

## **Sulphide mass-transport limited corrosion**

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## Summary

In the SR-Site safety assessment, the rate of corrosion of copper canisters during the long-term anaerobic phase is calculated on the assumption that the limiting process is the supply of sulphide ions to the canister surface. The evidence in support of that assumption is summarised here, along with a discussion of whether rates calculated on the basis of transport control could be non-conservative.

A critical flux has been determined up to which the corrosion rate is limited by the rate of transport of sulphide which is then compared to the sulphide fluxes expected in the repository. The critical flux is estimated in two ways: first, from a comparison of the experimental rates of sulphide depletion and mass transport and, second, from the rate of  $\text{Cu}_2\text{S}$  film growth under conditions where the corrosion rate is believed to be transport limited. Based on these analyses, the critical sulphide flux for mass-transport control of the corrosion rate is estimated to be between  $2 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$  respectively.

In comparison, the flux required to corrode a 5 cm copper shell in  $10^6$  years would be  $1.1 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . In SR-Site, all calculation cases where the bentonite buffer is assumed to be intact demonstrate considerable margins to penetration due to sulphide corrosion after one million years, i.e. the sulphide fluxes are considerably lower than  $10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . For the case where the buffer is lost due to erosion, the overwhelming majority of combinations of ground water fluxes at deposition holes and sulphide concentrations also give sulphide fluxes below  $10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . When pessimistically combining the highest sulphide concentrations with the highest ground water fluxes from the hydrogeological modelling, sulphide fluxes around  $2 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$  are estimated. These highly unlikely fluxes are within the range of estimated critical sulphide fluxes of  $2 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$  to  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . For these few cases, therefore, the corrosion rate may not be limited by the rate of supply of  $\text{HS}^-$ . However, for intact bentonite and for the majority of cases for the eroded bentonite, the expected  $\text{HS}^-$  flux in the repository is several orders of magnitude lower than the critical flux and the corrosion rate of the canister will be determined by the rate of supply of sulphide.

For conditions where the sulphide flux is below the critical flux for transport control, predictions based on the rate of supply of sulphide will provide reasonable estimates of the canister corrosion rate. For the relatively few conditions where the sulphide flux is predicted to be greater than the critical flux, the corresponding calculated corrosion rates will be pessimistic.

A consequence of the fact that the corrosion rate will (usually) be determined by the rate of supply of sulphide is that there is a low probability of passivation of the surface under anaerobic conditions and, hence, localised corrosion or SCC. Under transport-limited conditions, the  $\text{Cu}_2\text{S}$  film is porous and only partially protective. Only at higher sulphide fluxes is a coherent, passive  $\text{Cu}_2\text{S}$  film observed, with film breakdown and pitting only having been reported in 0.001 mol/L sulphide and higher. Furthermore, by definition, transport control of the corrosion reaction means that the concentration of sulphide at the canister surface will approach zero. Thus, the observation of the SCC of Cu in bulk solution with a sulphide concentration greater than 0.005 mol/L will not be applicable on the canister in the repository.

Calculation of the corrosion rate based on the rate of sulphide transport may be non-conservative if the sulphide is not irreversibly consumed, or sequestered, in the corrosion reaction or if it catalyses the corrosion reaction. All of the available evidence, however, indicates that sulphide ions are sequestered in the corrosion reaction. In addition, there is no evidence that the  $\text{Cu}_2\text{S}$  film that forms catalyses the  $\text{H}_2$  evolution reaction, which might otherwise lead to an increase in corrosion rate. Ground water species, such as chloride ions, do not significantly impact the corrosion of copper under repository conditions.

Under unsaturated conditions in the repository during the early thermal transient phase, the corrosion rate will be determined by sulphide transport through those regions of the bentonite or host rock that remain saturated.

Finally, there is no conceivable mechanism by which episodic formation of sulphide could lead to a higher corrosion rate.

In summary, therefore, it is concluded that the rate of corrosion of copper canisters during the long-term anaerobic phase will be controlled by the rate of supply of sulphide and that the rates presented in SR-Site are appropriate.

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# 1 Introduction

Following a period of aerobic conditions, the repository environment will become anaerobic and will remain so indefinitely. During this long-term anaerobic period, the corrosion behaviour of the canister will be dominated by the presence of sulphide ( $\text{HS}^-$ ) ions. Sulphide is present naturally in the ground water at Forsmark and may be produced by the microbially mediated reduction of sulphate (King et al. 2010, 2011a, b). Although it has been previously assumed that the dissolution of pyrite (present as an impurity in the bentonite clay) may also act as a source of  $\text{HS}^-$ , a detailed review of the behaviour of pyrite under repository conditions suggests that it will not be a significant source of sulphide (King 2013).

In the presence of  $\text{HS}^-$ , the general corrosion of copper can occur and is supported by the evolution of hydrogen  $\text{H}_2$  (King et al. 2010). The possibility of general corrosion accompanied by the formation of  $\text{Cu}_2\text{S}$  and the generation of  $\text{H}_2$  was recognised in the original assessment of the corrosion behaviour of copper canisters carried out by the Swedish Corrosion Institute in 1978 (SKBF/KBS 1978). In that, and the subsequent assessments of the corrosion behaviour of copper canisters (SKBF/KBS 1978, 1983a, b, Werme et al. 1992, SKB 1999, 2010a, b, 2011), it has been assumed that the rate of corrosion is limited by the rate of supply of  $\text{HS}^-$  to the canister surface.

The Swedish Radiation Safety Authority (SSM) has requested additional evidence to support the assumption that the rate of corrosion during the long-term anaerobic phase is controlled by the rate of supply of  $\text{HS}^-$  (SSM 2012). In addition to this specific request for additional information, SSM (2012) refers to the report by Scully and Hicks (2012). Scully and Hicks (2012) raise a number of ancillary issues that broadly fall into two categories:

- are there circumstances under which the assumption that the corrosion rate is transport limited could be non-conservative, and
- has the rate of  $\text{HS}^-$  transport been adequately estimated?

In their review of the SR-Site documentation, and in a similar review performed by Scully and Edwards (2013) for the Canadian nuclear waste management programme, Scully and Hicks (2012) define a number of specific issues within these two broad categories:

- Are there circumstances under which the  $\text{HS}^-$  is not sequestered (i.e., irreversibly consumed) in the corrosion reaction?
- What is the nature and location of the cathodic reaction and can the copper sulphide film catalyse the reaction?
- What are the effects of mixed ground water chemistry, specifically the presence of  $\text{Cl}^-$ ?
- What is the effect of the episodic formation and supply of  $\text{HS}^-$ ?
- Does sulphide transport occur more rapidly under unsaturated conditions?
- Does the treatment of mass transport using the concept of transport resistances and equivalent flow rates adequately describe the rate of supply of  $\text{HS}^-$  in all circumstances?

A number of these specific issues are addressed in this report. The focus of the discussion here is on the chemical and electrochemical aspects of copper corrosion in sulphide environments, and, for that reason, there is no discussion of the mathematical aspects

involving transport resistances and equivalent flows. Sections 2 to 4 present the available experimental evidence in support of a number of the questions defined above and, in particular, the question of under what conditions the corrosion rate of copper canisters will be limited by the rate of supply of  $\text{HS}^-$  (section 2). The question of whether corrosion rates calculated on this basis could be non-conservative is dealt with in section 3. Section 4 addresses other issues raised by Scully and Hicks (2012), including the role of the other ground water species, the episodic generation of  $\text{HS}^-$ , and the transport of sulphide under unsaturated conditions. The conclusions from these extended analyses are summarised in section 5.

## 2 Conditions under which the rate of corrosion is limited by the supply of sulphide

### 2.1 Data background

Whether the rate of canister corrosion is transport limited or not depends simply, of course, on the balance between the rate of  $\text{HS}^-$  supply and the rate at which it is consumed at the canister surface. In general, the rate of corrosion can be controlled by either the anodic or cathodic process. In turn, both the anodic and cathodic processes can be controlled either by the rate of the interfacial reaction (or of an individual step in a multi-step surface process) or by the rate of transport of a reactant to, or of a product away from, the corroding interface. Under freely corroding conditions, the rates of the anodic and cathodic interfacial and transport steps are the same and equal to the rate of corrosion.

Much of the evidence used below to determine under what conditions the corrosion rate of the canister is limited by the supply of  $\text{HS}^-$  is based on the results of electrochemical experiments carried out in the laboratory. Before discussing this evidence, it is important to understand the differences between the environment in the repository and the conditions used in bench-top studies. First, the primary source of sulphide in the repository is the ground water in the fractures of the host rock. At the Forsmark site, the ground water  $\text{HS}^-$  concentration was estimated to be typically up to 0.3 mg/L ( $10^{-5}$  mol/L) (King et al. 2010, Table 2-2), though a few higher values were measured (SKB 2010b). In laboratory studies, a range of  $[\text{HS}^-]$  has been used from  $10^{-5}$  mol/L to  $10^{-3}$  mol/L (Chen et al. 2010, 2011a, b, 2012, Smith et al. 2004, 2006, 2007, 2008, 2011). Second, the ground water  $\text{Cl}^-$  concentration at Forsmark is reported to be as high as 6,900 mg/L (0.194 mol/L) (King et al. 2010, Table 2-2). Again, to help investigate the mechanism, a wider range of  $[\text{Cl}^-]$  has been used in laboratory tests, from 0 mol/L to 5 mol/L. Third, and most significant, the mass-transport conditions in the repository are orders of magnitude more restrictive than those used in laboratory experiments. In terms of the steady-state mass-transfer coefficient  $k_m$  ( $k_m = D/\delta$ , where  $D$  is the diffusion coefficient and  $\delta$  is the diffusion layer thickness), the rate of mass transport in the repository ( $k_m = 5 \times 10^{-9}$  cm/s) is five to six orders of magnitude slower than that in some of the laboratory tests ( $k_m = 2 \times 10^{-3}$  cm/s). Thus, the flux of  $\text{HS}^-$  to the canister surface (i.e., the product of the  $[\text{HS}^-]$  and  $k_m$ ) could be up to 7-8 orders of magnitude slower than in some of the laboratory tests described below.

In using experimental data to infer the behaviour of the canister, it is important, therefore, to always bear in mind the differences in  $[\text{HS}^-]$ ,  $[\text{Cl}^-]$ ,  $[\text{Cl}^-]:[\text{HS}^-]$  ratio, and  $\text{HS}^-$  flux between the lab and repository situations.

### 2.2 Critical sulphide flux for mass-transport control

The critical flux at which the rate of supply of sulphide to the copper surface determines the rate of corrosion was determined by measuring the rate of  $\text{HS}^-$  consumption as a function of the rate of mass transport. Both rotating and stationary electrodes were used. For rotating electrodes, mass transport of species to and from the surface occurs by diffusion and a well-defined diffusion layer is established as a consequence of the hydrodynamics of the rotating electrode (Bard and Faulkner 1980). The thickness of this diffusion layer is inversely related to the rotation rate of the electrode and, for the rotation rate of 30 revolutions per minute (rpm) used in the current study, is of the order of 100  $\mu\text{m}$  thick. Under stagnant conditions,

mass transport also occurs primarily by diffusion, although the thickness of the diffusion layer is less well-defined but will be larger than that for the rotating electrode. For the stationary electrode, therefore, we have assumed steady-state diffusion layer thicknesses of 0.5 mm and 1 mm.

The rate of consumption of sulphide was monitored by measuring the time-dependent pH of the solution. The dissolution of Na<sub>2</sub>S in water can be written as

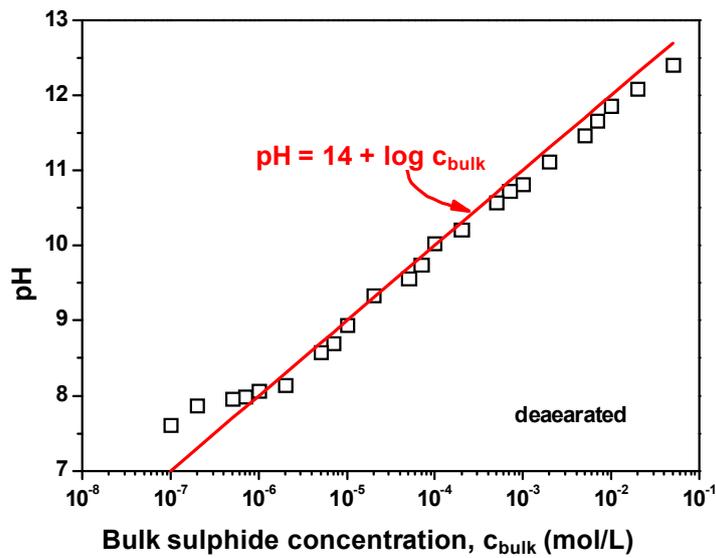


Because the concentration of S<sup>2-</sup> species is vanishingly small in aqueous solution (Rickard and Luther 2007), the solution pH can be used as a measure of the total sulphide concentration. The dependence of pH on the sulphide concentration was determined experimentally and a calibration curve established (Figure 2-1).

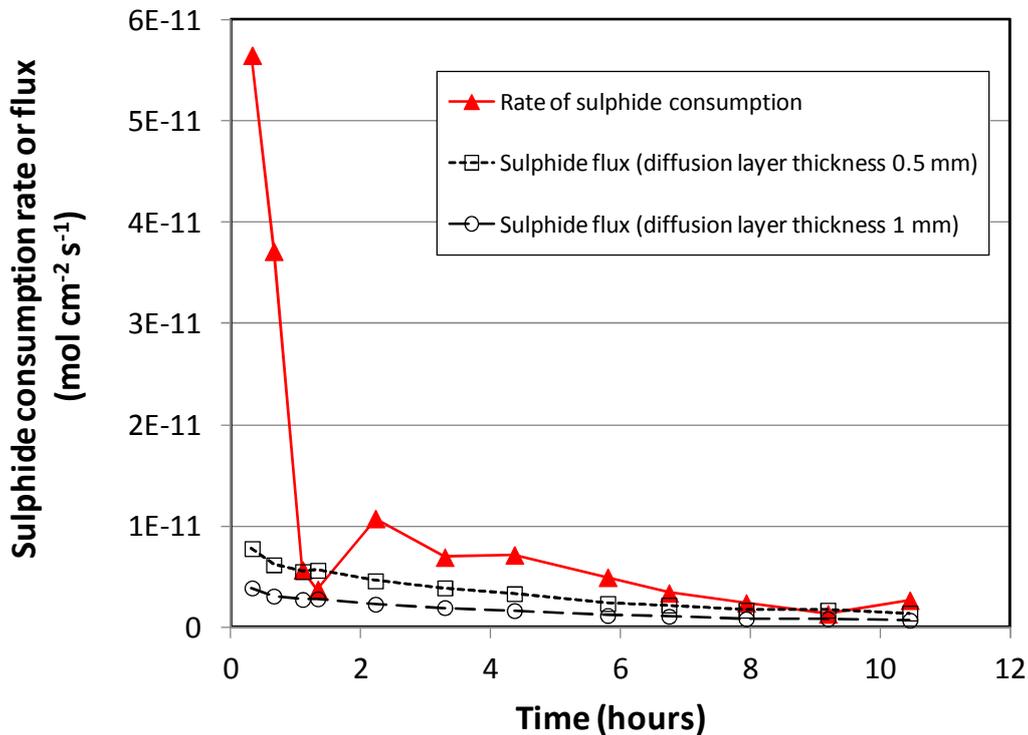
Figure 2-2 compares the measured sulphide consumption rate with the estimated rate of HS<sup>-</sup> supply for a stationary electrode in 0.1 mol/L NaCl plus 5×10<sup>-5</sup> mol/L Na<sub>2</sub>S. The consumption rate was calculated from the measured time-dependent [HS<sup>-</sup>] and the corresponding solution volume and electrode surface area. The steady-state diffusive flux was estimated based on the time-dependent [HS<sup>-</sup>], a sulphide diffusion coefficient of 1.7×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> (Lide 2003), and the assumed diffusion layer thickness of 0.5 mm or 1 mm. The initial HS<sup>-</sup> consumption rate exceeds the steady-state flux because sulphide transport occurs under transient diffusive conditions as the interfacial diffusion layer is depleted. Within a few hours, however, the consumption rates falls to a value equivalent to the steady-state HS<sup>-</sup> flux at which point the rate of HS<sup>-</sup> consumption (equivalent to the corrosion rate) is diffusive transport limited. Based on the data at times greater than 8 hours, the critical HS<sup>-</sup> flux at which the corrosion rate is transport limited is of the order of 2×10<sup>-12</sup> mol cm<sup>-2</sup> s<sup>-1</sup>.

The behaviour in stagnant solution is in contrast to that for the rotating electrode (Figure 2-3). At the higher rate of mass transport, the HS<sup>-</sup> consumption rate is always lower than the estimated rate of supply indicating interfacial control of the corrosion rate. In fact, the HS<sup>-</sup> consumption rate drops to near zero as a protective Cu<sub>2</sub>S film is formed (see section 2.3).

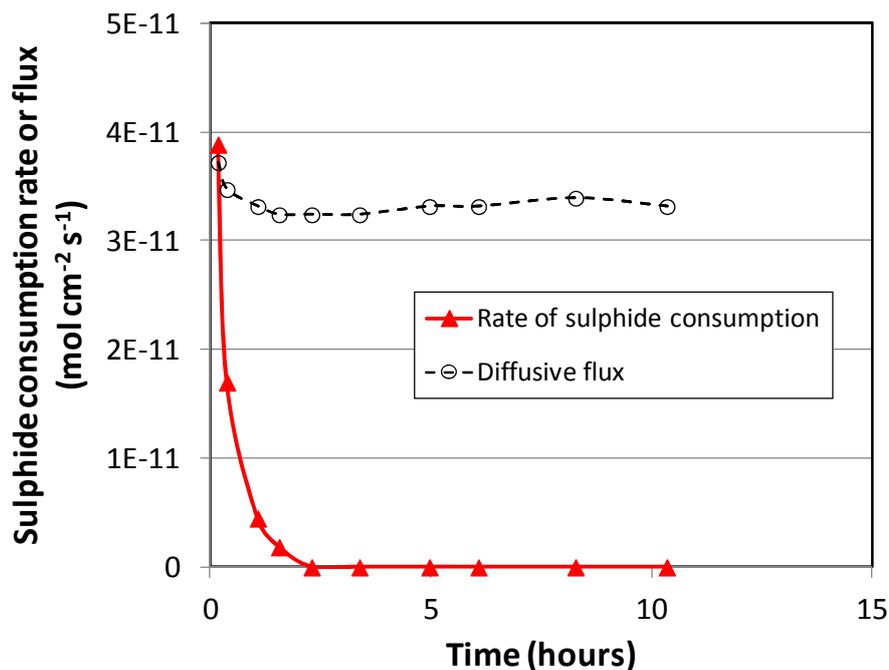
The critical HS<sup>-</sup> flux should then be compared with the mass-transport conditions for the canister in the repository, which is done in section 2.4.



**Figure 2-1.** Calibration curve of the dependence of the solution pH on sulphide concentration.



**Figure 2-2.** Comparison of the rate of sulphide consumption and the estimated sulphide flux for a stationary electrode in 0.1 mol/L NaCl plus  $5 \times 10^{-5}$  mol/L  $\text{Na}_2\text{S}$ . The  $\text{HS}^-$  flux is calculated for assumed diffusion layer thicknesses of 0.5 mm and 1 mm.



**Figure 2-3.** Comparison of the rate of sulphide consumption and the estimated sulphide flux for a rotating electrode in 0.1 mol/L NaCl plus  $5 \times 10^{-5}$  mol/L  $\text{Na}_2\text{S}$ . The  $\text{HS}^-$  flux is calculated based on a diffusion layer thickness of 100  $\mu\text{m}$  for the electrode rotation rate of 30 rpm.

### 2.3 Mechanism of copper corrosion in chloride-sulphide mixtures

Qualitative support for the conditions under which the rate of corrosion is under mass-transport control can also be obtained from the study of the mechanism of film formation in chloride-sulphide mixtures. It is implicitly assumed that the rate of film formation is equal to the rate of corrosion, i.e., that no other stable copper species are present and that all of the sulphide is sequestered in the formation of the film (see section 3.1).

Consistent with the results of the sulphide depletion experiments described above, at low  $\text{HS}^-$  fluxes the rate of film formation is transport limited (Smith et al. 2007). Figure 2-4 shows the voltammetric behaviour of copper in 0.1 mol/L NaCl solution containing  $10^{-3}$  mol/L  $\text{Na}_2\text{S}$ . A limiting current density is observed on the anodic scan due to the formation of a  $\text{Cu}_2\text{S}$  film, with the limiting current increasing with rotation rate (Figure 2-5). At low rotation rates (e.g., 1 Hz, 60 rpm), the observed current is equal to the predicted rate of the overall 2-electron process



on the assumption that the rate is limited by the rate of supply of  $\text{HS}^-$ . The corresponding steady-state flux at this rotation rate is approximately  $3 \times 10^{-9}$  mol  $\text{cm}^{-2}$   $\text{s}^{-1}$  ( $D = 1.7 \times 10^{-5}$   $\text{cm}^2$   $\text{s}^{-1}$ ,  $\delta = 64$   $\mu\text{m}$ , Bard and Faulkner 1980), which is higher than the critical flux under open-circuit conditions derived in section 2.2 because the electrode is being anodically polarised.

Under open-circuit conditions, the rate and mechanism of film growth is a function of the  $\text{HS}^-$  and  $\text{Cl}^-$  concentrations, the  $[\text{Cl}^-]:[\text{HS}^-]$  ratio, and the flux of  $\text{HS}^-$ . Three different types of film structure have been observed; two of which exhibit a porous structure (denoted P1 and P2

type films) and one exhibits a compact film (denoted C) (Chen et al. 2010, 2011a, b, 2012). In all cases, the film is composed entirely of  $\text{Cu}_2\text{S}$ . Table 2-1 lists the various experiments performed and the nature of the film observed. In some cases, interim film-thickness measurements were obtained, permitting the kinetics of film formation to be derived.

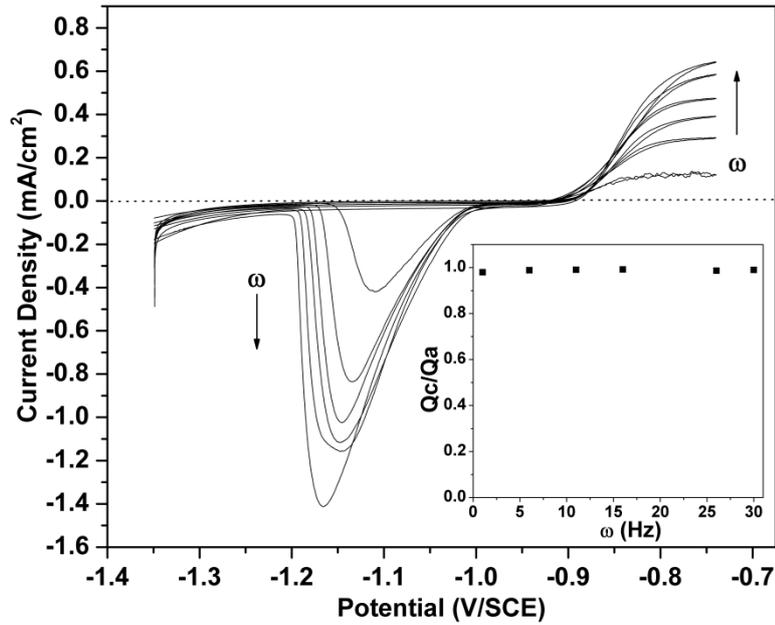
At high  $[\text{HS}^-]$  and/or high rates of mass transport (i.e., rotating electrode) and/or low  $[\text{Cl}^-]:[\text{HS}^-]$  ratio ( $\leq 1,000$  under stagnant conditions), a compact film (denoted type C) is formed and parabolic growth kinetics is observed (Figure 2-6). The rate of film growth is believed to be controlled by the transport of  $\text{Cu(I)}$  species through the film (Chen et al. 2010, 2011a). Figure 2-7(a), (b) shows a schematic of the proposed reaction scheme and an SEM of a cross-section cut using a focussed ion beam (FIB-SEM).

At lower  $[\text{HS}^-]$  and/or lower rates of mass transport and/or higher  $[\text{Cl}^-]:[\text{HS}^-]$ , the film is porous and exhibits linear growth kinetics (Chen et al. 2011a, b, 2012). Film growth is believed to be controlled by transport of  $\text{HS}^-$  either through the bulk solution or through the pores of the film. The film structure (denoted P1) is shown schematically in Figure 2-7(c) with a focussed-ion beam (FIB) image shown in Figure 2-7(d). Linear growth kinetics is consistent with a transport-limited corrosion reaction.

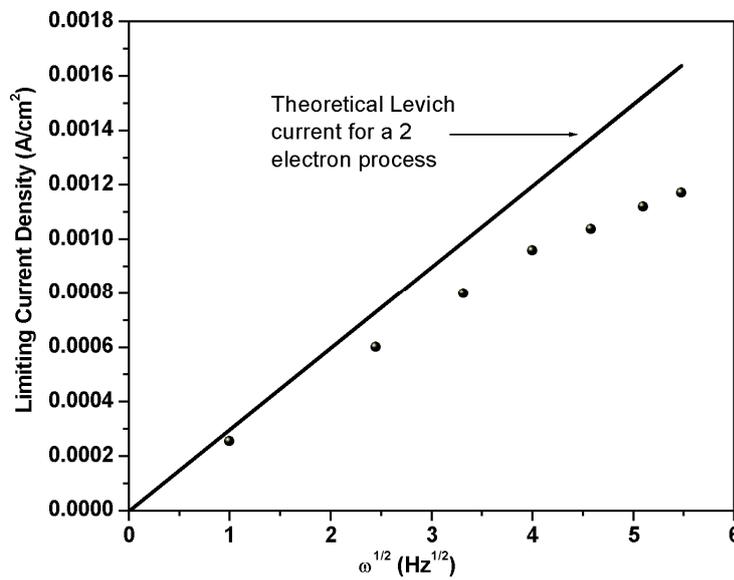
Finally, at high  $[\text{Cl}^-]$  (5 mol/L, Table 2-1), a columnar porous film (type P2) is observed (Figures 2-7(e) and (f)). The film growth kinetics are unknown, but it is suggested that a soluble  $\text{CuCl}_2^-$  species is involved in the process.

Figure 2-8 summarises the environmental conditions under which each type of film is observed, superimposed on the range of  $[\text{Cl}^-]$  and  $[\text{HS}^-]$  expected in the repository. For the ranges of  $[\text{Cl}^-]$  and  $[\text{HS}^-]$  expected for the repository and for the associated low rates of mass transport, it is apparent that  $\text{Cu}_2\text{S}$  films will be porous and grow linearly with time, consistent with mass-transport control by the supply of  $\text{HS}^-$ . As the film thickens after very long times in the repository (of the order of tens of thousands of years or longer), the rate controlling step may become transport of  $\text{HS}^-$  through the thick  $\text{Cu}_2\text{S}$  layer. Alternatively, the  $\text{Cu}_2\text{S}$  may periodically spall from the canister surface as it thickens due to the build up of internal stresses in the film. In this circumstance, rate control would likely revert to the rate of supply of  $\text{HS}^-$  through the bentonite. Regardless, the rate of corrosion cannot be higher than the corresponding rate of supply of  $\text{HS}^-$  and predictions based on this rate-limiting process will be conservative if the rate of supply of sulphide through a thick  $\text{Cu}_2\text{S}$  layer becomes rate controlling.

The linear film growth rate for the P1 porous film provides another estimate of the critical flux for transport control of the corrosion reaction. Since the linear kinetics is consistent with transport control, let us assume that the rate of film growth corresponds to the critical flux of  $\text{HS}^-$  for transport control of the corrosion reaction. The linear film growth rate from Figure 2-6 is  $6 \pm 4 \times 10^{-5}$   $\mu\text{m/h}$ . For a  $\text{Cu}_2\text{S}$  density of  $5.6 \text{ g/cm}^3$  (Lide 2003) and a molecular mass of  $159.14 \text{ g/mol}$  and a  $\text{Cu}_2\text{S}$  film with an assumed porosity of 0.5, the flux of  $\text{HS}^-$  corresponding to this rate of film growth is  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . This critical flux is a factor of 70 lower than the critical flux estimated on the basis of the short-term  $\text{HS}^-$  depletion experiments described in section 2.2. Because this value is based on a longer-term experiment it may represent a better estimate of the critical flux than that determined from the short-term depletion experiments. However, in the absence of more-definitive basis for selecting one of the two measurements, the critical  $\text{HS}^-$  flux is assumed to be within the range  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$  to  $2 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ .



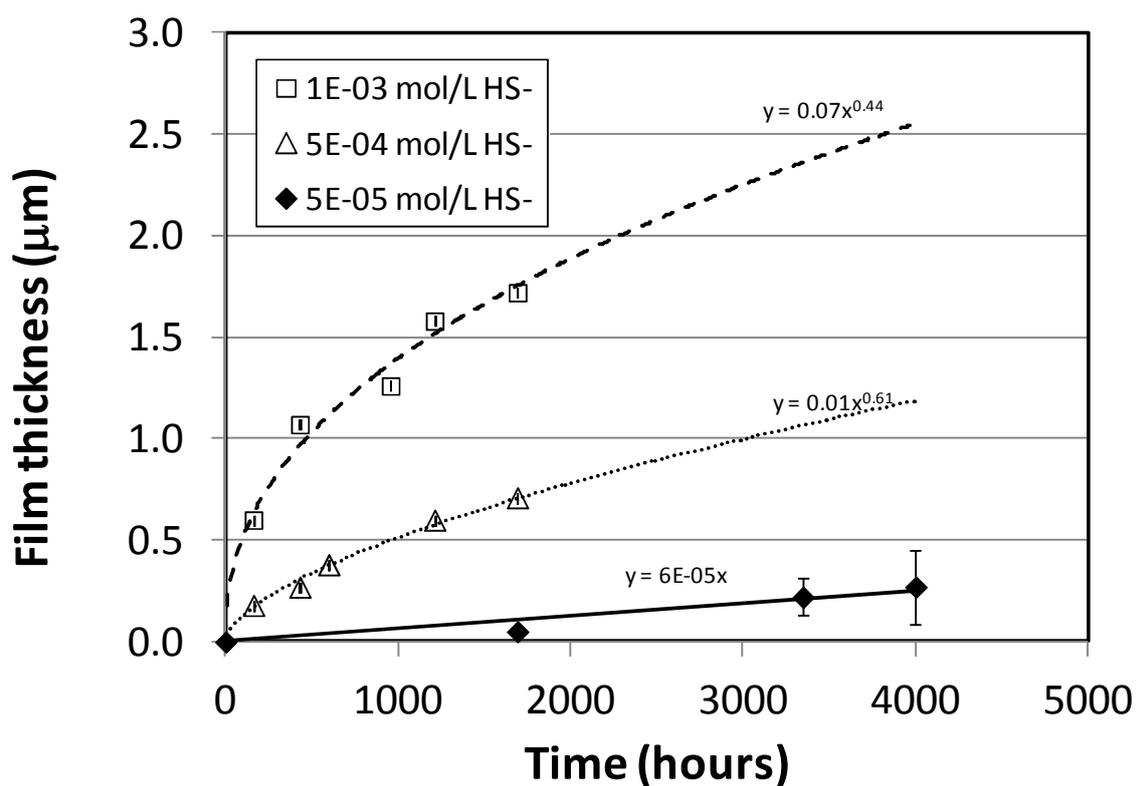
**Figure 2-4.** Voltammetric behaviour of a copper rotating electrode as a function of rotation rate  $\omega$  in 0.1 mol/L NaCl plus  $1 \times 10^{-3}$  mol/L Na<sub>2</sub>S (Smith et al. 2007). The inset shows the ratio of the cathodic ( $Q_c$ ) to anodic ( $Q_a$ ) charges.



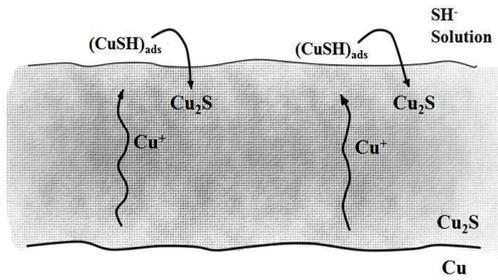
**Figure 2-5.** Levich plot of the anodic limiting current density of a copper rotating electrode in 0.1 mol/L NaCl plus  $1 \times 10^{-3}$  mol/L Na<sub>2</sub>S based on the data in Figure 2-4 (Smith et al. 2007).

**Table 2-1. Compilation of experiments at open-circuit potential at various sulphide and chloride concentrations and rates of mass transport and the resulting nature and kinetics of film growth.**

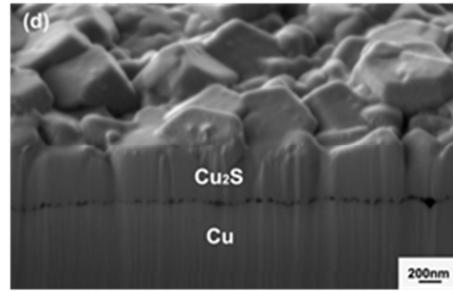
[HS <sup>-</sup> ] (mol/L)	[Cl <sup>-</sup> ] (mol/L)	[Cl <sup>-</sup> ]:[HS <sup>-</sup> ]	Mass transport conditions (Stagnant, rotation rate, ...)	Duration (hrs)	Film growth kinetics	Nature of film	Average film thickness and standard deviation (µm)
5×10 <sup>-5</sup>	0.1	2,000	stagnant	1691 3347 4000	linear	P1	0.050 ± 0.02 0.22 ± 0.09 0.27 ± 0.18
5×10 <sup>-4</sup>	0.1	200	stagnant	161 430 597 1211 1691	parabolic	C	0.18 ± 0.01 0.27 ± 0.10 0.38 ± 0.13 0.60 ± 0.11 0.71 ± 0.11
5×10 <sup>-4</sup>	0	0	stagnant	1691	-	C	1.31 ± 0.23
5×10 <sup>-4</sup>	0.1	200	168 h stagnant followed by 3h magnetic stirring (80 rpm)	1691	-	C	0.81 ± 0.15
1×10 <sup>-3</sup>	0.1	1,00	stagnant	161 430 956 1211 1691	parabolic	C	0.60 ± 0.10 1.07 ± 0.53 1.26 ± 0.38 1.58 ± 0.69 1.72 ± 0.39
1×10 <sup>-3</sup>	0.5	500	stagnant	430 1211 1691 3000	parabolic	C	0.22 ± 0.05 0.39 ± 0.06 0.39 ± 0.12 0.61 ± 0.22
1×10 <sup>-3</sup>	1.0	1,000	stagnant	3000	-	P1	-
1×10 <sup>-3</sup>	5.0	5,000	stagnant	1691	-	P2	-
1×10 <sup>-3</sup>	0.1	100	30 rpm	11	-	C	-
5×10 <sup>-5</sup>	0.1	2,000	30 rpm	11	-	C	-
1×10 <sup>-5</sup>	0.1	10,000	30 rpm	11	-	C	-
5×10 <sup>-5</sup>	1.0	20,000	30 rpm	11 and 24	-	C	-
1×10 <sup>-5</sup>	1.0	100,000	30 rpm	14	-	C	-



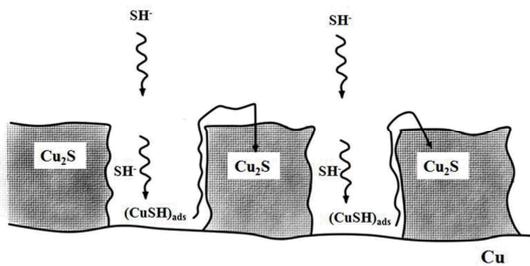
**Figure 2-6.** Film growth kinetics for a stationary copper electrode in 0.1 mol/L NaCl as a function of initial sulphide concentration. Parabolic film growth kinetics is observed at  $5 \times 10^{-4}$  mol/L and  $10^{-3}$  mol/L  $HS^-$  and linear kinetics at  $5 \times 10^{-5}$  mol/L  $HS^-$ .



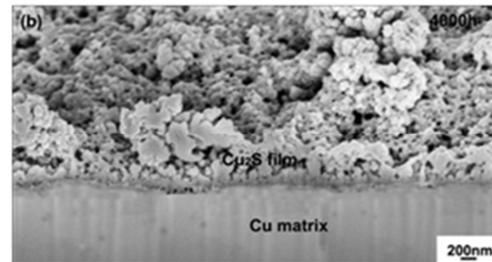
(a) Schematic of compact film C.



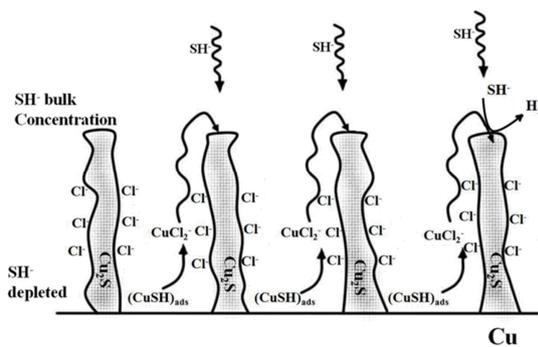
(b) FIB-SEM image of compact film C formed in  $5 \times 10^{-4}$  mol/L  $HS^-$  + 0.1 mol/L  $Cl^-$ .



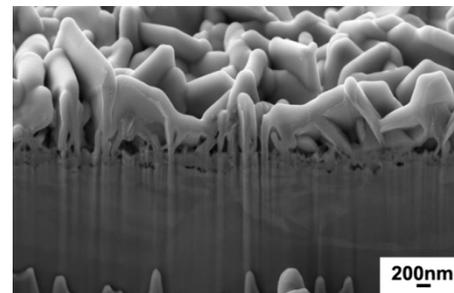
(c) Schematic of porous film P1.



(d) FIB-SEM image of porous film P1 formed in  $5 \times 10^{-5}$  mol/L  $HS^-$  + 0.1 mol/L  $Cl^-$ .

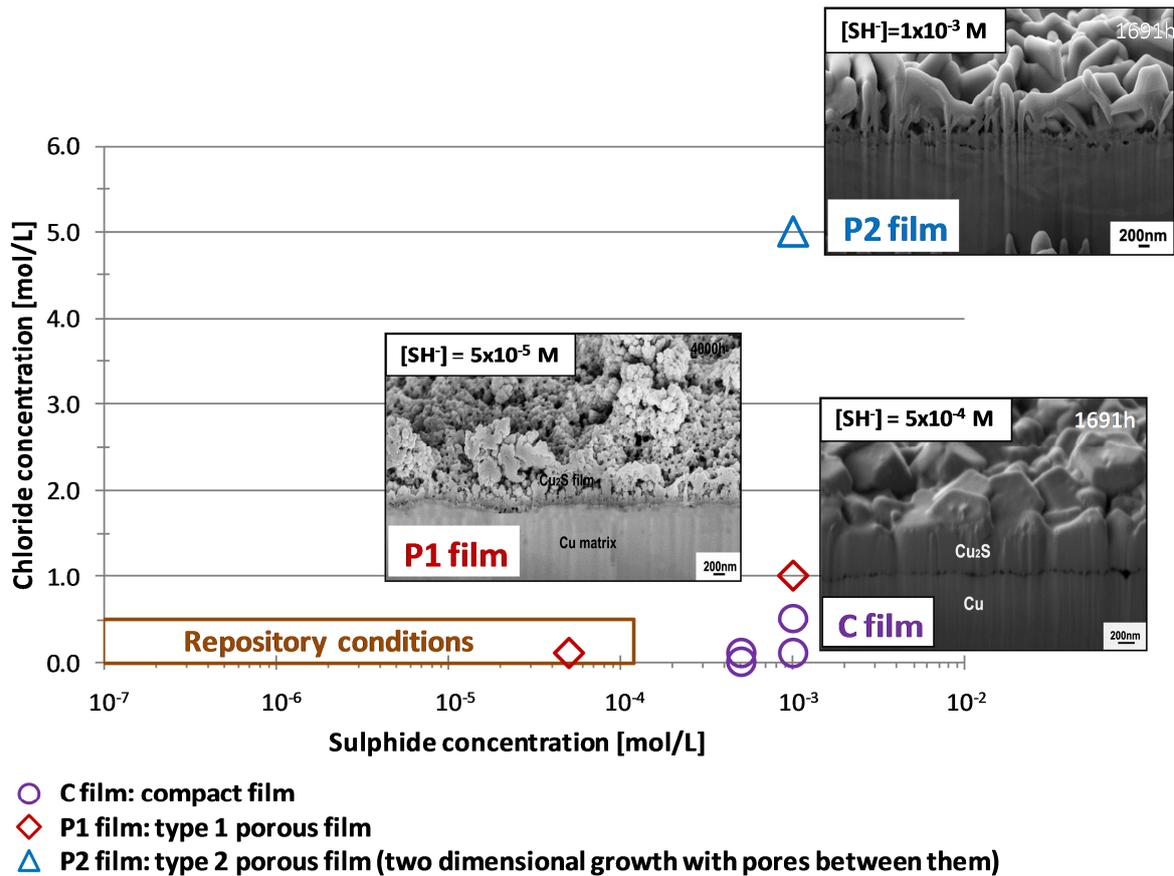


(e) Schematic of porous film P2.



(f) FIB-SEM image of porous film P2 formed in  $10^{-3}$  mol/L  $HS^-$  + 5 mol/L  $Cl^-$ .

**Figure 2-7.** Schematic illustrations and FIB-SEM images of the three types of cuprous sulphide film formed on copper at different sulphide and chloride ion concentrations.



**Figure 2-8.** Summary of the range of environmental conditions under which various types of  $\text{Cu}_2\text{S}$  film are formed in comparison to the range of conditions expected in the repository. The area marked “Repository conditions” indicates the maximum concentrations conceivable at the Forsmark site (SKB 2010c).

## 2.4 Comparison with sulphide fluxes in SR-Site

In order to understand the significance of the critical sulphide fluxes discussed in sections 2.2 and 2.3, a comparison should be made to the fluxes in the safety assessment SR-Site. A central aim with the corrosion analyses in SR-Site was to demonstrate that the copper canisters will maintain their containment capacity throughout the one million year assessment period. The sulphide flux required to just penetrate a copper shell of thickness  $d_{\text{Cu}}$  in time  $t$  is given by

$$J_{\text{HS}} = \frac{d_{\text{Cu}} \rho_{\text{Cu}}}{f_{\text{HS}} M_{\text{Cu}}} \frac{1}{t} \quad (2-3)$$

where  $\rho_{\text{Cu}}$  is the density of copper,  $f_{\text{HS}}$  a stoichiometric factor for the corrosion reaction, and  $M_{\text{Cu}}$  the molar mass of copper. For  $t=10^6$  years and the copper thickness 5 cm, and with  $\rho_{\text{Cu}}=8.9 \text{ g/cm}^3$ ,  $f_{\text{HS}}=2$  (1  $\text{HS}^-$  corrodes 2 Cu atoms) and  $M_{\text{Cu}}=63 \text{ g/mol}$ , the sulphide flux is about  $3.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ yr}^{-1} \approx 1.1 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . This is lower than the lower estimate given above ( $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ ) of the critical flux below which corrosion rates are transport controlled.

As demonstrated in SKB (2010b), all calculation cases where the bentonite buffer is assumed to be intact demonstrate considerable margins to penetration due to sulphide corrosion after one million years, i.e. the sulphide fluxes are considerably lower than  $10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . This is the case also for the overwhelming majority of combinations of ground water fluxes at deposition holes and sulphide concentrations considered in the analyses of cases where the buffer is assumed to be lost due to erosion.

When pessimistically combining the highest sulphide concentrations with the highest ground water fluxes from the hydrogeological modelling, penetration times as low as 50,000 years are obtained for the cases where the buffer is missing, equivalent to a  $\text{HS}^-$  flux of  $2 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$ . This is seen e.g. in Figure 13-39 of SKB (2011), where the onset of the dose curves mark the shortest time of canister failure due to corrosion in the probabilistic analyses where the entire ensemble of sulphide concentrations and ground water fluxes are considered. These highly unlikely fluxes are within the range of estimated critical sulphide fluxes of  $2 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$  to  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . For these few cases, therefore, the corrosion rate may not be limited by the rate of supply of  $\text{HS}^-$ . However, for intact bentonite and for the majority of cases for the eroded bentonite, the expected  $\text{HS}^-$  flux in the repository is several orders of magnitude lower than the critical flux and the corrosion rate of the canister will be determined by the rate of supply of sulphide.

For conditions where the sulphide flux is below the critical flux for transport control, predictions based on the rate of supply of sulphide will provide reasonable estimates of the canister corrosion rate. For the relatively few conditions where the sulphide flux is predicted to be greater than the critical flux, the corresponding calculated corrosion rates will be pessimistic.

A consequence of the fact that the corrosion rate will (usually) be determined by the rate of supply of sulphide is that there is a low probability of passivation of the surface under anaerobic conditions and, hence, localised corrosion or SCC. Under transport-limited conditions, the  $\text{Cu}_2\text{S}$  film is porous and only partially protective. Only at higher sulphide fluxes is a coherent, passive  $\text{Cu}_2\text{S}$  film observed, with film breakdown and pitting only having been reported in 0.001 mol/L sulphide and higher (Gennero De Chialvo and Arvia 1985). Furthermore, by definition, transport control of the corrosion reaction means that the concentration of sulphide at the canister surface will approach zero. Thus, the observation of the SCC of Cu in bulk solution with a sulphide concentration greater than 0.005 mol/L (Taniguchi and Kawasaki 2008) will not be applicable on the canister in the repository.

In summary, the expected  $\text{HS}^-$  flux in the repository is generally several orders of magnitude lower than the critical fluxes and the corrosion rate of the canister will be determined by the rate of supply of sulphide under almost all conditions.

### 3 Reasons for the assumption of sulphide transport limitation to be non-conservative

The assumption that the rate of corrosion is limited by the rate of transport of  $\text{HS}^-$  is conservative provided that:

1. the  $\text{HS}^-$  is irreversibly consumed (or sequestered) in the corrosion reaction, and
2. the resulting  $\text{Cu}_2\text{S}$  film does not act as a catalyst for some other rate-determining process.

#### 3.1 Sequestration of sulphide

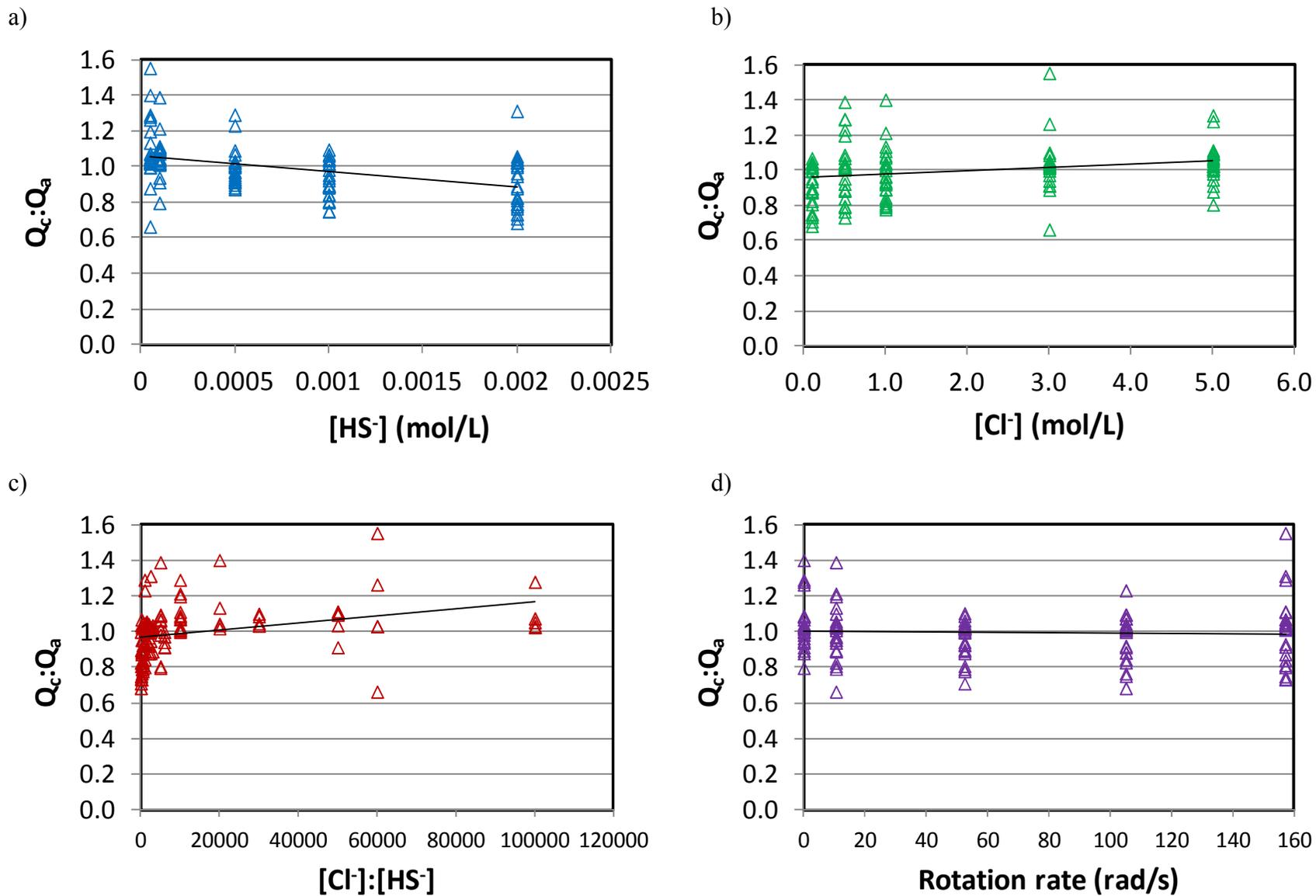
The primary evidence for the sequestration of  $\text{HS}^-$  is the observation that, during electrochemical polarisation experiments, the amount of charge required to reduce the  $\text{Cu}_2\text{S}$  film formed on the electrode is equal to the charge consumed in forming the film. The voltammogram shown in Figure 2-4 and the  $Q_c:Q_a$  ratio shown in the inset illustrate one such example. On the forward, anodic-going potential cycle a  $\text{Cu}_2\text{S}$  film is formed (the growth of which is transport limited, as described above) as indicated by the positive currents at potentials greater than approximately  $-1.0 V_{\text{SCE}}$  (Reaction (2-2)). On the reverse, cathodic-going scan, a corresponding reduction process is observed as a peak with a maximum at a potential of approximately  $-1.15 V_{\text{SCE}}$ , corresponding to the reverse process. The integrated areas under the cathodic and anodic curves is expressed as the charge ratio  $Q_c:Q_a$ , shown in the inset in Figure 2-4. Within experimental error, this ratio is equal to one, indicating that all  $\text{HS}^-$  that reacts on the electrode remains on the surface until it is subsequently cathodically reduced. Furthermore, the observed ratio is independent of the electrode rotation rate; which is significant as the formation of a soluble intermediate (indicative of non-sequestration of  $\text{HS}^-$ ) would be expected to lead to a decrease in  $Q_c:Q_a$  with increasing  $\omega$ .

A more-extensive series of such experiments has been performed as a function of:

- $\text{HS}^-$  concentration ( $5 \times 10^{-5}$ - $2 \times 10^{-3}$  mol/L)
- $\text{Cl}^-$  concentration (0.1-5.0 mol/L)
- $[\text{Cl}^-]:[\text{HS}^-]$  ratio (50-100,000)
- Rotation rate (0-157 rad/s, equivalent to 0-25 Hz or 0-1500 rpm).

Although there is some scatter in the data, there is no apparent trend with any of the variables studied (Figure 3-1). Thus, there is no evidence for the formation of a soluble copper ion, either as a dissolved sulphide complex ion, such as  $\text{Cu}(\text{HS})_2^-$ , or the corresponding chloride species,  $\text{CuCl}_2^-$ .

The behaviour at high  $[\text{Cl}^-]$  and high  $[\text{Cl}^-]:[\text{HS}^-]$  ratios is of particular interest, since the proposed mechanism for the formation of type P2 porous films (Figure 2-7(e), (f)) involves a dissolved  $\text{CuCl}_2^-$  species. The formation of a dissolved Cu species is consistent with the maintenance of open pores and the columnar growth of the  $\text{Cu}_2\text{S}$  film, with the walls of the pores blocked by adsorbed  $\text{Cl}^-$  and film growth occurring by precipitation of the dissolved  $\text{CuCl}_2^-$  at the film solution interface (Figure 2-7(e)). It has been suggested that  $\text{CuCl}_2^-$  could be formed from adsorbed  $\text{Cu}(\text{HS})_{\text{ads}}$  formed as an intermediate in the sulphidation of Cu (Chen et al. 2010, 2011b)



**Figure 3-1.** Effect of a) sulphide concentration, b) chloride concentration, c) their ratios, and d) the rate of mass transport on the charge ratio for the formation and reduction of  $Cu_2S$  films.



In essence,  $\text{Cl}^-$  and  $\text{HS}^-$  compete for the adsorbed  $\text{Cu}(\text{HS})_{\text{ads}}$  intermediate, with the end product being either  $\text{CuCl}_2^-$  (reaction (3-3)) or  $\text{Cu}_2\text{S}$  (reaction (3-2)), depending upon whether  $\text{Cl}^-$  or  $\text{HS}^-$  is the predominant anion. Cuprous sulphide may also form from the reaction between dissolved  $\text{CuCl}_2^-$  and  $\text{HS}^-$  (reaction (3-4)). A combination of reactions (3-1) and (3-3) does, however, represent a mechanism by which  $\text{HS}^-$  promotes the dissolution of copper without itself being irreversibly consumed (sequestered) in the corrosion reaction, *provided the  $\text{CuCl}_2^-$  end product is stable*. This latter caveat is crucial as, although  $\text{CuCl}_2^-$  may be formed as an intermediate, the subsequent reaction with  $\text{HS}^-$  (reaction (3-4)) does lead to the sequestration of  $\text{HS}^-$ .

Although the concentration of dissolved  $\text{CuCl}_2^-$  would be expected to be very low in the presence of  $\text{HS}^-$ , such species could be stable within the pores of a  $\text{Cu}_2\text{S}$  film if the  $\text{HS}^-$  is depleted because of limited transport into the pores. Based on thermodynamic considerations, however, sulphide would have to be almost entirely depleted in the pores for  $\text{CuCl}_2^-$  to be present in significant concentration. The dissolution of  $\text{Cu}_2\text{S}$  can be expressed as



for which the solubility product  $*K_{\text{sp}}^0$  is given by

$$*K_{\text{sp}}^0 = \frac{[\text{Cu}^+]^2[\text{HS}^-]}{[\text{H}^+]} \quad (3-6)$$

and has a value of  $10^{-34.02}$  (Puigdomenech and Taxén 2000). The overall stability constant for  $\text{CuCl}_2^-$  ( $\beta_2^0$ )



is given by

$$\beta_2^0 = \frac{[\text{CuCl}_2^-]}{[\text{Cu}^+][\text{Cl}^-]^2} \quad (3-8)$$

and has a value of  $10^{5.62}$  (Puigdomenech and Taxén 2000). The corresponding stability constant for the  $\text{CuCl}_3^{2-}$  species formed at high chloride concentrations is  $\beta_3^0 = 10^{4.86}$ .

Combining equations (3-6) and (3-8) gives the concentration of  $\text{CuCl}_2^-$  in equilibrium with  $\text{Cu}_2\text{S}(\text{cr})$  as a function of  $[\text{Cl}^-]$ ,  $[\text{HS}^-]$ , and pH

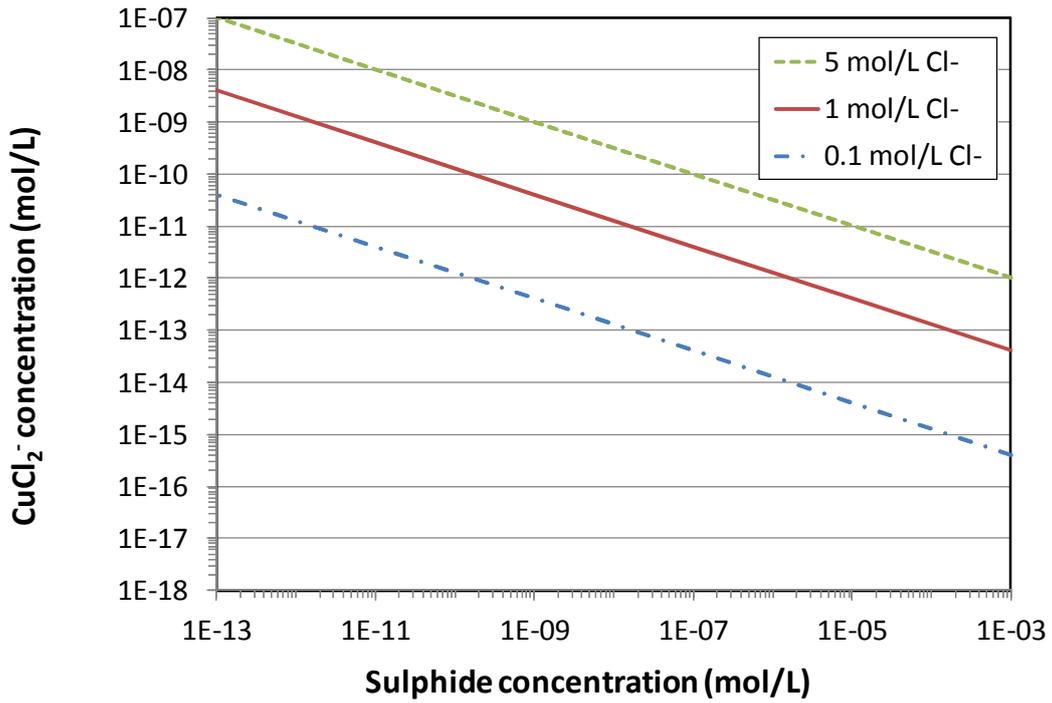
$$[\text{CuCl}_2^-] = \frac{\beta_2^{\circ} (*K_{\text{sp}}^{\circ})^{1/2} [\text{Cl}^-]^2 [\text{H}^+]^{1/2}}{[\text{HS}^-]^{1/2}} \quad (3-9)$$

and, for the  $\text{CuCl}_3^{2-}$  complex ions

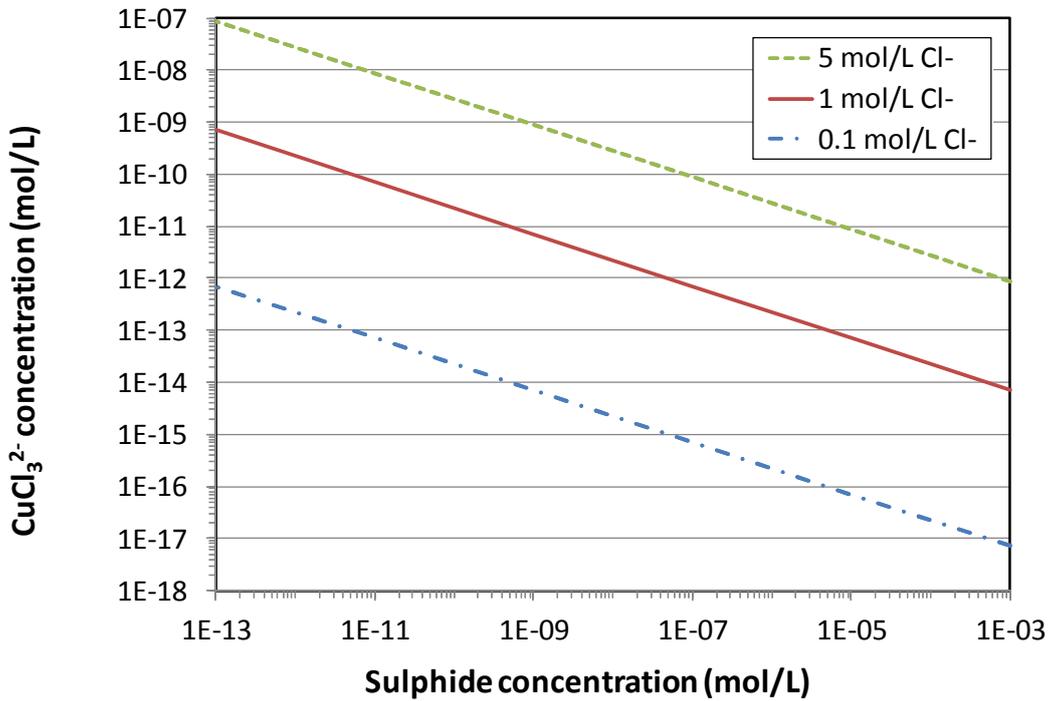
$$[\text{CuCl}_3^{2-}] = \frac{\beta_3^{\circ} (*K_{\text{sp}}^{\circ})^{1/2} [\text{Cl}^-]^3 [\text{H}^+]^{1/2}}{[\text{HS}^-]^{1/2}} \quad (3-10)$$

Figure 3-2 shows the dependence of  $[\text{CuCl}_2^-]$  and  $[\text{CuCl}_3^{2-}]$  on the sulphide concentration for three different  $\text{Cl}^-$  concentrations at pH 7, a pH value selected as representative of that in a sulphide-depleted pore. It is apparent that the concentration of the dissolved cuprous-chloro complex ions is extremely small. In the bulk of the solution, characterised by  $[\text{HS}^-]$  of  $10^{-6}$ - $10^{-5}$  mol/L or higher, the concentration of  $\text{CuCl}_2^-$  would be  $<10^{-10}$  mol/L even in 5 mol/L  $\text{Cl}^-$ . Even at the base of a pore in the  $\text{Cu}_2\text{S}$  film where the  $\text{HS}^-$  could be depleted (characterised by, say, a sulphide concentration of  $10^{-13}$  mol/L), the equilibrium  $\text{CuCl}_2^-$  concentration ranges from  $10^{-7}$  mol/L in 5 mol/L  $\text{Cl}^-$  solution to  $10^{-11}$ - $10^{-9}$  mol/L in 0.1-1 mol/L  $\text{Cl}^-$  solutions more characteristic of those expected in the repository. The concentrations of  $\text{CuCl}_3^{2-}$  are lower, even in 5 mol/L  $\text{Cl}^-$  solution.

Based on this analysis, therefore, it seems unlikely that there would be significant dissolution of copper as dissolved  $\text{CuCl}_2^-$  (or  $\text{CuCl}_3^{2-}$ ) formed via reaction between  $\text{Cl}^-$  and a  $\text{Cu}(\text{HS})_{\text{ads}}$  intermediate. Even if such a species were to form in the sulphide-depleted solution at the copper-solution interface in the pores of a  $\text{Cu}_2\text{S}$  film, it seems certain that it would precipitate at the film-solution interface once dissolved  $\text{CuCl}_2^-$  species encountered the sulphide-rich environment in the “bulk” solution. Therefore, there appears to be no evidence to suggest that sulphide can promote copper dissolution and not be sequestered in the corrosion reaction, even if it proceeds via a dissolved cuprous-chloro intermediate.



(a) Dependence of the  $\text{CuCl}_2^-$  concentration.



(b) Dependence of the  $\text{CuCl}_3^{2-}$  concentration.

**Figure 3-2.** Dependence of the concentration of dissolved cuprous-chloro complex ions in equilibrium with  $\text{Cu}_2\text{S}$  on the sulphide concentration at pH 7 for three chloride concentrations.

### 3.2 Location and nature of the cathodic reaction

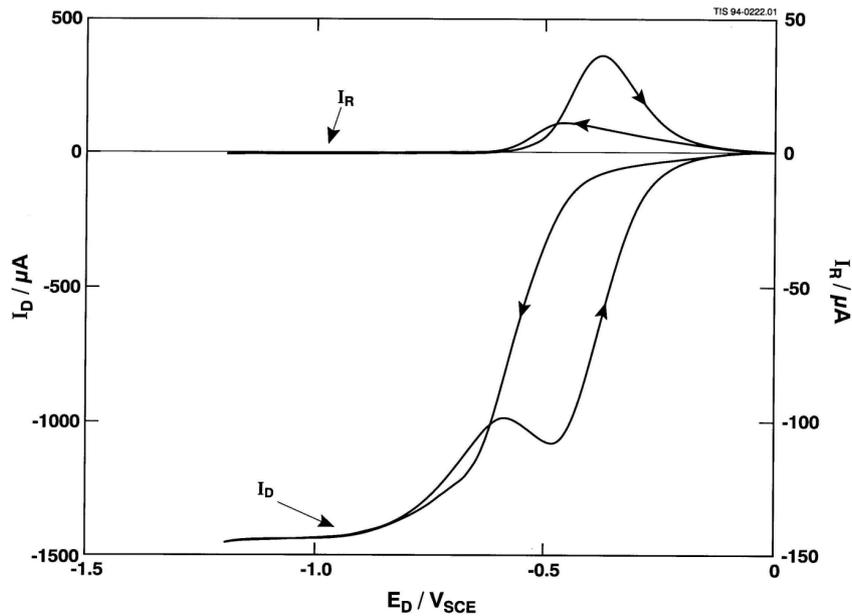
In aerobic systems,  $\text{Cu}_2\text{S}$  films are known to catalyse the cathodic reduction of  $\text{O}_2$  leading to an increase in corrosion rate. The catalysis of the  $\text{O}_2$  reduction reaction is responsible for the enhanced corrosion of brass condenser tubing in ships in polluted seawater, with a catalytic  $\text{Cu}_2\text{S}$  film forming during stagnant polluted conditions, which then enhances corrosion when replaced by unpolluted aerated water (Syrett 1981). Similar catalytic processes have been observed in sulphide-contaminated potable water (Jacobs and Edwards 2000). Whilst the catalysis of cathodic processes and corrosion reactions under aerobic conditions is well established, there is little evidence available for anoxic environments.

We have little information regarding the nature or location of the cathodic reaction under anaerobic conditions, but the available evidence suggests that  $\text{Cu}_2\text{S}$  neither catalyses the cathodic reaction nor leads to an enhancement of the corrosion rate. Unlike the catalysis of the  $\text{O}_2$  reduction reaction by sub-monolayer adsorbed species (King et al. 1995a, b), there is no evidence that the  $\text{Cu}_2\text{S}$  film catalyses the evolution of  $\text{H}_2$  (Figure 3-3). In  $\text{O}_2$ -containing solution (Figure 3-3(a)), the reduction of  $\text{O}_2$  is catalysed on the forward, anodic-going scan starting at potentials more positive than approximately  $-0.6 V_{\text{SCE}}$ , believed to be due to the presence of catalytic  $\text{Cu}(0)/\text{Cu}(I)$  surface sites (King and Litke 1994, King et al. 1995a, b). As the potential is scanned in the positive direction, the current decreases (resulting in an apparent peak at  $-0.45 V_{\text{SCE}}$ ). The catalytic activity is lost on the reverse scan (believed to be due to the elimination of Cu surface sites with two oxidation states), resulting in hysteresis on the  $\text{O}_2$  reduction curve and a lower current on the reverse scan.

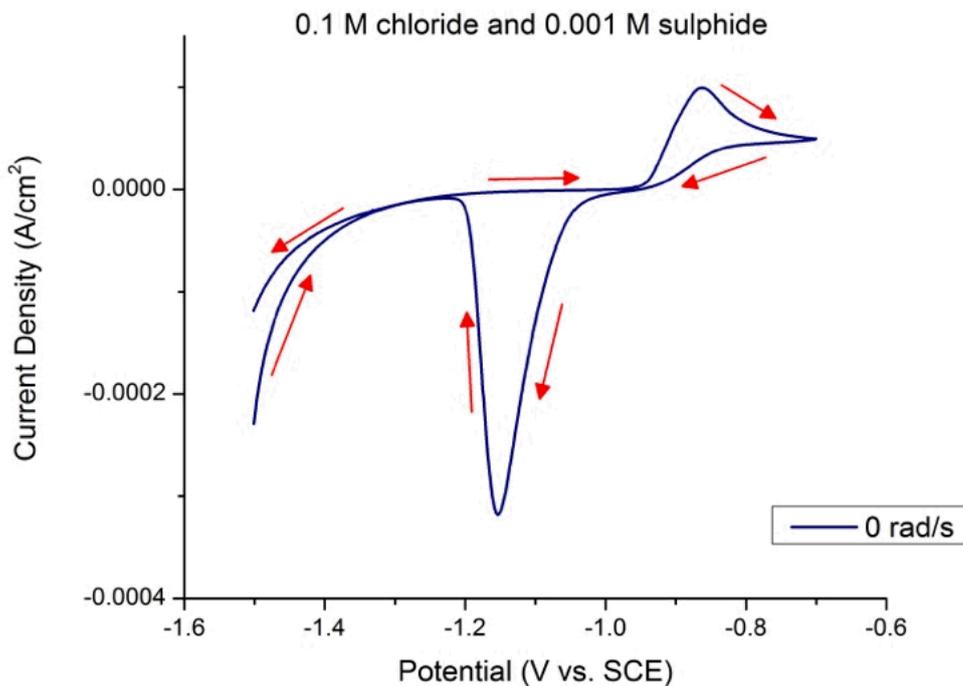
No such catalysis or current hysteresis is observed in the potential region for the evolution of  $\text{H}_2$  (approximately  $-1.1 V_{\text{SCE}}$  and more negative) in sulphide-containing solution (Figure 3-3(b)). On the forward potential scan, the  $\text{H}_2$  evolution reaction occurs on a "bare" copper surface (produced by cathodically cleaning the electrode at  $-1.5 V_{\text{SCE}}$ ). Film formation occurs at potentials more-positive than approximately  $-1.0 V_{\text{SCE}}$ . On the reverse, cathodic-going, potential scan the  $\text{Cu}_2\text{S}$  film is totally reduced (as evidenced by the  $Q_c:Q_a$  ratio of  $\sim 1$ , discussed above) prior to the onset of  $\text{H}_2$  evolution, which then occurs at a rate similar to that on the forward scan. If the  $\text{Cu}_2\text{S}$  film acted as a catalyst for the  $\text{H}_2$  evolution reaction then an enhanced cathodic current (and corresponding current hysteresis) would be expected prior to the reduction of the  $\text{Cu}_2\text{S}$  film, but this is not observed. Therefore, there is no evidence that  $\text{Cu}_2\text{S}$  catalyses the evolution of  $\text{H}_2$ , as it does the reduction of  $\text{O}_2$  (Syrett 1981). The available evidence suggests, therefore, that the cathodic reaction is most likely to occur at exposed Cu surfaces at the metal/film interface.

This behaviour is in contrast to that observed for iron sulphide films involved in the microbiologically influenced external corrosion of pipeline steels (Jack 2002). For this system, the corrosion rate is found to increase with increasing concentration of iron sulphide in the soil because the corrosion product is believed to act as a cathode of increasing surface area. For the  $\text{Cu}_2\text{S}$  system, however, there is no evidence that the corrosion rate increases as the film thickens (i.e., as the effective surface area of the porous film increases); in fact, the film growth rate is either constant or decreases with time (Figure 2-6).

We have no definitive information regarding the identity of the cathodic reactant, i.e., the source of the hydrogen evolved. Simply based on the respective concentrations of  $\text{H}^+$ ,  $\text{HS}^-$ , and  $\text{H}_2\text{O}$ , the most likely species undergoing reduction is  $\text{H}_2\text{O}$ .



(a) Reduction of  $O_2$  on Cu in  $NaClO_4$  solution (King and Litke 1994). The lower pane shows the current for  $O_2$  reduction on a rotating Cu disc electrode ( $I_D$ ) as the potential is scanned from  $-1.2 V_{SCE}$  to  $0 V_{SCE}$  and back again. The upper pane shows the corresponding ring current ( $I_R$ ) for the oxidation of peroxide intermediates. Electrode rotation rate 14.3 Hz, disc electrode surface area  $0.33 cm^2$ , potential scan rate 10 mV/s, second scan shown,  $[O_2] = 1.3 \times 10^{-3} mol/L$ , Pt ring electrode collection efficiency 0.4, ring potential  $+0.6 V_{SCE}$ .



(b) Cyclic voltammogram in 0.1 mol/L NaCl plus  $1 \times 10^{-3} mol/L Na_2S$  for a stationary Cu electrode. Potential scan rate 2 mV/s.

**Figure 3-3.** Comparison of the catalytic behaviour of copper surfaces to the cathodic reduction of  $O_2$  and the absence of catalysis of the  $H_2$  evolution reaction in sulphide-containing solution.

## 4 Associated issues

### 4.1 Effect of unsaturated conditions

During the initial warm, aerobic transient period in the evolution of the repository environment, the bentonite surrounding the canister will partially desiccate. The extent of this dry-out depends on a number of factors, including the heat output from the canister and the hydraulic conditions in the surrounding rock. The bentonite buffer may thus be partially unsaturated, while saturated conditions are maintained further from the canister surface.

For species that can partition into the gas phase, the rate of transport through partially saturated bentonite is higher than that in saturated buffer (King et al. 1996). Depending upon the pH, sulphide may exist as  $\text{HS}^-$  or  $\text{H}_2\text{S}$ . (The dissociation constant for  $\text{HS}^-$  is uncertain, with an estimated value of  $\text{p}K_2 > 18$  (Rickard and Luther 2007). Thus, the un-protonated ion  $\text{S}^{2-}$  does not exist in natural waters). The dissociation constant for the  $\text{HS}^-/\text{H}_2\text{S}$  equilibrium is  $10^{-6.98}$  at  $25^\circ\text{C}$  (Rickard and Luther 2007), so that  $\text{H}_2\text{S}$ , which could partition into the gas phase, only predominates at  $\text{pH} < 7$ . Since the pH of bentonite pore water is buffered in the range pH 8-9 by the presence of calcite in the bentonite (Sena et al. 2010), the sulphide in the bentonite pore water will tend to be in the form of  $\text{HS}^-$ . However, some partitioning of  $\text{H}_2\text{S}$  into the vapour phase in unsaturated bentonite may occur.

Even if gaseous  $\text{H}_2\text{S}$  does occur in unsaturated bentonite, the rate of supply of sulphide to the canister surface will still be controlled by  $\text{HS}^-$  transport across the *saturated* part of the bentonite and/or surrounding host rock. Therefore, partial desiccation of the bentonite will not lead to a higher rate of supply of sulphide to the canister surface.

### 4.2 Effect of ground water composition

Naturally occurring ground water (or, more correctly, the bentonite pore water in contact with the canister) is chemically more complex than the simple chloride solutions typically used in laboratory studies. Of those species present in the pore water (Sena et al. 2010), only  $\text{Cl}^-$  is likely to participate in the corrosion of copper in sulphide-containing environments.

The role of  $\text{Cl}^-$  ions has been discussed in some detail in sections 2.3 and 3.1. Even in 5 mol/L  $\text{Cl}^-$ , the relative concentration of dissolved  $\text{CuCl}_2^-$  and/or  $\text{CuCl}_3^{2-}$  species is too low to be significant. For repository-relevant  $\text{Cl}^-$  concentrations ( $< 1$  mol/L  $\text{Cl}^-$ ), the corrosion behaviour of copper will be dominated by the effect of  $\text{HS}^-$ .

### 4.3 Effect of episodic sulphide formation

The episodic formation of  $\text{HS}^-$  is only important if it is interspersed with the presence of  $\text{O}_2$ . As noted above,  $\text{Cu}_2\text{S}$  films catalyse the reduction of  $\text{O}_2$  and can lead to accelerated corrosion of copper alloys if the system is subject to alternating reducing (sulphide-dominated) and aerobic conditions (Syrett 1981).

In the SR-Site safety assessment, the possibility that oxygen may reach the canisters during certain conditions of glacial advances and retreats is not completely excluded (SKB 2011, section 10.4.7). The corrosion effects are evaluated with a mass balance approach, using several pessimistic assumptions (SKB 2011, section 12.6.2). The corrosion depth was calculated to be of the order of mm based on the amount of  $\text{O}_2$  that could pessimistically reach the canisters. In the case where the corrosion is limited by a mass balance of oxidants

transported to the canister, any catalytic effects would only change the rate, not the total extent of corrosion.

The sulphide content in groundwater at the Forsmark site was thoroughly investigated in support of the SR-Site safety assessment (Tullborg et al. 2010), giving both an estimate of present day conditions and proposed changes in values (or lack of change) for different future time periods. From the discussion in Tullborg et al. (2010, chapter 6) it may be concluded that sulphide concentrations in ground waters, including the potential input from methane and hydrogen, and the uncertain contribution from “natural” dissolved organic carbon and bentonite organic carbon, will be at levels found at present in the Forsmark site, or lower, during a complete glacial cycle. Naturally, for any given deposition location, variations in sulphide levels may take place. During the operational phase and during a marine transgression, the overall sulphide levels are expected to increase but these periods are relatively short compared with the temperate, periglacial and glacial periods. In addition, the sulphide concentrations in general are expected to decrease during the glacial periods.

Even if the rate of  $\text{HS}^-$  formation does vary over time, the only consequence will be variation in the rate of supply of  $\text{HS}^-$  to the canister surface, but still within the range of what was discussed in SR-Site (see section 2.4). It is therefore concluded that there is no viable episodic process that could lead to enhanced corrosion of the canister by sulphide compared to the estimates in SR-Site.

## 5 Summary and conclusions

Evidence has been presented that demonstrates that the rate of supply of sulphide to the canister surface will limit the rate of corrosion during the long-term anaerobic phase in the case of both intact and eroded bentonite buffer. The critical flux of  $\text{HS}^-$  at which the corrosion rate is under transport control has been estimated in two ways: first, from a comparison of the rate of sulphide consumption and the rate of supply from a short-term (of the order of 10 hours) test and, second, from the rate of film growth in longer-term (of the order of 1000's of hours) test under conditions where the mechanism of film growth is consistent with transport control. The resulting critical sulphide fluxes for transport control are  $2 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $3 \pm 2 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ , respectively. In comparison, the flux required to corrode a 5 cm copper shell in  $10^6$  years would be  $1.1 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ .

In the SR-Site safety assessment, all calculation cases where the bentonite buffer is assumed to be intact, demonstrate sulphide fluxes considerably lower than  $10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . For the case where the buffer is lost due to erosion, the overwhelming majority of combinations of ground water fluxes at deposition holes and sulphide concentrations also give fluxes below  $10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ . When pessimistically combining the highest sulphide concentrations with the highest ground water fluxes from the hydrogeological modelling, the sulphide fluxes are within the range of experimentally determined critical fluxes given above. The expected  $\text{HS}^-$  flux in the repository is thus generally several orders of magnitude lower than the critical fluxes and the corrosion rate of the canister will be determined by the rate of supply of sulphide under almost all conditions.

For intact bentonite and for the majority of cases with eroded bentonite, therefore, estimates based on the rate of supply of  $\text{HS}^-$  to the canister will provide a realistic prediction of the canister corrosion rate. For those few cases for eroded bentonite for which the estimated flux is greater than the critical flux for transport control, the predicted corrosion rate will over-estimate the actual rate. Thus, the earliest canister failures in SR-Site corresponding to the highest sulphide fluxes are likely to occur later than currently predicted.

Based on the results of short-term electrochemical polarization studies and thermodynamic considerations of the relative stability of  $\text{Cu}_2\text{S}$  and dissolved copper-chloro complex ions, there is no evidence to suggest that sulphide ions will not be permanently sequestered by the corrosion process. Furthermore, the  $\text{Cu}_2\text{S}$  film does not appear to catalyse the cathodic evolution of  $\text{H}_2$ , a process that might otherwise lead to a non-conservative estimate of the corrosion rate.

It is believed that the rate of sulphide transport is correctly estimated in the corrosion assessment presented in support of SKB's license application. Although the rate of gaseous  $\text{H}_2\text{S}$  transport in unsaturated bentonite formed during the early thermal transient would be higher, rate control of the corrosion reaction would simply be determined by the transport of dissolved  $\text{HS}^-$  across that part of the bentonite and/or host rock that remained saturated. Episodic changes of sulphide concentrations in ground water will most probably occur, but will be within the concentration ranges already analysed. In the unlikely case of oxygen penetrating all the way to the canister surface during a glacial event, accelerated corrosion due to the catalysis of the  $\text{O}_2$  reduction reaction by a pre-existing  $\text{Cu}_2\text{S}$  film may occur, but will not increase the total corrosion by oxygen as this is limited by the amount of oxygen that can reach repository depth.

It is concluded, therefore, that the rate of corrosion of copper canisters during the long-term anaerobic phase will be bounded by the rate of supply of sulphide at all times.

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## Audit list

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