Internal information

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Effects of chloride on "what if" calculation of copper corrosion

1 Background

Data from Szakálos et al. (2007) and Hultquist et al (2011) was interpreted by these authors as the formation of a solid copper corrosion product in pure water having an equilibrium partial pressure of molecular hydrogen of ≈ 1 mbar at 73 °C, (Szakálos et al 2007) and 0.395 mbar at 21°C (Hultquist et al 2011).

In TR-10-66, section 5.4 in pp. 42-43, a “what if” case was calculated showing that such a process, in the case of an eroded buffer and for the deposition hole with the highest flow rate, could result in a corrosion depth of 3.1 mm in 10^6 years. In the calculation the transport of hydrogen gas was assumed to be the rate-limiting process for the corrosion, and the hydrogen equilibrium pressure of 1 mbar was used as the driving force.

SSM has requested that SKB supplies additional information on the effects of dissolved salts in the groundwater. In the following, the example of chloride ions that might complex dissolved copper and enhance the overall corrosion process, is discussed.

2 The effect of chloride ions

2.1 Chloride concentrations

The highest chloride concentrations in Forsmark are slightly below 15 g/L (i.e. ≈ 0.42 mol/L), see for example Fig. 3-3, p. 55 of R-08-47.

2.2 Classical thermodynamic approach

No new information has recently appeared on this subject, which has been dealt with in many publications, including Macdonald and Sharifi-Asl (2011). It may be useful to present a summary of the effects of chloride ions here.

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The corrosion of Cu in water proceeds until a p_{H2} (equilibrium partial pressure of H_2) is reached such that there is equilibrium between dissolved Cu^+ and copper metal. This is described for example in section III, p. 15, of Macdonald and Sharifi-Asl (2011). For pure water at 25°C it may be shown, using available thermodynamic data, that $\log p_{H2} \approx -8.6$ and $\log\{Cu^+\} \approx -11.5$. The quantity $\log(p_{H2})^{0.5} + \log\{Cu^+\} \approx -16$ (at pH = 7) may be seen in Fig. 1 of Macdonald and Sharifi-Asl (2011). The total concentration of copper is calculated to be $\approx 4\times10^{-12}$ mol/L.

The effect of chloride can be seen by comparing Figs 11 and 16, etc of (Macdonald and Sharifi-Asl, 2011). Using the chloride concentration equal to 0.42 mol/L, it is possible to calculate $\log p_{H2} = -5.5$ (using the PhreeqC computer code with the Minteq.v4.dat database). The total concentration of copper is in this case calculated to be $\approx 4\times10^{-9}$ mol/L. Qualitatively this agrees well with the results of other studies, including Macdonald and Sharifi-Asl (2011), although other temperatures and chloride concentrations produce correspondingly different results.

It may be concluded that chloride ions enhance the corrosion of copper metal, as well as the calculated partial pressure of hydrogen. The extent of corrosion would nevertheless be limited for the calculated equilibrium concentration with chloride ions present in a repository environment. These results agree well with data and assumptions used in SR-Site.

2.3 Considerations for the “what if” case

Hultquist et al (2011) reported an equilibrium partial pressure of H_2 for the system oxygen free pure water and copper of 0.395 mbar at 21°C, which is much higher than the 2.5×10^{-6} mbar (i.e. the $\log p_{H2} \approx -8.6$, where the H_2 pressure is given in bar) calculated in the previous section. There is no satisfactory explanation for this discrepancy. The formation of some kind of solid product has been proposed (Szakálos et al. 2007 and Hultquist et al 2011), but there is no known crystalline species consisting of Cu, O and H with thermodynamic data corresponding to the reported equilibrium pressures.

By analogy with the oxides of copper, the composition of a hypothetical solid product, whose formation is suggested in (Szakálos et al. 2007 and Hultquist et al 2011), would be essentially unaffected by chloride concentrations, as there are no dissolved phases in the reaction in addition to the dissolved hydrogen gas. The influence of chloride ions would therefore be expected to be limited to small ionic strength effects on the solubility of molecular hydrogen. Although it may be possible to hypothesise a composition for the solid product, and in that way calculate its solubility and ionic strength effects, the result would still be a speculation.

2.4 Conclusion

The possible effect of chloride ions to the “what if” case presented in TR-10-66 can not be evaluated with certainty because of the speculative nature of the process and mechanisms that the “what if” case tries to capture. Under the assumption that the reaction product is a solid phase as claimed by Hultquist et al., it may be concluded that the effect of chloride ions in the solution is limited. Similar conclusions can be drawn for other groundwater constituents.

References

Hultquist, G., Graham, M., J., Szakalos, P., Sproule, G.,I., Rosengren, A., and Gråsjö, L., 2011, Hydrogen gas production during corrosion of copper by water, Corrosion Science Volume, 53 (1), pp. 310-319.

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