SITE-94

Revised Pourbaix Diagrams for Copper at 5-150 °C

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This report concerns a study which has been conducted for the Swedish Nuclear Power Inspectorate (SKI). The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of SKI.
This report concerns a study which is part of the SKI performance assessment project SITE-94. SITE-94 is a performance assessment of a hypothetical repository at a real site. The main objective of the project is to determine how site specific data should be assimilated into the performance assessment process and to evaluate how uncertainties inherent in site characterization will influence performance assessment results. Other important elements of SITE-94 are the development of a practical and defensible methodology for defining, constructing and analyzing scenarios, the development of approaches for treatment of uncertainties, evaluation of canister integrity, and the development and application of an appropriate Quality Assurance plan for Performance Assessments.

Johan Andersson
Project Manager
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Abstract

Pourbaix diagrams for copper in the temperature interval 5–150 °C have been revised. Predominance diagrams for dissolved copper species have also been calculated. Five different total concentrations (10^{-3}, 10^{-4}, 10^{-6}, 10^{-8} and 10^{-9} molal) for dissolved copper have been used in the calculations.

Copper is a noble metal, but it corrodes with hydrogen evolution at low pH, both at a concentration level of 10^{-6} m at T ≥ 125 °C, and at a concentration of 10^{-8} m from T ≥ 50 °C. The oxides (Cu_{2}O(cr) and CuO(cr)) are stable at all temperatures and concentration levels ≥ 10^{-8} m, with the exception of 10^{-8} m at T ≥ 100 °C where the oxides are not stable. The copper(II) hydroxide, Cu(OH)_{2}(cr), is not thermodynamically stable in the interval investigated. Cu^{+} predominates at T > 80 °C at all concentrations levels. CuOH(aq) appears in the Pourbaix diagrams only at the lowest concentrations, and in the predominance diagram for dissolved species at 125 and 150 °C. Cu(OH)_{2}^{−} predominates at all temperatures and concentrations investigated. The complete hydrolysis series of copper(I) and (II) have not been included in earlier published Pourbaix diagrams, and these species are covered for the first time in this work.

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

The calculated diagrams are used as a base for the discussion of the corrosion behaviour of the copper canisters in the Swedish radioactive waste management program.
1 Introduction

According to the concept KBS-3 developed by SKB\textsuperscript{1} project, spent nuclear fuel will be disposed in a system of several safety barriers. One of these is a duplex metal canister consisting of an outer copper vessel and an inner steel vessel. Copper has been chosen as the reference material for the ongoing development work mainly due to its excellent corrosion behaviour.

The expected life time of the 5.0 cm thick copper vessel is high. Life times of several hundred thousands to millions of years have been estimated. Material lifetimes of these orders of magnitude are unique and can only be found in the field of final disposal of spent nuclear fuel.

To be able to discuss lifetimes of these orders of magnitude in a serious way, a baseplate of knowledge is needed. One way to create a basis for this knowledge is to study the thermodynamics of the system.

Thermodynamics give the connection between heat energy and other forms of energy. Nature will always try to be in its lowest energy condition. Thermodynamic considerations show that the species with the lowest energy for a given set of conditions is the most stable. Thermodynamic calculations can predict if a chemical or electrochemical reaction can proceed or not.

The corrosion properties of the copper-water system have been studied from a thermodynamic stand-point in a number of instances. However, the choice of aqueous copper species are very similar in these publications. Furthermore, there has been a large progress in the chemical analysis of aqueous copper species, and the aqueous complexes of copper in the published reports are not always in agreement with modern conceptions of these species. This motivates to revise again the thermodynamic corrosion properties for the aqueous system of copper.

The temperature in the final repository for spent nuclear fuel may change in the future by a climate change, such as a glaciation. Glacier water might decrease the temperature of the ground water surrounding the repository to slightly above the freezing point for water (Sjöblom et al. 1994). As Pourbaix diagrams for copper at temperatures below 25 °C are lacking in the literature, a low temperature (5 °C) diagram has also been produced in this study.

The aims of this work are to revise the Pourbaix diagram for copper at elevated temperatures and to calculate temperature effects below 25 °C, which have not been published before. This report is the base for ongoing studies where sulphur, chlorine and carbon are intended to be included in the study of the corrosion properties of copper. The thermodynamic calculations for copper in different aquatic environments will also be used to simulate the corrosion behaviour of a copper vessels in the expected environment of the Swedish final repository for spent nuclear fuel.

\textsuperscript{1} SKB: Swedish Nuclear Fuel and Waste Management Co.
2 Pourbaix diagram

2.1 General

A Pourbaix diagram is a two dimensional representation of a multi-dimensional space (potential, pH, concentration, temperature, etc.). The diagram shows the equilibrium condition for all possible redox reactions. This type of diagram existed already in the 1930’s (Gatty and Spooner, 1938), but it was Marcel Pourbaix who in 1944 developed the potential-pH diagram applied to corrosion conditions (Pourbaix, 1945, 1965). Among people working in the field of metallic corrosion this diagram type is known as Pourbaix diagram and is characterised by:

- potential and pH on the axes
- aqueous chemical systems
- contains both solid and dissolved species, but also gaseous species can be included
- may contain three thermodynamic stability areas: immunity, passivity and corrosion
- the temperature is 25 °C if nothing else is indicated
- the concentration of dissolved species is $10^{-6}$ M if nothing else is indicated
- $10^{-6}$ M is per definition the limit for corrosion

Pourbaix diagrams can be seen as maps in the chemical space, summarising thermo-dynamic information in a compact and useful way. The diagram shows whether a chemical reaction can proceed or not. A Pourbaix diagram can also be seen as a map in a snowy landscape with a partly frozen lake in the darkness of a winter night, Fig. 1. The snow dwells the ground but also the ice, which may be more or less robust. The darkness represents the ignorance and the ground represents immunity, the ice passivity and the open water corrosion. With the help of this map it is possible to travel safely in the chemical landscape.

A Pourbaix diagram contains three different areas of thermodynamic stability: immunity, passivity and corrosion, Fig. 2. Immunity means that the metal itself is the stable phase and can therefore by definition not corrode. Passivity is the existence area where the metal is passivated by formation of a coating, usually a solid reaction product like an oxide or a hydroxide. This coating is called passive film or layer (depending on the thickness of the coating). The passive layer serves as a diffusion barrier for the reacting species and thereby decreases the chemical reaction rate (corrosion) sometimes with several orders of magnitude. A good passive film protects the metal from further degradation and gives a negligible corrosion rate. Corrosion is the state where the thermodynamically stable species is a dissolved reaction product, which does not protect the metal from further dissolution (corrosion) as no diffusion barrier is formed.
For a deeper description of the basis of the Pourbaix diagram, consult Pourbaix (1973, 1974) and Garrels and Christ (1965).

Figure 1. Map of a winterly landscape.

Figure 2. Pourbaix diagram for copper (S. Beverskog).
The Pourbaix diagram is often complemented by a predominance diagram for dissolved aqueous species in the system. This chemical equilibrium diagram contains only dissolved species and is used to determine the predominance of dissolved species, specially when a solid phase is thermodynamically stable and would hide the aqueous species in the corresponding Pourbaix diagram.

2.2 Copper

Pourbaix diagrams for copper can be found in a number of publications, while studies which include calculations to create Pourbaix diagrams are relatively few (Pourbaix, 1945; Garrels and Christ, 1964; Brook, 1972; Macdonald et al., 1972; Pourbaix, 1973; de Zubov et al., 1974; Duby, 1977; Chen et al., 1983; Daniel and Harper, 1986; Angus and Angus, 1984; Brookins, 1988; Cubicciotti, 1988; Skrifvars, 1993). The reason for this might be that the designer of this type of diagrams, Marcel Pourbaix, obviously had copper as a favourite system and has published these diagrams in a number of reports. At temperatures > 25 °C there are only four published Pourbaix diagrams for copper (Macdonald et al., 1972, Chen et al., 1983, Daniel and Harper 1986, Cubicciotti 1988).

The choice of copper species, which is the basis for the construction of the diagram, was made in a very traditional and routine manner in earlier publications, cf. Table 1. The choice of species was mostly the same as in Pourbaix’ thesis in 1945. The first and second hydrolysis steps for Cu(I) and Cu(II), respectively, have not been included in previous publications. The nomenclature \( \text{Cu(OH)}_{n}^{2-n} \) for the third and fourth hydrolysis steps for Cu(II) has only been used in one study (Skrifvars, 1993).

Most of these publications contain three solid phases: \( \text{Cu(cr)} \), \( \text{Cu}_{2}\text{O(cr)} \) and \( \text{CuO(cr)} \). The hydroxide is included in six publications. Of the dissolved species, only \( \text{Cu}^{+} \), \( \text{Cu}^{2+} \) and \( \text{HCOO}^{-} \) and/or \( \text{CuO}_{2}^{2-} \) were included in the majority of cases. Skrifvars (1993) uses the nomenclature \( \text{Cu(OH)}_{n}^{2-n} \) for the third and the fourth hydrolysis steps for copper(II). There seems to be no publication which included the first two hydrolysis steps for either copper(I) or copper(II). A polynuclear hydrolysis species was included in Duby (1977). Copper(III) species were included in two publications.

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2 The phase designators "(cr)", "(s)" and "(aq)" are used for crystalline and solid phases and aqueous species according to the IUPAC rules (Cox et al., 1982).
Table 1. Copper species included in previously published Pourbaix diagrams.

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<td>6</td>
<td>8</td>
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</table>

cr: crystalline solid, s: solid, aq: aqueous, g: gaseous
x': Cu₂O₃ hydrated; x*: HCuO₂⁻; x**: CuO₂⁻²

3 Hydration and hydrolysis

Cations in aqueous solutions form complexes with the solvent molecules. These complexed water molecules form a hydration sphere around the central metal cation. Most cations, with perhaps the exception of the largest ones, form a second hydration sphere of water molecules outside the first. The co-ordination number (the number of co-ordinated or complexed molecules in the first hydration sphere) is six for most metallic cations. The smallest cations have co-ordination numbers of four and the largest metal cations may have co-ordination numbers of eight or more. The coordination number for copper(II) is six, but the bonding distances are not equally long due to Jan-Teller distortion. Four of the co-ordination axes are equally long and form a plane, while the other two are longer and orthogonal to that plane, cf. Fig. 3.

Figure 3. Coordination for copper (II).

The chemical notation for a metallic cation in aqueous solution is: Me\(^{n+}\)(aq). The spheres of co-ordinated water molecules are generally not included in the notation. Although they are always present (the correct notation should be Me(H\(_2\)O)\(_n\)\(^{n+}\)(aq)), the simpler notation is usually used for convenience. Furthermore, because in this work no gaseous ions are considered, the notation “(aq)” will be omitted for aqueous ions.

The stability of a metal cation co-ordinated by H\(_2\)O molecules in aqueous solution is pH-dependent. The reaction of the complex with the bulk of water is stepwise where each co-ordinated water molecule releases a hydrogen ion, leaving a hydroxide ion. The general hydrolysis reaction is:

\[
\text{Me(H}_2\text{O)}_{\text{c}}^{\text{n}^+} \rightleftharpoons \text{Me(H}_2\text{O)}_{\text{c}-\text{m}}(\text{OH})_{\text{m}^n} + \text{m H}^+
\]

where \(m\) (usually \(\leq 4\)) is the number of hydrolysis steps or hydroxide ions coordinated (or hydrogen ions released).

Depending on the oxidation number of the metallic cation, uncharged aqueous hydrolysis complexes may be formed. Copper, which has the oxidation numbers I and II in aqueous solution, forms the uncharged complexes CuOH(aq) and Cu(OH)\(_2\)(aq). The suffix (aq) is used to distinguish these hydrolysis complexes from solid hydroxides. Hydrolysis of more than four steps are rare for metal ions in aqueous solutions, and usually highly alkaline solutions are need to release the last hydrogen ions. Due to the asymmetric configuration of the complexed water molecules around the copper(II) ion, the water molecules in the quadratic plane are the first to hydrolyse.
4 Choice of copper species in an aqueous system

It is of fundamental importance which species (solid phases, fluids, aqua ions, and aqua complexes) are included in the thermodynamic calculations in a given chemical system. Some species are not stable in water solutions while others can only form at high temperatures or at extreme compositions. It is therefore of the greatest importance to critically evaluate the species which are expected to exist in a system before they are allowed to be the fundament for the thermodynamic calculations. Calculations based on wrong species give misleading information of chemical equilibria.

Copper has the electron configuration \([\text{Ar}]3d^{10}4s^1\), i.e. one lonely 4s-electron outside a full 3d-scale. As a consequence, the first ionisation enthalpy is high compared with other elements with the oxidation number +1 like the alkali metals. The ionisation enthalpies for the second and the third oxidation step for copper are much lower than those for the alkali metals and this partly contributes to its character of transition metal. The oxidation numbers for copper in aqueous solution are 0, I and II. Three valent copper is a very strong oxidation agent and thereby not stable in water solution.

The copper species which are considered in the system of Cu-O-H are indicated in Table 2, which shows both included and excluded formulae. Eight dissolved species and four solid compounds have been selected in this work as the ground for thermodynamic calculations in the copper-water system.

The justifications for excluding species are as follows: The copper(I) hydride and hydroxide are not stable in aqueous solution. The existence of the suboxide \(\text{Cu}_4\text{O}(\text{cr})\) is very doubtful in contact with water and the same is true for \(\text{Cu}_4\text{O}_3(\text{cr})\). \(\text{Cu}^{6+}\) is a totally hydrolysed copper(II) ion, i.e. all six water molecules in the inner sphere of hydration have all given a hydrogen ion each. Its existence is very doubtful and if it should exist it can only be at extremely high pH-values. The oxidation number (III) is known in solid phases such as copper(III) hydroxide, \(\text{Cu}^{(OH)}_3(\text{cr})\), and copper(III) oxide, \(\text{Cu}_2\text{O}_3(\text{cr})\). Such compounds are very strong oxidising agents in water and thereby not stable in aqueous solutions. The same is true for the three valent copper ion and its fourth hydrolysis step \(\text{Cu}^{(OH)}_4^{-}\). The latter is reported in the literature as \(\text{CuO}_2^{2-}\), which is not consistent with theoretical hydration models for metal cations. The four valent copper oxide \(\text{CuO}_2(\text{cr})\) is not stable either in aqueous solutions.

The aqua ions of copper(II) with the charges -1 and -2 are in this work denoted as the third and forth hydrolysis steps for copper(II). This is instead of the notations \(\text{HCuO}_2^{-}\) and \(\text{CuO}_2^{2-}\) traditionally used in Pourbaix diagrams since Pourbaix published his first potential/pH-diagram (Pourbaix, 1945). The difference between these notations is one or two water molecules. The former notation is also in agreement with Baes and Mesmer (1976). The formulas \(\text{HCuO}_2^{-}\) and \(\text{CuO}_2^{2-}\) are not consistent with theoretical models for metal cations in water solutions as well as the hydrolysis series for copper (II), where every hydrolysis step add one hydroxide ion (Cotton and Wilkinson, 1980).
The complex Cu$_2$OH$_3^{2+}$ has been detected at quite high (≥0.1 M) Cu(II) concentrations (Ohtaki and Kawai, 1972; Burkov et al., 1982; Néher-Neumann, 1984). These studies have also been performed at high ionic strengths of background electrolyte. For these reasons, the species Cu$_2$OH$_3^{2+}$ has not been included in this study.

Table 2. Considered copper species in the copper-water system.

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</tbody>
</table>
5 Thermochemical data

A critical review of published thermochemical data has been performed for the solids and aqueous species described in previous Section. Data is usually available only for a reference temperature of 25 °C in the form of standard molar Gibbs free energy of formation from the elements ($\Delta_f^0 G^\circ_m$), standard molar entropy ($S^\circ_m$), and standard molar heat capacity ($C^\circ_{p,m}$). The standard partial molar properties are used for aqueous species. Extrapolation of these data to other temperatures is performed with the methodology described later in the "Calculations" section. Missing entropy and heat capacity values at 25 °C have been estimated as described below in this Section.

The data selected for the calculations performed in this report are summarised in Table 3. The data for solid compounds agree with other compilations (Gedansky et al., 1970; Wagman et al., 1982; Bertocci and Wagman, 1985; Chase et al., 1985; Knacke et al., 1991; Kubaschewski et al., 1993; Plyasunov et al., 1995; etc.). For aqueous species, our $\Delta_f^0 G^\circ_m$ values agree well with other compilations (Baes and Mesmer, 1976; Gedansky et al., 1970; Plyasunov et al., 1995). Values for entropy (and enthalpy) changes selected in different studies depend on the equations used for the temperature variation of $C^\circ_{p,m}$ for aqueous solutes, and therefore, some of the $S^\circ_m$ values selected here differ substantially from those in other compilations, as discussed below.

5.1 Solids

The standard molar Gibbs free energy of formation for Cu(cr) is by definition zero at all temperatures. The value of $S^\circ_m$ selected in this work for elemental copper are those listed in CODATA's Key Values (Cox et al., 1989), while parameters for temperature equations of the heat capacity are taken from Knacke et al. (1991). Values of $\Delta_f^0 G^\circ_m$, $S^\circ_m$ and $C^\circ_{p,m}$ for the oxides are those given in Knacke et al. (1991). These values do not differ substantially from those in other compilations of thermodynamic data (e.g., Kubaschewski et al. (1993), Chase et al. (1985), the NBS tables of Wagman et al. (1982), etc.).

The value of $\Delta_f^0 G^\circ_m$ for Cu(OH)$_2$(cr) has been calculated from the solubility product recommended by Baes and Mesmer (1976), while $S^\circ_m$ and the temperature equation for $C^\circ_{p,m}$ are those tabulated in Kubaschewski et al. (1993).
Table 3. Thermodynamic data at 25 °C for the system copper-water.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta_r G_m^\circ ) (kJ·mol(^{-1}))</th>
<th>( S_m^\circ ) (J·K(^{-1})·mol(^{-1}))</th>
<th>( C_{p,m}(T)/(J\cdot K^{-1}\cdot mol^{-1}) = a + bT + cT^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(cr)</td>
<td>0</td>
<td>33.15</td>
<td>20.531 8.611 0.155</td>
</tr>
<tr>
<td>Cu(_2)O(cr)</td>
<td>-147.90</td>
<td>92.36</td>
<td>58.199 23.974 -0.159</td>
</tr>
<tr>
<td>CuO(cr)</td>
<td>-128.29</td>
<td>42.6</td>
<td>48.597 7.427 -0.761</td>
</tr>
<tr>
<td>Cu(OH)(_2)(cr)</td>
<td>-359.92</td>
<td>87.0</td>
<td>86.99 23.26 -0.54</td>
</tr>
<tr>
<td>Cu(^+)</td>
<td>48.87</td>
<td>40.6</td>
<td>57.3</td>
</tr>
<tr>
<td>CuOH(aq)</td>
<td>-122.32</td>
<td>226</td>
<td>-280</td>
</tr>
<tr>
<td>Cu(OH)(_2)^-</td>
<td>-333.05</td>
<td>-135</td>
<td>562</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>65.04</td>
<td>-98.0</td>
<td>-23.8</td>
</tr>
<tr>
<td>CuOH(^+)</td>
<td>-126.66</td>
<td>-61</td>
<td>382</td>
</tr>
<tr>
<td>Cu(OH)(_2)(aq)</td>
<td>-316.54</td>
<td>26</td>
<td>214</td>
</tr>
<tr>
<td>Cu(OH)(_3)^-</td>
<td>-493.98</td>
<td>-14</td>
<td>105</td>
</tr>
<tr>
<td>Cu(OH)(_4)^2-</td>
<td>-657.48</td>
<td>-175</td>
<td>800</td>
</tr>
<tr>
<td>Cu(_2)(OH)(_2)^{2+}\</td>
<td>-285.1</td>
<td>-4</td>
<td>190</td>
</tr>
<tr>
<td>Cu(_3)(OH)(_4)^{2+}\</td>
<td>-633.0</td>
<td>-59</td>
<td>404</td>
</tr>
</tbody>
</table>

\( ^\dagger \) 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.

5.2 Aqueous species

The thermodynamic properties of \( \text{H}_2\text{O}(l) \) at 25 °C recommended by CODATA (Cox et al., 1989) have been used in this work. The temperature dependence of these properties has been calculated with the model of Saul and Wagner (1989). The dielectric constant of water (which is needed for the revised Helgeson-Kirkham-Flowers model described below) has been obtained with the equations given by Archer and Wang (1990).

Data for \( \text{Cu}^{2+} \), which is a key species in this system, are those recommended by CODATA (Cox et al., 1989). However, the standard partial molar heat capacity, which is not included in the CODATA Key Values, has been taken from the work of Helgeson et al. (Shock and Helgeson, 1988).
\( \Delta_f G_m^* \) for Cu\(^+\) has been obtained from the redox equilibrium constant reported by Ciavatta et al. (1980), while the value for \( S_m^* \) is that listed in the NBS tables (Wagman et al., 1982), and that of \( C_{p,m}^* \) is taken from Shock and Helgeson (1988), who list the same value for \( S_m^* (\text{Cu}^+, 25 \, ^\circ\text{C}) \) as the NBS.

### 5.2.1 Mononuclear hydrolysis species

Values of \( \Delta_f G_m^* \) for Cu(OH)\(_3^-\) and Cu(OH)\(_4^{2-}\) have been calculated from the hydrolysis constants recommended by Baes and Mesmer (1976), while the values of \( \Delta_f G_m^* \) for CuOH\(^+\) and Cu(OH)\(_2\)(aq) have been calculated from the equilibrium constants reported by Paulson and Kester (1980), as this high quality study appeared after the critical review of Baes and Mesmer.

The value of \( S_m^* \) for CuOH\(^+\) has been calculated from the results obtained by a calorimetric technique by Arena et al. (1976). Values of \( S_m^* \) for the other mononuclear Cu(II) hydrolysis complexes, and values of \( C_{p,m}^* \) for all the mononuclear hydrolysis complexes of Cu\(^{2+}\) have been calculated by fitting the solubility of CuO(cr) measured at several temperatures by Var'yash (1986). A comparison between experimental and calculated solubilities at 200 \, ^\circ\text{C} is shown in Fig. 4. It must be noted however, that the solubilities reported by Var'yash do not agree completely with the data obtained in other studies (Hayward et al., 1967; Hearn et al., 1969; Styrikovich et al., 1973), cf. Fig. 5. The reason for this discrepancy is not clear, and the data by Var'yash (1986) are preferred here because more experimental details are reported.

Values for \( \Delta_f G_m^* \), \( S_m^* \) and \( C_{p,m}^* \) for the hydrolysis complexes of Cu(I), CuOH(aq) and Cu(OH)\(_2\)\(^+\) have been calculated by fitting the temperature dependence of the aqueous solubility of Cu\(_2\)O(cr)/Cu(cr) mixtures obtained by Var'yash (1989). A comparison between experimental and calculated solubilities at 150 and 200 \, ^\circ\text{C} is shown in Fig. 6.

Some of the selected values of \( S_m^* \) and all \( C_{p,m}^* \) values listed in Table 3 for the mononuclear aqueous hydrolysis complexes are fitting parameters, and as such they naturally depend on the experimental data fitted (in this case the data of Var'yash (1986) and Var'yash (1989)). Furthermore, they also depend on the mathematical model used to describe the temperature dependence of \( C_{p,m}^* \). It is therefore desirable to check how the \( S_m^* \) and \( C_{p,m}^* \) values compare with other sources of information, and whether the values obtained here have chemically meaningful values. Values for \( \Delta_f S_m^* \) for the general reaction

\[
\text{Cu}^{2+} + n \, \text{H}_2\text{O}(l) \rightleftharpoons \text{Cu(OH)}_{(2-n)}^n + n \, \text{H}^+
\]

are plotted in Fig. 7 as a function of \( n \), and they show a relatively smooth dependence between \( \Delta_f S_m^* \) and \( n \).
**Figure 4.** Comparison between calculated and experimental solubility of CuO(cr). Data taken from Var'yash (1986).

**Figure 5.** Comparison between calculated and experimental solubility of CuO(cr) in pure water. Data taken from Hearn et al. (1969); Styrikovich et al. (1973); Var'yash (1986).
Figure 6. Comparison between calculated and experimental solubility of Cu$_2$O(cr)/Cu(cr) mixtures. Data taken from Var'yash (1989).

\[ \Delta_r S_m^o/(J \cdot K^{-1} \cdot mol^{-1}) \]

Figure 7. Selected values of $\Delta_r S_m^o$ for copper(II) hydrolysis.
The solubility of CuO(cr) has also been determined in alkaline phosphate solutions (Ziemniak et al., 1992). From the temperature dependence of the copper(II) concentrations, the authors of that study reported:

\[
\text{CuO(cr) + 2 H}_2\text{O(l) }\rightleftharpoons \text{Cu(OH)}_3^- + \text{H}^+ \tag{1}
\]

\[
\log K_{eq}^0 = -18.0 \pm 0.4
\]

\[
\Delta_rS_m^o = -(119 \pm 64) \text{ J-K}^{-1}\text{-mol}^{-1}
\]

\[
\Delta_rC_{p,m}^o = -(51 \pm 8) \text{ J-K}^{-1}\text{-mol}^{-1}.
\]

These values are not too far from the data selected in this study (\(\log K_{eq}^0 = -19.02\), \(\Delta_rS_m^o = -197 \text{ J-K}^{-1}\text{-mol}^{-1}\), and \(\Delta_rC_{p,m}^o = -85 \text{ J-K}^{-1}\text{-mol}^{-1}\)). The discrepancies can be attributed to the fact that Ziemniak et al. had to fit many parameters for mixed phosphate-hydroxide copper complexes in their complicated system.

Values of heat capacity changes close to zero are expected for aqueous "isocoulombic" reactions (Baes and Mesmer, 1981; Cobble et al., 1982; Phillips and Silvester, 1983; Jackson and Helgeson, 1985; Mesmer et al., 1988; Ruaya, 1988), that is, for reactions where the electric charge of the reactant ions is compensated by equal electric charges in the product ions. An example of a reaction which is not isocoulombic is Eq. (1). For the copper(II) hydrolysis system, it is possible to write the following isocoulombic reactions:

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O(l)} &\rightleftharpoons \text{CuOH}^+ + \text{H}^+ \\
\text{Cu}^{2+} + 2 \text{H}_2\text{O(l)} &\rightleftharpoons \text{Cu(OH)}_2(\text{aq}) + 2 \text{H}^+ \\
\text{CuOH}^+ + \text{H}_2\text{O(l)} &\rightleftharpoons \text{Cu(OH)}_2(\text{aq}) + \text{H}^+ \\
\text{Cu(OH)}_2(\text{aq}) + \text{OH}^- &\rightleftharpoons \text{Cu(OH)}_3^- \\
\text{Cu(OH)}_3^- + \text{OH}^- &\rightleftharpoons \text{Cu(OH)}_4^{2-}
\end{align*}
\]

While the isocoulombic approximation predicts that the values of \(\Delta_rC_{p,m}^o\) should be close to zero for the above reactions, the model of Ryzhenko and Bryzgalin (Ryzhenko and Bryzgalin, 1987; Bryzgalin, 1989; Plyasunov and Grenthe, 1994) which is based on simple electrostatic assumptions, predicts \(\Delta_rC_{p,m}^o\) values of: +79, +121, +43, +70, and +16, respectively. In comparison, the values of \(\Delta_rC_{p,m}^o\) obtained from the data in Table 3 for the above reactions are: +330, +87, -243, +28, and +832, respectively.

In conclusion, although the selected \(C_{p,m}^o\) values for mononuclear Cu(II) hydrolysis complexes should be considered only to be fitting parameters with large uncertainties, their magnitude appears not to be unreasonable.

### 5.2.2 Polynuclear hydrolysis species

The value of \(\Delta_rG_m^o\) for Cu_2(OH)_2^{2+} was derived from the equilibrium constant recommended by Baes and Mesmer (1976). The value of \(\Delta_rS_m^o(2) = -44.5 \text{ J-K}^{-1}\text{-mol}^{-1}\) reported by Arena et al. (1976) at 0.1 M NaClO_4 for the reaction
\[ 2 \text{Cu}^{2+} + 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2 \text{H}^+ \] (2)

is assumed to be valid at $I = 0$, allowing the calculation of $S_m^{\text{Cu}_2(\text{OH})_2^{2+}}$.

For $\text{Cu}_3(\text{OH})_4^{2+}$, the equilibrium constant reported by Arena et al. (1976) for the reaction

\[ 3 \text{Cu}^{2+} + 4 \text{H}_2\text{O}(l) \rightleftharpoons \text{Cu}_3(\text{OH})_4^{2+} + 4 \text{H}^+ \] (3)

at $I = 0.1 \text{ M}$ is extrapolated to $I = 0$ using the specific ion interaction equations given in (Grenthe et al., 1992, Appendix B), resulting in $\log K^\circ(3) = -21.1$, and this, together with the value of $\Delta_S^m$ for the above reaction given by Arena et al. (1976) (assumed to be valid at $I = 0$), results in the data listed in Table 3. Values of $C_{p,m}^\circ$ have been obtained assuming zero values for $\Delta S_{p,m}^\circ$ for the following isocoulombic equations:

\[ \text{Cu}^{2+} + \text{Cu}(\text{OH})_2(aq) \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} \]
\[ \text{Cu}^{2+} + 2 \text{Cu}(\text{OH})_2(aq) \rightleftharpoons \text{Cu}_3(\text{OH})_4^{2+} \]

The predominance of copper(II) hydrolysis products, calculated with the data given in Table 3, is shown in Fig. 8 as a function of pH and temperature.

**Figure 8.** The calculated predominance of copper(II) hydrolysis products as a function of pH and temperature. Thinner lines indicate the calculated predominance of aqueous species when Cu(II) oxides and hydroxides are not allowed to precipitate (supersaturated solutions).
Figure 8. (Continued).
**Fig. 8** illustrates the general tendency of polynuclear hydrolysis complexes to dissociate with increasing temperature (Baes and Mesmer, 1981; Plyasunov and Grenthe, 1994). The Figure also shows the general shift towards lower pH values for all hydrolysis species, which implies that for some low and constant pH values, the average fraction of polynuclear complexes in fact increases with temperature (for example at pH = 6, cf. **Fig. 8**), even though the total fraction of polynuclear species over the whole pH-range decreases with $T$. 
6 Calculations

6.1 Temperature extrapolations

The equilibrium composition of an aqueous system can be calculated from the law of mass action (see e.g. Alberty, 1987). For example:

\[ \text{Cu}^{2+} + \text{H}_2\text{O(l)} \rightarrow \text{CuOH}^+ + \text{H}^+ \]

\[ \log K^\circ_{eq} = \log \{\text{CuOH}^+\} - \text{pH} - \log \{\text{Cu}^{2+}\} - \log \{\text{H}_2\text{O(l)}\} \]

where "{}" denote activities. The equilibrium constant, \( K^\circ_{eq} \), is an expression of the change in a thermodynamic function, the Gibbs energy:

\[ \Delta_r G^\circ_m = -RT \ln K^\circ_{eq} \] (4)

where \( T \) is the absolute temperature and \( R \) is the gas constant. The Gibbs energy of a species (solid or aqueous) can not be determined in its absolute value. Only relative values have a physical meaning and can be determined experimentally. By convention, the chemical elements and the aqueous \( \text{H}^+ \) ion are used as reference, and standard Gibbs energies of formation (from the elements) are tabulated in thermodynamic publications. As the Gibbs energies of the elements cancel with each other in a chemical reaction, this allows the calculation of reaction changes, for example in the reaction given above,

\[ \Delta_r G^\circ_m = \Delta_r G^\circ_m (\text{CuOH}^+) + \Delta_r G^\circ_m (\text{H}^+) - \Delta_r G^\circ_m (\text{Cu}^{2+}) - \Delta_r G^\circ_m (\text{H}_2\text{O(l)}) \] (5)

and by convention \( \Delta_r G^\circ_m (\text{H}^+) = 0 \) at all temperatures.

Entropy is a thermodynamic function which indicates the variation with temperature of the Gibbs energy of a chemical species

\[ (\partial G/\partial T)_P = -S \]

and the variation of entropy with temperature is given by the heat capacity

\[ (\partial S/\partial T)_P = C_p/T \]

(similarly, \( (\partial \Delta_r G^\circ_m /\partial T)_P = -\Delta_r S^\circ_m \) and \( (\partial \Delta_r S^\circ_m /\partial T)_P = \Delta_r C^\circ_{p,m}/T, \text{etc.} \)). Finally, the temperature variation of the heat capacity must be taken into account. For solids and gases, \( C_p(T) \) is usually given by a polynomial equation (which can be integrated analytically to perform temperature extrapolations of the Gibbs energy), while for aqueous species different approximations may be used for the heat capacity depending on the temperature interval and the type of chemical reaction involved. For example, it might be assumed that \( \Delta_r S^\circ_m \) is constant for small temperature intervals (\( \pm 10 \text{ °C} \)), or that \( \Delta_r C^\circ_{p,m} \) does not vary at temperatures below 100 °C.
At higher temperatures, electrostatic models are adequate to describe the temperature variation of the Gibbs energy of aqueous species. The dielectric constant of liquid water decreases with temperature, and reaches values that are similar to those that some organic solvents have at room temperature. Owing to this, charged aqueous species become less stable with increasing temperature and ion pairs become more stable (for example, CuOH\(^+\) is more stable at higher temperature than Cu\(^{2+}\) and OH\(^-\)). This change in stability (which implies a change in Gibbs energy) corresponds to changes in the entropy and heat capacity of aqueous species. As the temperature increases, the pressure must increase to keep equilibrium between water and steam, and at the critical point (for \(H_2O\) \(T=374\) °C and \(p\approx221\) bar) the two phases (gas and liquid) have the same density and can not be distinguished. The heat capacity of water approaches infinity as the \(T\) comes closer to the critical point, while the standard partial molar heat capacities and volumes of aqueous species approach negative infinity.

Methods for temperature extrapolations of thermodynamic data for aqueous species must take into account the change in dielectric properties of water, and the peculiar behaviour of the heat capacity of solutes as the temperature increases. The revised Helgeson-Kirkham-Flowers model developed by Helgeson \textit{et al.} (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock \textit{et al.}, 1989, 1992) has been used in this work. Ignoring pressure effects, this model gives the following temperature variation for the standard partial molar heat capacity of aqueous ions

\[
C_{p,m}^\circ = c_1 + c_2/(T-228) + T \omega(T) X(T)
\]

\[
+ (2T/e(T)) \left\{ \left( \frac{\partial \ln T}{\partial T} \right) \frac{(\partial \omega(T)}{\partial T} + \right\}

\[
+ T \left\{ \left( 1-(1/e(T)) \right) \left( \frac{\partial^2 \omega(T)}{\partial T^2} \right) \right\}
\]

where \(T\) is the temperature in degrees Kelvin, \(e(T)\) is the dielectric constant of liquid water, \(c_1\) and \(c_2\) are model parameters, \(X(T)\) is a function of the dielectric constant:

\[
X(T) = \left( 1/e(T) \right) \left( \frac{\partial^2 \ln e(T)}{\partial T^2} \right) \left( \frac{\partial \ln e(T)}{\partial T} \right)
\]

and \(\omega(T)\) is an electrostatic Born coefficient, which depends on the electric charge, \(z_i\), and ionic radius, \(r_i\),

\[
\omega(T) = \eta \left[ (z_i^2/(r_i + |z_i|k_i + g(T))) - (z_i/(3.08 \times 10^{-10} + g(T))) \right]
\]

where \(\eta = 6.95 \times 10^{-5} \text{ m} \cdot \text{J} \cdot \text{mol}^{-1}\) (if \(r_i\) is in m), \(g(T)\) is a function which accounts for the temperature dependence of ionic radius (\(g(T)\) is zero below 175 °C, see Shock \textit{et al.}, 1992, Table 5), and \(k_i\) is zero for anions and \(=0.94 \times 10^{-10} \text{ m}\) for cations.

The revised Helgeson-Kirkham-Flowers model, as expressed in Eqs. (6) and (7) contains three parameters, \(c_1\), \(c_2\), and \(r_i\) (in addition to \(\Delta_f G_m^\circ\) and \(S_m^\circ\)) for each aqueous ions.

Shock and Helgeson (1988) have proposed methods to estimate values of \(c_1\), \(c_2\), and \(r_i\) from the values of \(S_m^\circ\) and \(C_{p,m}^\circ\).
where \( \alpha_2 \) is a charge dependent fitting parameter given in Shock and Helgeson (1988, their Eq. (56)).

Thermodynamic data for aqueous copper ions, given in Table 3, have been introduced in Eqs. (8) to (10) to calculate the standard partial molar heat capacity of the aqueous ions as a function of temperature according to Eqs. (6) and (7). Integration of Eq. (6) in its turn has permitted the temperature extrapolation of the Gibbs energies for aqueous ions of copper, and the calculation of equilibrium constants as a function of temperature with Eq. (4) and with expressions similar to Eq. (5). Further details on this procedure are given in Tanger and Helgeson (1988), Shock and Helgeson (1988) and Shock et al. (1992).

A similar procedure has been used for neutral aqueous complexes of copper, as described in Shock et al. (1989). For inorganic neutral aqueous species Eq. (6) is slightly modified, and an alternative version of Eq. (10) has to be used.

### 6.2 Pourbaix diagrams

The technique used to draw Pourbaix diagrams has been described in the literature exhaustively, we cite here only three refs.: Delahay et al., 1950; Garrels and Christ, 1965; Stumm and Morgan, 1981. The method may be summarised as follows.

For a general redox reaction between an oxidised and a reduced form of a chemical species,

\[
\text{Ox} + n \text{e}^- \rightleftharpoons \text{Red},
\]

the equilibrium constant is given as

\[
\log K^\circ = \log \{\text{Red}\} - \log \{\text{Ox}\} - n \log \{\text{e}^-\}
\]

(“{“} represents thermodynamic activities), and

\[- \log \{\text{e}^-\} = (1/n) \log K^\circ + (1/n) (\log \{\text{Ox}\} - \log \{\text{Red}\})\]

Multiplying by \((RT \ln(10)/F)\) we obtain the half cell electrode potential relative to the standard hydrogen electrode:

\[
E_H = E_H^\circ + (RT \ln(10)/nF) (\log \{\text{Ox}\} - \log \{\text{Red}\})
\]

where \( T \) is the absolute temperature, and \( R \) and \( F \) are the universal gas and Faraday constants respectively. The following equivalencies have been used:

\[- \log \{\text{e}^-\} = E_H^\circ / (RT \ln(10)/F)\]

\[
E_H^\circ = (RT \ln(10)/nF) \log K^\circ = -\Delta G_m^\circ / nF
\]

The electrochemical potentials reported in this work are always related to that of the standard hydrogen electrode \((E_{SHE})\), which is considered to be zero at all temperatures. As a first example of a redox reaction, the equilibrium taking place at the standard hydrogen electrode may be used:

\[
H^+ + e^- \rightleftharpoons 0.5 \text{H}_2(\text{g})
\]
\[
\log K^o = 0.5 \log p_{H2} - \log \{e^-\} + \text{pH} \\
- \log \{e^-\} = \log K^o - 0.5 \log p_{H2} - \text{pH}
\]

and as the equilibrium constant for this reaction is one by definition (and therefore \(E_H^o = 0\)), we obtain

\[
E_H = (RT \ln(10)/F) (-\text{pH} - 0.5 \log p_{H2})
\]

By setting the partial pressure of hydrogen gas to 1 atm, this equation represents a line with slope \(-1\) in the \(E_H/\text{pH}\) diagram, and the lower sloping dashed line in the Pourbaix diagrams of the Appendix is obtained. At potentials below this line \(H_2(g)\) evolution is possible (\(p_{H2} > 1\) atm) at ambient pressure. The parallel dashed line in the Pourbaix diagrams at higher potentials is that corresponding to

\[
0.5 \text{O}_2(g) + 2 \text{H}^+ + e^- \rightleftharpoons \text{H}_2\text{O}(l)
\]

\[
E_H = E_H^o + (RT \ln(10)/F) (-2 \text{pH} + 0.5 \log p_{O2})
\]

Again, by setting the partial pressure of oxygen gas to 1 atm, this equation represents a line with slope \(-1\) in the \(E_H/\text{pH}\) diagram.

Another example is:

\[
\text{Cu}^{2+} + 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{CuO}(s) + 2 \text{H}^+
\]

\[
\log K^o = -2 \text{pH} - \log \{\text{Cu}^{2+}\}
\]

in this case, setting the activity of \(\text{Cu}^{2+}\) to \(10^{-4}, 10^{-6}, 10^{-8}, \text{etc.}\), gives a pH value (\(E_H\)-independent) which represents a vertical line in the corresponding Pourbaix diagrams.

As a final example, two competing reactions may be used:

\[
\text{Cu}^+ + e^- \rightleftharpoons \text{Cu(cr)} \quad (11)
\]

\[
\log K^o(11) = -\log \{\text{Cu}^+\} - \log \{e^-\}
\]

\[
E_H(11) = E_H^o(11) + (RT \ln(10)/F) \log \{\text{Cu}^+\}
\]

\[
\text{Cu}^{2+} + 2 e^- \rightleftharpoons \text{Cu(cr)} \quad (12)
\]

\[
\log K^o(12) = -\log \{\text{Cu}^{2+}\} - 2 \log \{e^-\}
\]

\[
E_H(12) = E_H^o(12) + (RT \ln(10)/2F) \log \{\text{Cu}^{2+}\}
\]

These two reactions result in electrode potentials which are pH-independent. Because in a Pourbaix diagram the activity level is fixed: \(\log (\{\text{Cu}^{2+}\} + \{\text{Cu}^+\}) = -4, -6, -8, \text{etc.}\) (the activity level at which the diagram is drawn). If the potential in a given coordinate of the Pourbaix diagram is above \(E_H(11)\), then \(\{\text{Cu}^+\}\) in equilibrium with \(\text{Cu(cr)}\) will be larger than the activity level chosen (for example \(10^{-6}\)). Similar conditions apply to \(E_H(12)\) and \(\{\text{Cu}^{2+}\}\). Therefore, \(\text{Cu}^+\) will only appear in the Pourbaix diagram if \(E_H^o(11) < 2E_H^o(12)\). From the data in Table 3, the values of the potentials at 25 °C are \(E_H^o(11) = 0.507\) V and \(E_H^o(12) = 0.337\) V, and therefore \(\text{Cu}^+\) must appear in Pourbaix diagrams at 25°C. How much the \(\text{Cu}^+\) predominance will extend on the potential direction will depend on the equilibrium constant for

\[
\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+
\]

etc. The entire Pourbaix diagram of copper can be completed following this kind of reasoning, which was developed in the 1940's, and well used already in the 1950's. Chemical equilibrium diagrams in this report (including Pourbaix diagrams and predominance diagrams for dissolved species), Figs. 4-8, have been drawn with computer software (Puigdomenech, 1983) using the chemical compositions calculated with the SOLGASWATER algorithm (Eriksson, 1979). This technique differs slightly
from the procedure described above because the computer programs must be able to deal with a wide range of chemical possibilities. Nevertheless, the basic principles behind the programs are the those given above.

Calculations to draw the Pourbaix diagrams presented in the Appendix have been performed for seven temperatures in the interval 5–150 °C (i.e., at 5, 25, 50, 80, 100, 125, and 150 °C), which covers adequately the temperature range which copper canisters will experience in the expected environment of the Swedish final repository for spent nuclear fuel.

The concentration of dissolved metallic species used in Pourbaix diagrams is 10^{-6} M, if nothing else is mentioned. The value was stipulated by Pourbaix as a limit for practical corrosion. At concentrations of dissolved metallic species > 10^{-6} M the metal is considered to corrode and at concentrations < 10^{-6} M the metal is considered not to corrode. This boundary value is a definition for aqueous corrosion that is useful for practical applications.

However, in aquatic systems under special or extreme conditions the conventional definition of corrosion is not sufficient. In these systems other concentrations are needed to give the limits of corrosion. Such a system is the cooling media in nuclear boiling water reactors, where the impurity contents is on the ppb level. These levels correspond to concentrations of 10^{-8} M (Beverskog, 1992; Beverskog and Puigdomenech, 1992). Another system where the conventional definition of corrosion is not adequate is in systems for the final disposal of spent nuclear fuel. The concentrations of dissolved species can in this case vary considerably as the time scales considered are extremely long. At certain time periods the concentrations of dissolved materials may be very high, while during others periods of time they can be extremely low. Therefore four other concentrations have been included in the calculations (10^{-3}, 10^{-4}, 10^{-9} and 10^{-10}) besides the traditional 10^{-6} M. These values are considered to be extreme but important in the discussion of the corrosion behaviour of the copper canisters as well as in the ongoing modelling work of the near field of the nuclear repository.

Thus, Pourbaix diagrams have been calculated in this work at five concentration levels, 10^{-3}, 10^{-4}, 10^{-6}, 10^{-8} and 10^{-9} molal at every temperature. These concentrations are total concentrations, i.e. the sum of all aqueous species containing copper at each coordinate point ($E_{\text{redox}}$/pH-value). Because they are temperature-independent, molal concentration units (mol · (kg of water)^{-1}) are used in the calculations.

Activity factors for aqueous species have been neglected in the construction of the Pourbaix diagrams given in the Appendix, and similarly, the activity of water has been fixed to unity. This is in agreement with the frequently used assumption when drawing and using chemical equilibria diagrams that thermodynamic activity may be used instead of concentration. However, this does not hold for concentrated solutions, for example those with very low or high pH. The activity coefficient of these solutions will probably be large and will change quickly with pH, and concentration ratios might deviate strongly from the corresponding activity ratios obtained from the thermodynamic equations. For this reason, lines in chemical equilibrium diagrams based on activity ratios might lack significance, when the lines are below pH ~ 2 and beyond pH ~ 12. The lines in these
regions, which should perhaps be dotted, have been included in this work due to reasons of construction.

The parallel sloping dotted lines in the Pourbaix diagrams given in the Appendix limit the stability area of water at atmospheric pressure of gaseous species. The upper line represents the oxygen equilibrium line (O₂(g)/H₂O(l)) and potentials above this line will oxidise water with oxygen evolution. The lower line represents the hydrogen line (H⁺/H₂(g)) and potentials below this line will result in hydrogen evolution.

The pH values given in this work are pH values at the temperature of interest. The temperature dependence for the ion product of water,

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^- \]

changes the neutral pH value of pure water with the temperature (neutral environment = 1/2 \( pK_w,T \)). To facilitate reading the Pourbaix diagrams in the Appendix, the neutral pH value for the temperature of each diagram is given as a vertical dotted line.
7 Results and discussion

Two general remarks can be concluded regarding the temperature and concentration dependence in the diagrams. Firstly, temperature affects the different stability areas of immunity, passivity and corrosion. The immunity area (stability of the metal itself) decreases with increasing temperature. The passivity area (the oxides) is almost temperature independent. With increasing temperature the corrosion area at acidic pH changes due to a slight decrease of the passivity area and a decrease of the immunity area, while the corrosion area at alkaline pH increases. The reason for this behaviour is related to the temperature dependence of the ion product of water. Secondly, the concentration of dissolved metallic species changes also the different stability areas. The immunity and passivity areas increase with increasing concentration at increasing temperature, while the corrosion areas decrease.

The Pourbaix diagrams for copper show that copper is a noble metal, as the immunity area is situated above the hydrogen line (H/H2) at most temperatures, Figs. 9-12. This means that copper does not dissolve (corrode) with hydrogen evolution in deaerated water free from oxidising agents, owing to the fact that the potential of Cu/Cu+(or Cu/Cu+) is more noble than the redox couple in the hydrogen electrode (H/H2). However, there are some exceptions such as at low pH where copper corrodes with hydrogen evolution and formation of Cu+ at the concentration of 10^-6 m and T ≥ 125 °C as well as at the concentration of 10^-8 m from T ≥ 50 °C, see Figures 9F-G and 10C-G. Other exceptions to immunity are strong alkaline solutions at T ≥ 125 °C at the concentration of 10^-8 m, see Figures 10F-G.

In oxidising environments at low pH copper is dissolved and copper(I) ions are formed, which can oxidise to Cu++. The stability area of the Cu+ ion increases with increasing temperature, at the expense of the Cu++ ion. Oxidising environments at slightly alkaline pH oxidise elementary copper to Cu2O(cr), which at higher potential can be further oxidised to CuO(cr). The hydroxide of copper(II) is not stable compared to the oxide and therefore the hydroxide does not appear in the diagrams. Oxidising environments at alkaline pH oxidise elementary copper to Cu(OH)2+, which at higher potentials can oxidise further to the third or fourth hydrolysis step of Cu(II): Cu(OH)3~ or Cu(OH)4^2-.

The third and fourth hydrolysis steps Cu(OH)5~ and Cu(OH)4^2-, had previously only been included in one work (Skrifvars, 1993) but only at 25 °C. The predominance line between these two species is in god agreement with our calculations.

The predominance diagrams for dissolved copper species are shown in Figure 12. All considered copper species predominate at the calculated temperatures with the exception of the mono valent uncharged copper complex (CuOH(aq)) which predominate only at T ≥ 125 °C.

Calculations for the concentrations of 10^-3 and 10^-9 m have also been performed, but are not shown in the figures, because they are very similar to 10^-4 and 10^-8 m, respectively. The boundary lines are of course slightly displaced. Concerning the predominating species, the following comments can be made. Cu+ predominates at 80 °C and 10^-4 but
not at $10^{-3}$ m. There are no solid copper compounds stable at the lowest concentrations ($10^{-9}$ m). Cu(OH)$_2$(aq) predominate at $10^{-9}$ m at $\leq 25$ °C, but not at $10^{-8}$. This is due to the stability of the solid Cu(II) oxide at concentrations $\geq 10^{-8}$ m.

The Pourbaix diagram for copper at 25 °C and $10^{-6}$ m obtained in the present study deviates from all other publications. The stability areas differ slightly due to a "new" set of aqueous copper complexes. Another difference is the form of the stability area of Cu$_2$O in alkaline pH. This is due to the second hydrolysis step of Cu$^+$ (Cu(OH)$_2^-$), which had not been included in earlier works.
To be able to discuss the corrosion of copper canisters, there is a need to know the expected values for the redox potential as well as pH in the repository environment. The redox potential is anticipated to be in the interval $-300$ to $-400 \text{ mV}_{\text{SHE}}$ and the pH is expected to be around $8.4$. It is also pertinent to study the copper chemistry for parameter combinations somewhat outside the expected values, in order to obtain an adequate knowledge base. Therefore the base should include variations in pH and redox potential that might occur as a result of conceivable but unlikely events as processes (e.g. failure of the bentonite buffer or inflow of oxygen rich water).

The corrosion behaviour will be discussed in connection with three different concentrations of dissolved copper. The concentrations are denoted high, medium and low, i.e. $10^{-4}$, $10^{-6}$ and $10^{-8}$ m.

**High concentration ($10^{-4}$ m):** Copper is immune at the presumed redox potentials ($-300$ to $-400 \text{ mV}_{\text{SHE}}$) of the copper canister in the repository environment. In the presence of oxidising agents the potential will increase and a solid reaction product forms on the surface in the form of either CuO(cr) or Cu$_2$O(cr) (depending on the potential). At this high concentration of dissolved copper species the corrosion areas are situated far away from the presumed environmental conditions. This means that copper canisters should be free from corrosion from the thermodynamic point of view.

**Medium concentration ($10^{-6}$ m):** Copper is immune also at the concentration of $10^{-6}$ m in the expected range of redox potentials in the repository environment. In the presence of oxidising agents solid reaction products (oxides) will be formed. Oxidising agents and increasing temperature stabilise the Cu$^+$ ion on the acidic side of Cu$_2$O(cr) implying that the environment is corrosive for the copper canister. The predominance area of the Cu$^+$ ion at elevated temperatures is in fair agreement with the work of Chen et al., (1983). As the presence of this species implies corrosion, the Cu$^+$ ion has to be taken into account in the future modelling work on the corrosion behaviour of the copper canisters. However, if the pH is 6.9-12.7 (at 25 °C) this environment should also be safe from thermodynamical point of view.

**Low concentration ($10^{-8}$ m):** Copper is also immune at the low concentration of $10^{-8}$ m of dissolved species. However, oxidising agents which increase the redox potential can form a risky situation for the copper canister. At $T \geq 80$ °C CuO is not stable and Cu$_2$O only appears at $\leq 80$ °C, resulting in corrosion independently of pH in the presence of oxidising agents. These low copper concentrations might occur due to complexing agents, precipitation of secondary minerals, sorption, ion exchange, etc., all of which decrease the copper concentration perhaps to this low value. The effect of ion exchange of copper ions in the bentonite buffer on canister corrosion has not been investigated. If the bentonite clay surrounding the copper canister is undamaged, the complexing agents will soon be consumed due to their low migration rate through the clay. Copper will then continue to dissolve until the concentration is high enough to form a new equilibria with a solid phase and precipitate it on the copper surface and thereby reducing or eliminating the corrosion attack. In the postulated case where the bentonite...
clay is damaged and there is free access of oxidising agents then the copper canisters will undergo a faster corrosion.
9 Conclusions

The following points summarise the results of the thermodynamic calculations of this work:

- The Pourbaix diagram for copper at 5 °C is shown for the first time.

- The calculations are based on a "new" set of aqueous species which are in agreement with modern theories of cation hydrolysis.

- Inclusion of Cu(OH)$_2^+$ (for the first time in a Pourbaix diagram) changes the form of the stability area of Cu$_2$O(cr).

- Cu(OH)$_2$ is less stable than CuO(cr).

- The stability area of Cu$^+$ increases with the temperature and with decreasing total copper concentration.

- The stability areas of the two first hydrolysis products of Cu(I) are shown for the first time in Pourbaix diagrams.

- Copper is a noble metal, but it can corrode at extreme pH and low concentrations of dissolved copper with hydrogen evolution.

- According to the thermodynamic calculations copper canisters will not corrode in the repository environment at the expected pH-values and redox potentials. Deviating environmental conditions can, however, cause corrosion.

- Increasing temperature intensifies the corrosion of copper.
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References


Appendix: Diagrams
Figure 9A.
Pourbaix diagram for copper at 5 °C. The total concentration for soluble species is $10^4$ m.
Figure 9B.
Pourbaix diagram for copper at 25 °C. The total concentration for soluble species is $10^{-4}$ m.
Figure 9C.
Pourbaix diagram for copper at 50 °C. The total concentration for soluble species is $10^{-4}$ m.
Figure 9D.
Pourbaix diagram for copper at 80 °C. The total concentration for soluble species is $10^4$ m.
Figure 9E.
Pourbaix diagram for copper at 100 °C. The total concentration for soluble species is 10⁻⁴ m.
Figure 9F.
Pourbaix diagram for copper at 125 °C. The total concentration for soluble species is $10^{-4}$ m.
Figure 9G. Pourbaix diagram for copper at 150 °C. The total concentration for soluble species is $10^{-3}$ m.
Figure 10A.
Pourbaix diagram for copper at 5 °C. The total concentration for soluble species is $10^{-6}$ m.
Figure 10B.
Pourbaix diagram for copper at 25 °C. The total concentration for soluble species is $10^6$ m.
Figure 10C. Pourbaix diagram for copper at 50 °C. The total concentration for soluble species is $10^{-2}$ m.
Figure 10D.
Pourbaix diagram for copper at 80 °C. The total concentration for soluble species is $10^6$ m.
Figure 10E. Pourbaix diagram for copper at 100 °C. The total concentration for soluble species is $10^{-6}$ m.
Figure 10F. Pourbaix diagram for copper at 125 °C. The total concentration for soluble species is $10^6$ m.
Figure 10G.
Pourbaix diagram for copper at 150 °C. The total concentration for soluble species is $10^{-6}$ m.
Figure 11A.
Pourbaix diagram for copper at 5 °C. The total concentration for soluble species is $10^{-8}$ m.
Figure 11B. Pourbaix diagram for copper at 25 °C. The total concentration for soluble species is 10^{-3} m.
Figure 11C. Pourbaix diagram for copper at 50 °C. The total concentration for soluble species is $10^{-3}$ m.
Figure 11D.
Pourbaix diagram for copper at 80 °C. The total concentration for soluble species is $10^{-8}$ m.
Figure 11E.
Pourbaix diagram for copper at 100 °C. The total concentration for soluble species is $10^{-8}$ m.
Figure 11F.
Pourbaix diagram for copper at 125 °C. The total concentration for soluble species is $10^8$ m.
Figure 11G.
Pourbaix diagram for copper at 150 °C. The total concentration for soluble species is $10^{-8}$ m.
Figure 12A.
Pourbaix diagram for dissolved copper species at 5 °C. Gas fugacity is atmospheric pressure.
Figure 12B.
Pourbaix diagram for dissolved copper species at 25 °C. Gas fugacity is atmospheric pressure.
Figure 12C.
Pourbaix diagram for dissolved copper species at 50 °C. Gas fugacity is atmospheric pressure.
Figure 12D.
Pourbaix diagram for dissolved copper species at 80 °C. Gas fugacity is atmospheric pressure.
Figure 12E.
Pourbaix diagram for dissolved copper species at 100 °C. Gas fugacity is atmospheric pressure.
Figure 12F. Pourbaix diagram for dissolved copper species at 125 °C. Gas fugacity is atmospheric pressure.
Pourbaix diagram for dissolved copper species at 150 °C. Gas fugacity is atmospheric pressure.