Effect of saline water on metallic copper

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October 1999
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ABSTRACT

The disposal concept for high-active nuclear waste from Finnish nuclear power plants envisages encapsulation of the spent fuel in thick-walled copper-iron canisters, and burial deep into the crystalline bedrock. Many observations indicate that the deep-bedrock groundwaters may be very saline. The aim of the present report is to study the behavior of copper canister in deep-disposal conditions, if the groundwater around is saline.

The results indicate that soluble Cu(I) chloride complexes are the most important potential corrosion products of copper corrosion in saline water.

Based on the knowledge on the conditions and properties of the deep saline waters, and on the mineral composition of the bedrock and buffer material, two theoretical scenarios were identified for further study: oxidation of copper by ferric iron, and oxidation of copper by water with the formation of hydrogen.

The role of ferric as oxidizer was ruled out due to its very low solubility in water. Thermodynamic equilibrium considerations indicate that the hydrogen-evolving corrosion of copper can not leach more than $10^{-6}$ M copper at pH 6, 100 °C until equilibrium is attained. Hydrogen is formed as a product of this corrosion reaction, thus, if originally present in water, it will further suppress the corrosion reaction.

Avainsanat: copper corrosion, saline groundwater
SUOLAISEN VEDEN VAikutus KuparinMettaLiin

TIIVISTELMÄ

Suomen ydinvoimalaitoksissa syntyvän korkea-aktiivisen ydinjätteen loppusijoitus on suunniteltu toteutettavaksi pakkaamalla käytetty polttoaine paksuseinäisiin kuparirautakanistereihin ja hautamaalla ne syvälle kiteiseen kallioperään. Useat havainnot viittaavat siihen, että pohjavesi syvällä kallioperässä voi olla hyvin suolaista. Tämän raportin tarkoituksena on tutkia kuparikanisterin käyttäytymistä syvän kallioperän olosuhteissa suolaisessa pohjavedessä.

Tulosten perusteella liukoiset Cu(I) kloridikompleksit ovat tärkeimmät potentiaaliset kuparin korroosiotuotteet suolaisessa vedessä.

Perustuen tietoon syvien suolaisten pohjavesien ominaisuuksista ja olosuhteista, sekä tietoon kallioperän täyteaineen mineraalikoostumuksesta, havaittiin kaksi teoreettista skenaaristi tarkemmin tutkittaviksi: kuparin hapettuminen ferriraudan vaikutuksesta ja vetyä kehittävä kuparin korroosio, jossa vesi hapettimen Ferriraudan rooli hapettimena on poissuljettavissa, koska sen liukoisuus veteen on äärimmäisen pieni. Termodynaamisten tasapainotarkastelujen perusteella kuparin vetyä kehittävä korrosio ei voi liuottaa enempää kuin $10^{-6}$ M kuparia pH:ssa 6, 100 °C lämpötilassa ennenkuin tasapainotila on saavutettu. Vetyä muodostuu korroosiotuotteena ja siten, esiintyessään veden alkuperäisenä komponenttinä, se estää edelleen korroosiorakhtioita.

Avainsanat: kuparin korroosio, suolainen pohjavesi
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PREFACE

This study is based on research contract between Posiva Oy and the Geological Survey of Finland (GTK). The contact persons were Jukka-Pekka Salo and Margit Snellman from Posiva Oy, and Lasse Ahonen from GTK.

The author wishes to thank Dr. Timo Laitinen from VTT Manufacturing Technology for the constructive discussions, which improved considerably the content of this study.
1 INTRODUCTION

The Finnish disposal concept for nuclear waste is based on the encapsulation of the spent nuclear fuel bundles in thick-walled copper canisters with cast iron insert, and deep burial of these canister in a repository excavated at a depth of about 300 - 800 meters in crystalline bedrock.

In general, circulation of meteoric water is most effective in the uppermost bedrock. Bedrock fracturing and hydraulic pressure gradient decrease with increasing depth and, consequently, the groundwater content and the movement of groundwater in bedrock decreases gradually with increasing depth. The composition and properties of deep groundwaters are strongly affected by the long-term groundwater-bedrock interaction processes. As observed in many studies, deep groundwaters are often saline.

The choice of copper as the outer-wall material of the canister was mainly based on its chemical durability against corrosion. Thermodynamic foundations were presented together with the introduction of the Swedish KBS-3 concept (The Swedish Corrosion Research Institute and its reference group 1983), and later considered in numerous reports (e.g., Taxen 1990, Werme et al. 1992, Ahonen 1995, Beverskog and Puigdomenech 1998). Sulfide has been considered as the only important copper-corroding agent available in deep groundwaters (e.g., Ahonen 1995). However, the possible corrosive role of high groundwater salinity (1.5 M Cl) together with increased temperature near the canister surface (about 80 °C) was pointed out by Beverskog and Puigdomenech (1998).

In this report, the behavior of metallic copper in saline water is discussed. The term 'saline water' refers here to all types of oxygen-free waters and brines having chloride concentration of the order of 1 to 3 moles per liter. More detailed properties on the chemistry and physico-chemical properties of these waters are given in chapter 2. Design and properties of the disposal system and its near field are presented in chapter 3, with special reference to the components possibly having effect on copper corrosion.

The aim of the present report is make a systematic study of all possible processes, which may affect the integrity of copper canister in saline water. The calculations and conclusions are based on concepts defined prior to their use in chapter 4. The emphasis of this work in on the thermodynamic considerations, but also some key questions of kinetics are briefly dealt with.
2 COMPOSITION AND PROPERTIES OF SALINE WATERS

Based on the amount of total dissolved solids (TDS), groundwaters are often described as fresh, brackish, saline or brine. The following limits are generally used for salinity classification (e.g., Lampén 1994):

1) fresh  TDS < 1000 mg/l
2) brackish  1000 mg/l < TDS < 10000 mg/l
3) saline  10000 mg/l < TDS < 100000 mg/l
4) brine  TDS > 100000 mg/l

In this report the term saline water is used colloquially for the categories saline and brine.

Saline waters have been frequently found and well studied in deep crystalline bedrock of Precambrian Shield areas, especially in Fennoscandian and Canadian Shields (Fritz and Frape 1987). The main anion of saline waters is chloride, while the main cations are calcium, sodium and, less often, magnesium. As a rule, probability to meet saline waters in the bedrock increases with depth (Figure 2-1).

Figure 2-1. The relationship of depth and chloride concentration for groundwaters from the Canadian Shield (Modified from Frape and Fritz 1987).
The most saline waters (brines) in Canadian Shield contain chloride up to 200-300 g/l, Ca 50-100 g/l, and Na 30 - 50 g/l at a depth of about 1500 m (Frape and Fritz 1987. Gascoyne et al. 1987). Methane is the predominant component of the dissolved gas phase (up to 90 percent), while hydrogen content varies substantially, the highest values being about 30 percent of the gas phase (Fritz et al 1987).

Deep saline groundwaters have been detected in many locations in Finland (Nurmi et al. 1988, Blomqvist 1990, Halonen et al 1990). The most saline waters reported in Finland are found in Juuka (Miihkali) in Eastern Finland (Halonen et al 1990), where the following concentrations were analyzed: Na 48 g/l, Ca 18 g/l, and Cl 110 g/l (TDS 168 g/l) at the depth of 1100 m. Several occurrences of saline waters are known from Outokumpu region, Eastern Finland (Blomqvist et al 1987) with TDS values up to 27 g/l. Other known occurrences comprise for example Ylivieska, Central Finland (TDS up to 90 g/l at the depth of 600 m), Pori in Western Finland (TDS up to 120 g/l at depth of 300 m (Halonen et al, op. cit., Blomqvist et al. 1986). The gas phase released from deep groundwaters is mainly methane-dominated (40 - 80 %), while hydrogen is normally present in smaller amounts (less than 10 %) (Nurmi et al., op. cit.).

The highest TDS-values analyzed in Canadian Shield sites exceed those measured in Finland. This can be attributed to the deeper boreholes available there, often reaching the depth of 1.5 km, while the deepest boreholes in Finland are about 1 km deep. In Sweden, Laxemar, boreholes have been drilled to the depth of more than 1.5 km. Saline water observed in the deepest part of one of those drillholes contained Ca 19 g/l, Na 8 g/l, Cl 46 g/l (TDS about 74 g/l) (Laaksoharju et al 1995).

In the more than 10 km deep borehole of Kola Peninsula, groundwater was fresh to the depth of 800 meters, saline waters down to about 4.5 km contained up to about 150 g/l dissolved components, deeper down the TDS values increased to more than 300 g/l (Nurmi et al. 1988 and references therein).

In the Finnish site characterization program for disposal of spent nuclear fuel, bedrock has been studied to the depth of more than 1 km by deep drilling. The most saline waters so far obtained contain about 70 g/l and 32 g/l dissolved solids in Olkiluoto and Hästholmen sites, respectively. Based on the site investigation data, reference groundwaters have been selected for different bedrock-environments and conditions (Vuorinen and Snellman 1998). Compositions of the repository-farfield reference waters are presented in Table 2-1. Dissolved gas data of Table 2-1 were obtained using pressure-maintaining in-situ sampler "PAVE" (Ruotsalainen et al. 1996), so the data is given as volume (ml) of gas in NTP (i.e., 25 °C, 1 atm) extracted from one liter of water. The dominant dissolved volatile component of the brine reference water is methane (57 %), and the amount of hydrogen is 15 %. The concentration of dissolved hydrogen in this water is thus about 10 mM.

A synthetic saline reference water, "Standard Canadian Shield saline solution", SCSSS was used in the Canadian copper corrosion studies (Ogundele and Jain 1998). This solution contains: Cl 0.97 M (34 g/l), Ca 0.37 M (15 g/l) and Na 0.22 M (5 g/l), amount of total dissolved solids being thus about 54 g/l.
Table 2-1. Far-field reference waters for Finnish nuclear waste studies (Vuorinen and Snellman 1998).

<table>
<thead>
<tr>
<th></th>
<th>ALLARD Basic</th>
<th>ALLARD-OX log&lt;sub&gt;10&lt;/sub&gt;C&lt;sub&gt;02&lt;/sub&gt; =-4</th>
<th>ALLARD-OX log&lt;sub&gt;10&lt;/sub&gt;C&lt;sub&gt;02&lt;/sub&gt; =-3.5</th>
<th>BRACKISH-RE HH-KR3</th>
<th>SALINE-RE OL-KR1</th>
<th>SALINE-RE OL-SR</th>
<th>BRINE-RE OL-KR4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eh measured (mV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eh calculated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.3</td>
<td>8.8**</td>
<td>8.4**</td>
<td>7.7</td>
<td>8.3</td>
<td>9.0</td>
<td>7.8**</td>
</tr>
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<td>Alkalinity (meq/L)</td>
<td>2</td>
<td>1.07</td>
<td>1.49</td>
<td>1.61</td>
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<td>0.2</td>
<td></td>
</tr>
<tr>
<td>DIC (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (mg/L)</td>
<td>8</td>
<td>1.7</td>
<td>2.9</td>
<td>8.3</td>
<td>3.3</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>18</td>
<td>5.1</td>
<td>10</td>
<td>680</td>
<td>4 000</td>
<td>4 000</td>
<td>15 700</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>2 600</td>
<td>4 800</td>
<td>4 800</td>
<td>9 750</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>4.3</td>
<td>2.8</td>
<td>0.7</td>
<td>340</td>
<td>56</td>
<td>56</td>
<td>110</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>26</td>
<td>21</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>Fe (total)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (II)</td>
<td></td>
<td>max 2.7**</td>
<td></td>
<td>2.3</td>
<td>0.77</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.67</td>
<td>0.67</td>
<td>0.048</td>
<td>0.056</td>
</tr>
<tr>
<td>Br⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.68</td>
<td>0.68</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Sc⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.55</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>Sr (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.196</td>
<td>0.196</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Cs (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.034</td>
<td>0.034</td>
<td>&lt;0.02</td>
<td>0.12</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄⁺ (mg/L)</td>
<td>0.5</td>
<td>0.15</td>
<td>1.4</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>53</td>
<td>52</td>
<td>47</td>
<td>2 600</td>
<td>14 800</td>
<td>14 600</td>
<td>43 000</td>
</tr>
<tr>
<td>Br⁻ (mg/L)</td>
<td>5.2</td>
<td>5.2</td>
<td>1.6</td>
<td>12</td>
<td>12</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>I⁻ (mg/L)</td>
<td>0.41</td>
<td>0.41</td>
<td>0.05</td>
<td>0.85</td>
<td>0.9</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₃⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.02*</td>
<td>0.02*</td>
<td></td>
</tr>
<tr>
<td>NO₂⁻ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.02*</td>
<td>&lt;0.02*</td>
<td></td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td></td>
<td>1.1*</td>
<td>1.1*</td>
<td>0.17*</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>S(CO₃)⁻ (mg/L)</td>
<td></td>
<td>max 3 **</td>
<td></td>
<td>0.11</td>
<td>0.03</td>
<td>0.9</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>9.6</td>
<td>9.6*</td>
<td>9.6</td>
<td>710</td>
<td>0.84</td>
<td>4.2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>H-3 (TU)</td>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>U (μg/L)</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td></td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>U-234/U-238</td>
<td></td>
<td></td>
<td></td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rn (Bq/L)</td>
<td></td>
<td></td>
<td></td>
<td>44</td>
<td></td>
<td>47</td>
<td></td>
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<tr>
<td>C-14 (pm)</td>
<td></td>
<td></td>
<td></td>
<td>43.6</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>N₂ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40*</td>
<td>38*</td>
<td>480</td>
</tr>
<tr>
<td>CO₂ (mg/L)</td>
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<td></td>
<td></td>
<td></td>
<td>1.1*</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>H₂ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.381*</td>
<td></td>
<td>268</td>
</tr>
<tr>
<td>CH₄ (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.025*</td>
<td>26.2</td>
<td>990</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>220</td>
<td>185</td>
<td></td>
<td>9 778</td>
<td>24 000</td>
<td>20 000</td>
<td>70 000</td>
</tr>
</tbody>
</table>

*) uncertain values due to analytical problems.

**) these parameters are affected by the redox buffers acting in the system.
3 DISPOSAL CONCEPT AND NEAR-FIELD GEOCHEMISTRY

Nuclear waste to be disposed of is planned to be encapsulated in thick-walled copper canisters with cast iron insert, so that the minimum total thickness of the isolating metal wall is more than 10 centimeters (Raiko 1999). The outer copper wall provides shield against corrosion. Canister diameter is about 1 m and height 3.6 or 4.8 m depending on the spent fuel material. Each copper canister is to be placed in its own deposition hole, diameter about 1.7 m, and the space between the canister and rock will be filled with highly compacted bentonite.

Commercial sodium bentonite (MX-80, American Colloid Co) is selected as the reference material in Finnish nuclear waste research (MuuRinen 1992). Bulk MX-80 contains about 65 - 75% montmorillonite, 10 - 14% quartz, 5 - 9% feldspars, 2 - 4% mica and chlorite, 1 - 2% carbonates, and 1 - 4% heavy minerals, mainly pyrite and iron oxides. Chemical composition of bentonite is given in Table 3-1.

Table 3-1. Representative chemical analysis of MX-80 bentonite (Push and Karland, 1986).

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>63.0</td>
<td>Cl</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.1</td>
<td>S</td>
<td>0.12 - 0.23</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.0</td>
<td>Cu</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>1.1</td>
<td>Zn</td>
<td>0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>1.6</td>
<td>Cr</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.2</td>
<td>Ni</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.48</td>
<td>AsO₄</td>
<td>0.018</td>
</tr>
<tr>
<td>Li₂O</td>
<td>&lt;0.01</td>
<td>NO₃</td>
<td>none</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>PO₄</td>
<td>0.060</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.10</td>
<td>S²⁻</td>
<td>0.12</td>
</tr>
<tr>
<td>F</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The bedrock around the repository, regardless of the selection of actual disposal site, contains, in addition to the predominant silicate minerals, also accessory carbonates, iron oxides (hematite, magnetite) and sulfides (pyrite, pyrrhotite). During the excavation of the shaft, tunnels and deposition holes, and after that, during the operation of the repository, the rock mass is subjected to air intrusion, and a geochemically disturbed zone is going to be formed around the repository. The amount of ferric oxide minerals will be increased in the geochemically disturbed zone.

Based on available data on groundwater conditions in the bedrock (Table 2-1), two types of near-field reference waters has been suggested by Vuorinen and Snellman (1998) (Table 3-2). These are chosen on the basis of experimental results on bentonite interaction with fresh and saline groundwater.

Table 3-2. Proposed composition for the two near-field reference waters (Vuorinen and Snellman 1998).

<table>
<thead>
<tr>
<th></th>
<th>FRESH-NEAR-OX</th>
<th>FRESH-NEAR-RE</th>
<th>SALINE-NEAR-OX</th>
<th>SALINE-NEAR-RE</th>
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</thead>
<tbody>
<tr>
<td>Eh chosen</td>
<td>Np(V)</td>
<td>UO$_2$U$_2$O$_9$</td>
<td>Np(V)</td>
<td>UO$_2$U$_2$O$_9$</td>
</tr>
<tr>
<td>PH</td>
<td>7.0-10.0</td>
<td>7.0-9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkalinity</td>
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</tr>
<tr>
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<tr>
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<td>12 000</td>
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</tr>
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*) Uncertain values due to analytical problems
4 BEHAVIOR OF METALLIC Cu IN SALINE WATERS

4.1 Definition of the system and processes

Canister in saline water environment

The outer wall of the canister is manufactured of metallic copper, thermodynamic properties of the material are those presented in the literature for pure copper. The solid materials surrounding the canister are the bentonite buffer, and the bedrock consisting of typical silicate minerals with some accessory carbonate, sulfide and oxide minerals as described earlier. The backfill material in the tunnels is assumed to have similar geochemical properties as the wall rock.

In this report, the isolating properties of the bentonite buffer are neglected, and saline water is assumed to be in contact with the canister surface. Salinity of water is assumed to be at least as high as that of the brine presented in Table 2-1.

Redox conditions in saline water are assumed to be anoxic – reducing: free oxygen is absent, methane (CH₄) and hydrogen (H₂) may be present. Small amounts of ferric oxides (mainly hematite Fe₂O₃, goethite FeOOH and magnetite Fe₃O₄) are present in the surrounding rocks, as well as pyrite (FeS₂). Small amounts of ferrous iron can be dissolved from silicate minerals (e.g., micas), siderite FeCO₃, and pyrrhotite (Fe₁₋ₓS). Dissolved sulfide may also be present.

Due to the initial-phase heat-generation of the spent fuel, temperature in the disposal environment is assumed to be near 80 - 100 °C.

Concentrations and activities

The most important "input" parameters for the present study are the concentrations, especially that of chloride, measured in saline waters. In thermodynamic calculations, activities (aᵢ) are used instead of concentrations (mᵢ), which are related to each other by activity coefficients (γᵢ):

\[ aᵢ = γᵢ \cdot mᵢ \]  

For example chloride concentration 43 g/l (1.22 mol/l) corresponds to chloride activity of about 0.8-0.9, because the activity coefficient - estimated using Pitzer model - is of the order of 0.7 in NaCl solutions at ionic strengths 1 - 4 M (Falck and Read 1996). In general, at ionic strengths below 5 M, single-ion activities are smaller than corresponding molar concentrations, activity of chloride being always less than 80 % of the corresponding molar concentration at ionic strengths higher than 1 M (Langmuir 1997, pp. 124 -145).

In the following discussion, "effective concentrations" (i.e., activities, Langmuir 1997) are used instead of molar concentrations, and denoted by square brackets.
Canister corrosion: thermodynamic approach

Corrosion of copper canister means that copper changes its physicochemical state, the corrosion products may be either solids precipitating on the canister surface or they may dissolve to the groundwater and be transported away.

Corrosion of copper is an electrochemical reaction, in which electrons are transferred from the metal to some other species, capable to accept electrons. The process can be generalised as follows: 1) release of electron(s) from copper; 2) complexation or precipitation of the copper ion; 3) acceptance of the electron(s) by an oxidant:

1. \(\text{Cu}^o = \text{Cu}^{\scriptscriptstyle+n} + n\text{e}^- \quad (n = 1 \text{ or } 2)\)
2. \(\text{Cu}^{\scriptscriptstyle+n} + mL = \text{Cu}L^{\scriptscriptstyle+n} \)
3. \(\text{OX} + n\text{e}^- = \text{RED}^n \)

The initial release of the electron and the subsequent complexation/precipitation can be combined to a general 'anodic' process, while the acceptance of the electron(s) by the oxidant forms the general 'cathodic' process. The use of these half-cell reactions may be accompanied by the introduction of the concept 'electron activity', which is used formally analogous to the concept proton activity, so that \(pE = -\log[e^-]\). Essential difference between concepts \(pH\) (i.e., \(-\log[H^+])\) and \(pE\) is that free aqueous electrons are not stable in water. However, \(pE\) can be used as a formal measure of the oxidative or reductive potential of a system containing phases or species, which are able to accept or donate electrons. The electron activity is related to the reduction potential \((E)\) as follows:

\[
E = (2.303RT/nF) pE
\]

Consequently, any half cell reaction has a reduction potential. A generalised corrosion reaction of copper (eq. 4-4) can be constructed by combining imaginary anodic and cathodic half cell reactions with reduction potentials \(A\) and \(B\), respectively:

\[
\begin{align*}
\text{CuL} + \text{e}^- &= \text{Cu}^o + L^- \quad E = A \\
\text{OX} + \text{e}^- &= \text{RED}^- \quad E = B \\
\Rightarrow \text{Cu}^o + \text{OX} + L^- &= \text{CuL} + \text{RED}^- \quad E = B - A
\end{align*}
\]

The relation between electromotive force (EMF) and Gibbs energy change for the reaction (4-4) is defined by:

\[
E = -\frac{\Delta G}{[z]F}
\]

According to thermodynamics, spontaneous changes of a system can only proceed from higher chemical potential to lower \((\Delta G < 0)\) and, consequently, electrons can only be transferred, if the electron accepting (cathodic) half reaction has higher potential than the anodic half reaction. Possible corrosion reactions can thus be conveniently screened by the 'redox ladders', in which reduction potentials of all half reactions of importance are graphically compared.
The potentials, as used here, are the thermodynamic equilibrium potentials, being useful in estimating the directions of possible reactions. However, it must be pointed out that the redox potential is an intensive parameter like temperature and pH. If used as a master variable in the thermodynamic description of a system, as is the case for example in construction of the Pourbaix-diagrams (Eh vs. pH), no information can be obtained on the question, how far a reaction can proceed. The overall capability of a system to maintain stable redox conditions depends on its redox-buffering capacity, which is dependent on the availability and reactivity of the redox-active components in the system (e.g., Bruno et al. 1996).

Thermodynamic considerations are valid, if the reactions can be considered to be rapid and "reversible" (i.e., are able to go in both directions) within the time scale, in which amounts of system components do not change, i.e., system can be considered to be closed. If the inflow/outflow of some component is rapid compared to its equilibration in the system, kinetics of the reactions may control the system behavior.

**Canister corrosion: comments about kinetics**

Various electrochemical methods can be used in studying the kinetics of the copper corrosion. The knowledge on the kinetics of the corrosion processes is important - and complementary to the thermodynamics - for many reasons.

- All thermodynamically possible reactions do not take place; for example the anodic process of corrosion may be kinetically restricted.
- The kinetics of the electron accepting (cathodic) half reaction is also important. In principle, one can assume that the oxidizing agent can rapidly accept electron, but can not be oxidized back (release electron) within a time scale under which the total amount of this component remains constant (for example, if diffusion of the component is more rapid than the electron transfer). If such conditions, equilibrium thermodynamics can not be applied.
- Thermodynamic considerations are usually based on the knowledge of the overall properties of a macro-environment, while properties of microscopic environments on the metal surface may vary.
4.2 Speciation of dissolved copper in chloride waters

This section aims at giving an overall picture of possible corrosion products if copper is oxidized in saline water.

Cuprous copper (Cu) forms very stable complexes with chloride. In saline waters, dissolved copper is mainly bound in complexes CuCl$_2^-$ and CuCl$_3^-$. High chloride concentrations can even dissolve solid Cu$_2$O (Fig 4-1). In fresh waters dissolved copper is easily oxidized to Cu(II), but in chloride solutions copper is stable as Cu(I) even at very high concentrations (Fig 4-2).

![Figure 4-1. Speciation of Cu(I) as a function of pH and chloride activity (Ahonen 1995). Solubility limit used for Cu$_2$O is $10^{-7}$ M](image-url)
4.3 Thermodynamic evaluation of possible corrosion processes

Following figures 4-3 and 4-4 aim at giving a general picture of the copper corrosion processes relevant to be considered in the deep disposal environment. The figures are based on thermodynamic conceptualizations introduced in the previous chapters.

In figure 4-3 potential-levels of cathodic half-reactions are compared with various anodic processes of metallic copper. As indicated, dissolved oxygen is clearly able to oxidize copper, and the formation of all the different corrosion products indicated is theoretically possible, the most probable one being, however, Cu$_2$O.

Nitrate, when reduced to ammonium, is also an important oxidizer, and the reduced form ammonium forms strong complexes with Cu(II). Geochemical cycle of nitrogen is connected to biological processes: nitrate produced in oxic environment is reduced by organism to NH$_4^+$ (source of proteins), this process can take place both in aerobic and
anaerobic conditions (e.g., Correa and Germon 1991). In most cases, the source of nitrate in groundwater can be attributed to anthropogenic factors.

The existence of free oxygen or nitrate in deep saline waters can be ruled out, because these components are formed in the oxic ground-surface environments, and consumed mainly in the near-surface biological processes.

Figure 4-3 indicates that ferric iron is a potential oxidizer of metallic copper; the upper limit of potential range indicated corresponds to the dissolved ferric iron, while the lower limit corresponds to the mineral hematite. Because small amounts of ferric-iron minerals are probably present in the deep disposal environment, will the role of ferric iron as an electron acceptor be discussed further.

The potential of uranium(VI)/uranium(IV) pair is approximately on the same level as the potential of Cu/CuCl$_3^-$ pair and, consequently, U(VI) can theoretically oxidize metallic copper in saline solution. However, the solubility of uranium in reducing conditions is very low (Ollila and Ahonen 1998), and the amount of uranium in average bedrock is small (less than 4 g/ton, Mason 1966), mainly as U(IV). Natural hexavalent uranium outside the canister is unimportant with respect to the canister corrosion.

From the thermodynamic point of view, uranium of spent fuel (UO$_2$) and cast iron inside the canister can be considered to be "outside" the system studied here - provided that the copper wall of the canister is not penetrated and these materials are not together in contact with groundwater.

The potential of the sulfate/sulfide pair is very close to that of the cuprous trichloro complex formation in 1 M chloride solution (Fig 4-3). Concentration of sulfate is typically very low in deep saline waters studied in Finland (Table 2-1), but sulfate-containing brines are also known (Fritz et al. 1994). Inorganic sulfate reduction is an extremely slow process (Ohmoto and Lasaga 1982), while microbiological catalysis increases the rate of sulfate reduction by orders of magnitude. In microbiological sulfate reduction, organic compounds act as the ultimate electron acceptor. Consequently their possible negative effect for canister is due to the reaction product sulfide, which has been discussed earlier by Ahonen (1995).

The upper limit of the potential range of N$_2$/NH$_4^+$ pair (Fig 4-3) was calculated assuming that their chemical activity ratio would be 10$^6$:1. Using more realistic activity ratios, the electron acceptance capability of nitrogen/ammonium is of the same order as that of water. Compared to water, the amount of N$_2$ is negligible.

Even though water is the weakest oxidizer in aqueous system, its role as a possible electron acceptor from metallic copper has to be studied with scrutiny. The worst case is visualized in the Eh-pH diagram of Fig. 4-4, representing the situation in which metallic copper is in contact with hot saline water (100 °C). The anodic half reaction can be written as:

$$2 \text{Cu}^0 + 5\text{Cl}^- = \text{CuCl}_2^- + \text{CuCl}_3^- + 2\text{e}^-,$$

$$\log K (100^\circ \text{C}) = -3.3$$
The reduction potential of this reaction is, regardless of pH, less than about \(-300\) mV (pE \(< -5\)).

The cathodic reaction, water reduction, is represented by two dotted lines in the figure. Contrary to the conventional Eh-pH diagrams, water reduction lines are drawn here for two different H\(_2\) activities, not for H\(_2\) partial pressures. The reason is that these results have to be applicable up to total pressures of at least 100 bar. Activities of dissolved components are only little dependent on pressure, while the partial pressures of volatile components are linearly dependent on the total pressure, increasing with increasing depth.
Figure 4-3. Redox-ladders comparing potentials of cathodic (to the left) and anodic half-cell reactions of interest for copper corrosion. Half-cell potential of the "worst-case" reaction product is indicated by bold (modified from Ahonen 1995).
Figure 4-4. pE-pH diagram for the system Cu-Cl at 100 °C, [Cl] = 1, boundary between solid phase and solution represents activity of $10^{-7}$ for the predominant dissolved species. Dotted lines show the theoretical pE-range of water reduction (i.e., $H^+ + e^- = \frac{1}{2}H_2(aq)$ (Ahonen 1995).

Theoretical pE range of water reduction is delimited by dotted lines representing hydrogen activities between 1 and $10^{-9}$, the upper activity limit ($10^{-9}$) representing the situation, in which water is in equilibrium with atmosphere containing 0.5 ppm hydrogen gas (Ahonen 1995). As can be seen in the figure 4-4, there is a small range at which electron transfer from metallic copper to $H_2O$ is theoretically possible at 100 °C; this range is presented in the pE-pH space by the area above the line at pE $\approx -5.4$ (where anodic process of copper corrosion to cuprous chlorides exceeds $10^{-7}$ M) and between the hydrogen activity range defined by dotted lines. As also concluded by Beverskog and Puigdomenech (1998) this range is of special importance. The key question are: 1) how far can this process extend until equilibrium is attained, and, 2) what are the kinetic possibilities and requirements associated to the reaction.

The equilibrium conditions between metallic copper and saline water have been discussed earlier in details by Taxen (1990) and Ahonen (1995). Based on partially dissimilar thermodynamic databases these authors came to very similar conclusion being visualized in figures 4-5 and 4-6: Even at extremely low pH of 5, at 100 °C, equilibrium concentration of dissolved copper in contact with the canister is about $10^{-5}$ M decreasing with increasing pH.
The result presented in Figure 4-6 was obtained through the following discussion (according to Ahonen 1995): Corrosion of metallic copper in saline water leads to the formation of soluble cuprous complexes, their relative amount being dependent on the total chloride concentration (Fig. 4-1). If $H_2O$ ($H^+$) is assumed to be the electron acceptor (hydrogen is generated), following equation is obtained:

$$2Cu^0(s) + 2H^+ + 5Cl^- = CuCl_2^- + CuCl_3^{n-} + H_2(aq),$$

$$\log K_{25} = -10.05, \log K_{100} = -6.7$$

The reaction is promoted by low pH and high concentration of chloride, while the formation of reaction products has an opposite effect. Advancement of the corrosion reaction is possible if:

$$\log[CuCl_2^-] + \log[CuCl_3^{n-}] + \log[H_2(aq)] < -10.05 - 2pH + 5\log[Cl^-]$$

If the system does not contain hydrogen ($H_2(aq)$) from other sources than from this reaction, its amount is proportional to the amount of other reaction products:

$$[H_2(aq)] = [CuCl_2^-] + [CuCl_3^{n-}] = [Cu(aq,tot)]$$

Relative portion of cuprous complexes is a function of chloride concentration:

$$[CuCl_3^{n-}] = K\cdot[CuCl_2^-][Cl^-], \quad K_{25} = 10^{0.1}, K_{100} = 10^{0.3}$$

From these equations, formation of $CuCl_2^-$ due to the corrosion reaction can be calculated as a function of pH and chloride concentration as follows (25° C):

$$[CuCl_2^-] \cdot 10^{0.1}[Cl^-][CuCl_2^-][([CuCl_2^-] + 10^{0.1}[Cl^-][CuCl_2^-]) < 10^{(-10.05-2pH+5\log[Cl^-])}$$

This equation is valid at all chloride concentrations higher than about 0.01 M ($CuCl^0$ is not accounted for), and total concentration of copper corroded is the sum of $CuCl_2^-$ and $CuCl_3^{n-}$. Increase of temperature changes the values of stability constants, which were calculated from the corresponding reaction enthalpies. Details of construction of Figure 4-6 were presented by Ahonen (1995).
Figure 4-5. Equilibrium concentration of copper in 3 M chloride solution, if H$_2$O is the oxidizer (Taxen 1990).

Figure 4-6. The extent of corrosion as a function of pH until equilibrium is attained in eq. 4-7. Chloride activity is 1, different lines represent temperatures from 25 to 100 °C in 25° intervals (modified from Ahonen 1995).
Ferric iron minerals in the repository near-field are thermodynamically able to accept electrons from metallic copper. However, the solubility of ferric iron is very low. Figure 4-7 shows the solubility and speciation of ferric iron during the initial conditions after the closure of the repository: poorly crystallized ferric hydroxide ('rust') is probably available in the geochemically disturbed zone around the repository and the temperature has been increased. Recrystallization of the poorly crystallized ferric hydroxides to less soluble ferric oxides and oxyhydroxides takes place within a couple of years (Schwertmann and Murad 1983), and the solubility of ferric iron will still decrease.

Dissolved ferric iron is very strongly hydrolyzed, and the stability of ferric hydroxide complexes increases with temperature. Consequently, no matter what the salinity of water is, dissolved ferric iron concentration is not affected by the formation of ferric chloride complexes, except at pH below about 3.

The oxidative power of iron-bearing water is dependent on the ferric/ferrous ratio of the solution. The ability of iron-bearing solutions to oxidize metallic copper can be estimated as follows (thermodynamic data used in these equilibrium expressions is from Ahonen, 1995): Depending on the pH, different dissolved ferric species predominate as electron acceptor, assuming $T = 100 °C$, and $[Cl^-] \approx 1$

\[
\begin{align*}
\text{pH 4-7: } & 2\text{Fe(OH)}_2^+ + 2\text{Cu}^0 + 4\text{H}^+ + 5\text{Cl}^- = \text{CuCl}_2^- + \text{CuCl}_3^- + 2\text{Fe}^{2+} + 4\text{H}_2\text{O}, \\
\log K_{100} &= 26.1, \\
\text{pH 7-9: } & 2\text{Fe(OH)}_3^+ + 2\text{Cu}^0 + 6\text{H}^+ + 5\text{Cl}^- = \text{CuCl}_2^- + \text{CuCl}_3^- + 2\text{Fe}^{2+} + 6\text{H}_2\text{O}, \\
\log K_{100} &= 37.7 \\
\text{pH } &> 9: 2\text{Fe(OH)}_4^- + 2\text{Cu}^0 + 8\text{H}^+ + 5\text{Cl}^- = \text{CuCl}_2^- + \text{CuCl}_3^- + 2\text{Fe}^{2+} + 8\text{H}_2\text{O}, \\
\log K_{100} &= 53.6
\end{align*}
\]

Because at $[Cl^-] = 1$, $[\text{Cu(aq, tot)}] = 2[\text{CuCl}_2^-] = 2[\text{CuCl}_3^-]$, and following approximative relations are obtained:

\[
\begin{align*}
\text{pH 4 - 7: } & \log[\text{Fe(III)/Fe(II)}] \approx -30.5/2 + \log[\text{Cu(aq)}] - \log 2 + 2\text{pH} \\
\text{pH 7 - 9: } & \log[\text{Fe(III)/Fe(II)}] \approx -44.3/2 + \log[\text{Cu(aq)}] - \log 2 + 3\text{pH} \\
\text{pH } &> 9: \log[\text{Fe(III)/Fe(II)}] \approx -62.4/2 + \log[\text{Cu(aq)}] - \log 2 + 4\text{pH}
\end{align*}
\]

Based on these equations and earlier discussion by Ahonen (1995), the thermodynamic ability of iron-bearing solution is visualised in Figure 4-8. The main conclusions drawn from this figure are:

- In basic solutions (pH about 8.5 or higher), regardless of salinity, ferric iron can not oxidize metallic copper because dissolved Fe(III)/Fe(II) ratio has to be 1 or higher; such conditions can not be expected in deep disposal environment.
- Increase of salinity increases the oxidative power of dissolved iron at pH's lower than 8.5, if cuprous chloride complexes are corrosion products. At pH 6, 25 °C, ferric iron can act as electron acceptor even at Fe(III)/Fe(II) ratio $10^8 : 1$. The advancement of corrosion process is controlled by the availability of Fe(III).
- Increase of temperature decreases the oxidative power of dissolved iron, regardless of salinity. The reason is the increasing stability of the ferric hydroxide complexes.
Figure 4-7. Solubility and speciation of ferric iron as a function of pH at 100 °C, \([\text{Cl}^-]=1\). Details of construction of the figure are given in Appendix 1.

Figure 4-8. Stability field of metallic copper as a function of pH and Fe(III)/Fe(II) ratio. A) at \([\text{Cl}^-]=1, T=100 \, ^\circ\text{C}\); B) at \([\text{Cl}^-]=1, T=25 \, ^\circ\text{C}\); C) at \([\text{Cl}^-]=0, T=25 \, ^\circ\text{C}\).
4.4 Kinetic considerations

This section aims at commenting on some of the corrosion kinetic aspects related to the thermodynamic considerations of the present work. Basically, kinetics deals with the rates of the processes: In corrosion studies, the rates and rate limitations of anodic processes and cathodic processes can be studied separately, as well as the mass transport processes.

Originally the surface of the copper canister placed into the deposition hole is coated by a thin oxide layer. When coming into contact with saline water, oxide layer may disappear due to a chemical dissolution reaction (4-18) or it may be reduced (4-19):

\[
\begin{align*}
\text{Cu}_2\text{O} + 2\text{H}^+ &= 2\text{Cu}^+ + \text{H}_2\text{O} & \text{(4-18)} \\
\text{Cu}_2\text{O} + \text{H}_2 &= 2\text{Cu}^0 + \text{H}_2\text{O} & \text{(4-19)}
\end{align*}
\]

Both reactions lead to the stripping of the protective oxide coating from the metal surface. As long as the passivating oxide layer is present, it provides additional shield against corrosion. The rate and the mechanism of the possible disappearance of this coating in saline solution was beyond the scope of the present study.

The anodic corrosion process of the pure metallic copper surface immersed in chloride solution may described as follows (King and Tang, 1998 and references therein): 1) The release of electron is accompanied by adsorption of chloride anions on the metal surface; 2) The rate determining step is the outward diffusion copper chloride complex:

\[
\begin{align*}
\text{Cu}^+ + \text{Cl}^- &\rightleftharpoons \text{CuCl}_{\text{ADS}} + \text{e}^- \\
\text{CuCl}_{\text{ADS}} + \text{Cl}^- &\rightleftharpoons \text{CuCl}_2^-(s) \\
\text{CuCl}_2^-(s) &\rightarrow \text{CuCl}_2^-
\end{align*}
\]

Ogundele and Jain (1998) studied electrochemical kinetics of copper dissolution in the SCSSS (see chapter 2 for its composition) at different pH and temperature. Oxygen was present in most experiment, but some were reported to be carried out without oxygen. Corrosion potential settled typically to values about -150 - 0 mV (vs. SHE), decreasing with the temperature of the experiment. The rate of anodic reaction was estimated by polarization of the sample from -15 mV to +15 mV with respect to the corrosion potential. Interpretation of the result indicated copper corrosion rate of about 1 \mu m/year for the anodic reaction in those conditions.

As indicated by the thermodynamic considerations, the most important cathodic process for canister corrosion in saline water is the reduction of water to hydrogen. From the point of view of the previous thermodynamic considerations, probably the most important kinetic question to be clarified is the behavior of hydrogen in contact with metallic copper.
5 SUMMARY AND CONCLUSIONS

The aim of the present report was to conduct a systematic study of the behavior of copper canister in deep-disposal conditions, if the groundwater around is saline, meaning that the chloride concentration of water is in the range of 1-3 mol/l (i.e., up to 100 g/l). For convenience, the presented thermodynamic calculations were done for chloride activity of 1, which corresponds to chloride concentration of about 1.4 - 1.5 M (≈50 g/l).

This emphasis of this work was in thermodynamic considerations of equilibrium conditions in thermodynamic systems, which were defined according to the present knowledge on the hydrogeological and mineralogical conditions of the actual disposal system.

The main conclusion is that no relevant cathodic half reaction (i.e. oxidizer) was found, which could act as electron acceptor from metallic copper (i.e., oxidize metallic copper) in the conditions of deep disposal in saline water environment.

Solubility of ferric iron at the pH-range from 5 to 9 is below $10^{-6}$ M, being the upper limit for dissolved ferric iron availability. Realistic concentrations are still much lower because of the rapid recrystallization of ferric hydroxide compounds to less soluble forms. In alkaline conditions (pH > 8.5) dissolved ferric/ferrous ratio must be higher than 1 until this couple is able accept electrons from metallic copper. Ferric chloride complexes increase the solubility of ferric iron only at pH-values below 3.

As indicated by the Figure 4-6, there is a theoretical possibility at pH-values below 6 at 100 °C for water (i.e., H+) to accept electron from copper with subsequent formation of hydrogen gas. Thermodynamic equilibrium calculations clearly show, however, that this reaction can not leach more than $10^{-6}$ M copper at pH 6, 100 °C until equilibrium is attained. Hydrogen is formed as a product of this corrosion reaction, thus, if originally present in water, it will further suppress the corrosion reaction. Behavior (i.e., "reversibility") of the hydrogen/water redox pair in contact with metallic copper is a key question.
6 REFERENCES


APPENDIX 1.

THERMODYNAMIC DATA AND CONSTRUCTION OF Fig. 4-7.

Solubility of ferric iron in the system Fe$^{3+}$ — H$_2$O is controlled by some of the minerals in the sequence ferric hydroxide - oxyhydroxide - oxide: Fe(OH)$_3$ - FeOOH - Fe$_2$O$_3$. By assuming water activity of 1, solubility equation for all these minerals can be written as:

$$\text{Fe(OH)}_3(s) + 3 \text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O} \quad 1.$$ 

Depending of the grain size and crystallinity of the solid phase, solubility constant for this reaction at 25° C has been reported to be between about -1 to +5.5, but the reaction enthalpy is not well known (e.g. Nordstrom et al. 1990). Consequently, the zero-value of $\Delta H_r$ has been used in many recent computer data bases (e.g. Pearson and Waber 1999). However, $\Delta H_r$-values around -100 kJ/mol have been reported for the corresponding reactions of aluminum (e.g. Nordstrom et al 1990). In the database associated to the computer program HARPHRQ, stability constant value 5.54 and enthalpy value -85 kJ/mol were used for the solubility equation 1. Because the use of zero enthalpy would have given misleading values in extrapolating to 100° C, these values were used in the present work.

At the temperature range 25° - 100° C, temperature dependence of the stability constant can be well estimated using Van't Hoff equation assuming constant (not temperature-dependent) enthalpy. If the temperature increases from 25° C to 100° C, change of the stability constant is given by:

$$\log K_{100} = -\Delta H_r/(2.303 \times R) \times (1/373.15 - 1/298.15) + \log K_{25} \quad 2.$$ 

Where R is gas constant 8.314 J/(K·mol)

In construction of Figure 4-7., following data was used:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log $K_{25}$</th>
<th>$\Delta H_r$ kJ/mol</th>
<th>Log$K_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_3$(s) + 3 H$^+$ = Fe$^{3+}$ + 3H$_2$O</td>
<td>5.54</td>
<td>-85.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe$^{3+}$ + H$_2$O = FeOH$^{2+}$ + H$^+$</td>
<td>-2.19</td>
<td>43.5</td>
<td>-0.66</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 2H$_2$O = Fe(OH)$_2^+$ + 2 H$^+$</td>
<td>-5.67</td>
<td>71.6</td>
<td>-3.15</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 3H$_2$O = Fe(OH)$_3^0$ + 3 H$^+$</td>
<td>-12.56</td>
<td>104</td>
<td>-8.9</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 4H$_2$O = Fe(OH)$_4^-$ + 4 H$^+$</td>
<td>-21.6</td>
<td>134</td>
<td>-16.9</td>
</tr>
<tr>
<td>2Fe$^{2+}$ + 4H$_2$O = Fe$_2$(OH)$_2^{4+}$ + 2 H$^+$</td>
<td>-2.95</td>
<td>56.6</td>
<td>-0.96</td>
</tr>
<tr>
<td>Fe$^{3+}$ + Cl$^-$ = FeCl$_2^{2+}$</td>
<td>1.48</td>
<td>23</td>
<td>2.29</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 2 Cl$^-$ = Fe(Cl)$_2^-$</td>
<td>2.13</td>
<td>- **</td>
<td>2.94</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 3 Cl$^-$ = Fe(Cl)$_3^-$</td>
<td>1.13</td>
<td>- **</td>
<td>1.94</td>
</tr>
</tbody>
</table>

** The value 23 kJ/mol was used for the unknown values in extrapolating to 100° C
For each pH-value (-log [H⁺]), the activity of free [Fe³⁺] was first calculated from eq. 1. The activities of complexed Fe(III) species could then be calculated from known [Fe³⁺] and known [H⁺] values. Details of the calculation procedure were presented by Ahonen (1995).

REFERENCES

