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Influence of high chloride concentration on copper corrosion

This Memo is an extended description of the analyses performed in SR-Site concerning the effect of chloride on copper corrosion, and of the use of chloride concentration as one part of a safety assessment indicator criterion.

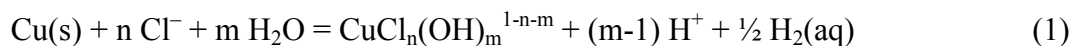
The assessment in SR-Site is mainly a thermodynamic approach, using conventional thermodynamic data. The analysis of the effect of chloride on copper corrosion was performed in steps, all according to the general safety assessment approach:

1. The general knowledge base of reactions and mechanisms was discussed in detail in the state-of-the-art report on copper corrosion (King et al. 2010) surveying calculations and experimental data in literature. In the report, Section 5.2.1.2 treats kinetic effects, while thermodynamic aspects are discussed in Section 5.2.2.
2. To express the thermodynamics as a “stability” or “immunity” of copper a total copper concentration needs to be set as the limit for corrosion. By one convention (Pourbaix 1974) a total concentration of the soluble metal of 10^{-6} M is used as the definition of corrosion.
3. Another approach to set this limit is by evaluating canister corrosion failures when the transport of copper corrosion products is calculated using the corrosion models from SR-Site for intact and eroded buffer respectively. This will indicate if a postulated copper concentration limit at the surface of the canister may or may not lead to canister failures.
4. With a chosen total copper concentration limit for corrosion, a simplified calculation to get one combination of pH and Cl^- concentration to be used as safety function indicator criterion was made.

The four steps are elaborated in more detail below.

1 Influence of chloride on copper corrosion

The point of departure for the analysis is the thermodynamic description of the system copper metal in contact with a chloride containing aqueous solution. As described in Section 5.2.2 in King et al. (2010) the corrosion of copper in Cl^- solution with water or (protons) as the only oxidant can be written



Chloride ions stabilise dissolved Cu(I) in the form of complex anions, such as CuCl_2^- and CuCl_3^{2-} . In the reaction, n and m denotes the different stoichiometries. At sufficiently low pH, Cu corrosion is accompanied by the evolution of H_2 in Cl^- solutions. The critical pH for $\text{H}^+/\text{H}_2\text{O}$ reduction can be seen as the crossing of the “hydrogen stability line” (the lower hatched line)

with the line separating CuCl_2^- and Cu in Figure 1(d). This critical pH increases with increasing chloride concentration and temperature. With increasing chloride concentration, also the stability of the solid phase $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ increases with respect to Cu_2O and CuO , as indicated by the growth in the size of the stability field of the former compared to the latter.

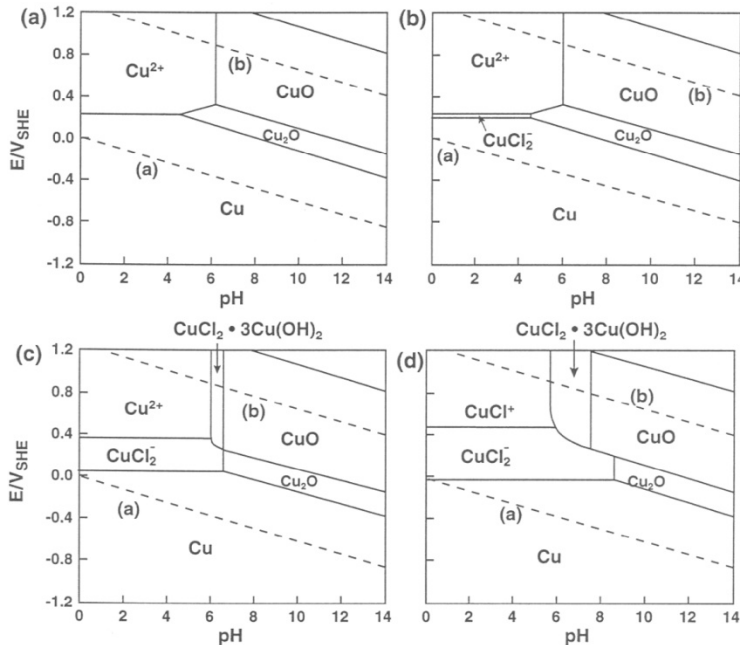


Figure 1. Potential/pH (Pourbaix) diagrams for the system $\text{Cu}/\text{Cl}/\text{H}_2\text{O}$ at 25°C for various chloride concentrations. (a) $10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, (b) $10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, (c) $0.1 \text{ mol}\cdot\text{dm}^{-3}$, (d) $1.0 \text{ mol}\cdot\text{dm}^{-3}$. Figures constructed for a total dissolved Cu activity of $10^{-6} \text{ mol}\cdot\text{dm}^{-3}$. The figure is identical to Figure 5-1 in King et al. (2010).

Kinetic effects, effects of rate-determining steps and the corrosion behaviour of copper in compacted bentonite are described in detail in Section 5.2.12 in King et al. (2010).

How this knowledge could be used for modelling of general corrosion is described in Section 5.2.4 in King et al. (2010), and both thermodynamic and kinetic approaches are possible. A thermodynamic approach generally involves an assumption of rapid interfacial kinetics and rate control by the rate of (diffusive) mass transport and represent a “worst-case” assessment and produce a conservative estimate of the corrosion. Kinetically based lifetime-prediction models combine the finite kinetics of interfacial reactions with possible limitation by mass transport to and from the corroding surface.

In the SR-Site assessment published thermodynamic data for copper in water was used. For the experiments showing a larger hydrogen production from copper in pure water than what corresponds to the equilibrium constants of all known phase of oxidised copper (an updated presentation can be found in SKBdoc id 1396568) but no corrosion product, an no thermodynamic data has been presented, and these results cannot be included in any thermodynamic analysis.

2 Copper concentration at combinations of pH and chloride concentration

The effect of the complexation of Cl^- to $\text{Cu}(\text{I})$ can be seen in e.g. Pourbaix diagrams in that at high chloride concentrations the copper metal is not stable but will corrode under hydrogen

development. An example is shown in Figure 2, for a chloride concentration of 1.5 M, where the “hydrogen line” is crossing the stability line between Cu(s) and CuCl₂⁻ at a pH of about 3.3.

In Figure 2 the conventional corrosion limit of 10⁻⁶ M (Pourbaix 1974) is used. The hydrogen line represents a hydrogen pressure of 1 atm. For a lower pressure the hydrogen line is moved further up in the diagram, requiring a higher pH to reach the 10⁻⁶ limit for a specific chloride concentration.

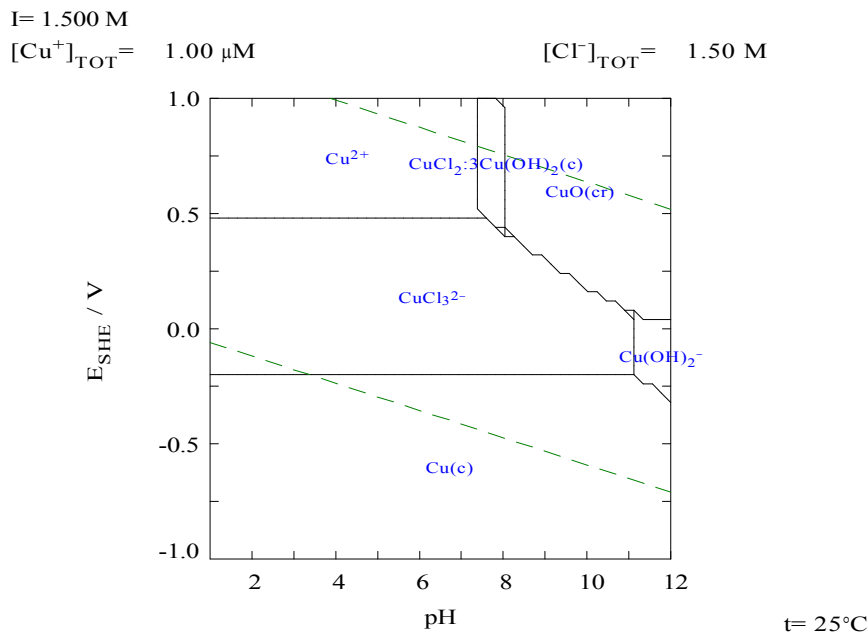


Figure 2. Potential-pH (Pourbaix) diagram for the Cu/Cl/H₂O system at 25°C and for a total copper concentration of 10⁻⁶ M and a total chloride concentration of 1.5 M. The diagram was derived with the Medusa software (Puigdomenech 2010).

3 The role of copper concentration in corrosion calculations in SR-Site

One way to bound the extent of a corrosion process is to look at the transport rate for any soluble corrosion product. At equilibrium in pure water for the reaction



and using available thermodynamic data it can be shown that for pure water the total concentration of copper is about 4 × 10⁻¹² M, while the equilibrium pressure of hydrogen gas is 2.5 × 10⁻⁹ bar, as discussed in earlier documentation to SSM (SKBdoc id 1339678)

With chloride complexing the copper(I) to mainly CuCl₂⁻ and CuCl₃²⁻ the concentration of copper in solution will be higher. To investigate the use of a 10⁻⁶ M total copper concentration as a bounding limit, the transport of copper-chloride complexes away from the canister can be investigated. The two different models used in SR-Site for evaluation of sulphide transport to the canister are then used. The models are applied to copper transported away instead of

sulphide brought to the canister by reversing the boundary conditions with the higher concentration at the canister surface and the zero concentration in the ground water. The parameter that needs to be adjusted is the stoichiometric factor that should be divided by two one copper atom in each copper complex ion, while each HS^- corrodes two copper atoms. As both HS^- and the copper complexes are anions the same diffusivity is applied in these comparisons.

For the case with an intact buffer, the mass transport model described in section 4.2 in SKB (2010) is used. This model assumes advection in a nearby fracture, diffusion in the bentonite and, as a separate case, also including a thermally induced rock spalling zone. Even for a concentration of 1.2×10^{-4} M of the transported species, no canister failures occurs, see Figure 5-4 in SKB (2010).

For the case with a partially eroded buffer, the model described in section 4.3 in SKB (2010) is applied. The model assumes advection in a fraction, and with erosion eventually giving advective conditions at the canister surface. Using the semi-correlated hydrogeological DFN model realisations in SR-Site it can be seen from Figure 5-9 in SKB (2010) that no canister failures due to corrosion for a sulphide concentration of $5 \cdot 10^{-6}$ M (marked as "Mean $[\text{HS}^-]$ " in the figure caption). As mentioned above, when evaluating the transport of copper(I) chloride complexes a factor of two must be applied, indicating no failures for a copper(I) concentration of 10^{-5} M.

Thus a copper concentration of 10^{-6} M will not cause corrosion failure for any of the deposition positions in Forsmark, either for intact or eroded buffer.

4 Deriving a safety function indicator criteria

In SR-Site the concept of safety function indicators are used. The set of safety functions provides understanding of the safety features of the system and a list of key issues to evaluate over time in the assessment, e.g. in the selection of scenarios, as described in section 2.5.8 in SKB (2011).

To arrive at a safety function indicator criterion for copper corrosion in high chloride concentrations a suitable combination of copper concentration, pH and chloride concentration was sought. In SR-Site a simplified calculation was done with data (thermodynamic data and activity coefficients) from Puigdomenech and Taxén (2000) which gave a CuCl_3^{2-} concentration close to 10^{-6} M for the combination of $\text{pH}=4$ and $[\text{Cl}^-]=2$ M. It was therefore suggested this combination to be used as the safety function indicator criteria in SR-Site.

Other combinations could have been chosen. In Figure 3 some combinations of pH and Cl^- that corresponds to three different total copper concentrations have been calculated, using both the complexes CuCl_2^- and CuCl_3^{2-} . Again, thermodynamic data were taken from Puigdomenech and Taxén (2000) to draw the figure. Two different models for calculating activity coefficients were applied (a modified model by Helgesson et al, and the Davies equation respectively), though outside their formal range of application. If a copper concentration of 10^{-6} M is used as the limit any point at the right of the 10^{-6} curve(s) is safe (i.e. $<10^{-6}$ M). For example, to allow $\text{pH}=3$ only about 0.6 M Cl^- is possible, while 3 M of Cl^- requires a pH of about 4.5 not to cause corrosion. In SR-Site, the combination of $\text{pH}>4$ and $[\text{Cl}^-]<2$ M (indicated with a cross in Figure 3) was chosen as the safety assessment indicator criterion. The simplified calculation approach still gave a value close to the curves derived with more sophisticated models for activity coefficients. These values were then used in comparisons to the description of the geochemistry development in SR-Site (e.g. Section 10.3.7 in SKB 2011) in the further assessment.

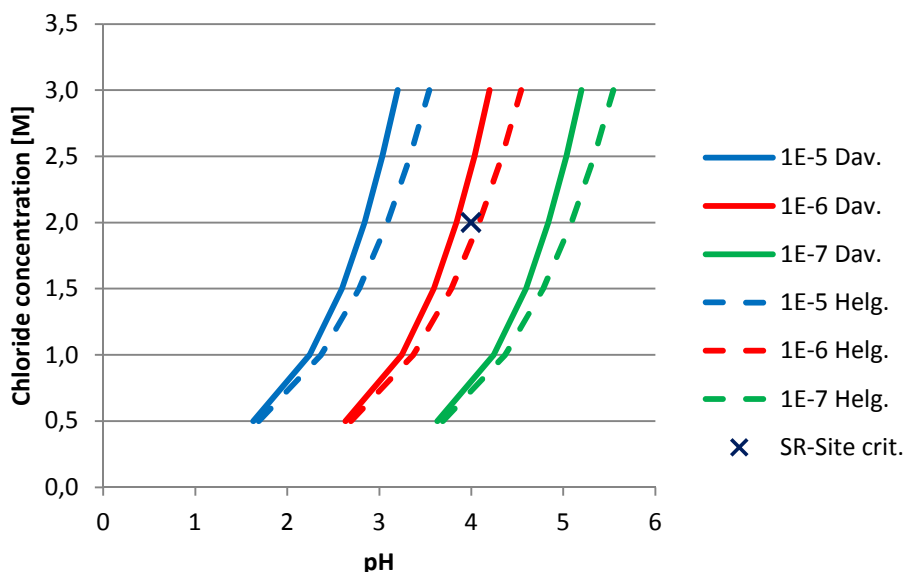


Figure 3. Different combinations of pH and Cl^- concentration at the total copper concentrations 10^{-5} , 10^{-6} and 10^{-7} M. Two different models to calculate activity coefficients were used (modified model by Helgesson et al. and the Davies equation respectively, see Puigdomenech and Taxén (2000)). The cross denotes the safety assessment indicator criterion used in SR-Site.

Conclusions

Chloride ions enhances copper corrosion by complexing Cu(I) ions in solution.

The safety assessment indicator criterion of $\text{pH} > 4$ and $[\text{Cl}^-] = < 2 \text{ M}$ in SR-Site is a criterion for comparison with the geochemistry descriptions and a tool to identify when a more detailed analysis of chloride assisted copper corrosion is warranted in the safety assessment, not a condition for the occurrence of the corrosion mechanism in question.

In the above assessment published thermodynamic data for copper compounds is used. From the discussion in the updated presentation on copper corrosion in pure water (SKBdoc id 1396568) the search for a mechanism for the hydrogen production in experiments in confined systems is described, but so far no new stable corrosion product has been identified. The thermodynamic approach can thus not include these results.

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