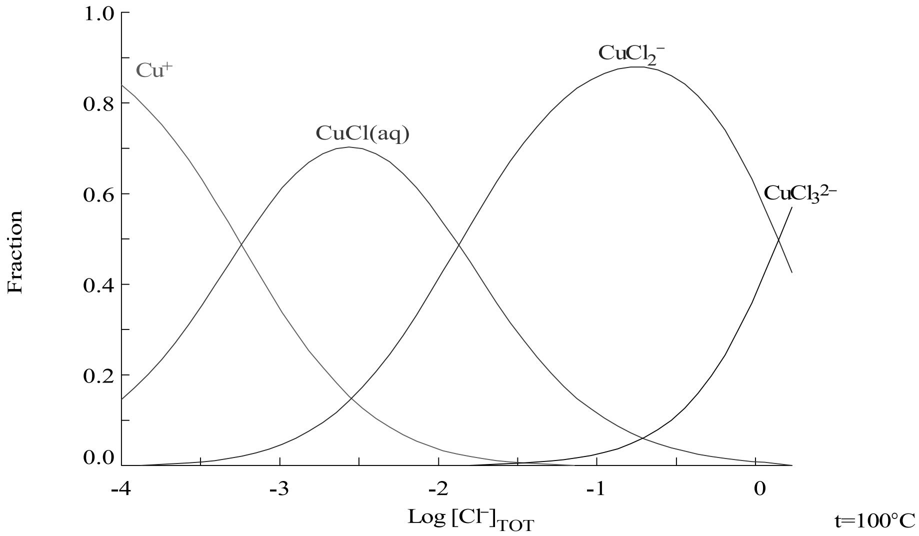


Figure 4.b. Fraction of copper(I) as chloride complexes: 100°C. Diagram calculated for pH = 3, $[Cu]_{TOT} = 10^{-5}$ mol/kg, and for $[Cl^{-}]_{TOT}$ between 10^{-4} and 1.7 mol/kg.

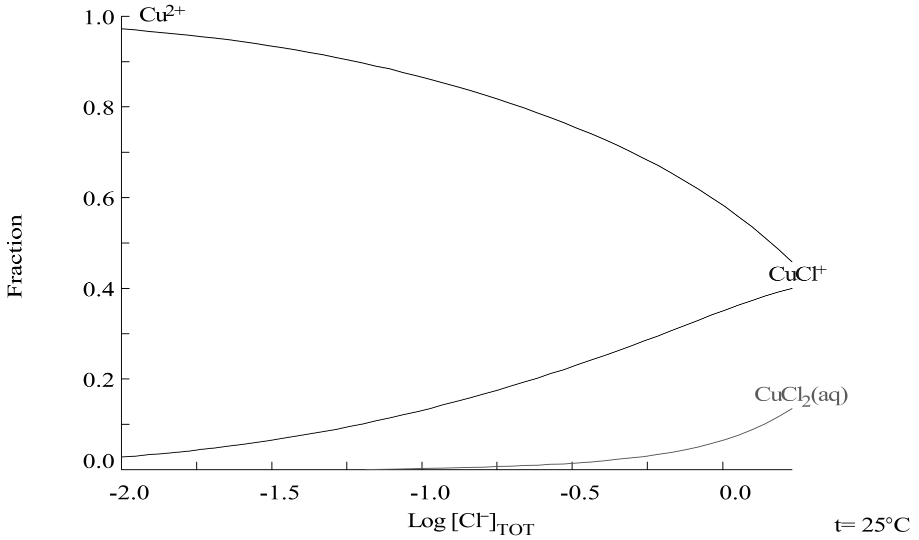


Figure 5.a. Fraction of copper(II) as chloride complexes: 25°C. Diagram calculated for pH = 3, $[Cu]_{TOT} = 10^{-5}$ mol/kg, and for $[Cl^{-}]_{TOT}$ between 0.01 and 1.7 mol/kg.

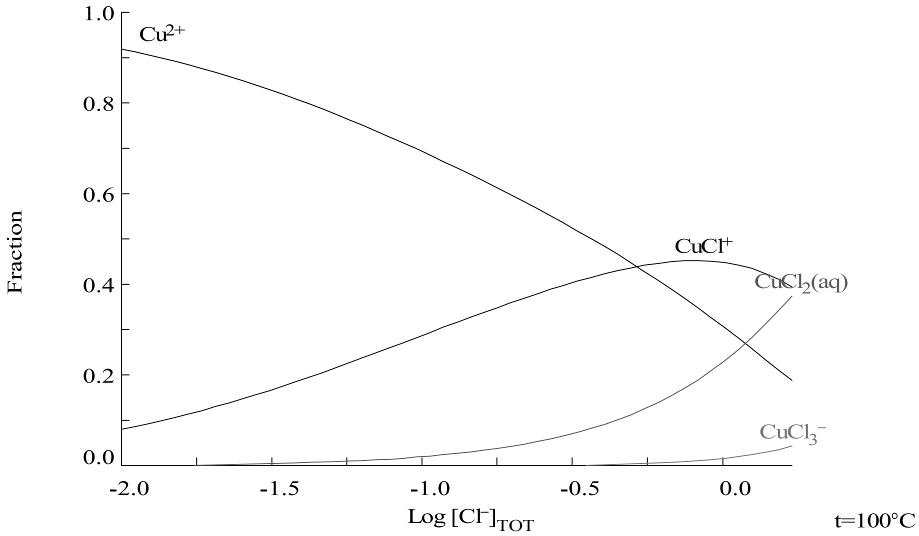


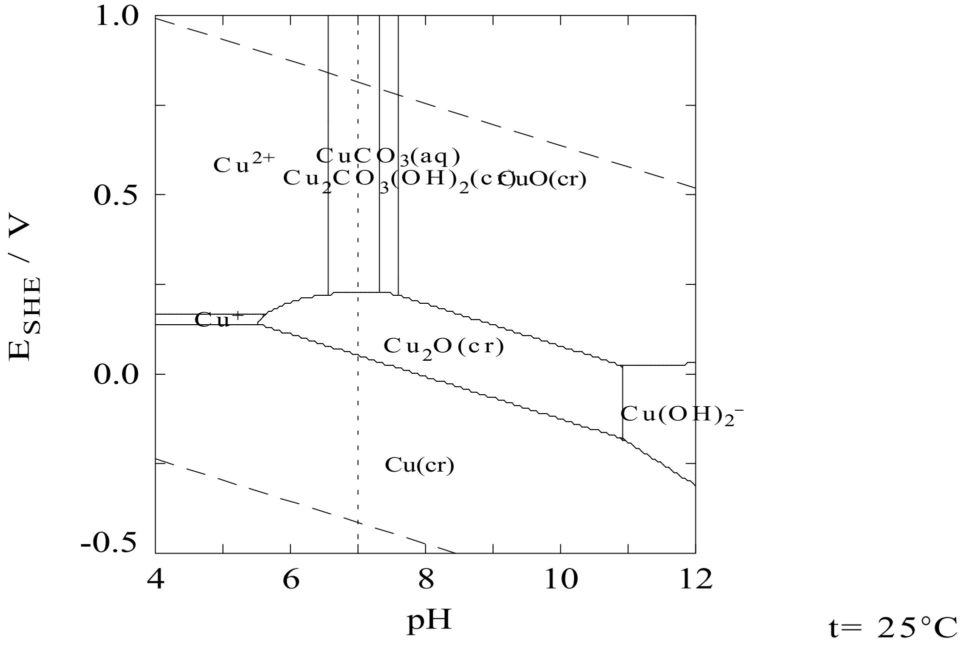
Figure 5.b. Fraction of copper(II) as chloride complexes: 100°C. Diagram calculated for pH = 3, $[Cu]_{TOT} = 10^{-5}$ mol/kg, and for $[Cl^-]_{TOT}$ between 0.01 and 1.7 mol/kg.

3.4.2 E_H/pH diagrams

Figure 6 and Figure 7 show the Pourbaix diagrams (E_H/pH diagrams) for copper in chloride solutions with $[CO_3^{2-}]_{TOT} = 0.002$ mol/kg. The diagrams for $[Cl^-] = 1.7$ mol/kg are essentially identical to those reported in (Beverskog and Puigdomenech, 1998), even if the thermodynamic data for the copper-chloride system is not exactly the same in the two studies. This reflects the fact that Pourbaix diagrams are in general not very sensitive to the thermodynamic data used in the calculations.

The E_H/pH diagrams in Figure 6 and Figure 7 show that Cl^- decreases the stability of copper metal in acidic solutions, for example, from $E_H = +0.2$ V in chloride-free solutions to $E_H \approx -0.2$ V in $[Cl^-] = 1.7$ mol/kg at 25°C. This is due to the stability of Cu(I) chloride complexes, which are also responsible for the decrease of the stability area for the Cu(I) oxide.

At intermediate redox potentials, Cu(I)-chloride complexes replace Cu(II) species as $[Cl^-]$ increases. This is shown in Figure 8 for $E_H = +0.3$ V



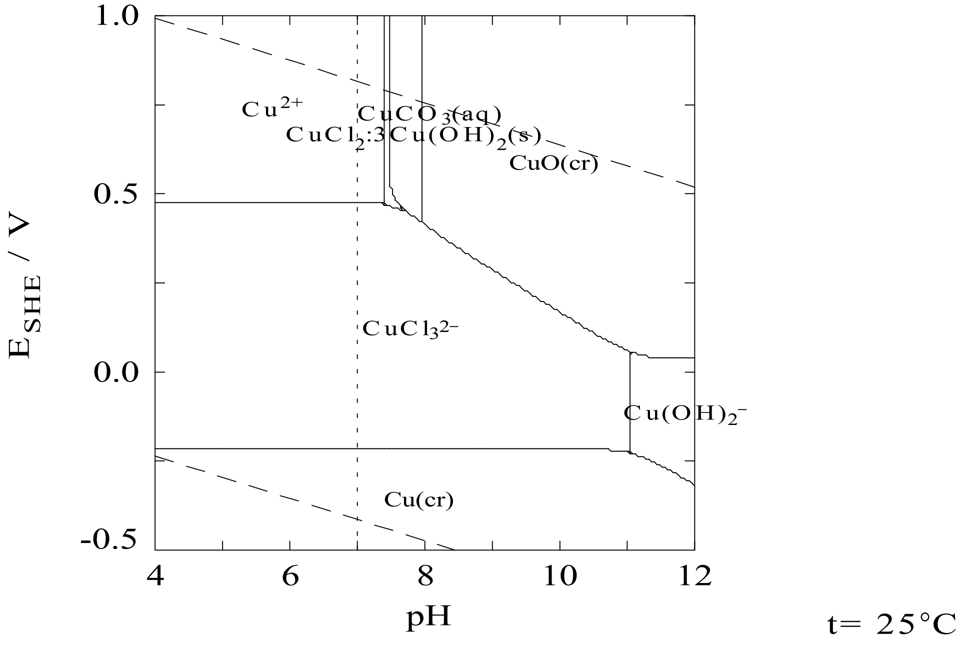


Figure 6. Pourbaix diagram for copper at 25°C and $[Cu]_{TOT} = 10^{-6}$ mol/kg in solutions containing: *a)* $[CO_3^{2-}]_{TOT}$ = 2 mmol/kg and $[Cl^-]_{TOT}$ = 0.2 mmol/kg (upper diagram) and *b)* $[CO_3^{2-}]_{TOT}$ = 2 mmol/kg and $[Cl^-]_{TOT}$ = 1.7 mol/kg (lower diagram).

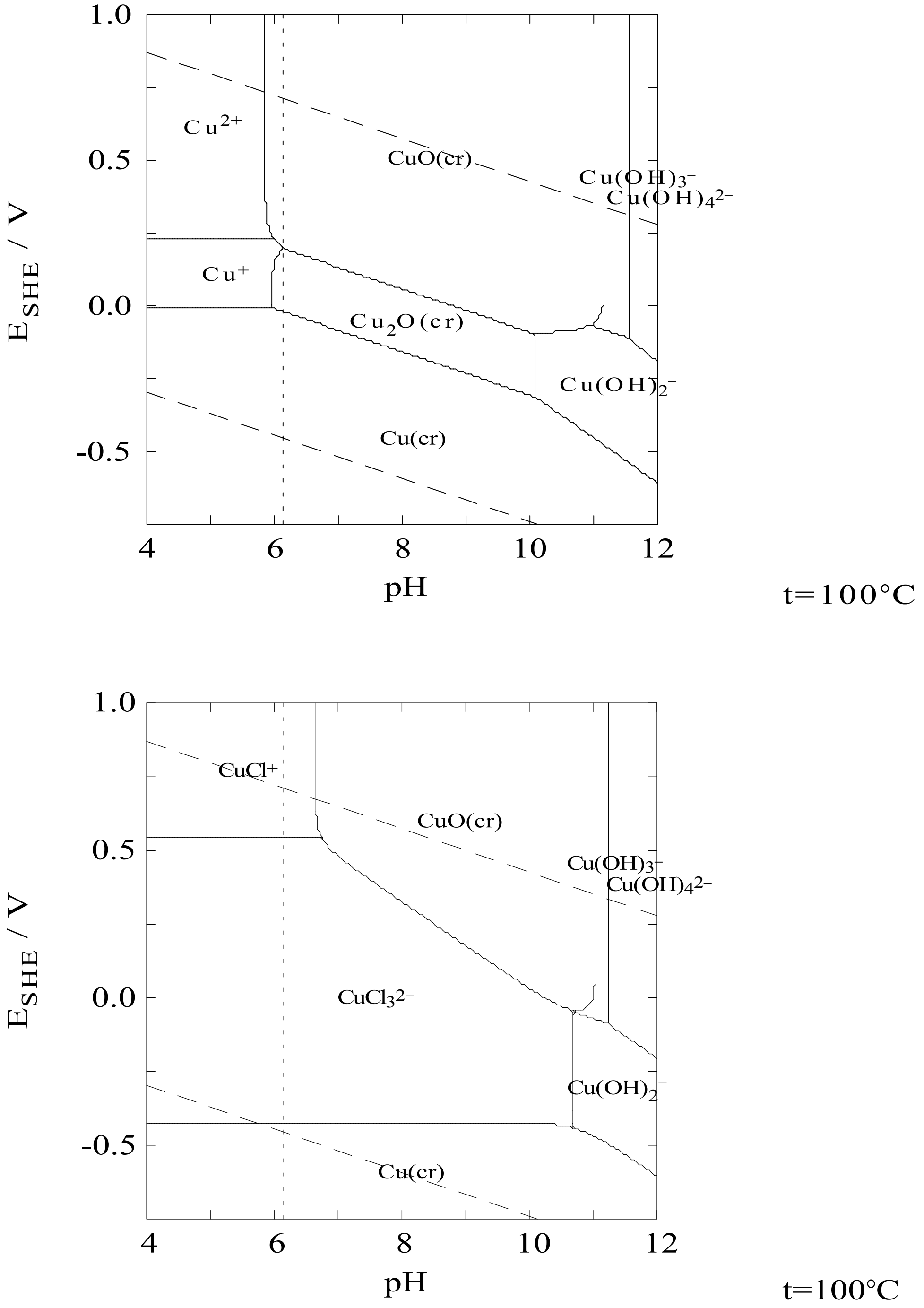
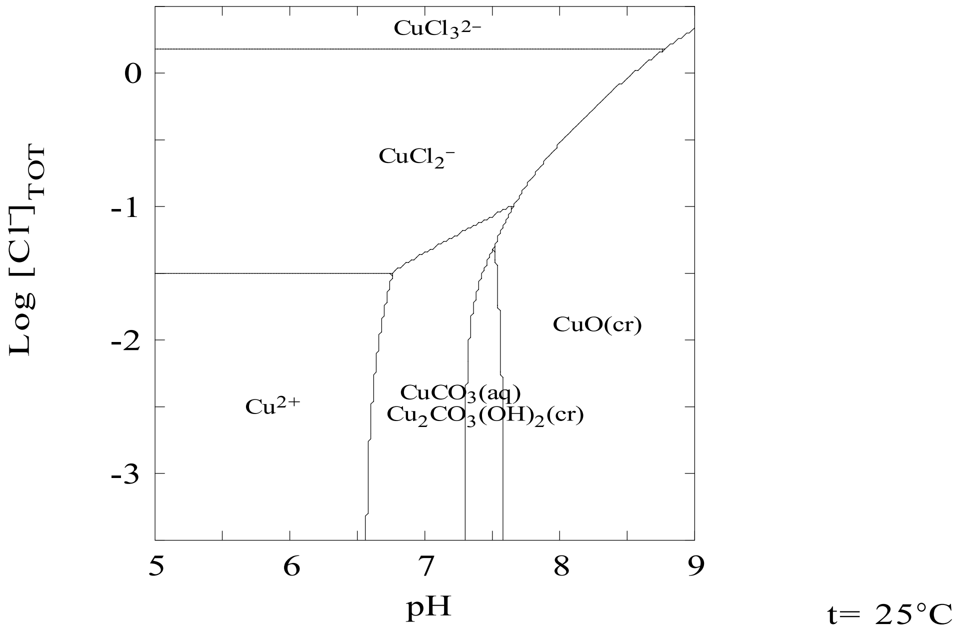


Figure 7. Pourbaix diagram for copper at 100°C and $[Cu]_{TOT} = 10^{-6}$ mol/kg in solutions containing *a)* $[CO_3^{2-}]_{TOT}$ = 2 mmol/kg and $[Cl^-]_{TOT}$ = 0.2 mmol/kg (upper diagram) and *b)* $[CO_3^{2-}]_{TOT}$ = 2 mmol/kg and $[Cl^-]_{TOT}$ = 1.7 mol/kg (lower diagram).



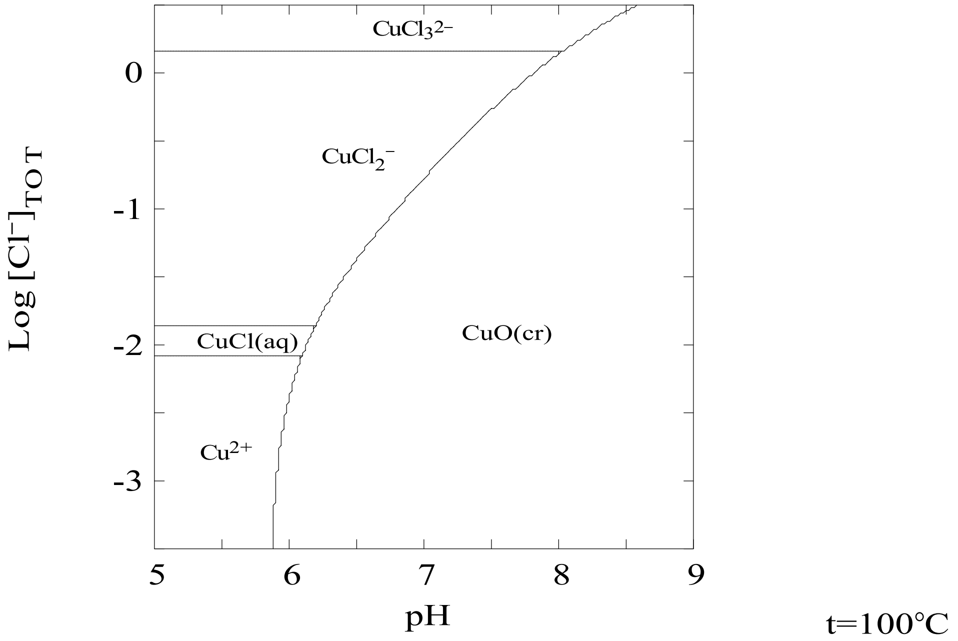


Figure 8. Predominance area diagrams for copper at 25°C (upper diagram) and 100°C (lower diagram) in solutions at E_H = +300 mV containing $[CO_3^{2-}]_{TOT}$ = 2 mmol/kg and $[Cu]_{TOT}$ = 1 μmol/kg.

3.4.3 Immunity, Passivity and Pitting Corrosion

Under conditions where the metal is thermodynamically stable against oxidation, it can be said to be immune against corrosion. Under conditions where there is no or little corrosion because of a protective oxide layer, passivity is the preferred term. Localised corrosion can under some circumstances take place when the major part of the metal is in its passive state.

The corrosion process can itself change the local environment from that of the bulk. As discussed earlier in section 3.1.3, the pH may be lower, the solution more concentrated and the potential may be lower. For example, the stability region for CuO(cr) in Figure 6 and Figure 7 represent non-corroding situations ($[\mathrm{Cu(aq)}]_{\mathrm{TOT}} < 10^{-6}$ mol/kg), but also for the case where the bulk concentration of Cl^- is low, a part of the metal surface may be in a corroding state and exposed to an acidic pit solution with high chloride concentration.

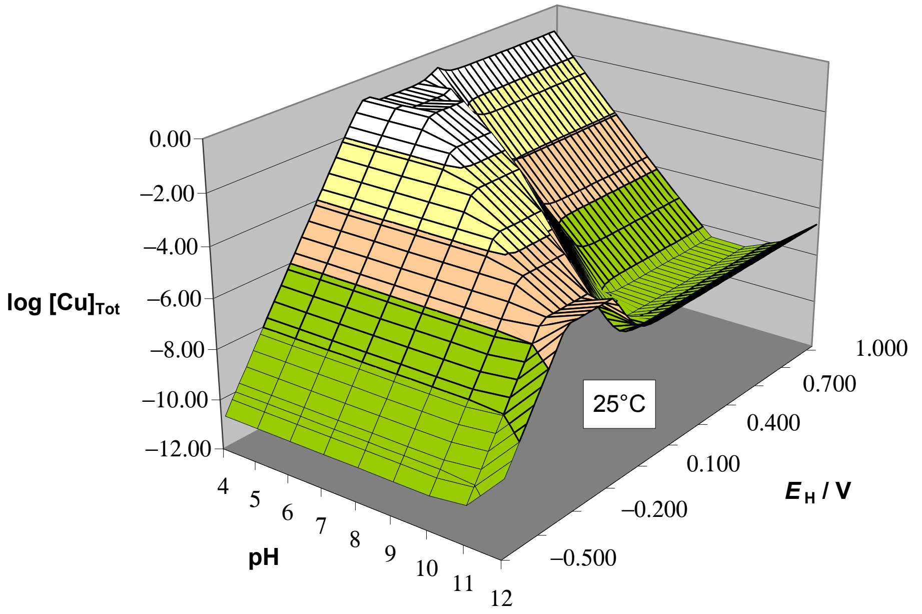
Pitting corrosion can not take place when the metal is in its immune state, because there are no processes occurring that can change the local environment.

3.4.4 Copper(II) Chloride Minerals

Several copper(II) chloride-containing minerals are found in nature, *cf.* Section 7.5.1. Some of these minerals contain other ligands: sulphate and hydroxide. The stability fields of these minerals are discussed in Sections 3.7 and 3.8.2.

3.4.5 Copper Corrosion in Chloride Media

As pointed out in (Beverskog and Puigdomenech, 1998), high chloride concentrations produce a corrosion area in the Pourbaix diagrams (E_{H}/pH diagrams). This corrosion area is located in a pH-potential region located between the stabilities of Cu(cr) and CuO(cr), as indicated in Figure 6 and Figure 7. The calculated solubility of copper at $[\mathrm{Cl}^-]_{\mathrm{TOT}} = 1.7$ mol/kg is shown in Figure 9 as a function of E_{H} and pH. This figure shows the regions where the Cu-solubility is lower than 10^{-6} mol/kg, which is the conventional limit for corrosion. Figure 9 is equivalent to the E_{H}/pH diagrams in Figure 6 and Figure 7, but it includes additional quantitative information on the possible extend of corrosion.



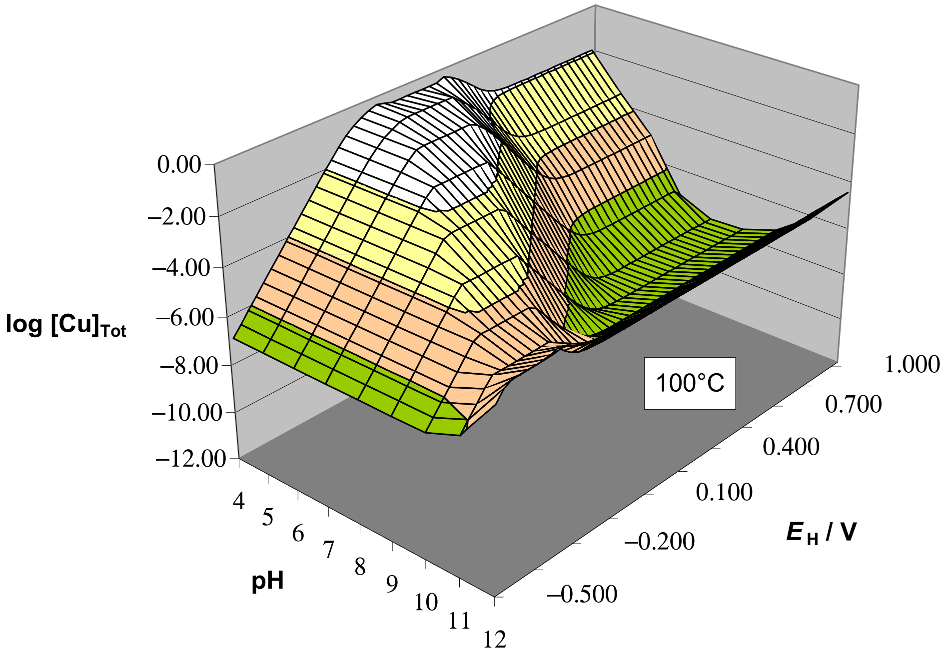


Figure 9. The solubility of copper as a function of pH and E_H, at $[Cl^-]_{TOT}$ = 1.7 mol/kg and at temperatures of 25°C (upper diagram) and 100°C (lower diagram). The figure illustrates the corrosion areas (where $[Cu]_{TOT} > 10^{-6}$ mol/kg) as well as the immunity and passivity regions. The corresponding solids and predominating complexes may be seen in the lower diagrams of Figure 6 and Figure 7.

If it is arbitrarily postulated that the redox potential in the repository is E_H = −200 to −400 mV, and that the pH is between 7 and 9, then the calculations show that at 25°C and for any chloride concentration copper does not corrode, *i.e.*, $[Cu]_{TOT} \lesssim 10^{-6}$ mol/kg. However, at 100°C and for $[Cl^-]_{TOT}$ = 1.7 mol/kg, the calculations given in Figure 7 and Figure 9 show that copper can corrode, *i.e.*, $[Cu]_{TOT} > 10^{-6}$ mol/kg. Similar results were obtained by (Wallin, 1983).

This conclusion is however affected by the following factors:

- Uncertainties in the thermodynamic data used for the calculations.
- The copper metal in a canister for nuclear waste is probably not uniform in activity. Local stress or strain is likely to be reflected in local variations in the chemical activity of the metal.
- The real E_H value in the vicinity of a copper canister in the bentonite buffer of a waste repository. Although there are no experimental measurements available, the redox potential will be affected by the presence of an excess of copper metal.
- Does a calculated solubility of *e.g.* $[Cu]_{TOT} \approx 10^{-5}$ mol/kg really implicate corrosion? Such solubilities are for example attained in the zinc-water system (Beverskog and Puigdomenech, 1997b), although in practice the corrosion of zinc metal in the presence of air is not considered to be a problem. To estimate life-times for the waste package it is necessary to use calculated Cu-solubilities, together with an evaluation of diffusion and flow transport of oxidants and corrosion products.

In any case, copper will not corrode in the absence of electron acceptors (*cf.* Section 3.1.1). The extent of "corrosion" in the absence of added oxidants may be found by calculating the amount of copper metal that must be added to a closed system to reach over-saturation. This has been calculated for $[Cl^-]_{TOT}$ = 0 and 1.7 mol/kg both at 25°C (Figure 10) and at 100°C (Figure 11). These calculations show that when copper metal is added to a system it becomes quickly oversaturated. The final concentration of copper in the aqueous phase is in all cases $\lesssim 10^{-6}$ mol/kg, implying a negligible extend of corrosion.

Figure 12 shows the calculated extent of "corrosion" when an excess H^+ is added to the system, by decreasing the initial pH of the solution. If large initial concentrations of $H_2(aq)$, (*e.g.*, 0.01 mol/kg) are added in the model, the calculated corrosion of copper is decreased.

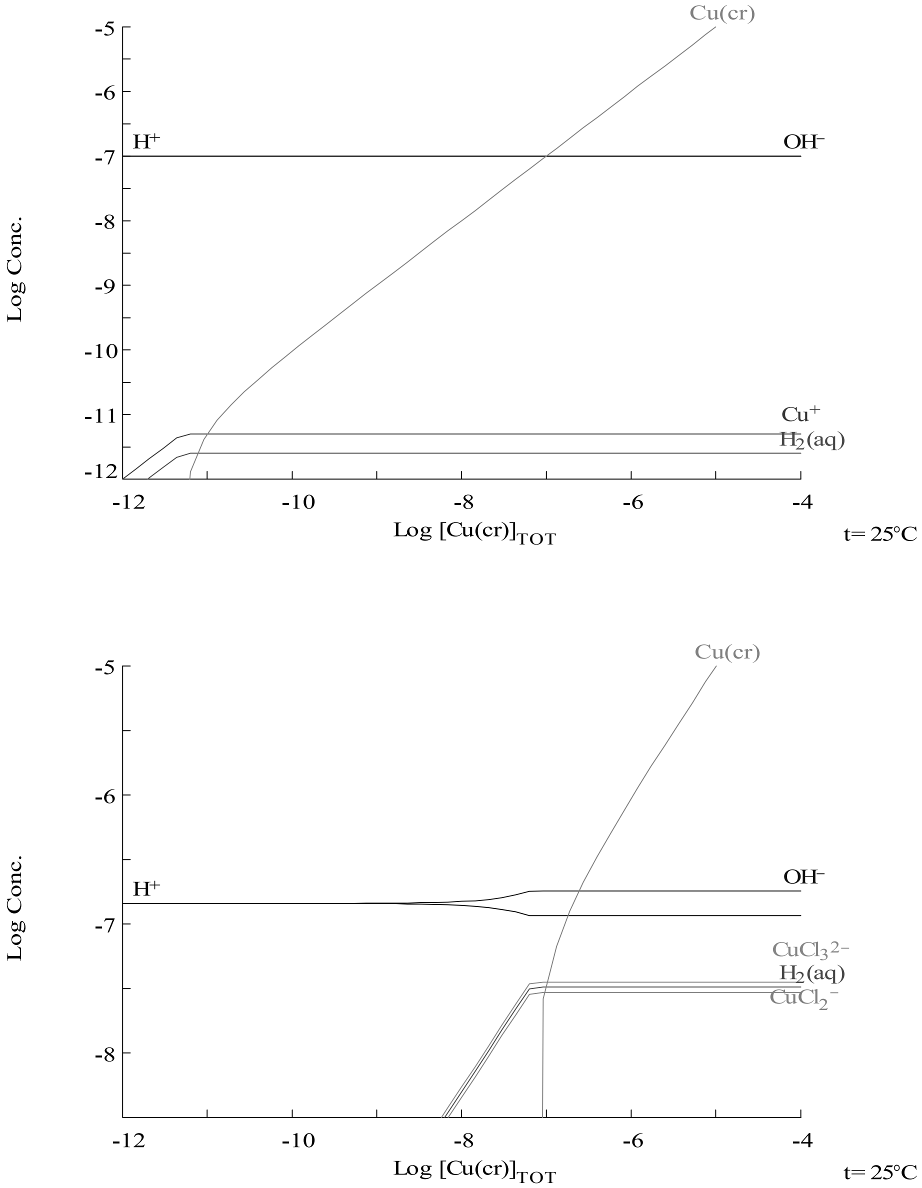
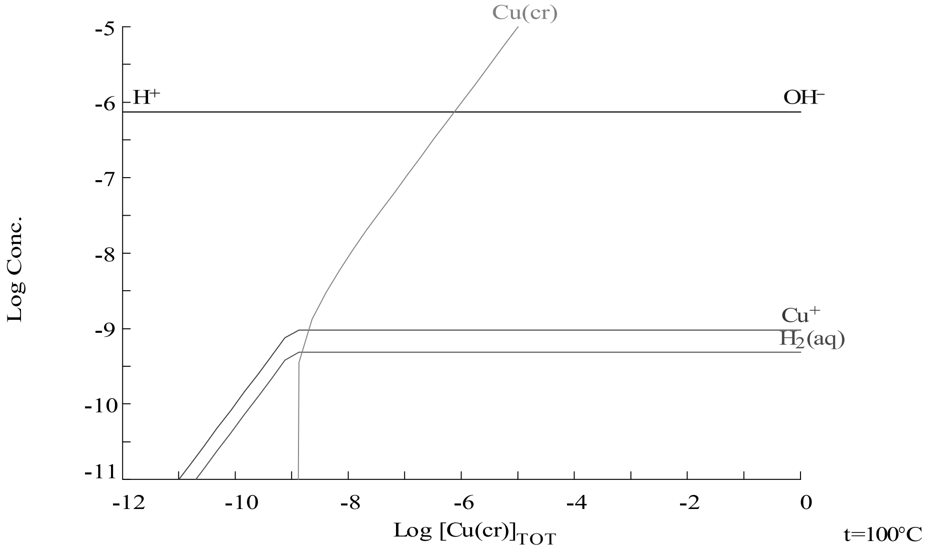


Figure 10. Calculated concentrations of species at 25°C when copper is added to pure water (upper diagram) and to a $[Cl^{-}]_{TOT}$ = 1.7 mol/kg (lower diagram) solution. In the presence of high chloride concentrations copper dissolves ("corrodes") to a larger extent, *i.e.*, the Cu(cr)-saturated solution reaches a copper content of $\approx 10^{-7}$ mol/kg.



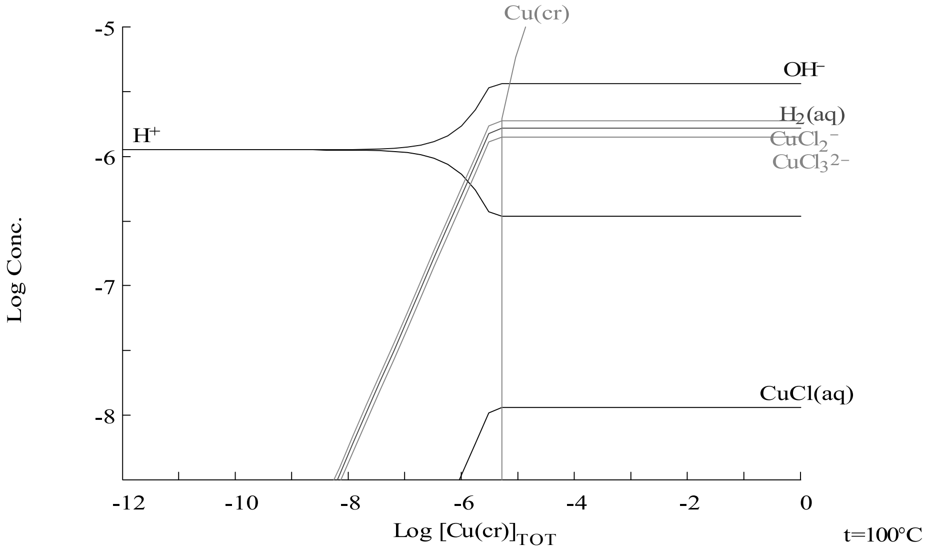


Figure 11. Calculated concentrations of species at 100°C when copper is added to pure water (upper diagram) and to a $[Cl^-]_{TOT}$ = 1.7 mol/kg solution (lower diagram). In the presence of high chloride concentrations copper dissolves (“corrodes”) to a larger extent, *i.e.*, the Cu(cr)-saturated solution reaches a copper content of $10^{-5.3}$ mol/kg.

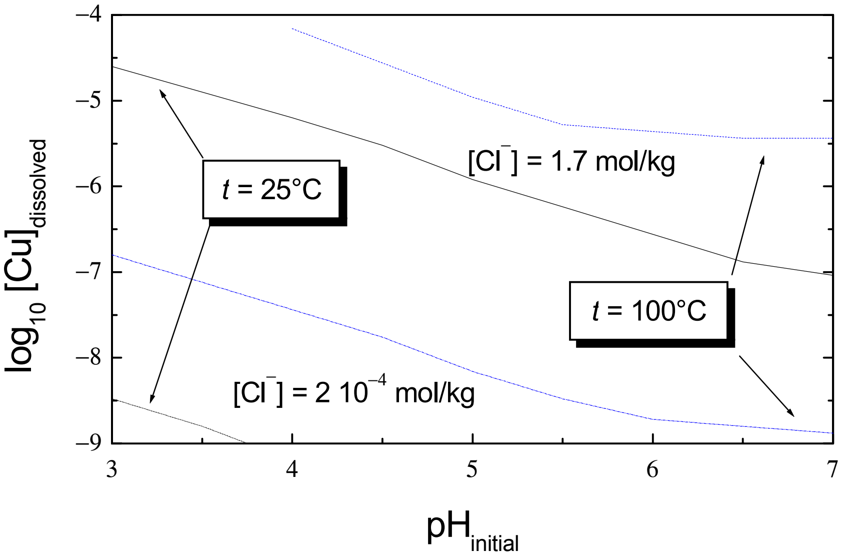


Figure 12. Calculated equilibrium concentrations of dissolved copper in chloride solutions as a function of the initial pH. In the presence of high chloride concentrations (the two upper curves) copper metal dissolves ("corrodes") to a larger extent.

3.5 THE INFLUENCE OF NITROGEN LIGANDS

Nitrogen is present only at trace amounts (as NO_3^-, NO_2^-, and NH_3) in deep granitic groundwaters in Sweden. The stability areas of these ligands at 25°C is shown in Figure 13. Redox disequilibrium usually prevails among nitrogen species, and N_2(g), N_2O(g), NO(g) and N_3^- have been excluded from the figure. Nitrate, nitrite, nitrogen, and ammonia are usually very reluctant to undergo redox reactions. However, there are observations that indicate that nitrate may be reduced electrochemically at a conducting surface or alternatively, oxidise dissolved Fe(II) to Fe(III) (Newman and Ajjawi, 1986). Stainless steels are frequently alloyed with small amounts of nitrogen. It has been shown that ammonia is produced when a nitrogen containing steel is corroded (Jargelius and Wallin, 1986). Nitrite as a corrosion inhibitor is classified as a passivating or oxidising inhibitive anion (Thomas, 1994). That is, nitrite works as an inhibitor by undergoing reduction. So, while there are many examples to the contrary, the general behaviour of the nitrogen species is that they are electrochemically inert. Transformations between nitrate, nitrite, nitrogen, and ammonia must frequently be "catalysed" by bacteria

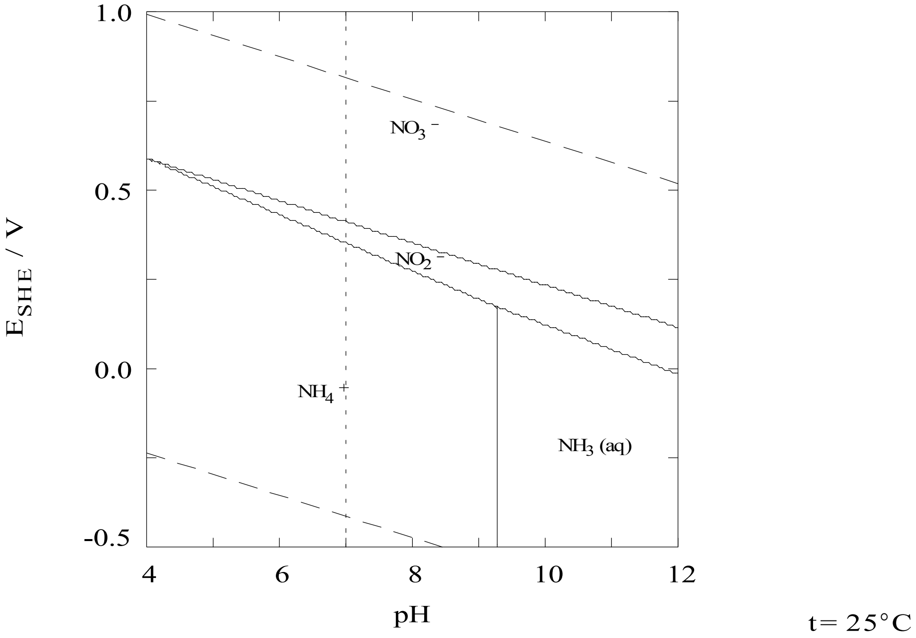


Figure 13. Pourbaix diagram for nitrogen at 25°C.

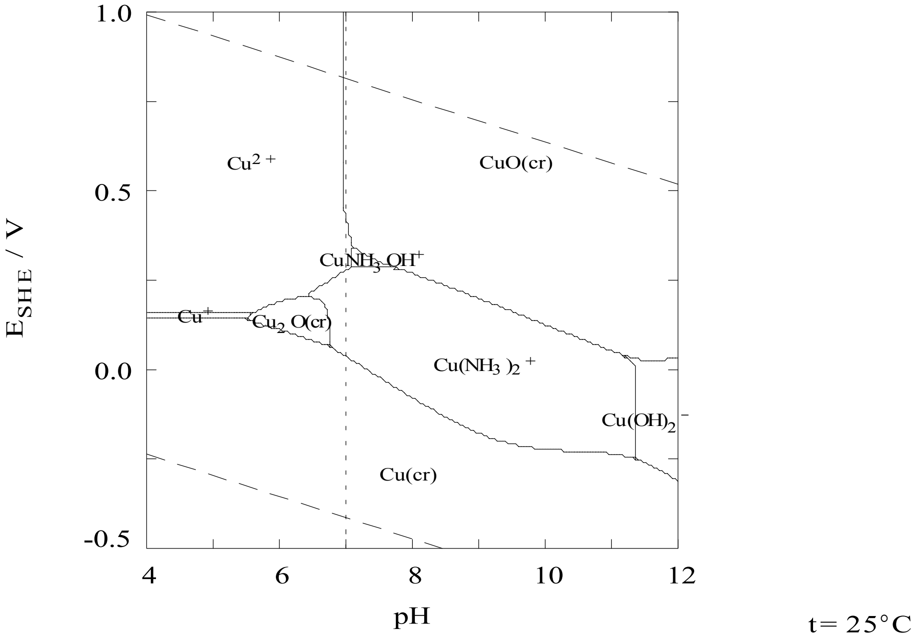


Figure 14. Pourbaix diagram for copper in solutions containing $[N]_{TOT}$ = 0.01 mol/kg and $[Cu]_{TOT} = 10^{-6}$ mol/kg, at 25°C.

Expected nitrogen concentrations in granitic groundwaters are in the order of a few µmol/kg. In exceptional cases concentrations up to 0.5 mmol/kg have been observed. However, due to the weak effects of nitrogen ligands, the nitrogen concentration in the diagrams of this section has been set to an unrealistic high value of 10 mmol/kg. The relative effect at such high concentrations of nitrogen ligands on the chemistry of copper may be seen in Figure 14. Ammonia complexes of copper(I) appear to be of importance.

At higher potentials, strong Cu(II)-ammonia complexes could be expected to predominate. These deep blue complexes are easily prepared in laboratory solutions. In nature, however, ammonia-nitrogen is (microbially) oxidised to nitrate. The fraction of complexes with nitrogen-ligands under mildly oxidising conditions, where Cu(II)-ammonia complexes might predominate, is given in Figure 15.

It has been proposed that transformations between ammonia complexes with Cu(II) and Cu(I) may be involved in stress corrosion cracking of copper (Mattsson, 1980), see also Section 3.1.4.

3.6 THE INFLUENCE OF PHOSPHATE

Because phosphate (PO_4^{3-}) is present only at trace amounts in deep granitic groundwaters, phosphorous from this source is not expected to influence the corrosion processes of copper canisters. However, a phosphorous containing copper alloy is considered as canister material for the Swedish spent nuclear fuel repository. The content of phosphorous in this alloy is in the order of 10-100 ppm (mg/kg). 100 ppm elementary phosphorous in copper metal would give a molar ratio of about 0.0002. During corrosion of the copper metal the elementary phosphorous can be oxidised to the thermodynamically stable oxidation state +V as in phosphate or, through more favourable kinetics, be reduced to the oxidation state –III as in phosphine, $PH_3(aq)$. The Pourbaix diagram of phosphorus is given in Figure 16.

The intermediate oxidation states of phosphorus +I, +III and +IV are also known (van Muylder and Pourbaix, 1974).

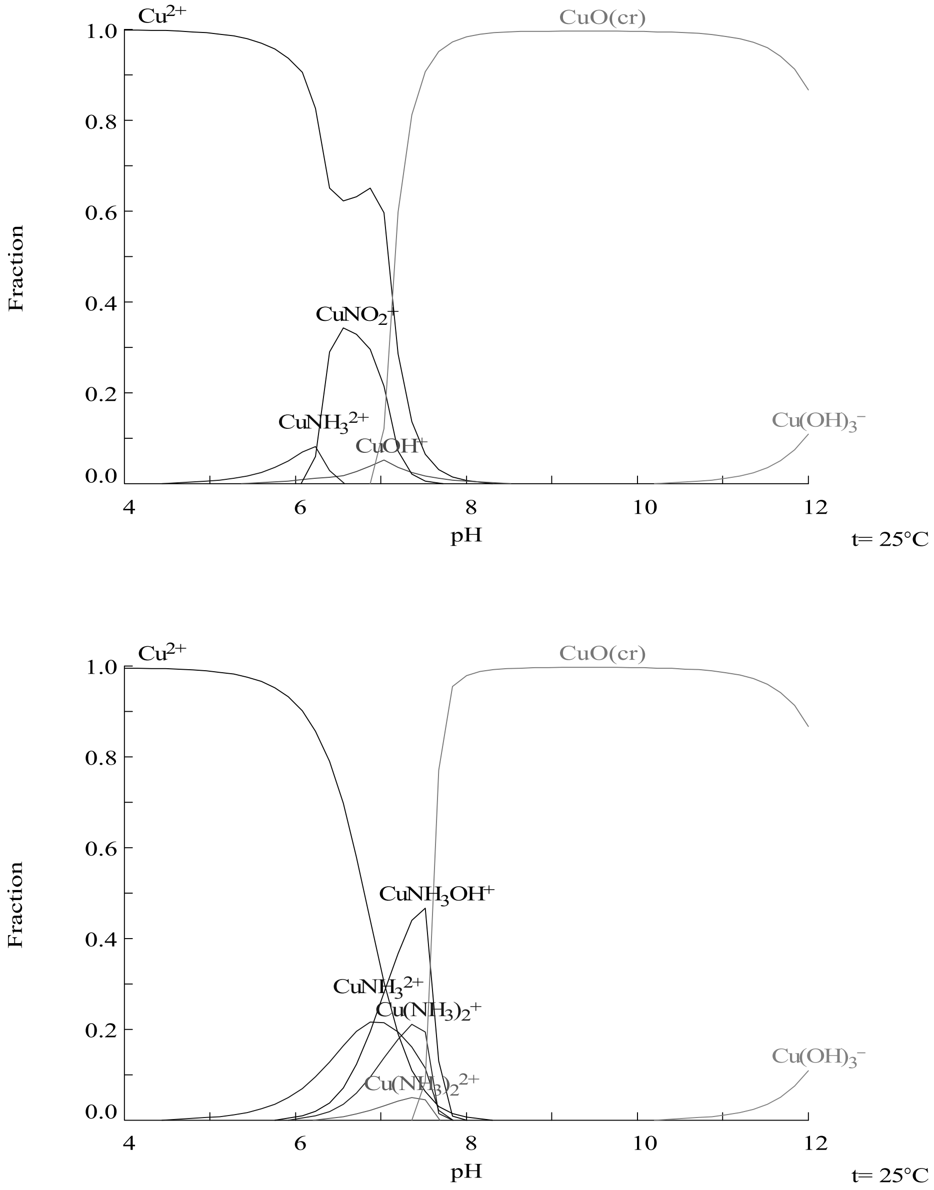


Figure 15. Fraction of ammonia and nitrite complexes of copper in solutions containing $[N]_{TOT}$ = 0.01 mol/kg and $[Cu]_{TOT} = 10^{-6}$ mol/kg, at E_H = +400 mV (upper diagram) or E_H = +300 mV (lower diagram), and at 25°C.

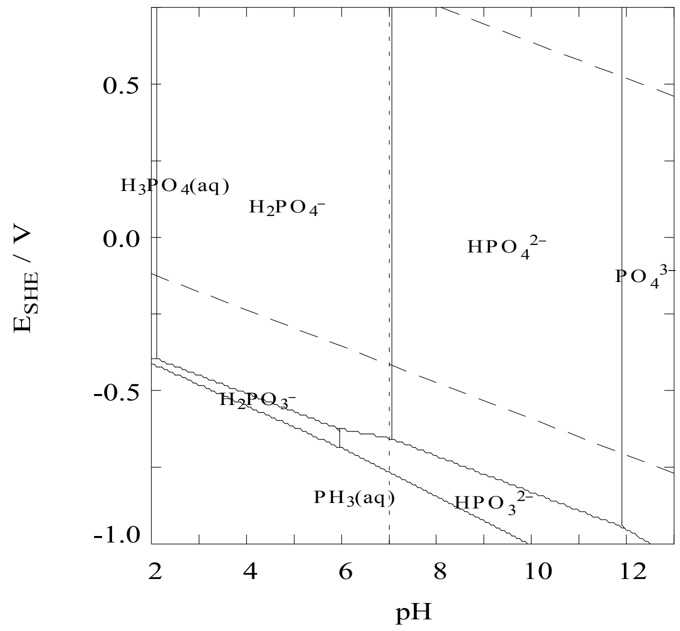


Figure 16. Pourbaix diagram for phosphorus at 25°C.

Both phosphate and phosphine form complexes with copper but considering the low molar ratio, phosphorous from corrosion of the canister can not increase significantly the solubility of copper through complex formation. But, because of the many protons involved when phosphorous is oxidised to phosphate, this reaction may have slightly acidifying effect in pit corrosion (Section 3.1.3.2).

Phosphate complexes with both Cu(I) and Cu(II) are reported in the literature, *cf.* Section 7.8. There is however some uncertainty concerning the speciation in this system. Nevertheless the phosphate complexes of Cu(I) appear to be weak. For Cu(II) the dominating complex is $CuHPO_4(aq)$, as illustrated in the Pourbaix diagram for $[PO_4^{3-}]_{TOT}$ = 0.01 mol/kg, *cf.* Figure 17.

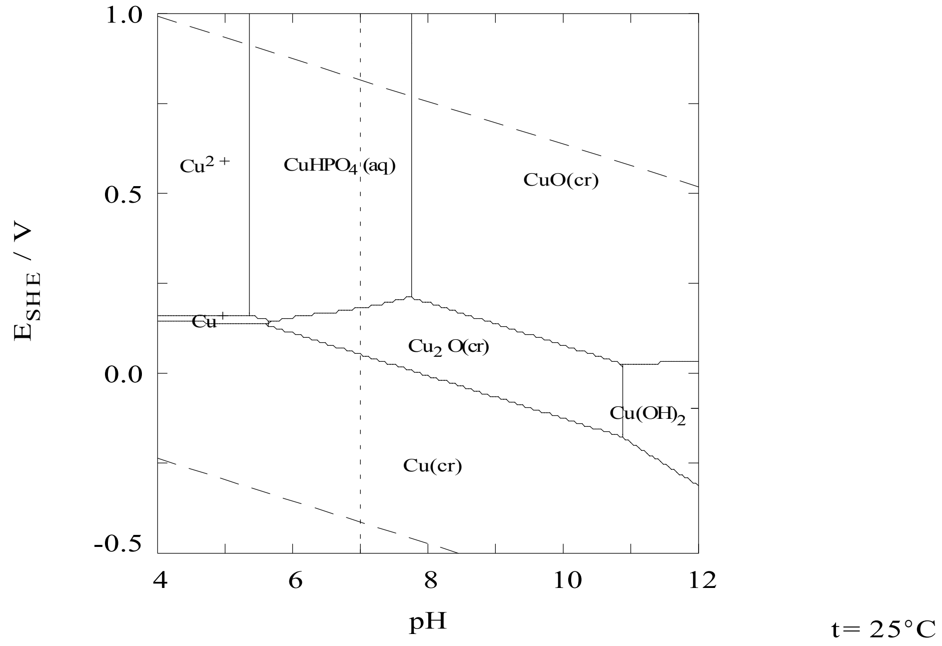


Figure 17. Pourbaix diagrams for copper at 25°C in solutions with $[PO_4^{3-}]_{TOT}$ = 0.01 mol/kg, and $[Cu]_{TOT}$ = 1 μmol/kg.

3.7 THE INFLUENCE OF CARBONATE

In deep granitic groundwaters of Sweden carbonate (CO_3^{2-}) is present in the range of 0.1 to 7.5 mmol/kg, *cf.* Table 1.

Two copper(II)-carbonate minerals are found in nature: malachite, $Cu_2CO_3(OH)_2(cr)$, and azurite, $Cu_3(CO_3)_2(OH)_2(cr)$. Only Cu(II) complexes are reported in the literature, *cf.* Section 7.9.

The behaviour of systems containing inorganic carbon may be described either as

- a function of the partial pressure of $CO_2(g)$, or
- using either $[CO_3^{2-}]_{TOT}$ or alkalinity as a master variable.

The predominating complexes and solid phases are shown in Figure 18 as a function of P_{CO2}, and in Figure 19 as a function of $[CO_3^{2-}]_{TOT}$.

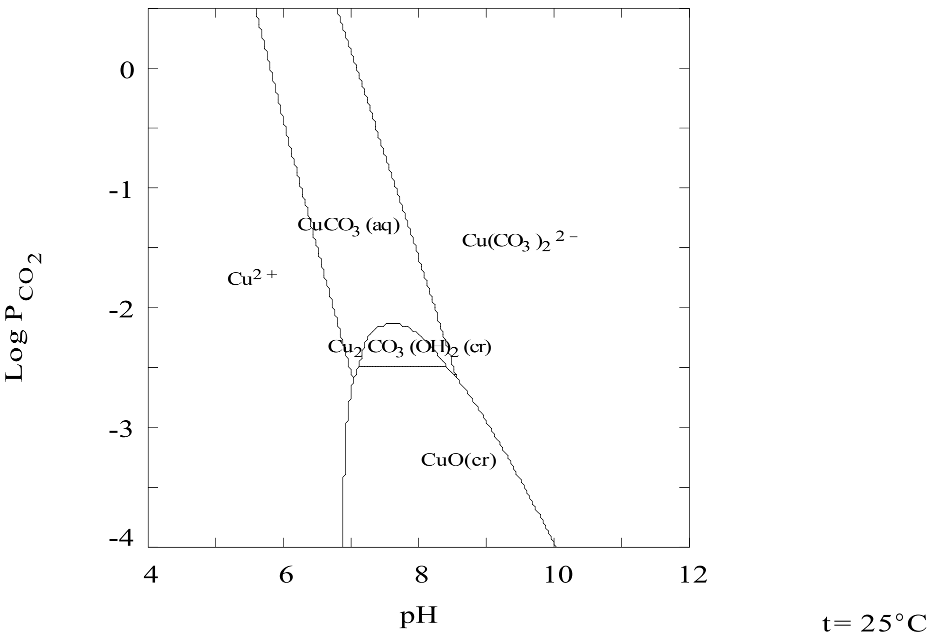


Figure 18.a. Predominance diagrams for copper species as a function of pH and the partial pressure of $CO_2(g)$ at $[Cu(II)]_{TOT} = 10^{-6}$ mol/kg and at 25°C.

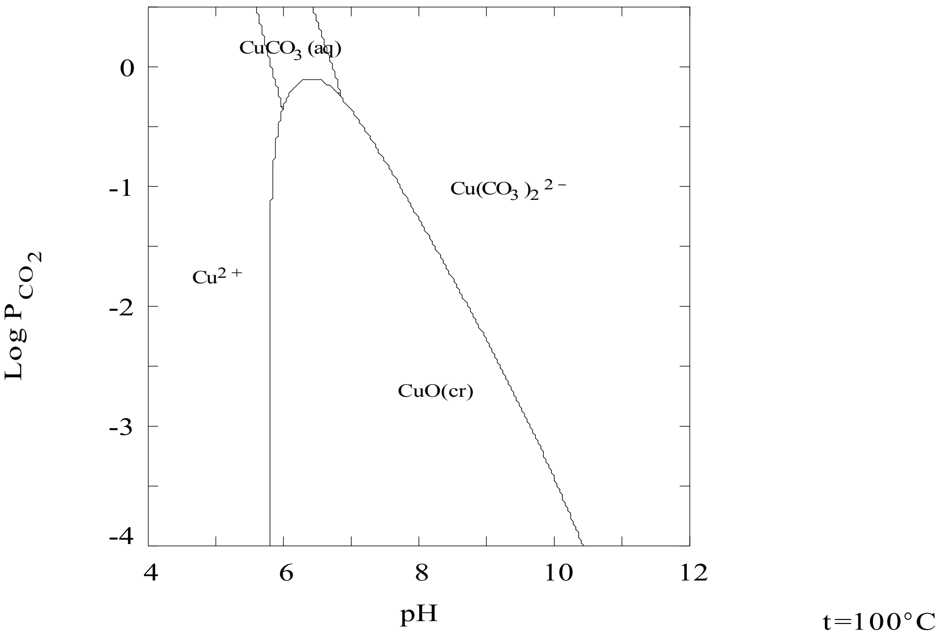


Figure 18.b. Predominance diagrams for copper species as a function of pH and the partial pressure of $CO_2(g)$ at $[Cu(II)]_{TOT} = 10^{-6}$ mol/kg and at 100°C.

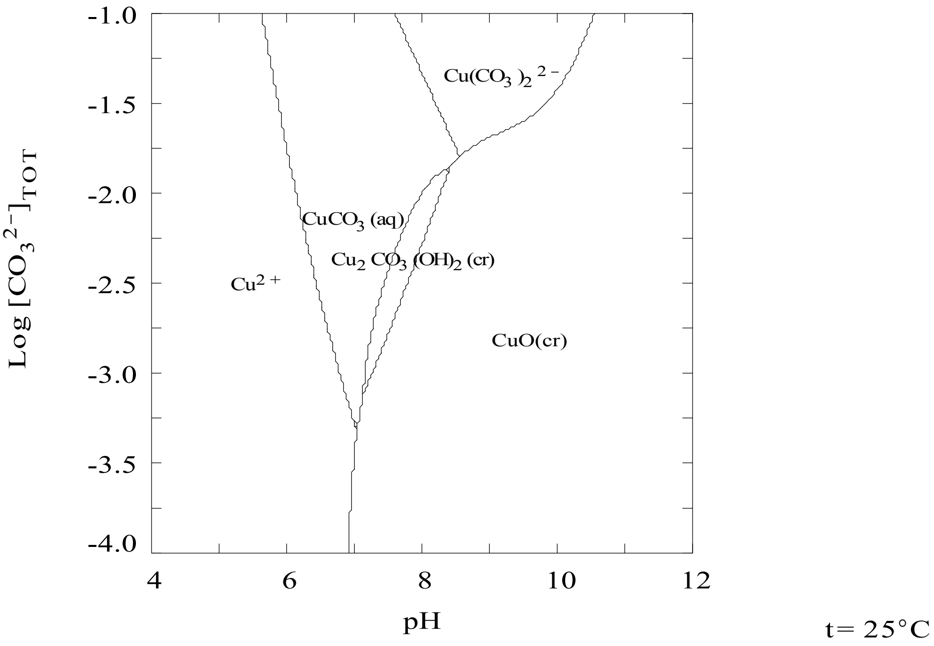


Figure 19.a. Predominance diagrams for copper species as a function of pH and the total carbonate concentration at $[Cu(II)]_{TOT}$ = 10^{-6} mol/kg and at 25°C (upper diagram) and 100°C (lower diagram).

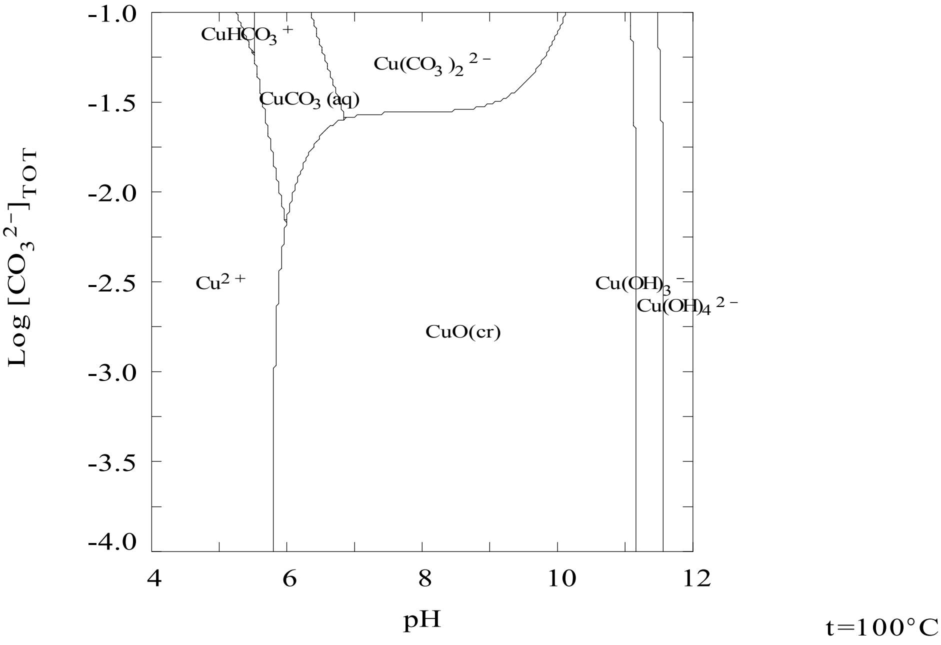


Figure 19.b. Predominance diagrams for copper species as a function of pH and the total carbonate concentration at $[Cu(II)]_{TOT}$ = 10^{-6} mol/kg and at 100°C.

The carbonate complexes of copper(II) become important at concentrations above those found in Swedish granitic groundwaters, as seen in Figure 18 and Figure 19.

The solubility of malachite ($Cu_2CO_3(OH)_2$(cr)) has been determined experimentally (Symes and Kester, 1985) at 25°C. The data is compared in Figure 20 together with the predicted values. The agreement between experiment and theory is satisfactory up to pH ≈ 8. At higher pH-values the deviations correspond to the formation of $Cu(CO_3)_2^{2-}$. The stability of this complex appears to be overestimated. As discussed in Section 7.9.2, the value for $\beta_2°$ is quite uncertain.

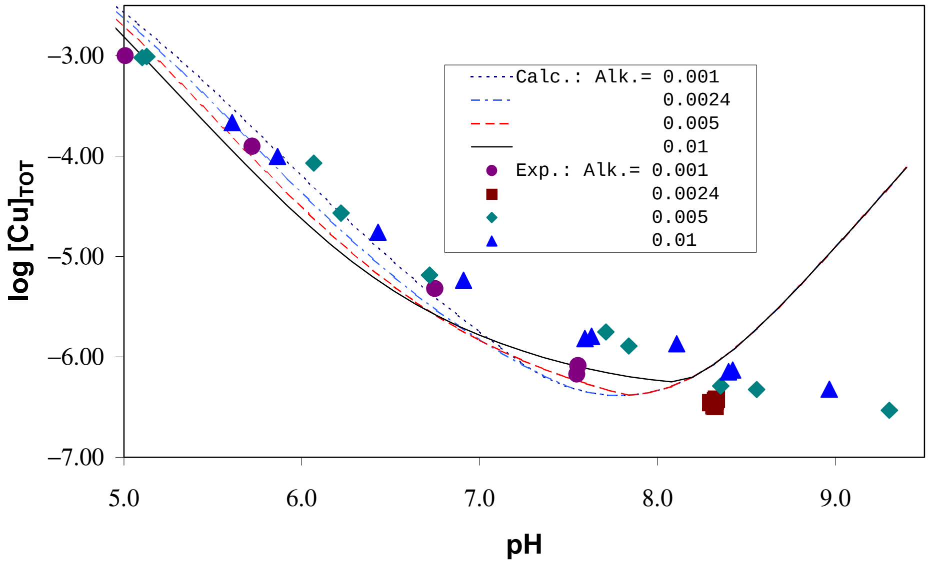


Figure 20. Experimental data on the solubility of malachite (Symes and Kester, 1985) at 25°C and $I = 0.72$ mol/kg, compared with calculated values at the corresponding total alkalinities. The model overestimates solubilities at pH ≳ 8.5, indicating that the formation of $Cu(CO_3)_2^{2-}$ is questionable.

The relative stability of malachite, $Cu_2CO_3(OH)_2$(cr), as compared to that of atacamite, $CuCl_2 \cdot 3Cu(OH)_2$(cr), is illustrated in Figure 21. The interface between the two solids is pH-dependent, starting at $[Cl^-]_{TOT} = 19$ g/kg at pH ≈ 6. The effect of temperature is to increase the stability of cupric oxide at the expense of malachite and atacamite, *cf.* Figure 21, as well as Figure 18 and Figure 19.

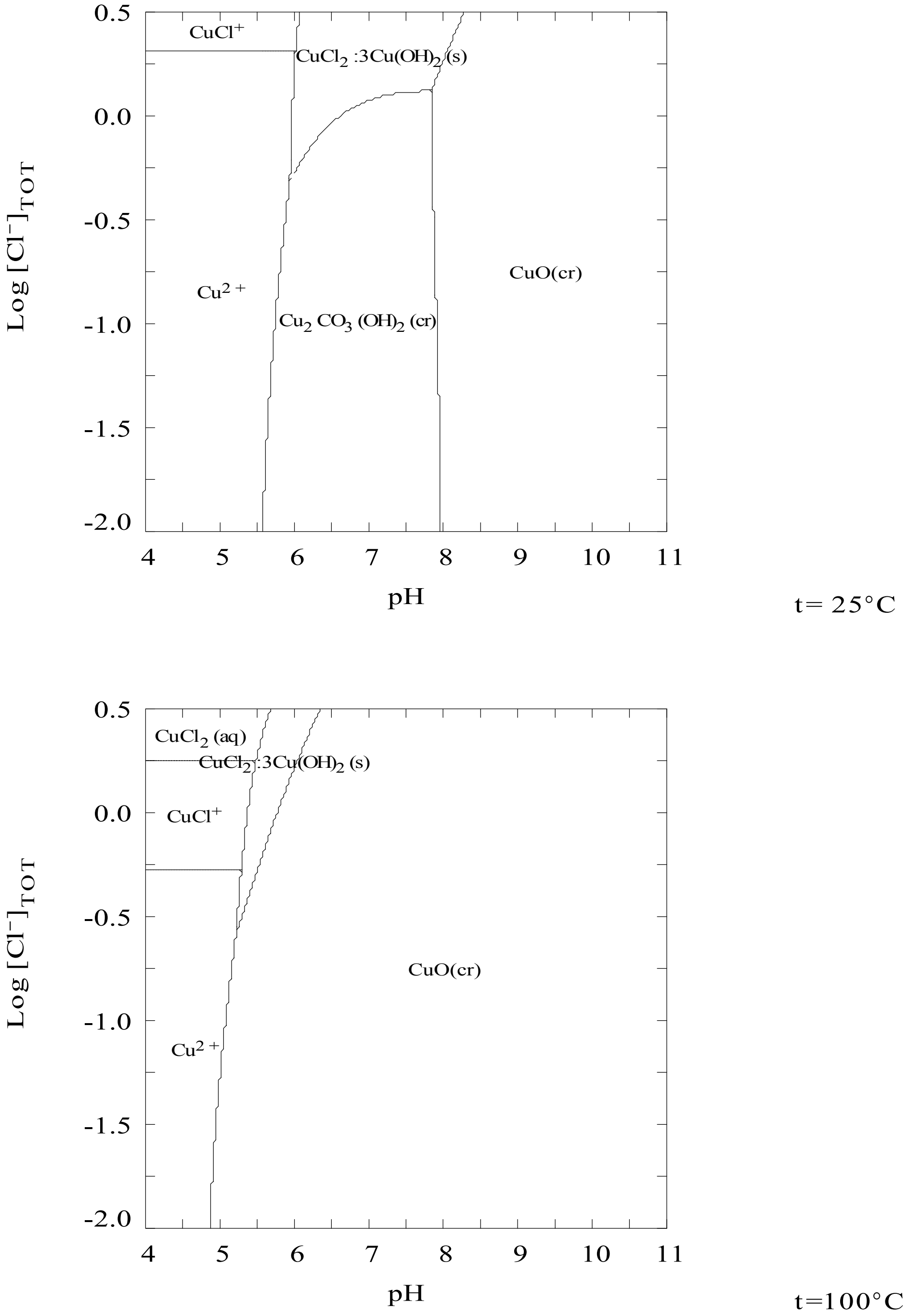


Figure 21. Predominance diagrams for copper species as a function of pH and the total chloride concentration at $[Cu(II)]_{TOT} = 10^{-4}$ mol/kg and $[CO_3^{2-}]_{TOT} = 10^{-4}$ mol/kg, both at 25°C (upper diagram) and at 100°C (lower diagram).

3.8 THE INFLUENCE OF SULPHUR

Granitic Swedish groundwaters may have a total sulphur content up to 0.011 mol/kg, *cf.* Table 1.

The geochemistry of sulphur is dominated by sulphur(VI) in the form of sulphate (SO_4^{2-}), sulphur(0) in the form of either crystalline or colloidal rhombic sulphur (S_8), and sulphur(−II) in the form of hydrogen sulphide (HS^-). The E_H/pH regions where these species dominate may be seen in Figure 22. In addition, several metastable sulphur species may be found in natural waters: sulfite (SO_3^{2-}), thiosulphate ($S_2O_3^{2-}$), dithionite ($S_2O_4^{2-}$), *etc.*

The redox conversions between the different sulphur species are very slow, especially at low temperatures. Even if some bacteria catalyse these reactions, it is not unusual to find substantial concentrations of SO_4^{2-} in reducing environments where sulphide should be the stable sulphur component. On the other hand the chemical and microbial oxidation of HS^- is fast, and sulphide is not found in oxidising environments.

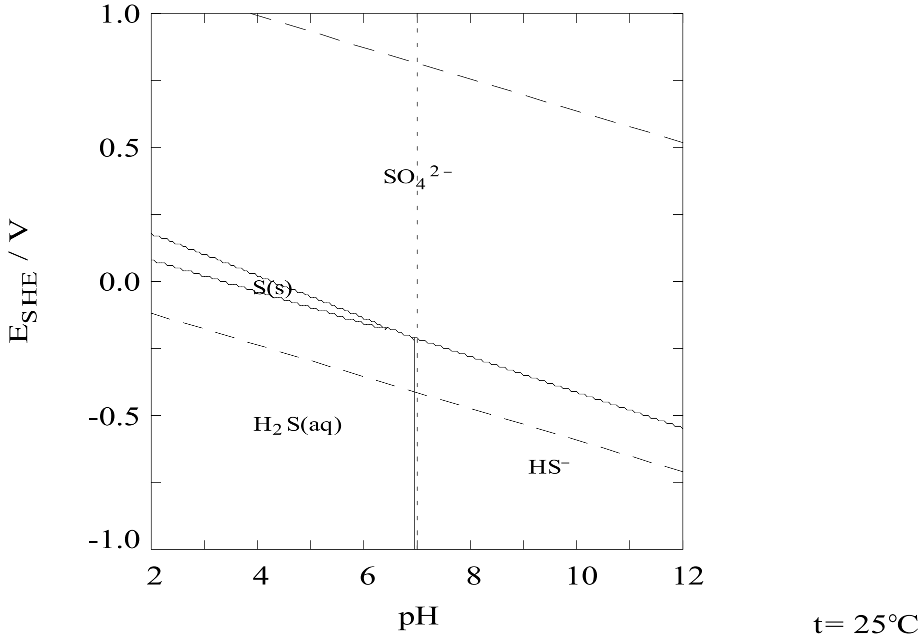


Figure 22. Pourbaix diagram for sulphur at a total sulphur concentration of 0.02 mol/kg and at 25°C.

3.8.1 The Effect of Sulphide

While the total sulphur content of granitic Swedish groundwaters is up to 0.011 mol/kg, sulphide concentrations are much lower, $[HS^-]_{TOT} \leq$

2×10^{-4} mol/kg, *cf.* Table 1. This is due to the low solubility of metal sulphides, for example pyrite, which is a relatively common fracture filling mineral in Swedish granitic environments. All diagrams in this section are therefore performed for $[HS^-]_{TOT}$ = 0.2 mmol/kg.

Sulphide is the groundwater component most detrimental for copper corrosion, perhaps followed by chloride. The action of sulphide is to form very insoluble corrosion products with copper, like chalcocite, $Cu_2S(cr)$. This increases the energy gain for the oxidation of copper metal to such a degree that hydrogen ions, which are always present in water, become adequate electron acceptors:

$$2\ Cu(cr) + S^{2-} \rightleftharpoons Cu_2S(cr) + 2\ e^-$$

$$2\ H^+ + 2\ e^- \rightleftharpoons H_2(g)$$

These two reactions may be combined into the following global reaction:

$$2\ Cu(cr) + S^{2-} + 2\ H^+ \rightleftharpoons Cu_2S(cr) + H_2(g)$$

In the presence of elemental or colloidal sulphur, other sulphides are produced, for example covellite:

$$2\ Cu(cr) + S(s) + S^{2-} + 2\ H^+ \rightleftharpoons 2\ CuS(cr) + H_2(g)$$

Figure 22 shows that in sufficiently oxidising environments sulphide and sulphur are unstable. The consequence is that in oxidising environments copper sulphides become thermodynamically unstable as well. This is illustrated in the Pourbaix diagrams of Figure 23.

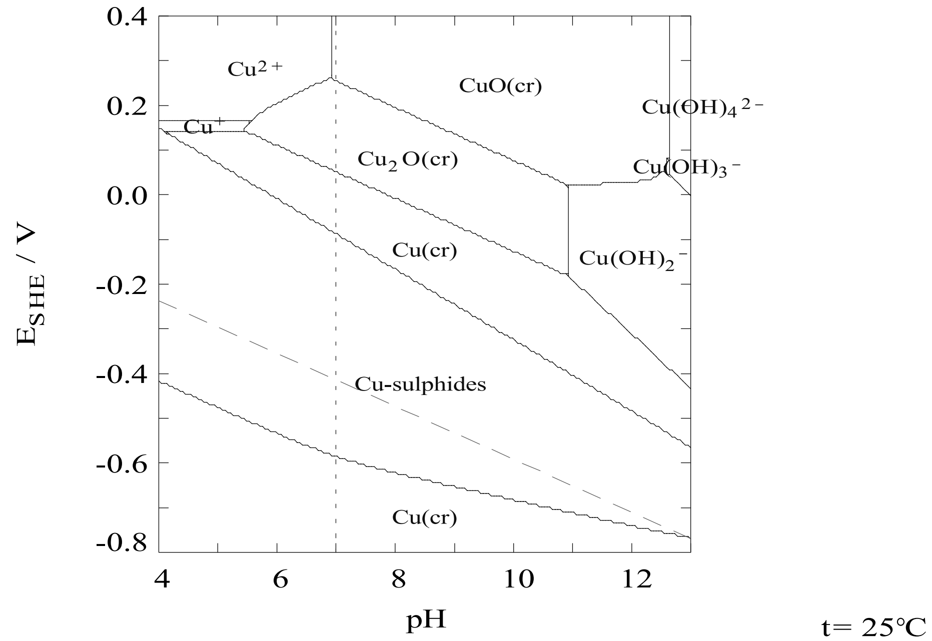


Figure 23.a. Pourbaix diagram for copper in solutions containing $[HS^-]_{TOT}$ = 0.2 mmol/kg and $[Cu]_{TOT} = 10^{-6}$ mol/kg, at 25°C.

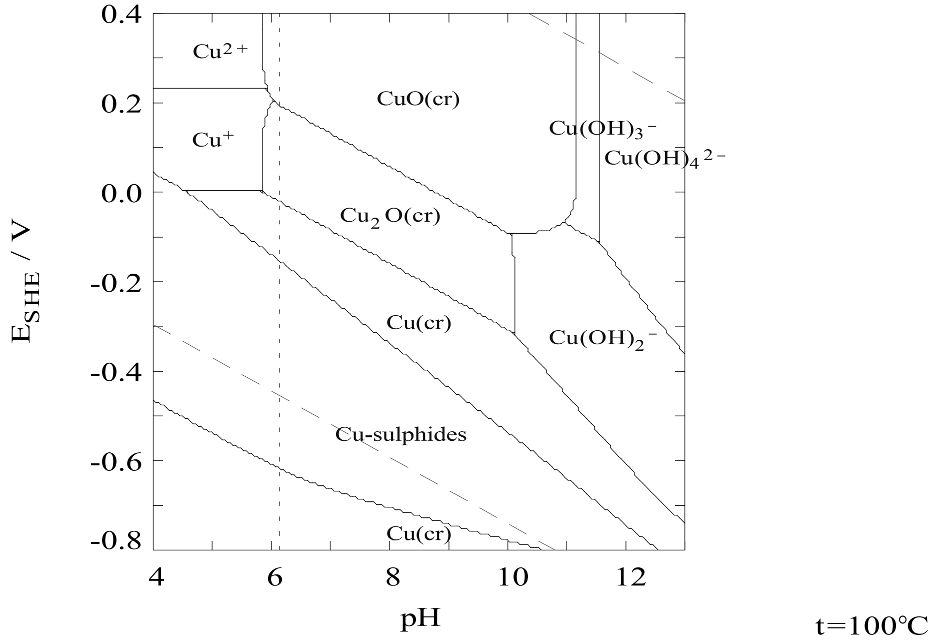
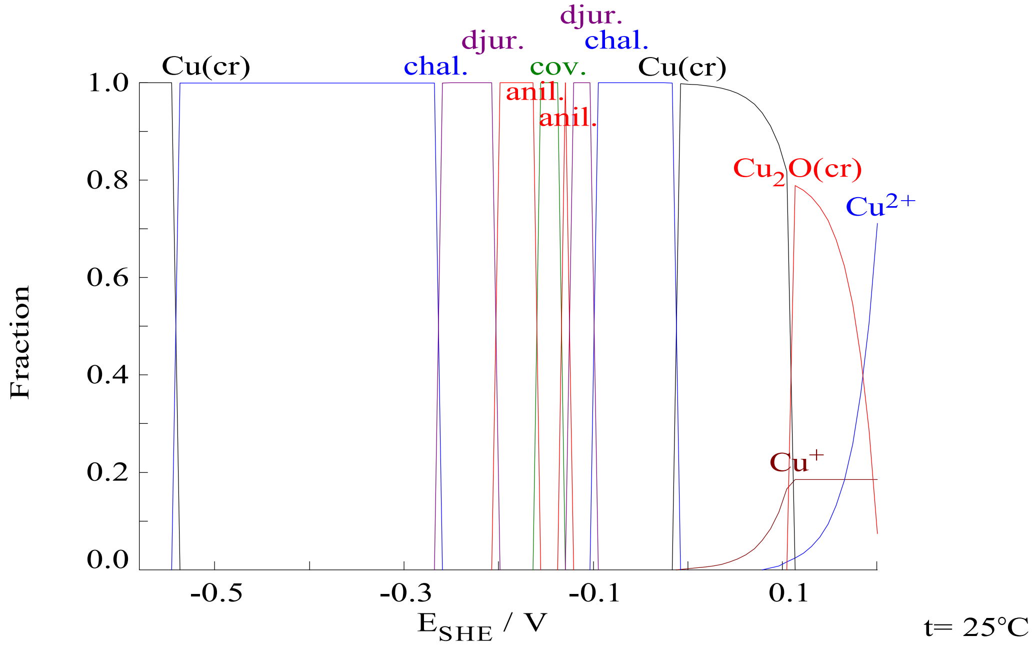


Figure 23.b. Pourbaix diagram for copper in solutions containing $[HS^-]_{TOT}$ = 0.2 mmol/kg and $[Cu]_{TOT} = 10^{-6}$ mol/kg, at 100°C.

For a given pH value, as the redox potential increases, the activity of elemental sulphur goes through a maximum. This results in *double* stability fields for several copper sulphides,

- covellite (CuS) is most stable in the E_H region where sulphur has the highest activity,
- chalcocite (Cu_2S) has two stability regions at E_H values above and below that of covellite.
- djurleite ($Cu_{1.934}S$) and anilite ($Cu_{1.75}S$) have symetric stability fields between those of covellite in the centre and chalcocite.

This is illustrated in Figure 24. It should be noted that both djurleite ($Cu_{1.934}S$) and anilite ($Cu_{1.75}S$) decompose between 75 and 100°C.



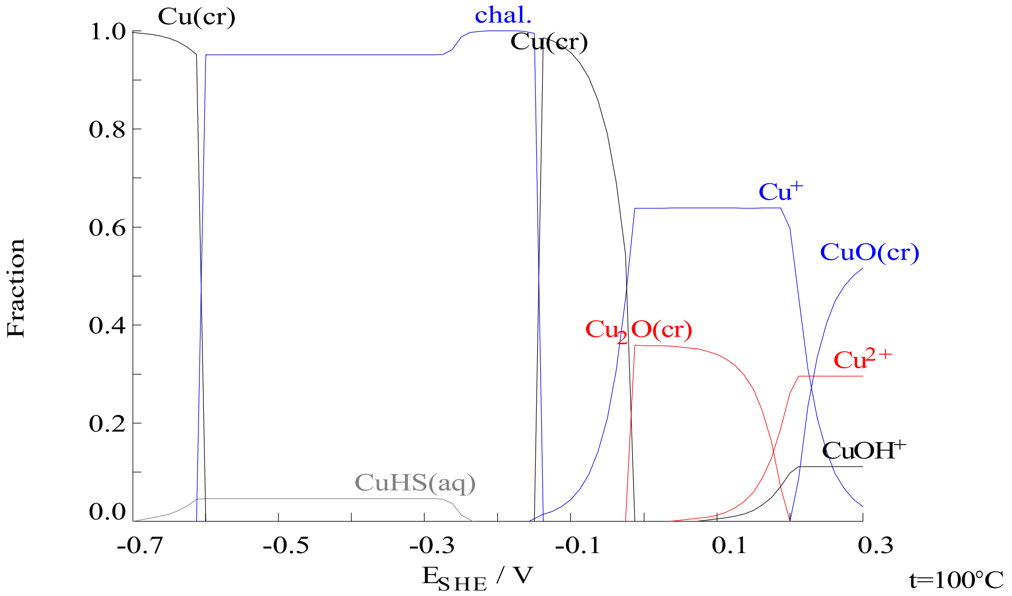


Figure 24. Fraction of copper species as a function of E_H at pH = 6 in solutions containing $[Cu]_{TOT}$ = 10^{-6} mol/kg, $[HS^-]_{TOT}$ = 0.2 mmol/kg, and at 25°C (upper diagram) and 100°C (lower diagram). Abbreviations: chal.= chalcocite (Cu_2S), djur.= djurleite ($Cu_{1.934}S$), anil.= anilite ($Cu_{1.75}S$), and cov.= covellite (CuS).

Copper(I) forms soluble sulphide complexes, which may be responsible for copper migration and mineralisation in reducing sulphide environments. The solubility of copper in sulphide solutions has been determined by several experimental laboratory studies (Crerar and Barnes, 1976; Mountain and Seward, 1999; Shea and Helz, 1988; Thompson and Helz, 1994).

The studies by (Crerar and Barnes, 1976; Mountain and Seward, 1999) have been selected here to evaluate the stability of the copper(I)-sulphide complexes: CuHS(aq), $Cu(HS)_2^-$, and $Cu_2S(HS)_2^{2-}$.

It is of interest to compare this model with the experimental measurements from earlier studies, that were interpreted with more “complex” models containing more complexes (Shea and Helz, 1988; Thompson and Helz, 1994), see Figure 25 and Figure 26. The simpler model model appears to overestimate slightly the experimental values, but it is to be preferred because only a few number of complexes are required. Because of the slightly higher solubilities, the predicted corrosion rates will be conservative (overestimated).

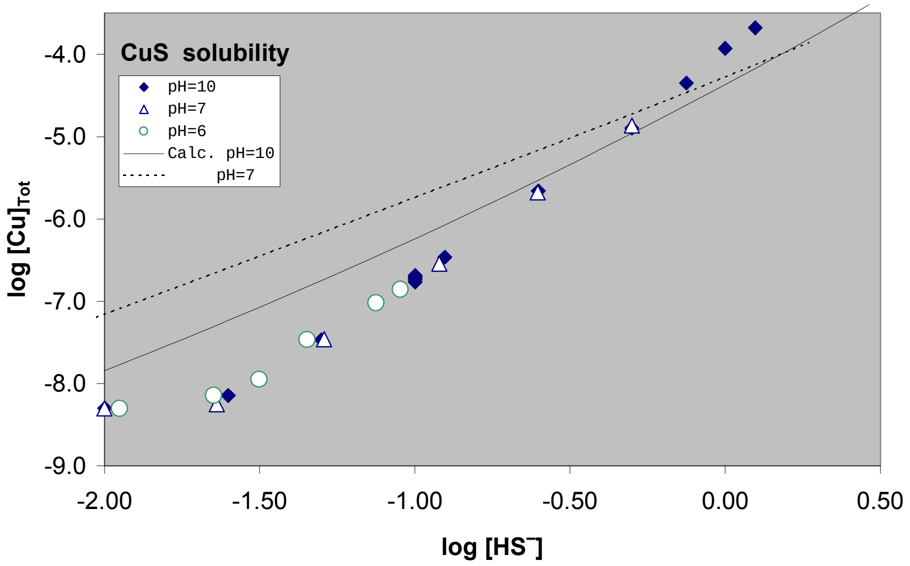
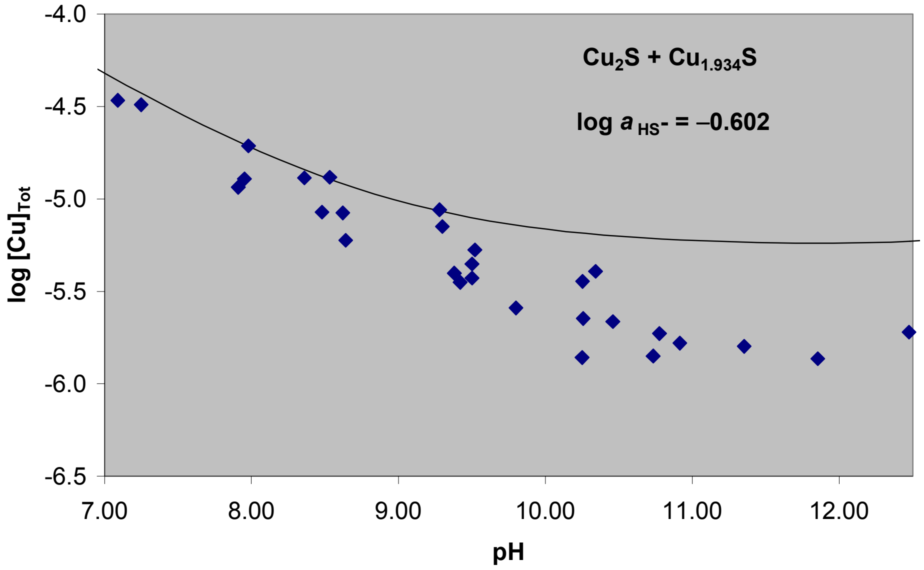


Figure 25. The solubility of the covellite determined by (Shea and Helz, 1988) as a function of $[HS^-]$. The curves show calculations for pH = 10 and 7 with the model proposed by (Mountain and Seward, 1999), involving the following Cu(I)-sulfide complexes: CuHS(aq), $Cu(HS)_2^-$, and $Cu_2S(HS)_2^{2-}$.



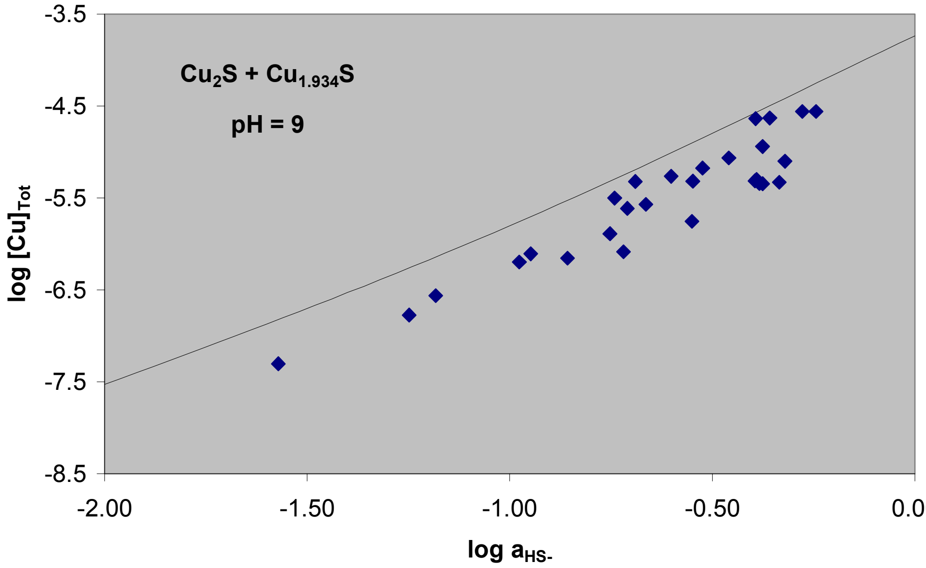


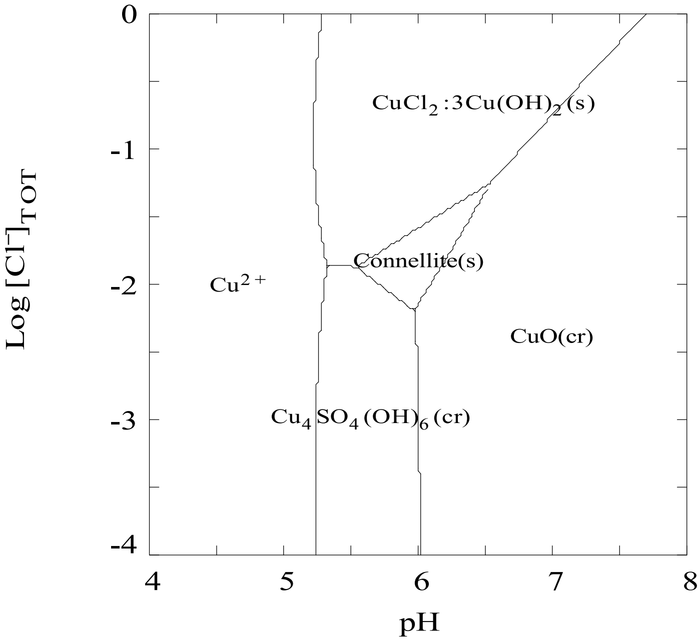
Figure 26. The solubility of the chalcodite-djurleite assemblage determined by (Thompson and Helz, 1994, their Fig. 2) as a function of pH (upper diagram) and of log a_{HS^-} (lower diagram). The curves show solubilities calculated with the model proposed by (Mountain and Seward, 1999).

3.8.2 The Effect of Sulphate

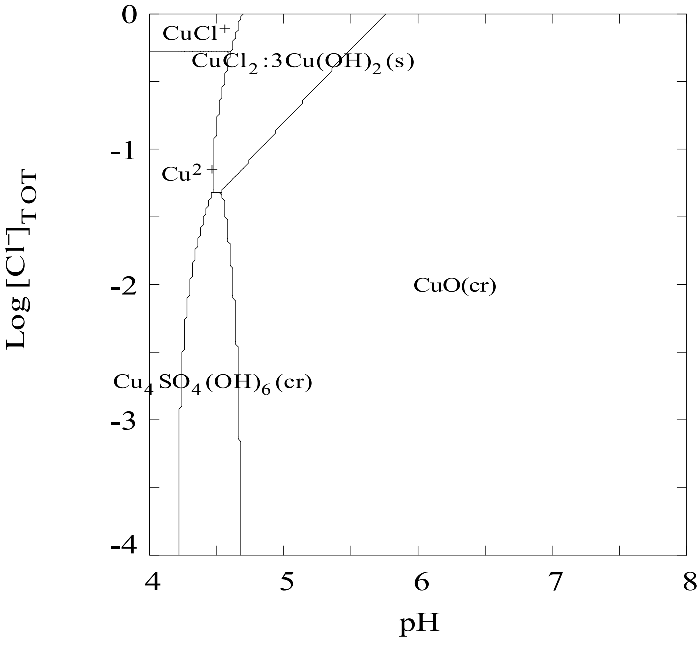
Several sulphate minerals of copper(II) are found in nature, *cf.* Section 7.6.1.1. Some of these solids also contain chloride and hydroxide ions. These solids may influence the corrosion of copper. Most of the granitic Swedish groundwaters have a SO_4^{2-} content up to 11 mmol/kg, *cf.* Table 1.

Calculated stability fields for the sulphate-containing minerals of copper(II) at 25 and 100°C are shown in Figure 27 and in Figure 28. These two figures illustrate the effect of temperature, and increasing concentrations of Cl^-, SO_4^{2-} and CO_3^{2-}. The calculations show that atacamite, $CuCl_2{\cdot}3Cu(OH)_2$, is formed at high chloride concentrations. Tenorite, CuO, is formed at neutral and slightly alkaline pH in the absence of carbonate both at 25 and 100°C, but it is replaced by malachite, $Cu_2CO_3(OH)_2$, at 25°C when $[CO_3^{2-}]_{TOT} = [SO_4^{2-}]_{TOT} = 10^{-2}$ M. Brochantite, $Cu_4SO_4(OH)_6$, and antlerite, $Cu_3SO_4(OH)_4$, are formed in slightly acidic solutions.

The formation of mixed sulphate-chloride-hydroxide corrosion by-products similar to connellite, $Cu_{37}Cl_8(SO_4)_2(OH)_{62}{\cdot}8H_2O$, has been reported from brass corrosion (Stoffyn-Egli et al., 1998). The relative stability of connellite, compared to that of tenorite, CuO, and atacamite, $CuCl_2{\cdot}3Cu(OH)_2$, has been reported by (Pollard et al., 1990). Our calculations produce however a more restricted stability field for connellite (Figure 27). A larger stability field would be in contradiction with the experimental Cu-solubilities (Pollard et al., 1990), *cf.* Section 7.5.1.4.



t= 25°C



t=100°C

Figure 27. Calculated stabilities of copper(II) minerals as a function of pH and Cl^- concentration, at $[SO_4^{2-}]_{TOT} = [Cu^{2+}]_{TOT} = 10^{-3}$ mol/kg and at 25°C (upper diagram) and 100°C (lower diagram).

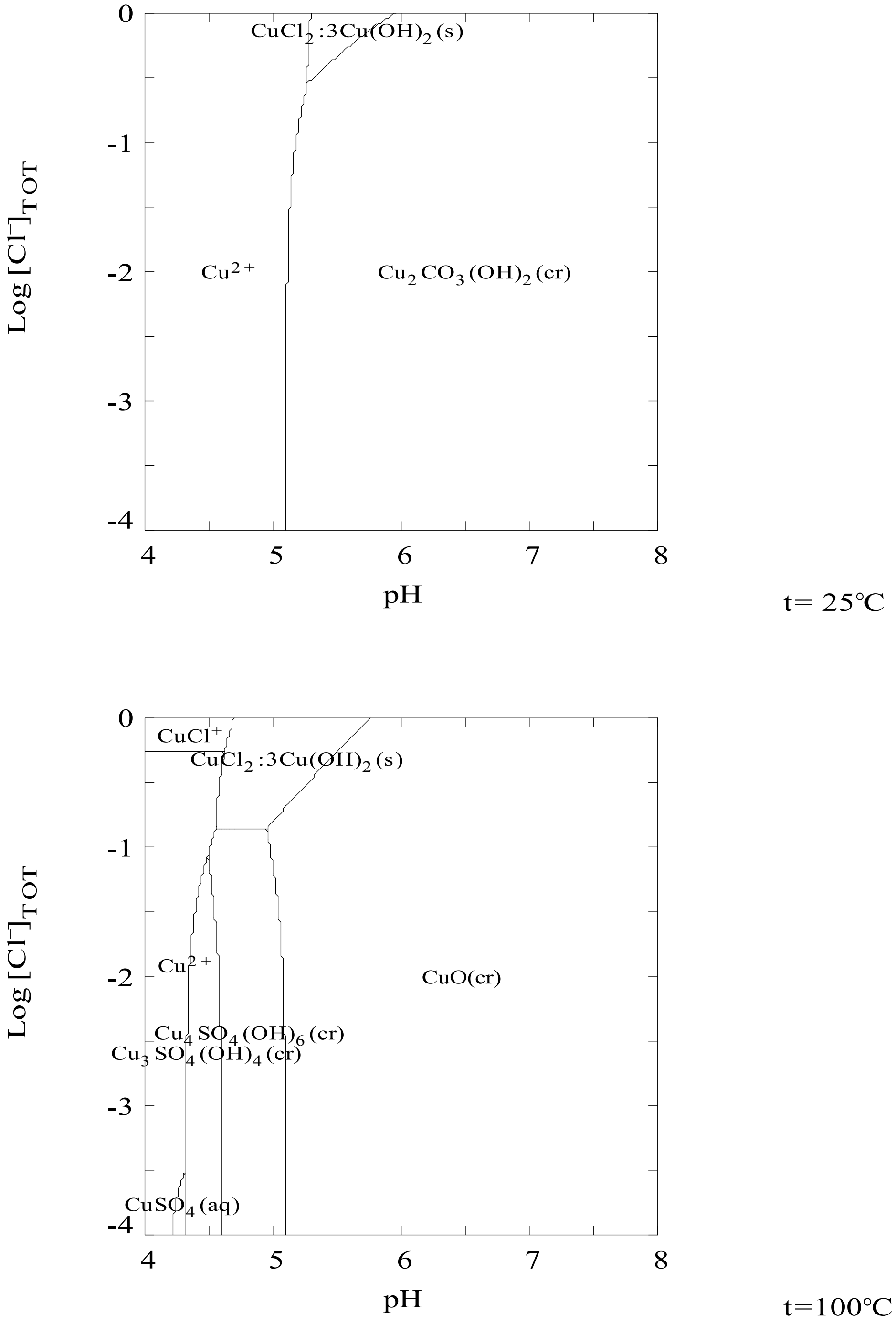


Figure 28. Calculated stability fields of copper(II) minerals as a function of pH and Cl^- concentration, at $[CO_3^{2-}]_{TOT} = [SO_4^{2-}]_{TOT} = 10^{-2}$ mol/kg, $[Cu^{2+}]_{TOT} = 10^{-3}$ mol/kg, and at 25°C.

4 DISCUSSION

The diagrams exposed in previous sections of this report indicate the relative importance of the different electron acceptors (oxidants) for copper corrosion. Only the following deserve further consideration:

- HS^- and O_2
- Cl^- in concentrations exceeding 1 M, especially at elevated temperatures, and in combination with larger $[H^+]$ (*i.e.*, low pH values)

The use of "master" variables, or intensive properties, such as pH and E_H also deserves some attention.

Other oxidants might be envisaged for copper. For example Fe(III). The interactions between the copper and the iron systems have not been discussed here, but they are described in (Ahonen, 1995; Ahonen, 1999). In general the solubility of Fe(III) oxides and hydroxides are too low for iron(III) to affect the integrity of the copper canister.

4.1 pH AND E_H

The concepts of pH and especially E_H are not adequate to describe the corrosion of canisters in nuclear repositories. The amounts of oxidants/reductants, and the stoichiometries of the corrosion reactions are instead the main variables in the system.

However, in some cases it may be justified to consider a given pH value to model the corrosion process. This may be for example in cases where the acidity of the system is buffered by other chemical reactions, such as ion-exchange or carbonate mineral dissolution and precipitation. Also a substantial alkalinity might poise the pH to a particular range.

An equivalent condition for E_H can seldom be claimed. This is due to the fact that the amounts of metal, oxidants, and corrosion products in general exceed or are of comparable magnitude to those of other active redox species, such as Fe(II)/Fe(III), $H_2(aq)$, *etc.*

Given that the amount of copper metal is in excess, only the amounts of oxidants and corrosion products may be considered to be "master" variables. Examples of the former are O_2, HS^- and H^+, and examples of the latter are CuO(cr) and H_2. Other variables of importance are the concentrations of ligands that might stabilise the formation of corrosion products, increasing the driving force for corrosion, *e.g.*, chloride ions.

4.2 SULPHIDE AND OXYGEN

Dissolved sulphide in groundwater is the most damaging component for copper corrosion. If available, dissolved HS^- will react quantitatively with copper to form a variety of sulphides. This applies to all chemical conditions of interest in the context of a nuclear repository (pH, *etc*).

However, sulphide concentrations in natural waters are usually low, owing to the fact that it forms sparingly soluble solids with transition metals, including iron(II), which is widespread in reducing environments.

O_2, if available, will also react quantitatively with copper to produce $Cu_2O(cr)$, Cu^+, *etc*, depending on pH. Molecular oxygen, however, is absent in the deep granitic environment of the nuclear repository.

4.3 CHLORIDE

Chloride can affect copper corrosion negatively. This is because Cl^- stabilises the formation of soluble Cu(I) species. At high chloride concentrations (*e.g.*, $[Cl^-]_{TOT} = 60$ g/ℓ) even H^+, which is always present in aqueous solutions, may oxidise copper to produce H_2. Note that the term "under hydrogen evolution" in this case is not really appropriate, because no gas evolution may occur due to the low amounts of hydrogen produced and the high prevailing pressure.

High Cl-concentrations may be unfavourable for the general corrosion of copper in combination with in the following circumstances:

- Low pH ($\lesssim 4$ at 25°C, or $\lesssim 5$ at 100°C, *cf.* Figure 12).
- The presence of other oxidants than H^+.

The "safe" pH-range indicated depends on temperature and $[Cl^-]_{TOT}$. Increasing amounts of dissolved H_2 (or increasing the corresponding equilibrium partial pressure) will be beneficial, because molecular hydrogen is one of the reaction products, and its presence will decrease the driving force for the reaction. However, quite large concentrations of H_2 are needed to substantially decrease the corrosion of copper. Nevertheless, the most conservative assumption is that no H_2 is present in the near field of the nuclear repository. Figure 12 shows the calculated extend of copper corrosion as a function of acidity when there is no excess H_2.

Models for the thermodynamic behaviour of aqueous solutions are unsatisfactory in concentrated solutions, and some judgement is required when using the results of model calculations for concentrated electrolytes. Results from calculations at high ionic strengths, especially at temperatures above 50°C, should be used bearing in mind this unknown uncertainty.

It should be pointed out however, that the chloride-enhancement of general corrosion may be beneficial for localised corrosion: pitting and stress corrosion cracking are less likely to take place simultaneously with general corrosion.

5 ACKNOWLEDGEMENTS

This work received support and inspiration from Lars Werme at SKB. The report was notably improved after discussions and criticism from several colleagues: Ingmar Grenthe (KTH), Lasse Ahonen (Geological Survey of Finland), and Margit Snellman and Jukka-Pekka Salo (Posiva Oy, Finland).

6 REFERENCES

Adeloju S. B. and Duan Y. Y. (1994) Influence of bicarbonate ions on stability of copper oxides and copper pitting corrosion. *Br. Corros. J.* **29**, 315-320.

Ahonen L. (1995) Chemical stability of copper canisters in deep repository, YJT-95-19, Nuclear Waste Commission of Finnish Power Companies, Finland.

Ahonen L. (1999) Effect of saline water on metallic copper, POSIVA WR 99-58, Posiva Oy, Helsinki, Finland.

Ahrland S. and Rawsthorne J. (1970) The stability of metal halide complexes in aqueous solution. VII. The chloride complexes of copper(I). *Acta Chem. Scand.* **24**, 157-172.

Al-Kharafi F., Shalaby H. M., and Gouda V. K. (1987) Failure of copper pipes in Kuwait's domestic tap water. In *Proc. 10th Internat. Congress on Metallic Corrosion*, pp. 767-781, Madras.

Anderson G. M., Castet S., Schott J., and Mesmer R. E. (1991) The density model for estimation of thermodynamic parameters of reactions at high temperatures and pressures. *Geochim. Cosmochim. Acta* **55**, 1769-1779.

Archer D. G. and Wang P. (1990) The dielectric constant of water and Debye-Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **19**, 371-411.

Arnek R., Puigdomenech I., and Valiente M. (1982) A calorimetric study of copper(II) chloride complexes in aqueous solution. *Acta Chem. Scand.* **A36**, 15-19.

Baes C. F., Jr. and Mesmer R. E. (1976) *The Hydrolysis of Cations*. J. Wiley & Sons, New York, 489 p.

Ball J. W. and Nordstrom D. K. (1991) User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters, USGS-OFR-91-183, U.S. Geological Survey, Menlo Park, California.

Ball J. W., Nordstrom D. K., and Zachmann D. W. (1987) WATEQ4F - a personal computer FORTRAN translation of the geochemical model WATEQ2 with revised data base, USGS/OFR-87-50, U.S. Geological Survey, Menlo Park, California.

Beavers J. A. (1992) Stress-corrosion cracking in copper alloys. In *Stress-corrosion cracking* (ed. R. H. Jones), pp. 211-231. The Materials Information Society.

Bertocci U. and Wagman D. D. (1985) Copper. In *Standard Potentials in Aqueous Solution* (eds. A. J. Bard, R. Parsons, and J. Jordan), pp. 287-293. Int. Union Pure Appl. Chem., Marcel Dekker, New York.

Beverskog B. and Puigdomenech I. (1997a) Revised Pourbaix diagrams for copper at 25 to 300°C. *J. Electrochem. Soc.* **144**, 3476-3483.

Beverskog B. and Puigdomenech I. (1997b) Revised Pourbaix diagrams for zinc at 25-300°C. *Corros. Sci.* **39**, 107-114.

Beverskog B. and Puigdomenech I. (1998) Pourbaix diagrams for the system copper-chlorine at 5-100 °C, SKI-TR-98:19, Swedish Nuclear Power Inspectorate, Stockholm, Sweden.

Bisengalieva M. R., Kiseleva I. A., Melchakova L. V., and Ogorodova L. P. (1993) Thermodynamic properties of malachite and azurite and analysis of sulfidization of oxide copper ores. *Vestn. Mosk. Univ., Ser. 4: Geol.*(2), 38-49. In Russian.

Bisengalieva M. R., Kiseleva I. A., Melchakova L. V., Ogorodova L. P., and Gurevich A. M. (1997) The molar heat capacity of hydrous copper chloride: atacamite $Cu_2Cl(OH)_3$. *J. Chem. Thermodynamics* **29**, 345-352.

Bjerrum J. (1972) On the usefulness and limitations of a "constant ionic medium" for the study of equilibria involving ions in salt solutions. In *Contributions to Coordination Chemistry in Solution*. Trans. Royal Inst. Technol. (ed. E. Högfeldt), pp. 69-77. Swedish Natural Science Research Council, Stockholm, Sweden.

Bjerrum J. (1987) Determination of small stability constants. A spectrophotometric study of copper(II) chloride complexes in hydrochloric acid. *Acta Chem. Scand.* **A41**, 328-334.

Bjerrum J. and Skibsted L. H. (1977) A contribution to our knowledge of weak chloro complex formation by copper(II) in aqueous chloride solutions. *Acta Chem. Scand.* **A31**, 673-677.

Bjerrum J. and Skibsted L. H. (1986) Weak chloro complex formation by copper(II) in aqueous chloride solutions. *Inorg. Chem.* **25**, 2479-2481.

Chase M. W., Jr., Davies C. A., Downey J. R., Jr., Frurip D. J., McDonald R. A., and Syverud A. N. (1985) JANAF Thermochemical tables, third edition. *J. Phys. Chem. Ref. Data* **14, Suppl. No. 1**, 1-1856.

Ciavatta L., Iuliano M., and Porto R. (1993a) Complex formation between copper(I) and phosphate ions. *Annal. Chim. (Roma)* **83**, 39-51.

Ciavatta L., Iuliano M., and Porto R. (1993b) Complex formation equilibria in copper(II) *ortho*phosphate solutions. *Annal. Chim. (Roma)* **83**, 19-38.

Cornwell F. J., Wildsmith G., and Gilbert P. T. (1973) Pitting corrosion of copper tubes in cold water service. *Br. Corros. J.* **8**, 202-209.

Cornwell F. J., Wildsmith G., and Gilbert P. T. (1976) Pitting corrosion of copper tubes in cold water service. In *Galvanic and Pitting Corrosion -*

Field and Laboratory Studies, pp. 155-179. American Society for Testing and Materials. ASTM STP 576.

Cox J. D., Wagman D. D., and Medvedev V. A. (1989) *CODATA Key Values for Thermodynamics*. Hemisphere Publ. Co., New York, 271 p.

Crerar D. A. and Barnes H. L. (1976) Ore solution chemistry V. Solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solution at 200° to 350°C. *Econ. Geol.* **71**, 772-794.

Drogowska M., Bossard L., and Ménard H. (1994) Comparative study of copper behaviour in bicarbonate and phosphate aqueous solutions and effect of chloride ions. *J. Applied Electrochem.* **24**, 344-349.

Edwards M., Chock M. R., and Meyer T. E. (1996) Alkalinity, pH and copper by-product release. *J. AWWA* **88**, 81-94.

Edwards M., Ferguson J. F., and Reiber S. H. (1994a) The pitting corrosion of copper. *J. AWWA* **86**, 74-90.

Edwards M., Rehring J., and Meyer T. (1994b) Inorganic ions and copper pitting. *Corrosion* **50**, 366-372.

Elfström Broo A., Berghult B., and Hedberg T. (1997) Copper corrosion in water distribution systems. The influence of water quality. *Corros. Sci.* **39**, 1119-1132.

Elfström Broo A., Berghult B., and Hedberg T. (1998) Copper corrosion in water distribution systems. The influence of natural organic matter on the solubility of copper corrosion products. *Corros. Sci.* **40**, 1-11.

Ellis A. J. and Giggenbach W. (1971) Hydrogen sulphide ionization and sulphur hydrolysis in high temperature solution. *Geochim. Cosmochim. Acta* **35**, 247-260.

Eriksen T. E., Ndalamba P., and Grenthe I. (1989) On the corrosion of copper in pure water. *Corros. Sci.* **29**, 1241-1250.

Eriksson G. (1979) An algorithm for the computation of aqueous multicomponent, multiphase equilibria. *Anal. Chim. Acta* **112**, 375-383.

Fisher J. F. and Hall J. L. (1967) Polarographic study of complexes of copper(II) ion with ammonia and various ethyl, ethanol, and ethylethanolamines. *Anal. Chem.* **39**, 1550-1556.

Francis P. E., Cheung W. K., and Pemberton R. C. (1990) Electrochemical measurements of the influence of sulphate/hydrogen carbonate ion ratio on the pit initiation process on copper. In *Proc. 11th Internat. Corrosion Congress*, pp. 363-370, Florence, Italy.

Fritz J. J. (1980) Chloride complexes of CuCl in aqueous solution. *J. Phys. Chem.* **84**, 2241-2246.

Gedansky L. M., Woolley E. M., and Hepler L. G. (1970) Thermochemistry of compounds and aqueous ions of copper. *J. Chem. Thermodynamics* **2**, 561-576.

Giggenbach W. (1971) The blue solutions of sulfur in water at elevated temperatures. *Inorg. Chem.* **10**, 1306-1308.

Giggenbach W. F. (1974) Equilibria involving polysulfide ions in aqueous sulfide solutions up to 240°. *Inorg. Chem.* **13**, 1724-1730.

Grauer R. and Berner U. (1999) Solubility products of M(II) - carbonates, PSI Bericht Nr. 99-04, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland. NAGRA-TR-95-08.

Grenthe I., Fuger J., Konings R. J. M., Lemire R. J., Muller A. B., Nguyen-Trung C., and Wanner H. (1992a) *Chemical Thermodynamics of Uranium*. North-Holland, Elsevier Sci. Publ. B.V., Amsterdam, 715 p.

Grenthe I. and Plyasunov A. (1997) On the use of semiempirical electrolyte theories for the modeling of solution chemical data. *Pure & Appl. Chem.* **69**, 951-958.

Grenthe I., Plyasunov A. V., and Spahiu K. (1997) Estimations of medium effects on thermodynamic data. In *Modelling in Aquatic Chemistry* (eds. I. Grenthe and I. Puigdomenech), pp. 325-426. OECD Nuclear Energy Agency, Paris, France.

Grenthe I., Stumm W., Laaksuharju M., Nilsson A.-C., and Wikberg P. (1992b) Redox potentials and redox reactions in deep groundwater systems. *Chem. Geol.* **98**, 131-150.

Gübeli A. O., Hébert J., Côté P. A., and Taillon R. (1970) L'action de l'ammoniac sur l'oxyde cuivrique et les hydroxo-complexes de cuivre (II). *Helv. Chim. Acta* **53**, 186-187.

Helgeson H. C., Kirkham D. H., and Flowers G. C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. *Am. J. Sci.* **281**, 1249-1516.

Hovey J. K. and Hepler L. G. (1990) Thermodynamics of sulphuric acid: apparent and partial molar heat capacities and volumes of aqueous HSO_4^- from 10-55 °C and calculation of the second dissociation constant to 350 °C. *J. Chem. Soc., Faraday Trans.* **86**, 2831-2839.

Hultquist G. (1986) Hydrogen evolution in corrosion of copper in pure water. *Corros. Sci.* **26**, 173-177.

Hultquist G., Chuah G. K., and Tan K. L. (1989) Comments on hydrogen evolution from the corrosion of pure copper. *Corros. Sci.* **29**, 1371-1377.

Högfeldt E. (1982) *Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands*. Int. Union Pure & Appl. Chem., Pergamon Press, Oxford.

Ingri N., Kakolowicz W., Sillén L. G., and Warnqvist B. (1967) High-speed computers as a supplement to graphical methods - V. HALTAFALL, a general program for calculating the composition of equilibrium mixtures. *Talanta* **14**, 1261-1286. *Errata:* 15 (1968) xi-xii. See also [Warnqvist, 1971 #384].

Izatt R. M., Christensen J. J., Oscarson J. L., and Gillespie S. E. (1989) Determination of thermodynamic data for modeling corrosion. Vol. 1: Sulfates (Revision 1), EPRI-NP-5708, Electric Power Research Inst., Palo Alto, California.

Jargelius R. F. A. and Wallin T. (1986) The effect of nitrogen alloying on the pitting and crevice corrosion resistance of CrNi and CrNiMo austenitic stainless steels. In *Proc. 10th Scandinavian Corrosion Congress*, pp. 161-164. Bulletin of the Swedish Corrosion Institute, Vol.101, Stockholm.

King E. G., Mah A. D., and Pankratz L. B. (1973) *Thermodynamic properties of copper and its inorganic compounds*. The International Copper Research Association (INCRA), New York.

Kiseleva I. A., Ogorodova L. P., Melchakova L. V., Bisengalieva M. R., and Bekturganov M. S. (1992) Thermodynamic properties of copper carbonates - Malachite $Cu_2(OH)_2CO_3$ and azurite $Cu_3(OH)_2(CO_3)_2$. *Phys. Chem. Mineral.* **19**, 322-333.

Knacke O., Kubaschewski O., and Hesselmann K. (1991) *Thermochemical Properties of Inorganic Substances*. Springer-Verlag, Berlin, 2412 p. 2 edition.

Kubaschewski O., Alcock C. B., and Spencer P. J. (1993) *Materials Thermochemistry*. Pergamon Press, Oxford, 363 p. 6 edition.

Langmuir D. (1997) *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle River, NJ.

Latimer W. M. (1952) *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*. Prentice-Hall, Englewood Cliffs, N.J., 392 p. 2 edition.

Martell A. E. and Smith R. M. (1974) *Critical Stability Constants, Vol. 1: Amino Acids*. Plenum Press, New York, 469 p.

Martell A. E. and Smith R. M. (1975) *Critical Stability Constants, Vol. 2: Amines*. Plenum Press, New York, 415 p.

Martell A. E. and Smith R. M. (1977) *Critical Stability Constants, Vol. 3: Other Organic Ligands*. Plenum Press, New York, 495 p.

Martell A. E. and Smith R. M. (1982) *Critical Stability Constants, Vol. 5: First Supplement*. Plenum Press, New York, 604 p.

Martell A. E., Smith R. M., and Motekaitis R. J. (1997) *Critically Selected Stability Constants of Metal Complexes Database. Version 4.0*. National Institute of Standards and Technology (NIST); Texas A & M University. (http://www.nist.gov/srd).

Mattsson E. (1980) Corrosion of copper and brass: Practical experience and basic data. *Br. Corros. J.* **15**, 6-13.

Mattsson E. and Fredriksson A.-M. (1968) Pitting corrosion in copper tubes - Causes and countermeasures. *Br. Corros. J.* **3**, 246-257.

Mills K. C. (1974) *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*. Butterworths, London.

Mountain B. W. and Seward T. M. (1999) The hydrosulphide/sulphide somplexes of copper(I): Experimental determination of stoichiometry and stability at 22°C and reassessment of high temperature data. *Geochim. Cosmochim. Acta* **63**, 11-29.

Möller K. (1995) Kopparkorrosion i rent syrefritt vatten, SKI R 95:72, Swedish Nuclear Power Inspectorate, Stockholm, Sweden. In Swedish.

Nakayama F. S. (1971) Thermodynamic functions for the dissociation of $NaHCO_3^0$, $NaCO_3^-$, H_2CO_3 and HCO_3^-. *J. Inorg. Nucl. Chem.* **33**, 1287-1291.

Newman R. C. and Ajjawi M. A. A. (1986) A micro-electrode study of the nitrate effect on pitting of stainless steels. *Corros. Sci.* **26**, 1057-1063.

Nordstrom D. K., Ball J. W., Donahoe R. J., and Whittemore D. (1989) Groundwater chemistry and water-rock interactions at Stripa. *Geochim. Cosmochim. Acta* **53**, 1727-1740.

Näsänen R. and Tamminen V. (1949) The equilibria of cupric hydroxysalts in mixed aqueous solutions of cupric and alkali salts at 25°. *J. Am. Chem. Soc.* **71**, 1994-1998.

Oelkers E. H. and Helgeson H. C. (1990) Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions. *Geochim. Cosmochim. Acta* **54**, 727-738.

Pedersen K. (1997) Investigations of subterranean microorganisms and their importance for performance assessment of radioactive waste disposal. Results and conclusions achieved during the period 1995 to 1997, SKB-TR-97-22, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

Perrin D. D. (1979) *Stability Constants of Metal-Ion Complexes. Part B: Organic Ligands*. Int. Union Pure & Appl. Chem., Pergamon Press, Oxford.

Pettit L. and Powell K. (1997) *The IUPAC Stability Constants Database*. IUPAC Commission on Equilibrium Data and Academic Software. http://www.cityscape.co.uk/users/gr71.

Pollard A. M., Thomas R. G., and Williams P. A. (1990) Connellite: stability relationships with other secondary copper minerals. *Mineral. Mag.* **54**, 425-430.

Potter I., R. W. (1977) An electrochemical investigation of the system copper-sulphur. *Econ. Geol.* **72**, 1524-1542.

Puigdomenech I. (1983) INPUT, SED and PREDOM: computer programs drawing equilibrium diagrams, TRITA-OOK-3010, Dept. Inorg. Chem., Royal Institute of Technology, 100 44 Stockholm, Sweden. 12 p.

Puigdomenech I. and Nordstrom D. K. (1987) Geochemical interpretation of groundwaters from Finnsjön, Sweden, SKB-TR-87-15, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. 36 p.

Puigdomenech I., Rard J. A., Plyasunov A. V., and Grenthe I. (1997) Temperature corrections to thermodynamic data and enthalpy calculations. In *Modelling in Aquatic Chemistry* (eds. I. Grenthe and I. Puigdomenech), pp. 427-493. OECD Nuclear Energy Agency, Paris, France.

Robie R. A. and Hemingway B. S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures, USGS Bull. 2131, U.S. Geological Survey. 461 p.

Robie R. A., Hemingway B. S., and Fisher J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures, USGS Bull. 1452, U.S. Geological Survey. 456 p.

Rose A. W. (1989) Mobility of copper and other heavy metals in sedimentary environments. In *Sediment-hosted Stratiform Copper Deposits* (eds. R. W. Boyle, A. C. Brown, C. W. Jefferson, E. C. Jowett, and R. V. Kirkhams), pp. 97-110. Geol. Assoc. Can. Special Paper 36.

Schumacher M. (1979) *Seawater Corrosion Handbook*. Noyes Data Corporation, Park Ridge, New Jersey.

Schwarzenbach G. and Fischer A. (1960) Die Acidität der Sulfane und die Zusammensetzung wässeriger Polysulfidlösungen. *Helv. Chim. Acta* **43**, 1365-1390. In German.

SCI. (1978) The Swedish Corrosion Institute and its reference group: Copper as canister material for unreprocessed nuclear waste - Evaluation with respect to corrosion, KBS-TR-90, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

SCI. (1983) The Swedish Corrosion Institute and its reference group: Corrosion resistance of a copper canister for spent nuclear fuel, SKBF/KBS-TR-83-24, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

Shalaby H. M., Al-Kharafi F., and Said A. J. (1990) Corrosion morphology of copper in dilute sulphate, chloride and bicarbonate solutions. *Br. Corros. J.* **25**, 292-298.

Sharma V. K. and Millero F. J. (1988) The oxidation of Cu(I) in electrolyte solutions. *J. Solution Chem.* **17**, 581-599.

Sharma V. K. and Millero F. J. (1990) Equilibrium constants for the formation of Cu(I) halide complexes. *J. Solution Chem.* **19**, 375-390.

Shea D. and Helz G. R. (1988) The solubility of copper in sulfidic waters: sulfide and polysulfide complexes in equilibrium with covellite. *Geochim. Cosmochim. Acta* **52**, 1815-1825.

Shea D. and Helz G. R. (1989) Solubility product constants of covellite and poorly crystalline copper sulfide precipitate at 298 K. *Geochim. Cosmochim. Acta* **53**, 229-236.

Shinohara T., Fujimoto S., Laycock N. J., Msallem A., Ezuber H., and Newman R. C. (1997) Numerical and experimental simulation of iron dissolution in a crevice with a very dilute bulk solution. *J. Electrochem. Soc.* **144**, 3791-3796.

Shock E. L. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. *Geochim. Cosmochim. Acta* **52**, 2009-2036. *Errata:* **53** (1989) 215.

Shock E. L. and Helgeson H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* **54**, 915-945.

Shock E. L., Helgeson H. C., and Sverjensky D. A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **53**, 2157-2183.

Shock E. L., Oelkers E. H., Johnson J. W., Sverjensky D. A., and Helgeson H. C. (1992) Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000 °C and 5 kbar. *J. Chem. Soc., Faraday Trans.* **88**, 803-826.

Shock E. L., Sassani D. C., Willis M., and Sverjensky D. A. (1997) Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* **61**, 907-950.

Sillén L. G. and Martell A. E. (1964) *Stability Constants of Metal-Ion Complexes*. The Chemical Society, London. Special Publ. No. 17.

Sillén L. G. and Martell A. E. (1971) *Stability Constants of Metal-Ion Complexes. Suppl. No 1*. The Chemical Society, London. Special Publ. No 25.

Silva R. J., Bidoglio G., Rand M. H., Robouch P. B., Wanner H., and Puigdomenech I. (1995) *Chemical Thermodynamics of Americium*. North-Holland, Elsevier Sci. Publ. B.V., Amsterdam, 374 p.

Simpson J. P. and Schenk R. (1987) Hydrogen evolution from corrosion of pure copper. *Corros. Sci.* **27**, 1365-1370.

SKB. (1998) Detailed programme for research and development 1999-2004, Background Report to RD & D-Programme 98, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

Smith R. M. and Martell A. E. (1976) *Critical Stability Constants, Vol. 4: Inorganic Complexes*. Plenum Press, New York, 257 p.

Smith R. M. and Martell A. E. (1989) *Critical Stability Constants, Vol. 6: Second Supplement*. Plenum Press, New York, 643 p.

Soli A. L. and Byrne R. H. (1989) Temperature dependence of Cu(II) carbonate complexation in natural seawater. *Limn. Ocean.* **34**, 239-244.

Spahiu K. and Puigdomenech I. (1998) On weak complex formation: Reinterpretation of literature data on the Np and Pu nitrate complexation. *Radiochim. Acta* **82**, 413-419. (*in print*).

Stoffyn-Egli P., Buckley D. E., and Clyburne J. A. C. (1998) Corrosion of brass in a marine environment: mineral products and their relationship to variable oxidation and reduction conditions. *Appl. Geochem.* **13**, 643-650.

Stumm W. and Morgan J. J. (1996) *Aquatic Chemistry,* 3*rd* edn. John Wiley & Sons, New York.

Suzuki Y. and Hisamatsu Y. (1981) Stress corrosion cracking of pure copper in dilute ammoniacal solutions. *Corrosion Sci.* **21**, 353-368.

Sverjensky D. A., Shock E. L., and Helgeson H. C. (1997) Prediction of the Thermodynamic Properties of Aqueous Metal Complexes to 1000° and 5 kb. *Geochim. Cosmochim. Acta* **61**, 1359-1412.

Symes J. L. and Kester D. R. (1985) Copper(II) interaction with carbonate species based on malachite solubility in perchlorate medium at the ionic strength of seawater. *Marine Chem.* **16**, 189-211.

Tanger J. C., IV and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.* **288**, 19-98.

Taxén C. (1996) Pitting corrosion of copper. An equilibirum - mass transport study, KI Rapport 1996:8-E, Swedish Corrosion Institute, Stockholm, Sweden. Presented in 13:*th* International Corrosion Conference, 25-29 November, Melbourne, Australia. Paper 141.

Thomas J. G. N. and Tiller A. K. (1972) Formation and breakdown of surface films on copper in sodium hydrogen carbonate and sodium chloride solutions. I. Effects of anion concentrations. *Br. Corros. J.* **7**, 256-263.

Thomas R. G. N. (1994) The mechanism of corrosion prevention by inhibitors. In *Corrosion, 3rd* edn., Vol. 2 (eds. L. L. Shrier, R. A. Jarman, and G. T. Burstein), pp. 17:40-17:65. Butterworth-Heinemann, Oxford.

Thompson R. A. and Helz G. R. (1994) Copper speciation in sulfidic solutions at low sulfur activity: Further evidence for cluster complexes? *Geochim. Cosmochim. Acta* **58**, 2971-2983.

Toropova V. F., Sirotina I. A., and Rotanova V. B. (1955) Thiosulfate complexes of copper and silver. *Uchenye Zapiski Kazanskogo Gosudarst. Univ. im. V.I.Ul'yanova-Lenina, Khim.* **115**(3), 53-60. In Russian.

Tremaine P. and Xiao C. (1995) Standard partial molar heat capacities and volumes of aqueous divalent and trivalent ions from measurements near 25°C. In *Physical Chemistry of Aqueous Systems. Meeting the Needs of Industry* (eds. H. J. White, Jr., J. V. Sengers, D. B. Neumann, and J. C. Bellows), pp. 511-517. Begell House, New York. Proc. 12*th* International Conference on the Properties of Water and Steam, 1994, Orlando, Fla.

Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., and Nuttall R. L. (1982) The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C_1 and C_2 organic substances in SI units. *J. Phys. Chem. Ref. Data* **11, Suppl. No. 2**, 1-392.

Wagner D., Tietz M., von Franqué O., and Fischer W. R. (1996) Remedial measures versus microbially influenced corrosion in copper potable water installations. In *Proc. 13th Internat. Corrosion Congress*, Vol. 40, Melbourne, Australia. Paper 143.

Wallin T. (1983) Thermodynamic estimates of the solubility of copper in contact with groundwaters of different composition, Appendix 3 in "Corrosion resistance of a copper canister for spent nuclear fuel" (The Swedish Corrosion Institute and its reference group), SKBF/KBS-TR-83-24, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

van Muylder J. and Pourbaix M. (1974) Phosphorus. In *Atlas of Electrochemical Equilibria in Aqueous Solutions,* 2*nd* edn. (ed. M. Pourbaix), pp. 504-515. Nat. Ass. Corrosion Engineers, Houston, Texas, and CEBELCOR, Brussels.

Wang M., Zhang Y., and Muhammed M. (1997) Critical evaluation of thermodynamics of complex formation of metal ions in aqueous systems. III. The system Cu(I,II)-Cl^--e at 298.15 K. *Hydrometal.* **45**, 53-72.

Xiao Z., Gammons C. H., and Williams-Jones A. E. (1998) Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300°C and saturated water vapor pressure. *Geochim. Cosmochim. Acta* **62**, 2949-2964.

7 APPENDIX: SELECTION OF THERMODYNAMIC DATA

A review of published thermodynamic data has been performed for solids and aqueous species of copper. Two types of data are of interest:

- Thermodynamic data: standard molar Gibbs free energy of formation from the elements ($\Delta G_f°$), standard molar entropy ($S°$), and standard molar heat capacity ($C_p°$). For aqueous species these data corresponds to the standard *partial* molar properties.

  From the values of $\Delta G_f°$, the Gibbs free energy change for a reaction can be calculated, and the equilibrium constant is then given by:

  $$\log K° = \frac{-\Delta G°}{RT\ln(10)}$$

  Extrapolation of $\Delta G_f°$ values to other temperatures than the reference value of 25°C is performed with the methodology described in Section 2.3.

  Missing values for entropies and heat capacities at 25°C have been estimated with the procedures described below in Section 7.2.

- Equilibrium constants, enthalpies, entropies, and heat capacities for reactions in aqueous solution. For complex formation, with a ligand “L”, a stepwise equilibrium constant, K_n, refers to a reaction:

  $$\mathrm{CuL}_{n-1} + \mathrm{L} \rightleftharpoons \mathrm{CuL}_n$$

  where electric charges are omitted for brevity. The global equilibrium constant, β_n, is used for a reaction like:

  $$\mathrm{Cu} + n\,\mathrm{L} \rightleftharpoons \mathrm{CuL}_n$$

  Extrapolation of values to (and from) the standard state of zero ionic strength is performed as described in Section 0. Values of $\Delta G_f°$ and $S°$ may be obtained from reaction data in combination with relevant auxiliary thermodynamic data (given in Table 4).

Thermodynamic data, mostly for solids and gases, are compiled for example in (Bertocci and Wagman, 1985; Chase et al., 1985; Cox et al., 1989; Gedansky et al., 1970; Knacke et al., 1991; Kubaschewski et al., 1993; Robie and Hemingway, 1995; Wagman et al., 1982).

Sources of equilibrium constants may be found in specialised reviews, like (Baes and Mesmer, 1976). The *Stability Constants* compilations (Högfeldt, 1982; Perrin, 1979; Sillén and Martell, 1964; Sillén and Martell, 1971) contain information on essentially all published values. Nearly all the reported equilibrium constants are expressed in concentration units, and therefore, the numerical values are only valid in the given ionic medium. The IUPAC Commission on Equilibrium Data maintains an electronic version of the Stability Constants (Pettit and Powell, 1997). In the *Critical Stability Constants* compilation (Martell and Smith, 1974; Martell and Smith, 1975; Martell and Smith, 1977; Martell and Smith, 1982; Smith and Martell, 1976; Smith and Martell, 1989) the authors have made a selection of the "best" values at certain specified ionic strengths. However, there is no information given on the method used to select the data. The National Institute of Standards and Technology maintains an electronic version of the Critical Stability Constants (Martell et al., 1997).

The data selected for the calculations performed in this report are summarised in Table 2.

Table 2. Thermodynamic data at 25°C for copper, copper compounds and aqueous species.

	ΔG_f°	S°	$C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = a + bT + cT^{-2}$		
Species	(kJ/mol)	$(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$a^\dagger$	$b \times 10^3$	$c \times 10^{-6}$
Cu(cr)	0.	33.15	20.531	8.611	0.155
Cu^+	48.87	40.6	57.3		
CuOH(aq)	−122.32	226	−280		
$Cu(OH)_2^-$	−333.05	−135	562		
Cu_2O(cr)	−147.90	92.36	58.199	23.974	−0.159
Cu^{2+}	65.04	−98.0	−23.8		
$CuOH^+$	−126.66	−61	382		
$Cu(OH)_2$(aq)	−316.54	26	214		
$Cu(OH)_3^-$	−493.98	−14	105		
$Cu(OH)_4^{2-}$	−657.48	−175	800		
$Cu_2(OH)_2^{2+}$	−285.1	−4	190		
$Cu_3(OH)_4^{2+}$	−633.0	−59	404		
CuO(cr)	−128.29	42.6	48.597	7.427	−0.761
$Cu(OH)_2$(cr)	−359.92	87.0	86.99	23.26	−0.54
CuF(cr)	−192.22	65.26	47.9		
CuF^+	−225.5	−38	99		
CuF_2(cr)	−501.5	73.0	72.01	19.96	−1.138

†: For aqueous ions and complexes "*a*" corresponds to the standard partial molar heat capacity at 25°C, and its temperature dependence has been calculated with the revised Helgeson-Kirkham-Flowers model as described in the text.

Table 2. (Continued)

	ΔG_f°	S°	$C_p^\circ(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = a + bT + cT^{-2}$		
Species	(kJ/mol)	$(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$	a	$b \times 10^3$	$c \times 10^{-6}$
$CuF_2{\cdot}2H_2O$(cr)	–998.21	152.75	152.3		
CuCl(aq)	–101.2	173.	–215		
$CuCl_2^-$	–245.6	202.	–20		
$CuCl_3^{2-}$	–372.48	217.	98		
$Cu_2Cl_4^{2-}$	–487.42	325	80		
$Cu_3Cl_6^{3-}$	–731.99	349	70		
CuCl(cr)	–120.	87.	38.28	34.98	
$CuCl^+$	–69.81	–3.25	88		
$CuCl_2$(aq)	–198.75	73.4	158		
$CuCl_3^-$	–321.25	121.6	187		
$CuCl_4^{2-}$	–437.05	145.9	174		
$CuCl_2$(cr)	–176.07	116.7	67.03	17.57	
$CuCl_2{\cdot}3Cu(OH)_2$(cr)	–1339.9	335.57	312.621	134.86	–3.10959
$Cu_{37}Cl_8(SO_4)_2(OH)_{62}{\cdot}8H_2O$(cr)	–15635.12	3409.	3525.3		
$CuClO_3^+$	55.14	36.3	161		
CuHS(aq)	–13.2	206	–209		
$Cu(HS)_2^-$	–22.98	239	32		
$Cu_2S(HS)_2^{2-}$	–32.59	80	–270		
Cu_2S(cr)	–84.11	116.2	52.84	78.74	
$Cu_{1.934}S$(cr)	–82.4	109.6	73.0		
$Cu_{1.75}S$(cr)	–76.4	98.3	68.4		
CuS(cr)	–48.65	64.4	44.35	11.05	
$CuS_2O_3^-$	–531.36	130	–35		
Cu_2SO_4(cr)	–657.4	201	126.8		
$CuSO_4$(aq)	–692.154	–18.15	–96		
$CuSO_4$(cr)	–662.2	109.2	152.84	–12.30	–7.159
$CuSO_4{\cdot}5H_2O$(cr)	–1880.0	301.2	70.88	–18.58	
$Cu_4SO_4(OH)_6$(cr)	–1818.0	339.7	258.57	387.23	–4.4649
$Cu_4SO_4(OH)_6{\cdot}H_2O$(cr)	–2044.0	335.	403.5		
$Cu_3SO_4(OH)_4$(cr)	–1446.6	266.4	362.7		

Table 2. (Continued)

	ΔG_f°	S°	$C_p^\circ(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = a + bT + cT^{-2}$		
Species	(kJ/mol)	($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	a	$b \times 10^3$	$c \times 10^{-6}$
$CuO{\cdot}CuSO_4$(cr)	−792.26	157.3	170.83	45.355	−3.925
$Cu(NH_3)_2^+$	−64.5	272	207		
$CuNH_3^{2+}$	15.0	12.1	51		
$Cu(NH_3)_2^{2+}$	−31.2	112	126		
$Cu(NH_3)_3^{2+}$	−73.9	197	201		
$Cu(NH_3)_4^{2+}$	−112.1	272	276		
$CuNH_3OH^+$	−183.4	68	126		
$Cu(NH_3)_2(OH)_2$(aq)	−399.8	191	276		
$Cu(NH_3)_3OH^+$	−257.9	210	275		
$CuNO_2^+$	21.64	43.5	115		
$Cu(NO_2)_2$(aq)	−14.01	166.	170		
$CuNO_3^+$	−48.61	34.	130		
$Cu(NO_3)_2$(aq)	−154.26	185	−160		
$Cu(NO_3)_2{\cdot}3Cu(OH)_2$(cr)	−1278.67	399.2	415.0		
CuH_2PO_4(aq)	−1093.25	150	0		
$Cu(H_2PO_4)_2^-$	−2235.71	230	0		
$Cu(HPO_4)(H_2PO_4)^{2-}$	−2208.31	170	0		
$CuHPO_4$(aq)	−1054.35	−20	−70		
$Cu(HPO_4)_2^{2-}$	−2168.94	−170	−200		
$Cu(HPO_4)(H_2PO_4)^-$	−2198.64	−40	−200		
$CuH_2PO_4^+$	−1078.62	0	200		
$Cu(H_2PO_4)_2$(aq)	−2220.34	100	0		
$Cu_3(PO_4)_2$(cr)	−2066.20	370	229		
$Cu_3(PO_4)_2{\cdot}3H_2O$(cr)	−2767.75	504	351		
$CuCO_3$(aq)	−501.50	−19	−117		
$Cu(CO_3)_2^{2-}$	−1048.98	122	−410		
$CuHCO_3^+$	−532.08	65.4	170		
$CuCO_3$(cr)	−528.20	87.9	92.05	38.91	−1.799
$Cu_2CO_3(OH)_2$(cr)	−902.35	166.3	49.57	328.36	−0.616
$Cu_3(CO_3)_2(OH)_2$(cr)	−1431.43	254.4	137.89	387.46	−2.205

7.1 IONIC STRENGTH EFFECTS

7.1.1 Extrapolations of Experimental log *K* Values to *I* = 0

When several values of K_{eq} at different ionic strengths are reported in the literature for a given equilibrium reaction, the best extrapolation method is the "SIT" model (Grenthe and Plyasunov, 1997; Grenthe et al., 1997). This allows the standard state value, $K°_{eq}$, to be calculated with an uncertainty which in general is better than ±0.1 log-units from values of K_{eq} determined at ionic strengths lower than about 3 M.

The SIT equation for the activity coefficient of an aqueous ion, γ_j, is given as:

$$\log \gamma_j = - z_j^2\, D_H(I) + \sum_k \varepsilon(j, k)\, m_k \qquad (6)$$

where z_j is the charge of the ion; m_i is the molality (mol/(kg of H_2O)); I is the ionic strength ($I = 0.5 \sum_i m_i z_i^2$); $D_H(I)$ is a Debye-Hückel term that accounts for long range electrostatic interactions:

$$D_H(I) = \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}},$$

where A is a temperature and pressure dependent parameter, equal to 0.5101 $(\mathrm{mol\ kg})^{-1/2}$ at 25°C and 1 bar (Archer and Wang, 1990).

The sum in Eq.(6) extends over all species k, of concentration m_k, present in solution. The $\varepsilon(j,k)$ terms are specific ion interaction coefficients between ions j and k. This coefficient is temperature and pressure dependent, but it is assumed not to be dependent on the ionic medium. The main assumption for the SIT model is that the $\varepsilon(j,k)$ coefficients are zero for ions of the same charge sign. This assumption, which is the basis of the "specific ion interaction" approach, has been found to be a good approximation for activity coefficients of mixtures of (1:1) electrolytes.

When only a single experimental determination of K_{eq} is available, and information on $\varepsilon(j,k)$ coefficients can not be obtained for many of the reactants, it may be necessary to use crude expressions, like the Davies equation

$$\log \gamma_i = -z_i^2 A\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right) \qquad (7)$$

7.2 TEMPERATURE EFFECTS: ESTIMATION OF ENTROPIES AND HEAT CAPACITIES

The temperature dependence of $\Delta G°$ values may be expressed as:

$$\Delta G°(T) = \Delta G°(T_0) - (T - T_0)\Delta S°(T_0) + \int_{T_0}^{T} \Delta C_{\mathrm{p}}^{\circ}\,\mathrm{d}T - T\int_{T_0}^{T} \frac{\Delta C_{\mathrm{p}}^{\circ}}{T}\,\mathrm{d}T$$

as described in Section 2.3. Therefore, to calculate equilibrium constants at $T \neq 25°\text{C}$, the following is needed:

- values of $\Delta G_f°$ and $S°$ (or of $\log K°$ and $\Delta S°$) at the reference temperature
- the temperature-function for the heat capacity: $\Delta C_p°(T)$. For small temperature intervals (for example 0 to 150°C) a constant value of $\Delta C_p°$ might give adequate results. For special kinds of reactions, the approximation $\Delta C_p° \approx 0$ may be used.

For solid phases the $C_p°(T)$ function is expressed as a polynomial function of T, usually $C_p° = a + bT + cT^{-2}$. For aqueous species however, different models are used to describe the $C_p°(T)$ function, for example, the method of Helgeson and co-workers (Sverjensky et al., 1997), and the “density” model (Anderson et al., 1991; Tremaine and Xiao, 1995).

Values of $S°$ or $\Delta C_p°(T)$ may be obtained from the T-variation of $\log K°$ when data is available for a sufficiently large temperature interval, at least 25 to 150°C, see for example (Sverjensky et al., 1997).

When there is no information on the temperature effects on a reaction, estimation methods must be used. The methods used will depend on the kind of reaction, and they are described in this section.

7.2.1 Entropies and Heat Capacities for Solid Phases

Entropies for ionic compounds may be estimated with the method proposed by (Latimer, 1952) which consists in adding contributions for ionic constituents. The parameters in (Puigdomenech et al., 1997, their Table X.12) are used in this work.

Heat capacities for solid compounds are as well estimated by adding contributions for cationic and anionic groups. The parameters given in (Kubaschewski et al., 1993) have been used here.

7.2.2 Entropies and Heat Capacities for Aqueous Species

Several estimation methods for $S°$ are based on correlations of entropies with ionic radii, molar volumes, mass, and electrical charge. These methods are useful for simple cations, anions, oxyanions and non-electrolytes, and they are described in (Puigdomenech et al., 1997; Shock et al., 1997). For these aqueous species the heat capacity may be estimated from correlations between $S°$ and $C_p°$ values (Puigdomenech et al., 1997).

$\Delta S°$ values for metal complexes of monovalent ligands involving reactions of type:

$$\mathrm{ML}_{y-1}^{Z+1} + \mathrm{L}^- \rightleftharpoons \mathrm{ML}_y^{Z}$$

can be estimated with the following equations (Sverjensky et al., 1997):

$$\Delta S_y^\circ = (a_Z S^\circ(\mathrm{L}^-) + a_Z')\, S^\circ(\mathrm{ML}_{y-1}^{Z+1}) + b_Z S^\circ(\mathrm{L}^-) + b_Z' \qquad (8)$$

$a_Z = 3.8817\times10^{-3}\, Z - 1.145\times10^{-4}$
$a_Z' = -0.36097\, Z + 0.3209$
$b_Z = 0.32102\, Z - 0.05996$
$b_Z' = 34.392\, Z - 6.514$

The resulting ΔS_y° values probably have an uncertainty of ±20 J/(K mol).

For SO_4^{2-} complexes, according to reaction $M^{Z+2} + SO_4^{2-} \rightleftharpoons MSO_4^{Z}$, estimates of ΔS° can be obtained from (Sverjensky et al., 1997):

$$\Delta S_1^\circ = (-0.055\, Z + 0.055)\, S^\circ(\mathrm{M}^{Z+2}) + 57.91\, Z + 76. \qquad (9)$$

while for carbonates, the corresponding expression is (Sverjensky et al., 1997):

$$\Delta S_1^\circ = (-1.617\, Z + 0.213)\, S^\circ(\mathrm{M}^{Z+2}) + 279.6\, Z + 120. \qquad (10)$$

ΔC_p° values for halide-metal complexes can be estimated with equations given by (Sverjensky et al., 1997):

- for reactions of type: $\mathrm{ML}_{y-1}^{Z+1} + \mathrm{L}^- \rightleftharpoons \mathrm{ML}y^{Z}$, with $y = 1$ or 2, and where the complex has stoichiometry ML^0, ML^+, or ML_2^0:

$$\Delta C_{p,}{}^\circ_{y=1\,\mathrm{or}\,2} = 1.25\, C_p^\circ(\mathrm{M}^{Z+1}) + 190\,(Z+1) - 114 \qquad (11)$$

- for reactions of type $\mathrm{ML}_{y-1}^{Z-(y-1)} + \mathrm{L}^- \rightleftharpoons \mathrm{ML}_y^{Z-y}$, with $y > 1$:

$$\Delta C_{p,}{}^\circ_{y>1} = (y-1)\,(0.89\, C_p^\circ(\mathrm{M}^{Z+}) - 20.5) + \Delta C_{p,}{}^\circ_{y=1} \qquad (12)$$

A different set of parameters for metal-acetate complexes is reported by (Sverjensky et al., 1997).

In *isocoulombic* reactions the magnitude of the electrical charge of each ionic species is balanced between reactants and products. An example of isocoulombic reaction is $M(OH)_2^+ + Cl^- \rightleftharpoons MClOH^+ + OH^-$; while $M^{3+} + OH^- \rightleftharpoons MOH^{2+}$ is not. For isocoulombic reactions it is found experimentally that ΔC_p° is ≈0 as discussed in (Puigdomenech et al., 1997). This may be used to estimate individual C_p° values for species participating in isocoulombic reactions.

7.3 COPPER, COPPER IONS, AND HYDROLYSIS PRODUCTS

The data for Cu(cr), Cu^+, Cu^{2+}, Cu_2O(cr), CuO(cr), $Cu(OH)_2$(cr), CuOH(aq), $Cu(OH)^{2-}$, $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$, $CuOH^+$, $Cu(OH)_2$(aq), $Cu(OH)_3^-$, and

$Cu(OH)_4^{2-}$ is that listed and discussed in (Beverskog and Puigdomenech, 1997a), where details are given on the selection of the data.

7.4 THE COPPER – FLUORINE SYSTEM

7.4.1 Solid Copper-Fluorides

CuF(cr) and CuF_2(cr) are quite soluble, and they will unlikely form in low temperature waters.

The data from the WATEQ4F data base (Ball and Nordstrom, 1991), which originates in the compilation by (Mills, 1974), has been used here:

$$\mathrm{CuF(cr)} \rightleftharpoons \mathrm{Cu}^{+} + \mathrm{F}^{-} \qquad \log K_{\mathrm{sp}}^{\circ} = 7.08, \quad \Delta S^{\circ} = -39\ \mathrm{J/(K\ mol)}$$

$$\mathrm{CuF_2(cr)} \rightleftharpoons \mathrm{Cu}^{+} + 2\,\mathrm{F}^{-} \qquad \log K_{\mathrm{sp}}^{\circ} = -0.62, \quad \Delta S^{\circ} = -199\ \mathrm{J/(K\ mol)}$$

$$\mathrm{CuF_2{\cdot}2H_2O(cr)} \rightleftharpoons \mathrm{Cu}^{+} + 2\,\mathrm{F}^{-} + 2\,\mathrm{H_2O}$$

$$\log K_{\mathrm{sp}}^{\circ} = -4.55, \quad \Delta S^{\circ} = -138\ \mathrm{J/(K\ mol)}$$

The heat capacity for CuF_2(cr) is that listed in (Kubaschewski et al., 1993). For CuF(cr) and $CuF_2{\cdot}2H_2O$(cr), C_p° values have been estimated using the methods given in (Kubaschewski et al., 1993).

7.4.2 Aqueous Copper-Fluoride Complexes

Only copper(II)-fluoride complexes are reported in the literature (Pettit and Powell, 1997). Several publications present a value for K_1. Extrapolation of these values to $I = 0$ using the SIT model, Eq.(6), gives $\log K_1^{\circ} = 1.58 \pm 0.10$ and $\varepsilon(\mathrm{CuF}^{+},\mathrm{ClO_4}^{-}) = 0.25 \pm 0.06$, see Figure 29.

The enthalpy change for the reaction: $\mathrm{Cu}^{2+} + \mathrm{F}^{-} \rightleftharpoons \mathrm{CuF}^{+}$, is given as $\Delta H_1 = +14.9$ kJ/mol at $I = 0.5$ (Pettit and Powell, 1997), which is extrapolated to $I = 0$ using the SIT equations (Grenthe et al., 1997) to $\Delta H_1^{\circ} = +13$ kJ/mol (giving $\Delta S_1^{\circ} = +74$ J/(K mol)). The heat capacity for CuF^+ has been estimated using the method of (Sverjensky et al., 1997), *cf.* Eq.(11), $\Delta C_p^{\circ} = +236$ J/(K mol).

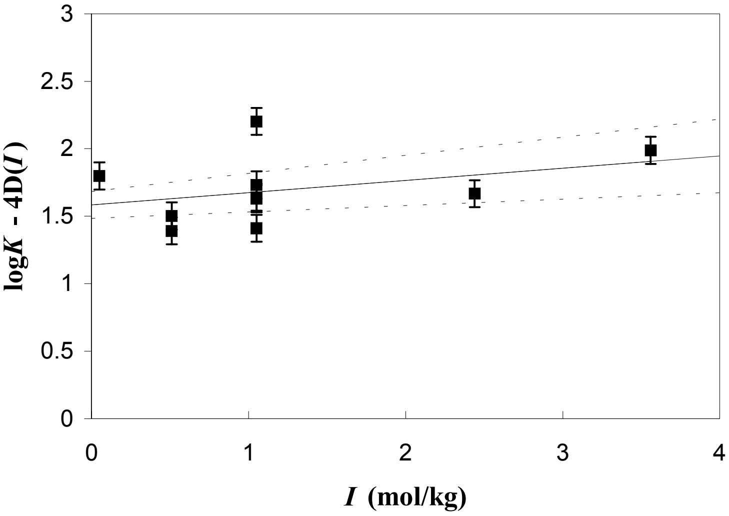


Figure 29. Extrapolation of equilibrium constants to $I = 0$ using the SIT method for reaction: $Cu^{2+} + F^- \rightleftharpoons CuF^+$.

7.5 THE COPPER – CHLORINE SYSTEM

7.5.1 Solid Copper-Chlorides

7.5.1.1 CuCl(cr)

This solid corresponds to the mineral nantokite. $\Delta G_f°$ and $S°$ are derived from data in (Chase et al., 1985; Kubaschewski et al., 1993; Robie and Hemingway, 1995). This gives

$$CuCl(cr) \rightleftharpoons Cu^+ + Cl^- \qquad \log K_{sp}° = -6.8 \pm 0.4$$

The $C_p°(T)$ function is that of (Kubaschewski et al., 1993).

7.5.1.2 $CuCl_2$(cr)

This solid corresponds to the mineral melanothallite. This is a soluble solid, which will unlikely form in low temperature environments. The solubility product and entropy change

$$CuCl_2(cr) \rightleftharpoons Cu^+ + 2\,Cl^- \quad \log K_{sp}° = 3.73, \; \Delta S° = -101.5 \text{ J/(K mol)}$$

are those selected in the WATEQ4F geochemical modelling code (Ball and Nordstrom, 1991; Ball et al., 1987). The $C_p°(T)$ function is that of (Kubaschewski et al., 1993).

7.5.1.3 $CuCl_2 \cdot 3Cu(OH)_2$(cr)

This solid corresponds to the mineral atacamite. All solubility constants available in the literature for atacamite, for example (King et al., 1973;

Wagman et al., 1982), apparently originate from the experiments by (Näsänen and Tamminen, 1949):

$$\mathrm{CuCl_2{\cdot}3Cu(OH)_2(cr)} + 6\ \mathrm{H^+} \rightleftharpoons 4\ \mathrm{Cu^{2+}} + 2\ \mathrm{Cl^-} + 6\ \mathrm{H_2O} \qquad \log {}^*K_{\mathrm{sp}} = 14.92$$

$\Delta G_f°$ has been calculated using this solubility constant. The value of $S°$ and the $C_p°(T)$ function are those determined by (Bisengalieva et al., 1997).

7.5.1.4 $\mathrm{Cu_{37}Cl_8(SO_4)_2(OH)_{62}{\cdot}8H_2O(cr)}$

This solid corresponds to the mineral connellite. The solubility equilibrium constant has been reported by (Pollard et al., 1990)

$$\mathrm{Cu_{37}Cl_8(SO_4)_2(OH)_{62}{\cdot}8H_2O(cr)} + 62\ \mathrm{H^+} \rightleftharpoons 37\ \mathrm{Cu^{2+}} + 8\ \mathrm{Cl^-} + 2\ \mathrm{SO_4^{2-}} + 70\ \mathrm{H_2O} \qquad \log {}^*K_{\mathrm{sp}} = 238.3$$

However, the equilibrium concentrations reported by these authors show that their solutions would have been supersaturated with the hydroxide $\mathrm{Cu(OH)_2(cr)}$. Furthermore, equilibrium calculations using the solubility constant for atacamite given in section 7.5.1.3, result in the constraint $\log {}^*K_{\mathrm{sp}} \leq 192$ for connellite to be more stable than atacamite at pH ≥ 6.75 when $[\mathrm{Cl^-}]_{\mathrm{TOT}} = 36$ mM and $[\mathrm{SO_4^{2-}}]_{\mathrm{TOT}} = 2.2$ mM, the conditions described by (Pollard et al., 1990).

The equilibrium calculations also show that connellite must be even more stable in order to have a stability field between tenorite (CuO) and atacamite ($\mathrm{CuCl_2{\cdot}3Cu(OH)_2}$) as indicated by (Pollard et al., 1990) in their stability field diagrams. The value $\log {}^*K_{\mathrm{sp}} = 188$ is therefore adopted here, which corresponds to a calculated stability field for connellite, but failing to reproduce the copper solubility reported by (Pollard et al., 1990), *cf.* Figure 30.

The value $\log {}^*K_{\mathrm{sp}} = 188$ is used to derive $\Delta G_f°$. The values at 25°C of $S°$ and $C_p°$ are estimated using the methodology described in (Kubaschewski et al., 1993).

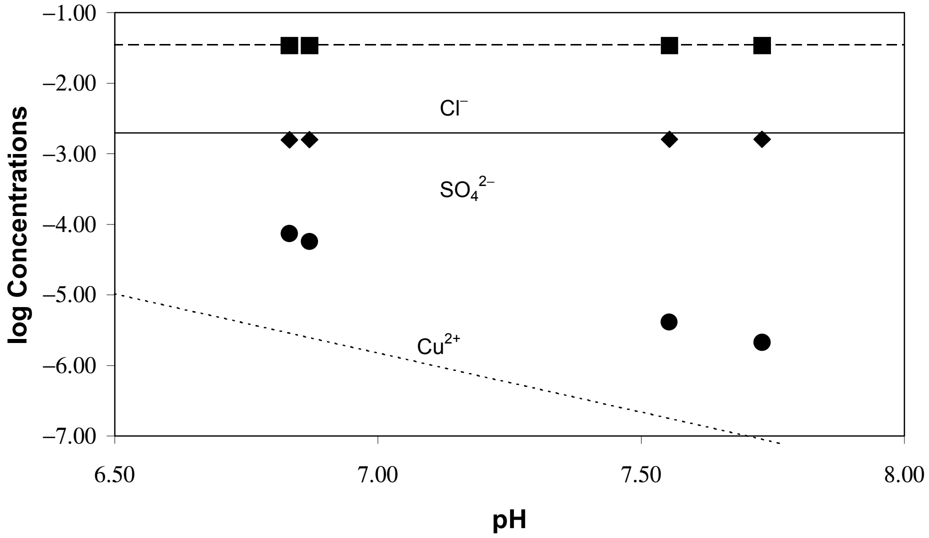


Figure 30. Comparison between the concentrations reported by (Pollard et al., 1990) for connellite-saturated solutions, and the values calculated using log $^{*}K_{sp}$ = 188 and suppressing the precipitation of tenorite (CuO).

7.5.2 Aqueous Copper(I)-Chloride Complexes

7.5.2.1 CuCl(aq)

The stability of this complex has been determined at 25°C in 5 M $NaClO_4$ by (Ahrland and Rawsthorne, 1970) who found $\log K_1 = 2.7$. This equilibrium constant has been extrapolated with Pitzer's equations (Sharma and Millero, 1988; Sharma and Millero, 1990), resulting in $\log K_1° = 3.10$ at $I = 0$.

This value was later confirmed by the study of (Fritz, 1980, Table III) who reported [CuCl(aq)] values in CuCl(cr) saturated solutions. A plot of log [CuCl(aq)] *versus* [HCl] results in

$$\text{CuCl(cr)} \rightleftharpoons \text{CuCl(aq)} \qquad \log K°_{s1} = -3.46$$

When combined with the solubility product of CuCl(cr) assigned in Section 7.5.1.1, $\log K_1° = 3.34$ is obtained.

The data in a recent study (Xiao et al., 1998) gives

$$\text{Cu}^{+} + \text{Cl}^{-} \rightleftharpoons \text{CuCl(aq)} \qquad \log K°_1 = 3.30;\ \Delta S_1° = +76 \text{ J/(K mol)}$$
$$\Delta C_{p,1}° = -150 \text{ J/(K mol)}$$

and these values are selected in Table 2.

7.5.2.2 $CuCl_2^-$ and $CuCl_3^{2-}$

The data from a recent study (Xiao et al., 1998) gives

$Cu^+ + 2\ Cl^- \rightleftharpoons CuCl_2^-$ $\log \beta°_2 = 5.62$; $\Delta S°_{\beta 2} = +48$ J/(K mol)
$\Delta C_p°{}_{\beta 2} = +169$ J/(K mol)

$Cu^+ + 3\ Cl^- \rightleftharpoons CuCl_3^{2-}$ $\log \beta°_3 = 4.86$; $\Delta S°_{\beta 3} = +6.6$ J/(K mol)
$\Delta C_p°{}_{\beta 3} = +410$ J/(K mol)

and these values are selected in Table 2. These equilibrium constants are in agreement with the literature review of (Wang et al., 1997), which reports $\log \beta°_2 = 5.66$ and $\log \beta°_3 = 4.91$.

7.5.2.3 Polynuclear Cu(I)-Cl^- Complexes: $Cu_2Cl_4^{2-}$ and $Cu_3Cl_6^{3-}$

$Cu_2Cl_4^{2-}$ and $Cu_3Cl_6^{3-}$ form in concentrated Cl^- solutions with [Cu(I)] > 1 M. The equilibrium constants are those determined by (Fritz, 1980):

$2\ CuCl(cr) + 2\ Cl^- \rightleftharpoons Cu_2Cl_4^{2-}$ $\log K° = -3.09$
$\Delta H° = 28.3$ kJ/mol

$3\ CuCl(cr) + 3\ Cl^- \rightleftharpoons Cu_3Cl_6^{3-}$ $\log K° = -4.47$
$\Delta H° = 0.23$ kJ/mol

while the enthalpy changes have been estimated here from the temperature variation of the equilibrium constants reported at 15, 25 and 35°C in (Fritz, 1980). A large uncertainty is associated to these $\Delta H°$ values.

Heat capacities for these polynuclear complexes have been estimated assuming $\Delta C_p° \approx 0$ (*cf.* Section 7.2.2) for the isocoulombic reactions:

$$CuCl_3^{2-} + CuCl(aq) \rightleftharpoons Cu_2Cl_4^{2-}$$

$$2\ CuCl_3^{2-} + CuCl_2^- \rightleftharpoons Cu_3Cl_6^{3-} + 2\ Cl^-$$

7.5.3 Aqueous Copper(II)-Chloride Complexes

Cu^{2+} forms weak complexes with Cl^-. Nevertheless these complexes are important in natural waters, where chloride may be abundant. A very large number of UV spectrophotometric studies have shown the existence of $CuCl^+$, $CuCl_2(aq)$, $CuCl_3^-$, and $CuCl_4^{2-}$. However, the intrinsic nature of systems with weak complexation is such that large uncertainties are always associated with the experimental determination of equilibrium constants (Bjerrum, 1972; Spahiu and Puigdomenech, 1998).

Furthermore, even if reliable equilibrium constants should be available, their usefulness would be limited: the results of calculations will differ substantially depending on the equation used to calculate activity coefficients in aqueous solutions of relatively high Cl^- concentrations.

Nevertheless, an attempt is made here to obtain data on the Cu(II)-Cl^- system in order to be able to model this system at least qualitatively. The equilibrium constants for the chlorocomplexes of Cu(II) have been selected here according to the following three criteria:

1. For $CuCl^+$ the equilibrium constant is known from studies with low chloride concentrations. An evaluation of the literature data using the SIT equation (Wang et al., 1997) has resulted in $\log K_1° = 0.64 \pm 0.06$.
2. For $CuCl_4^{2-}$, the procedure proposed by (Bjerrum, 1987; Bjerrum and Skibsted, 1977; Bjerrum and Skibsted, 1986) is used. With this method the stability of $CuCl_4^{2-}$ is determined spectrophotometrically in the wavelength range where only this complex absorbs, using the extinction coefficient determined independently in solutions with very high chloride concentration. Using this approximation the copper fraction for $CuCl_4^{2-}$ in 5 M NaCl is found to be $\alpha_4 = 0.05$ (Bjerrum and Skibsted, 1977).
3. For $CuCl_2(aq)$ and $CuCl_3^-$ equilibrium constants are estimated to produce a reasonably constant ligand effect (Bjerrum and Skibsted, 1977; Bjerrum and Skibsted, 1986). Several possible combinations of $K_2°$ and $K_3°$ can in principle satisfy this condition. Furthermore, the ligand effect will be influenced by the temperature dependence of $K_2°$ and $K_3°$.

In order to combine the first and second criterion above, activity coefficients must be considered. The medium effects in 5 M $Na(ClO_4)$ have been calculated with the SIT model, Eq.(6), using the following estimated interaction coefficients:

$\varepsilon(Cu^{2+}, ClO_4^-) = \varepsilon(Cu^{2+}, Cl^-) = 0.32 \pm 0.02$
$\varepsilon(CuCl^+, ClO_4^-) = \varepsilon(CuCl^+, Cl^-) = 0.2 \pm 0.1$
$\varepsilon(CuCl_2(aq), NaClO_4) = \varepsilon(CuCl_2(aq), NaCl) = 0.1 \pm 0.1$
$\varepsilon(CuCl_3^-, Na^+) = 0 \pm 0.1$
$\varepsilon(CuCl_4^{2-}, Na^+) = -0.05 \pm 0.1$

These ε-values have been estimated by inspection of the tables in (Grenthe et al., 1997), and they include the implicit assumption that K_1 and K_2 have the same values in 5 M NaCl and in 5 M $NaClO_4$. However, the uncertainty introduced by this assumption is not influential, and for example, it is less than that originating from the third criterion listed above.

The constraints and assumptions given above result in the equilibrium constants reported in Table 3.

Table 3. Equilibrium constants at 25°C for the system copper(II)-chloride both in standard conditions ($I = 0$) and in 5 M Na(ClO_4,Cl).

Complex	$K°$	$\log K^{5M}$	$\log \beta°$	$\log \beta^{5M}$
$CuCl^+$	4.37	0.494	0.640	0.494
$CuCl_2(aq)$	0.4	−0.126	0.243	0.367
$CuCl_3^-$	0.03	−0.721	−1.280	−0.354
$CuCl_4^{2-}$	0.002	−1.647	−3.979	−2.000

The equilibrium constants selected here at $I = 0$ result in the following ligand effects at 25°C: $L_{1,2}$=0.61, $L_{2,3}$=0.77 and $L_{3,4}$=0.75. As required by the second criterion, the β^{5M}-values give $\alpha_4 = 0.05$ in 5 M NaCl.

Although large uncertainties are associated with the constants listed in Table 3, they adequately describe the complex formation between Cu(II) and chloride.

The calorimetric data published by (Arnek et al., 1982) is reinterpreted here using the same least-squares technique. This results in the following values for the thermodynamic quantities

Complex	$\log K^{5M}$	ΔH_K^{5M}	ΔS_K^{5M}	$\log \beta^{5M}$	ΔH_β^{5M}	ΔS_β^{5M}
$CuCl^+$	0.494	7.74	35.4	0.494	7.74	35.4
$CuCl_2(aq)$	−0.126	8.27	25.3	0.367	16.01	60.7
$CuCl_3^-$	−0.721	6.2	6.9	−0.354	22.2	67.7
$CuCl_4^{2-}$	−1.647	(5.8)	(−12)	−2.000	(28)	(56)

where the units for enthalpies and entropies are kJ/mol and J/(K mol), respectively. Because of the low fraction for the tetrachloro complex in the calorimetric investigation, the thermodynamic quantities for $CuCl_4^{2-}$ are estimated from the dependence of ΔH_β^{5M} with the number of ligands in the complexs. The values of ΔH_β^{5M} have been used without extrapolation to zero ionic strength.

Heat capacities for the formation of $CuCl^+$, $CuCl_2(aq)$, $CuCl_3^-$, and $CuCl_4^{2-}$ have been estimated with Eqs.(11) and (12): $\Delta C_{p,}°_{\beta n}$ = 235, 428, 580, and 690 J/(K mol) for n = 1 to 4, respectively.

7.5.4 Copper-Chlorate Complexes

Chlorate is not expected to be a ligand that affects the corrosion of copper in nuclear waste repositories. For reaction

$$Cu^{2+} + ClO_3^- \rightleftharpoons CuClO_3^+$$

$\log K_1 = -0.34$ and $\Delta S_1 = -28$ J/(K mol) are reported for 1.0 M $NaClO_4$ (Martell et al., 1997; Pettit and Powell, 1997). The equilibrium constant is extrapolated to $I = 0$ using the SIT model, Eq.(6), resulting in $\log K_1° = 0.35±0.15$. $\Delta C_p°$ is estimated to be +236 J/(K mol) with the equations given by (Sverjensky et al., 1997), *cf.* Section 7.2.2.

7.6 THE COPPER – SULPHUR SYSTEM

7.6.1 The Copper-Sulphate System

7.6.1.1 Solid Copper Sulphates

7.6.1.1.1 $Cu_2SO_4(cr)$

The values of $\Delta G_f°$ and $S°$ are derived from the equilibrium constant and enthalpy change, respectively, selected in the WATEQ4F geochemical modelling code (Ball and Nordstrom, 1991; Ball et al., 1987):

$$Cu_2SO_4(cr) \rightleftharpoons 2\,Cu^+ + SO_4^{2-} \qquad \log K° = -1.95$$
$$\Delta H° = -19.1 \text{ kJ/mol}$$

The value of $C_p°$ has been estimated using the methodology described in (Kubaschewski et al., 1993).

7.6.1.1.2 $CuSO_4(cr)$

This corresponds to the mineral chalcocyanite. The values of $\Delta G_f°$ and $S°$ are those from CODATA (Cox et al., 1989). The $C_p°(T)$ function is that listed in (Kubaschewski et al., 1993).

7.6.1.1.3 $CuSO_4{\cdot}5H_2O(cr)$

This corresponds to the mineral chalcanthite. The values of $\Delta G_f°$ and $S°$ are those compiled by (Robie and Hemingway, 1995). The $C_p°(T)$ function is that listed in (Kubaschewski et al., 1993).

7.6.1.1.4 $Cu_4SO_4(OH)_6(cr)$

This corresponds to the mineral brochantite. The value of $\Delta G_f°$ is that compiled by (Robie and Hemingway, 1995). The value of $S°$ and the $C_p°(T)$ function are those given by (Bisengalieva et al., 1993).

7.6.1.1.5 $Cu_4SO_4(OH)_6{\cdot}H_2O(cr)$

This corresponds to the mineral langite. The data from the NBS tables (Wagman et al., 1982) are used here. $C_p°$ has been estimated using the methodology described in (Kubaschewski et al., 1993).

7.6.1.1.6 *$Cu_3SO_4(OH)_4(cr)$*

This corresponds to the mineral antlerite. The data from the NBS tables (Wagman et al., 1982) are used here. $S°$ and $C_p°$ have been estimated using the methodology described in (Kubaschewski et al., 1993).

7.6.1.1.7 *$CuO{\cdot}CuSO_4(cr)$*

The data for this solid is that listed in (Knacke et al., 1991).

7.6.1.1.8 *$Cu_{37}Cl_8(SO_4)_2(OH)_{62}{\cdot}8H_2O(cr)$*

See the discussion on connellite in Section 7.5.1.4.

7.6.1.2 Copper Sulphate Complexes

Only $CuSO_4(aq)$ has been reported (Pettit and Powell, 1997). The equilibrium constant and enthalpy change for the reaction: $Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4(aq)$, are those selected in the WATEQ4F geochemical modelling code (Ball and Nordstrom, 1991; Ball et al., 1987): $\log K_1° = 2.31$; $\Delta H_1° = +5.1$ kJ/mol. The value of $\Delta C_p°$ at 25°C is estimated to be +197 J/(K mol), *i.e.*, that of the corresponding reaction for the complexation of Ca^{2+} (Sverjensky et al., 1997).

7.6.2 The Copper-Sulphide System

7.6.2.1 Solid Copper Sulphides

A series of copper sulphides are formed with compositions varying between chalcocite (Cu_2S) and covellite (CuS), *cf.* (Potter, 1977). Only two intermediate sulphides are considered here: djurleite ($Cu_{1.934}S$) which decomposes at 93°C, and anilite ($Cu_{1.75}S$) which decomposes at 75°C.

For chalcocite and covellite the $\Delta G_f°$ values are derived from the solubility constants (Shea and Helz, 1989; Thompson and Helz, 1994):

$$Cu_2S(cr) + H^+ \rightleftharpoons 2\,Cu^+ + HS^- \qquad \log {}^*K_{sp}° = -34.02$$

$$CuS(cr) + H^+ \rightleftharpoons Cu^+ + HS^- \qquad \log {}^*K_{sp}° = -22.06$$

The entropy values for these two sulphides used are those of (Robie and Hemingway, 1995), while the $C_p°$ (T) functions are those listed in (Kubaschewski et al., 1993).

For djurleite and anilite the $\Delta G_f°$ values are adjusted to obtain the relative stabilities reported in (Thompson and Helz, 1994, their Fig.1). The corresponding solubility constants are:

$$Cu_{1.75}S(cr) + H^+ \rightleftharpoons 0.25\,Cu^+ + 1.5\,Cu^{2+} + HS^- \qquad \log {}^*K_{sp}° = -31.22$$

$$Cu_{1.934}S(cr) + H^+ \rightleftharpoons 0.066\,Cu^+ + 1.868\,Cu^{2+} + HS^- \qquad \log {}^*K_{sp}° = -33.33$$

The $S°$ values for these two sulphides are those of (Potter, 1977), while $C_p°$ values at 25°C have been estimated using the methods described in (Kubaschewski et al., 1993).

7.6.2.2 Copper Sulphide Complexes

The following equilibrium constants result from the experimental investigation by (Mountain and Seward, 1999):

$$\tfrac{1}{2}\,Cu_2S(cr) + \tfrac{1}{2}\,HS^- + \tfrac{1}{2}\,H^+ \rightleftharpoons CuHS(aq) \qquad \log K_s° \approx -4$$

$$\tfrac{1}{2}\,Cu_2S(cr) + 1.5\,HS^- + \tfrac{1}{2}\,H^+ \rightleftharpoons Cu(HS)_2^- \qquad \log K_s° = -0.13\pm0.02$$

$$Cu_2S(cr) + 2\,HS^- \rightleftharpoons Cu_2S(HS)_2^{2-} \qquad \log K_s° = -4.75\pm0.04$$

These equilibrium constants have been used to derive $\Delta G_f°$ values for the corresponding complexes.

The data in (Crerar and Barnes, 1976) has been re-evaluated by (Mountain and Seward, 1999). The reported temperature dependence for the stability of CuHS(aq) and $Cu(HS)_2^-$ has been used here to obtain values of $S°$ and $\Delta C_p°$ for these two complexes.

For $Cu_2S(HS)_2^{2-}$ there is no information on temperature effects, and entropy and heat capacity values had to be chosen on uncertain grounds. For the formation reaction of $Cu_2S(HS)_2^{2-}$,

$$2\,Cu^+ + 3\,HS^- \rightleftharpoons Cu_2S(HS)_2^{2-} + H^+ \qquad \log \beta° = 29.3\pm0.14$$

$\Delta S°$ was set to −202 J/(K mol) and $\Delta C_p° = -105$ J/(K mol). These values suppress the formation of the polynuclear sulphide complex in model calculations at higher temperatures. It should be pointed out that the contribution of sulphide complexes (*i.e.*, $Cu(HS)_2^-$) to copper(I) speciation is expected to be negligible at 200–350°C in seafloor hydrothermal fluids (Xiao et al., 1998).

7.6.3 Other Sulphur Ligands

7.6.3.1 Thiosulphate

Thiosulphate is not an important ligand in chemical equilibrium modelling, because it is thermodynamically unstable. For example in acid solutions it disproportionates according to:

$$S_2O_3^{2-} + {}^{4}\!/_{3}\,H^+ \rightleftharpoons {}^{4}\!/_{3}\,S(cr) + {}^{2}\!/_{3}\,HSO_4^- + {}^{1}\!/_{3}\,H_2O$$

and at pH > 6.3:

$$S_2O_3^{2-} + OH^- \rightleftharpoons HS^- + SO_4^{2-}$$

7.6.3.1.1 Copper(I)-Thiosulphate Complexes

The experimental data available on this system shows that: $K_1 \gg K_2 \gtrapprox K_3 \gtrapprox K_4$. Because the concentration of $S_2O_3^{2-}$ in natural waters is not expected to be large, only the first complex is included in the database to check that thiosulphate complexes do not appear in model calculations.

The equilibrium constant for $CuS_2O_3^-$, $\log K_1° = 10.1$, selected in the compilation by (Rose, 1989) is also used here. The entropy and heat capacity values are estimated to be $\Delta S_1° = +23$ J/(K mol) and $\Delta C_{p,1}° = +147$ J/(K mol) using the methods in (Sverjensky et al., 1997), Eqs.(9) and (11).

7.6.3.1.2 Copper(II)-Thiosulphate Complexes

There are studies indicating some complex formation between Cu^{2+} and $S_2O_3^{2-}$ (Pettit and Powell, 1997). These results were obtained from kinetic and ultrasound absorption experiments. Further studies using other techniques, for example spectrophotometry, are needed to justify the recommendation of data for Cu(II)-thiosulphate complexes.

7.6.3.2 Dithionite

No copper complexes with dithionite, $S_2O_4^{2-}$, have been reported (Pettit and Powell, 1997).

7.6.3.3 Sulphite

Equilibrium constants for the complex formation between Cu(I) and SO_3^{2-} have only been determined by (Toropova et al., 1955) in Na_2SO_4 medium. The data indicates that $K_1 \gg K_2 \gtrapprox K_3$. These data have not been confirmed by additional studies, and because SO_3^{2-} is not thermodynamically stable, sulphite complexes are not included in the data set.

7.7 THE COPPER – NITROGEN SYSTEM

7.7.1 Copper-Ammonia Complexes

7.7.1.1 Copper(I)-Ammonia Complexes

Similarly to the copper(I)-chloride system, the second complex ($Cu(NH_3)_2^+$) is much more stable than the first, and there is practically no data available on K_1 (Pettit and Powell, 1997). Owing to this, the first complex is not included in the data set. The value of $\log \beta_2° = 10.5$ is that listed in (Bertocci and Wagman, 1985). Because there is no information on temperature effects, the enthalpy for

$$Cu^+ + 2\ NH_3 \rightleftharpoons Cu(NH_3)_2^+$$

is estimated to be equal to that of the equivalent reaction with silver(I), $\Delta H_{\beta 2}° = -56$ kJ/mol (Martell et al., 1997). A value of $\Delta C_{p,\beta 2}° \approx 0$ is estimated for this reaction, according to the isocoulombic approach (Section 7.2.2).

Although there are some publications reporting mixed complexes of copper(I) with ammonia and either chloride or hydroxide, the data is too scarce to be considered reliable.

7.7.1.2 Copper(II)-Ammonia Complexes

The data for $CuNH_3^{2+}$ to $Cu(NH3)_4^{2+}$ is that listed in (Bertocci and Wagman, 1985):

$$Cu^{2+} + NH_3 \rightleftharpoons CuNH_3^{2+} \qquad \log K_1° = 4.10; \quad \Delta H_1° = -24 \text{ kJ/mol}$$

$$Cu^{2+} + 2\ NH_3 \rightleftharpoons Cu(NH_3)_2^{2+} \qquad \log \beta_2° = 7.51; \quad \Delta H_{\beta 2}° = -45 \text{ kJ/mol}$$

$$Cu^{2+} + 3\ NH_3 \rightleftharpoons Cu(NH_3)_3^{2+} \qquad \log \beta_3° = 10.31; \quad \Delta H_{\beta 3}° = -68 \text{ kJ/mol}$$

$$Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \qquad \log \beta_4° = 12.35; \quad \Delta H_{\beta 4}° = -90 \text{ kJ/mol}$$

The heat capacity changes for these isocoulombic reactions are estimated to be $\Delta C_{p,\beta n}° \approx 0$ as discussed in Section 7.2.2.

Mixed complexes of copper(II) with ammonia and hydroxide have been reported. The equilibrium constants determined by (Gübeli et al., 1970) for $CuNH_3OH^+$, $Cu(NH_3)_3OH^+$, and $Cu(NH_3)_2(OH)_2(aq)$ in 1 M $NaClO_4$ at 25°C are in reasonable agreement with the results from (Fisher and Hall, 1967) at 0.5 M KNO_3 and 30°C.

The constants given by (Gübeli et al., 1970) have been extrapolated to $I = 0$ using the SIT equations, Eq.(6), and the following estimates: $\varepsilon(NH_3, NaClO_4) = \varepsilon(Cu(NH_3)_2(OH)_2, NaClO_4) = 0$, and $\varepsilon(CuNH_3OH^+, ClO_4^-) = \varepsilon(Cu(NH_3)_3OH^+, ClO_4^-) = 0.2$. The uncertainty introduced with these ε-estimates should be less than ±0.2 in the value of $\log K°$. The extrapolation of the equilibrium constants for the following reactions:

$$Cu^{2+} + NH_3(aq) + OH^- \rightleftharpoons CuNH_3OH^+ \qquad (13)$$

$$Cu^{2+} + 2\ NH_3(aq) + 2\ OH^- \rightleftharpoons Cu(NH_3)_2(OH)_2(aq) \qquad (14)$$

$$Cu^{2+} + 3\ NH_3(aq) + OH^- \rightleftharpoons Cu(NH_3)_3OH^+ \qquad (15)$$

gives the following values: $\log K°_{(13)} = 11.3$; $\log K°_{(14)} = 17.0$; and $\log K°_{(15)} = 15.0$.

Because there is no information on temperature effects for these mixed complexes, values for $\Delta H°$ have been roughly estimated as the sum of enthalpies for the single-ligand complex reactions. For example, for $Cu(NH_3)_3OH^+$, $\Delta H°_{(15)} = \Delta H_{\beta 3}°(Cu(NH_3)_3^{2+}) + \Delta H_1°(CuOH^+)$. This crude estimation gives $\Delta H^\circ_{(13)} = -44$; $\Delta H^\circ_{(14)} = -69$; and $\Delta H^\circ_{(15)} = -88$ (all in kJ/mol). The heat capacity changes for the isocoulombic reactions:

$$Cu^{2+} + NH_3(aq) + H_2O \rightleftharpoons CuNH_3OH^+ + H^+$$

$$Cu^{2+} + 2\ NH_3(aq) + 2\ H_2O \rightleftharpoons Cu(NH_3)_2(OH)_2(aq) + 2\ H^+$$

$$Cu^{2+} + 3\ NH_3(aq) + H_2O \rightleftharpoons Cu(NH_3)_3OH^+ + H^+$$

are estimated to be $\Delta C_{p,\beta n}^\circ \approx 0$ as discussed in Section 7.2.2.

7.7.2 Copper-Nitrite Complexes

NO_2^- has a limited thermodynamic stability. Although it is widespread in nature, it is usually a minor nitrogen species because nitrite is an intermediate in the bacterial oxidation of ammonia to nitrate..

Only Cu(II) complexes with NO_2^- have been reported (Pettit and Powell, 1997). Although data for five complexes are given in the literature, only $CuNO_2^+$ and $Cu(NO_2)_2(aq)$ are included in this work. Extrapolation of literature data on K_1 and β_2 to $I = 0$ using the SIT model, Eq.(6), gives $\log K_1^\circ = 1.96\pm0.14$ and $\varepsilon(CuNO_2^+, ClO_4^-) = 0.24\pm0.04$, and $\log \beta_2^\circ = 2.56\pm0.14$ and $\varepsilon(Cu(NO_2)_2, NaClO_4) = 0.23\pm0.03$, see Figure 31.

Values for the entropies ($\Delta S_{K1}^\circ = +18.5$ and $\Delta S_{\beta2}^\circ = +18.0$ J/(K mol)) and heat capacity ($\Delta C_{p,K1}^\circ = +236$ and $\Delta C_{p,\beta2}^\circ = +390$ J/(K mol)) have been estimated using the equations in (Sverjensky et al., 1997), see Section 7.2.2.

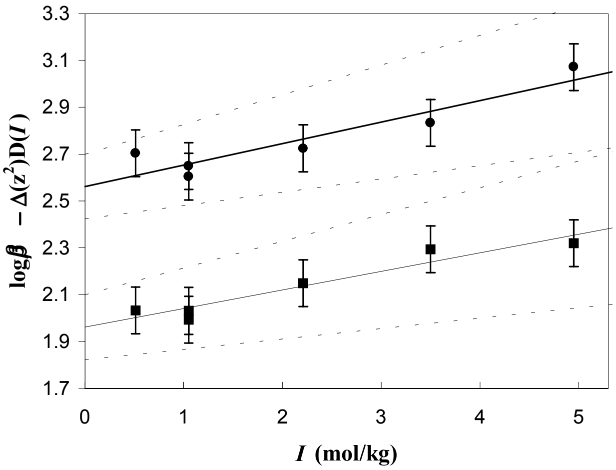


Figure 31. Extrapolation of equilibrium constants to $I = 0$ using the SIT method for reactions: $Cu^{2+} + NO_2^- \rightleftharpoons CuNO_2^+$ (lower set of data), and $Cu^{2+} + 2\ NO_2^- \rightleftharpoons Cu(NO_2)_2(aq)$ (upper set of data).

7.7.3 The Copper-Nitrate System

7.7.3.1 $Cu(NO_3)_2 \cdot 3Cu(OH)_2(cr)$

The solubility constant for this solid has been determined by (Näsänen and Tamminen, 1949):

$$Cu(NO_3)_2 \cdot 3Cu(OH)_2(cr) + 6\ H^+ \rightleftharpoons 4\ Cu^{2+} + 2\ NO_3^- + 6\ H_2O \qquad \log K° = 14.5$$

who also investigated the solubility of atacamite ($CuCl_2 \cdot 3Cu(OH)_2$, see Section 7.5.1.3). The value for $S°$ is that listed by the NBS (Wagman et al., 1982). A value of $C_p°$ has been estimated using the methods in (Kubaschewski et al., 1993).

7.7.3.2 Cu(II)-Nitrate Complexes

Only Cu(II) complexes with NO_3^- have been reported (Pettit and Powell, 1997). These complexes appear to be quite weak. It seems possible that the experimental effects observed are not due to complex formation, but that instead the data result from changes in activity coefficients, due to the large values of $[NO_3^-]$ employed. Nevertheless, the equilibrium constants selected in (Martell et al., 1997) are adopted here ($\log K_1° = 0.5$ and $\log \beta_2° = -0.4$).

The value of $\Delta S_{K1}° = -14$ J/(K mol) at $I = 1$ M (Martell et al., 1997) is used. In the abscence of more information, values of $\Delta C_{p,K1}°$, $\Delta S_{\beta 2}°$, and $\Delta C_{p,\beta 2}°$ are assigned to obtain negligible temperature variation for $K_1°$ and $\beta_2°$ between 25 and 100°C.

7.8 THE COPPER – PHOSPHATE SYSTEM

Data on phosphate complex formation is in general difficult to interpret and correlate among different studies because equilibrium constants for metal complexes depend strongly on the acid-base data used for H_3PO_4. Furthermore, phosphoric acid produces three anions, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, all of which can act as ligands towards metal cations. Therefore, a large number of complexes may in principle be formed, and this makes data interpretation quite difficult.

However, phosphate is a minor ligand in most natural waters, because it forms insoluble solids with calcium and other cations. Large uncertainties in the constitution and stability of copper-phosphate complexes will therefore not have a serious interference on the assessment of the suitability of copper canisters for spent nuclear fuel disposal.

7.8.1 Copper(I)-Phosphate Complexes

The formation constants determined by (Ciavatta et al., 1993a) are accepted:

$$Cu^+ + H_2PO_4^- \rightleftharpoons CuH_2PO_4(aq) \qquad \log K° = 0.87$$

$$Cu^+ + 2\ H_2PO_4^- \rightleftharpoons Cu(H_2PO_4)_2^- \qquad \log K° = 1.8$$

$$Cu^+ + 2\ H_2PO_4^- \rightleftharpoons Cu(HPO_4)(H_2PO_4)^{2-} + H^+ \qquad \log K° = -3.0$$

In the absence of any information on temperature effects, values of $\Delta S°$ and $\Delta C_p°$ have been arbitrarily assigned that minimise the T-variation for these equilibrium constants.

7.8.2 The Copper(II) – Phosphate System

7.8.2.1 Solid Cu(II)-Phosphates

The solubility constants for $Cu_3(PO_4)_2(cr)$ and $Cu_3(PO_4)_2{\cdot}3H_2O(cr)$ are from the WATEQ4F database (Ball and Nordstrom, 1991)

$$Cu_3(PO_4)_2(cr) \rightleftharpoons 3\ Cu^{2+} + 2\ PO_4^{3-} \qquad \log K_{sp}° = -36.85$$

$$Cu_3(PO_4)_2{\cdot}3H_2O(cr) \rightleftharpoons 3\ Cu^{2+} + 2\ PO_4^{3-} + 3\ H_2O \qquad \log K_{sp}° = -35.12$$

The values of $S°$ and $C_p°$ for these two phosphates have been estimated with the methods outlined in Section 7.2.1.

7.8.2.2 Cu(II)-Phosphate Complexes

The formation constants determined by (Ciavatta et al., 1993b) are accepted:

$$Cu^{2+} + H_2PO_4^- \rightleftharpoons CuH_2PO_4^+ \qquad \log K° = 1.14$$

$$Cu^{2+} + 2\ H_2PO_4^- \rightleftharpoons Cu(H_2PO_4)_2(aq) \qquad \log K° = 1.94$$

$$Cu^{2+} + HPO_4^{2-} + H_2PO_4^- \rightleftharpoons Cu(HPO_4)(H_2PO_4)^- \qquad \log K° = 5.35$$

$$Cu^{2+} + 2\ HPO_4^{2-} \rightleftharpoons Cu(HPO_4)_2^{2-} \qquad \log K° = 7.36$$

For the complex $CuHPO_4(aq)$, the data selected in (Martell et al., 1997) has been extrapolated to $I = 0$ to give:

$$Cu^{2+} + HPO_4^{2-} \rightleftharpoons CuHPO_4(aq) \qquad \log K° = 4.1$$

In the absence of any information on temperature effects, values of $\Delta S°$ and $\Delta C_p°$ have been assigned that minimise the T-variation for these equilibrium constants.

7.9 THE COPPER – CARBONATE SYSTEM

7.9.1 Solid Copper(II)-Carbonates

7.9.1.1 $CuCO_3(cr)$

The data for this solid is that of (Kubaschewski et al., 1993), except for the solubility product ($\log K_{sp}° = -11.45$) which is that recommended by (Grauer and Berner, 1999). This value is close to that selected in (Martell et al., 1997): $\log K_{sp}° = -11.5$.

7.9.1.2 $Cu_2CO_3(OH)_2(cr)$

This corresponds to the mineral malachite. The solubility constant for reaction:

$$Cu_2CO_3(OH)_2(cr) + 2\ H^+ \rightleftharpoons 2\ Cu^{2+} + CO_3^- + 2\ H_2O \qquad \log K° = -5.3$$

has been selected by (Martell et al., 1997), and can be compared with the value, $\log K° = -5.18$, given in the WATEQ4F database (Ball and Nordstrom, 1991). The value of $S°$ for malachite is that determined by (Kiseleva et al., 1992), while the $C_p°(T)$ function is given by (Bisengalieva et al., 1993).

7.9.1.3 $Cu_3(CO_3)_2(OH)_2(cr)$

This corresponds to the mineral azurite (= chessylite). The solubility constant for reaction:

$$Cu_3(CO_3)_2(OH)_2(cr) + 2\ H^+ \rightleftharpoons 3\ Cu^{2+} + 2\ CO_3^- + 2\ H_2O$$
$$\log K° = -16.91$$

has been selected in the WATEQ4F database (Ball and Nordstrom, 1991), as well as by (Baes and Mesmer, 1976; Martell et al., 1997). The value of $S°$ for azurite is that determined by (Kiseleva et al., 1992), while the $C_p°(T)$ function is given by (Bisengalieva et al., 1993).

7.9.2 Copper(II)-Carbonate Complexes

The equilibrium constants for the complex formation between Cu(II) and carbonate/bicarbonate:

$$Cu^{2+} + CO_3^{2-} \rightleftharpoons CuCO_3(aq) \qquad \log \beta_1° = 6.77$$
$$Cu^{2+} + 2\ CO_3^{2-} \rightleftharpoons Cu(CO_3)_2^{2-} \qquad \log \beta_2° = 10.2$$
$$Cu^{2+} + HCO_3^- \rightleftharpoons CuHCO_3^+ \qquad \log K_{HL}° = 1.8$$

have been selected by (Martell et al., 1997). A comparison with the constants selected in the WATEQ4F database: 6.73, 9.83 and 2.7 respectively (Ball and Nordstrom, 1991) and other literature data (Pettit and Powell, 1997) indicates that the values of $\beta_2°$ and $K_{HL}°$ are somewhat uncertain.

The complex $CuCO_3OH^-$ has been proposed by (Symes and Kester, 1985). However, these authors have also reported equilibrium constants for $CuCO_3(aq)$ and $CuHCO_3^+$ which differ from the other literature values.

The enthalpy change for the formation of $CuCO_3(aq)$ has been determined by (Soli and Byrne, 1989) in seawater: $\Delta H_{\beta 1} = +10.4 \pm 1.2$ kJ/mol ($\Delta S_{\beta 1} = +129 \pm 4$ J/(K mol)). This entropy change may be compared with $\Delta S_{\beta 1}° = +120$ J/(K mol) estimated using Eq.(10). The value of $\Delta S_{\beta 1}$ determined by (Soli and Byrne, 1989) is selected here, neglecting medium effects. The value of $\Delta C_{p,\beta 1}°$ for $CuCO_3(aq)$ has been assumed to be the same as that for the formation of $CaSO_4(aq)$, *cf.* (Sverjensky et al., 1997).

For $Cu(CO_3)_2^{2-}$ the value of $\Delta S_{\beta 2}° = +320$ J/(K mol) has been estimated by similarity with the complex formation for UO_2^{2+}. The value of $C_p°$ has been estimated assuming that $\Delta C_p° \approx 0$ for the isocoulombic reaction:

$$CuCO_3(aq) + CO_3^{2-} \rightleftharpoons Cu(CO_3)_2^{2-}$$

as discussed in Section 7.2.2.

For $CuHCO_3^+$ the value of $\Delta S_{HL}° = +65$ J/(K mol) has been estimated by comparison with the corresponding experimental values for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Mn^{2+} listed in (Martell et al., 1997). A crude estimate of $\Delta C_p°$ for the formation of $CuHCO_3^+$ has been obtained from Eq.(11), although this equation was designed for metal-halide complexes (Sverjensky et al., 1997).

7.10 AUXILIARY DATA

Thermodynamic data for auxiliary species are needed in two contexts. Firstly, to calculate log *K* values from $\Delta G_f°$ data for reactions involving copper species. For example, reaction $Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ requires data for the chloride ion. The other use for data on auxiliary species is to obtain equilibrium constants for ligand protonation and for reactions that involve Na^+ and Ca^{2+}.

Table 4 contains the thermodynamic data selected for auxiliary species.

Data for ligands is that selected by CODATA (Cox et al., 1989) and by the NEA (Grenthe et al., 1992a; Silva et al., 1995). Other sources of information are (Robie and Hemingway, 1995; Shock et al., 1997; Wagman et al., 1982). Heat capacities for aqueous species have been taken from (Shock et al., 1997; Sverjensky et al., 1997).

Other sources of data have been (Robie et al., 1978) for $H_2(g)$; (Shock and Helgeson, 1990) for $CH_4(aq)$; (Robie and Hemingway, 1995) for $CH_4(g)$; (Ellis and Giggenbach, 1971; Giggenbach, 1971; Giggenbach, 1974; Schwarzenbach and Fischer, 1960) for polysulphides; (Hovey and Hepler, 1990; Izatt et al., 1989) for HSO_4^- and $H_2SO_4(aq)$; (Nakayama, 1971) for $NaCO_3^-$ and $NaHCO_3(aq)$.

7.10.1 Carbonic Acid

CO_2 is present in aqueous solutions both as $CO_2(aq)$ and as $H_2CO_3(aq)$. The equilibrium reaction

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$

is shifted far to the right, and the fraction of carbonic acid as $CO_2(aq)$ is very close to 100%. In Table 4 the formula "$CO_2(aq)$" is used to denote the sum of all dissolved and non-dissociated carbon dioxide (*i.e.*, $H_2CO_3(aq)$ + $CO_2(aq)$). For example, the equilibrium constant, K°_{eq}, for the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^- + H^+$$

calculated using the data in Table 4 corresponds to:

$$K^{o}_{eq} = \frac{[HCO_3^-][H^+]}{["CO_2(aq)"]\, a_{H_2O}} = \frac{[HCO_3^-][H^+]}{\left([CO_2(aq)] + [H_2CO_3(aq)]\right) a_{H_2O}}$$

Table 4. Thermodynamic data at 25°C for auxiliary species.

Species	ΔG_f° $(\mathrm{kJ\cdot mol^{-1}})$	S° $(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	$C_p^{\circ\dagger}$ $(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$
$H_2(g)$	0.	130.68	‡
H^+	0.	0.	0.
OH^-	–157.22	–10.9	–125.
F^-	–281.5	–13.8	–113.9
$HF(g)$	–275.4	173.78	29.14
$HF(aq)$	–299.675	88.	–58.6
HF_2^-	–583.709	92.68	–138.9
Cl^-	–131.20	56.6	–123.2
ClO_3^-	–7.903	162.3	–51.5
$S(cr)$	0.	32.05	‡
$H_2S(g)$	–33.4	205.81	‡
$H_2S(aq)$	–27.648	126.0	178.7
HS^-	12.243	67.0	–93.
S^{2-}	120.7	–14.6	–300.
S_5^{2-}	66.96	187.	–180.
HS_5^-	32.14	269.	27.
$H_2S_5(aq)$	9.88	328.	297.
S_4^{2-}	66.22	165.	–210.
HS_4^-	27.98	247.	267.
$H_2S_4(aq)$	4.0	306.	273.
S_3^{2-}	78.2	95.	–240.
S_2^{2-}	97.17	5.	–210.
S_2^-	58.18	144.	–105.
$S_2O_3^{2-}$	–522.58	66.94	–240.
$HS_2O_3^-$	–532.21	127.6	14.6
$H_2S_2O_3(aq)$	–535.55	188.3	115.1

†: For aqueous ions and complexes "*a*" corresponds to the standard partial molar heat capacity at 25°C, and its temperature dependence has been calculated with the revised Helgeson-Kirkham-Flowers model as described in the text.

‡: Heat capacity functions:

$H_2(g)$ $\quad C_p^\circ(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 7.442 + 0.011707\,T - 1.3899\times10^{-6}\,T^2 - 5.1041\times10^{5}\,T^{-2} + 410.17\,T^{-0.5}$

$S(cr)$ $\quad C_p^\circ(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 14.795 + 0.024075\,T + 7.1\times10^{4}\,T^{-2}$

$H_2S(g)$ $\quad C_p^\circ(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 26.356 + 0.026497\,T - 6.0244\times10^{-6}\,T^2 + 2.6599\times10^{5}\,T^{-2} - 43.559\,T^{-0.5}$

Table 4 (Continued)

Species	$\Delta G_f°$ (kJ·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$C_p°$ (J·K^{-1}·mol^{-1})
SO_3^{2-}	–487.47	–29.	–318.
HSO_3^-	–528.69	139.7	–6.
H_2SO_3(aq)	–539.19	231.9	270.
SO_4^{2-}	–744.00	18.5	–269.
HSO_4^-	–755.32	131.7	–18.
H_2SO_4(aq)	–748.47	83.5	250.
NO_3^-	–110.79	146.7	–69.
NO_2^-	–32.22	123.0	–97.5
HNO_2(aq)	–50.63	135.56	28.
NH_3(g)	–16.41	192.77	‡
NH_3(aq)	–26.67	109.04	74.9
NH_4^+	–79.40	111.17	65.9
PH_3(g)	13.4	210.23	‡
PH_3(aq)	25.36	120.1	188.
H_3PO_4(aq)	–1149.367	161.91	98.7
$H_2PO_4^-$	–1137.15	92.5	–29.3
HPO_4^{2-}	–1095.99	–33.5	–243.9
PO_4^{3-}	–1025.49	–220.97	–480.7
CO_2(g)	–394.37	213.79	‡
"CO_2(aq)"	–385.97	119.36	243.1
HCO_3^-	–586.845	98.4	–35.4
CO_3^{2-}	–527.899	–50.0	–290.8
C(cr)	0.	5.74	‡
CH_4(g)	–50.7	186.26	‡
CH_4(aq)	–34.451	87.82	277.4
Na^+	–262.00	58.45	37.9
NaOH(aq)	–417.98	44.8	–13.4
NaF(aq)	–537.94	50.2	46.9

‡: Heat capacity functions:

for NH_3(g) $C_p°(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 51.39 + 0.0266\,T - 4.90\times10^{-6}\,T^2 + 7.584\times10^{5}\,T^{-2} - 548.0\,T^{-0.5}$

for PH_3(g) $C_p°(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 26.3 + 0.04048\,T - 1.14\times10^{5}\,T^{-2}$

for CO_2(g) $C_p°(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 87.82 - 0.0026442\,T + 7.064\times10^{5}\,T^{-2} - 99.886\,T^{-0.5}$

for C(cr) $C_p°(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 60.86 - 0.01024\,T + 1.669\times10^{-6}\,T^2 + 7.139\times10^{5}\,T^{-2} - 99.22\,T^{-0.5}$

for CH_4(g) $C_p°(T)/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 119.4 + 0.02055\,T - 5.0\times10^{-6}\,T^2 + 2.814\times10^{6}\,T^{-2} - 2090\,T^{-0.5}$

Table 4 (Continued)

Species	ΔG_f° ($\mathrm{kJ \cdot mol^{-1}}$)	S° ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	C_p° ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
$\mathrm{NaCl(aq)}$	–388.74	117.2	35.6
$\mathrm{NaSO_4^-}$	–1010.12	95.	–16.1
$\mathrm{NaCO_3^-}$	–792.99	–43.9	–37.9
$\mathrm{NaHCO_3(aq)}$	–847.89	120.9	89.5
$\mathrm{NaPO_4^{2-}}$	–1295.61	–100.5	–192.8
$\mathrm{NaHPO_4^-}$	–1360.79	–27.4	9.0
$\mathrm{Ca^{2+}}$	–552.8	–56.2	–31.5
$\mathrm{CaOH^+}$	–716.72	28.0	5.9
$\mathrm{Ca(OH)_2(cr)}$	–898.0	83.4	‡
$\mathrm{CaF^+}$	–838.43	–37.7	125.9
$\mathrm{CaF_2(cr)}$	–1175.3	68.9	‡
$\mathrm{CaCl^+}$	–682.41	18.8	73.1
$\mathrm{CaCl_2(aq)}$	–811.70	25.1	129.5
$\mathrm{CaSO_4(aq)}$	–1309.3	20.9	–104.6
$\mathrm{CaSO_4(cr)}$	–1321.8	107.4	‡
$\mathrm{CaSO_4 \cdot 2H_2O(cr)}$	–1797.0	193.8	183.
$\mathrm{CaCO_3(aq)}$	–1099.76	10.5	–123.9
$\mathrm{CaHCO_3^+}$	–1145.99	101.1	163.1
$\mathrm{CaCO_3(cr)}$	–1129.10	91.71	‡
$\mathrm{CaPO_4^-}$	–1615.17	–110.0	–212.2
$\mathrm{CaHPO_4(aq)}$	–1664.43	9.1	–78.4
$\mathrm{CaH_2PO_4^+}$	–1698.01	111.02	89.2
$\mathrm{Ca_5(PO_4)_3OH(cr)}$	–6337.1	390.4	‡
$\mathrm{Ca_5(PO_4)_3F(cr)}$	–6489.7	387.9	‡

‡: Heat capacity functions:

for $\mathrm{Ca(OH)_2(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 186.7 - 0.02191\,T - 1600\,T^{-0.5}$

for $\mathrm{CaF_2(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 2033 - 1.436\,T + 5.04\times10^{-4}\,T^2 + 2.988\times10^7\,T^{-2} - 33120\,T^{-0.5}$

for $\mathrm{CaSO_4(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 372.8 - 0.1574\,T + 7.99\times10^{-5}\,T^2 + 1.695\times10^6\,T^{-2} - 4330.8\,T^{-0.5}$

for $\mathrm{CaCO_3(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 99.546 + 0.027137\,T - 2.1481\times10^6\,T^{-2}$

for $\mathrm{Ca_5(PO_4)_3OH(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 387.8 + 0.1186\,T - 1.27\times10^7\,T^{-2} + 1811\,T^{-0.5}$

for $\mathrm{Ca_5(PO_4)_3F(cr)}$ $C_p^\circ(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 754.3 - 0.03026\,T - 9.084\times10^5\,T^{-2} - 6201\,T^{-0.5}$