Sulphide-transport control of the corrosion of copper canisters

Fraser King, Jian Chen, Zack Qin, David Shoesmith & Christina Lilja

Published online: 23 Aug 2017.

Submit your article to this journal ↗

Article views: 112

View related articles ↗

View Crossmark data ↗

The Institute of Materials,
Minerals and Mining

Taylor & Francis
Taylor & Francis Group

Sulphide-transport control of the corrosion of copper canisters

Fraser King[a], Jian Chen[b], Zack Qin[b], David Shoesmith[b] and Christina Lilja[c]

[a]Integrity Corrosion Consulting Ltd, Nanaimo, BC, Canada; [b]Department of Chemistry, University of Western Ontario, London, ON, Canada; [c]Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden

ABSTRACT
The long-term anaerobic corrosion rate of copper canisters in a KBS-3 repository is calculated on the basis of sulphide-transport control. The nature of the anodic and cathodic rate-determining steps, as well as the controlling process for the overall corrosion reaction of copper in sulphide environments, are considered. Evidence indicates that the assumption of sulphide-transport control is valid for the overwhelming majority of ground water flow rates and sulphide concentrations considered in the Swedish SR-Site safety assessment. There is no evidence that canister lifetimes calculated on the basis of sulphide-transport control are non-conservative.

This paper is part of a supplement on the 6th International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems.

Introduction

The copper canister is an important component of the KBS-3 concept for the deep geological disposal of spent nuclear fuel [1]. Because of the small quantity of oxidants and the limited rate of mass transport in the repository, the canister is expected to remain intact from corrosion for periods exceeding 10^5 years with the vast majority of the canisters surviving for periods in excess of 10^6 years [2]. These lifetime predictions are supported by a mechanistic understanding of the general and localised corrosion behaviour of copper under repository conditions, as well as of processes such as stress corrosion cracking that are not expected to occur [3].

After a brief period of aerobic conditions, the repository environment is expected to become anaerobic and to remain so. During this anaerobic period, which will prevail for >99.9% of the lifetime of the canister, the repository environment will be dominated by the presence of sulphide ions (HS^-) naturally present in deep Fennoscandian Shield ground waters [3]. In the presence of HS^-, copper will corrode under anaerobic conditions accompanied by the evolution of H_2:

$$2Cu + HS^- + H_2O \rightarrow Cu_2S + H_2 + OH^- \qquad (1)$$
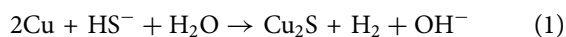
The extent of general corrosion during the aerobic period, due to the presence of O_2 trapped in the pores of the buffer and backfill materials in which the canisters are emplaced and of oxidising radiolysis products produced by the irradiation of moist air and/or bentonite pore water immediately adjacent to the canister, is treated in the safety assessment using mass-balance arguments [2]. Since the development of the KBS-3 disposal concept, it has been conservatively assumed that the rate of corrosion due to the presence of HS^- during the anaerobic period is determined by the rate of supply of sulphide to the canister surface through the surrounding highly compacted bentonite buffer [1,2].

In separate reviews of the Swedish [4] and Canadian [5] nuclear waste programmes, reviewers have asked for evidence for the conditions under which Reaction (1) can be expected to be under mass-transport control. In addition, the question has been raised whether there are any circumstances under which the assumption of transport control may be non-conservative. The assumption of transport control can only be non-conservative if the HS^- plays the role of a catalyst in the corrosion process, i.e. it participates in the reaction but is not consumed.
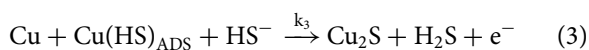
Here, evidence is presented to confirm that the rate of corrosion of the copper canisters by Reaction (1) will be under mass-transport control for the overwhelming majority of hydrogeological conditions possible in the repository. Electrochemical data are used to define the rate of the interfacial reactions, which are then compared with estimates of the sulphide flux used in the SR-Site safety assessment [1,2]. Then, evidence is presented to demonstrate that HS^- does not act as a catalyst in the corrosion reaction. Catalysis of the corrosion reaction by sulphide could occur in one of two ways; first, if HS^- participates in the oxidation (sulphidation) of Cu but is not consumed (not sequestered) in the reaction (i.e. contrary to the stoichiometry in Reaction (1), one HS^- ion leads to the oxidation of more than two Cu atoms) and, second, if the Cu_2S film catalyses the cathodic reaction and if the overall rate of corrosion is under cathodic control (for which there is some evidence in *aerobic* systems [6,7]). The current analysis is based on existing data from the literature, and no new experimental results are presented here.

## Rate-controlling process for the corrosion of copper in sulphide environments

Kinetic versus transport control

The mechanism of the anodic interfacial reaction between copper and HS^- at potentials close to the corrosion potential (E_{CORR}) is given by [8–10]

$$Cu + HS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cu(HS)_{ADS} + e^- \qquad (2)$$

$$Cu + Cu(HS)_{ADS} + HS^- \xrightarrow{k_3} Cu_2S + H_2S + e^- \quad (3)$$

where ks denote the respective interfacial rate constants. The overall anodic reaction is, therefore,

$$2Cu + 2HS^- \rightarrow Cu_2S + H_2S + 2e^- \quad (4)$$
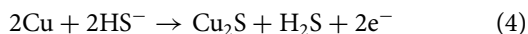
where the second step is rate-controlling and the two-step mechanism accounts for the observed Tafel slope of 40 mV and the second-order dependence of the reaction rate on $[HS^-]$ [8,9].

The rate of the overall reaction (expressed as a current density i_S) can be limited by the kinetics of the interfacial processes ($i_{kinetic}$) or by the rate of transport of HS^- to the surface ($i_{transport}$). (Because Reaction (3) is the slow step, the overall process is unlikely to be limited by the rate of transport of the corrosion product H_2S *away* from the surface). The rate of the interfacial process is determined by the concentration of reactant at the corroding surface c_0. This concentration may differ from that in the bulk c_∞ because of the limited rate of mass transport. At steady-state, the general expression for the overall reaction rate is given by [11]

$$\frac{1}{i_S} = \frac{1}{i_{kinetic}} + \frac{1}{i_{transport}} \quad (5)$$

Thus, if the interfacial kinetics are fast, the overall reaction rate is determined by the rate of transport, and vice versa. Mixed-control is also possible if the rates of the kinetic and transport processes are comparable.

The cathodic reaction involves the evolution of H_2. Although H_2O is present in excess, we believe that the species being reduced is actually HS^-

$$2HS^- + 2e^- \rightarrow H_2 + 2S^{2-} \quad (6)$$
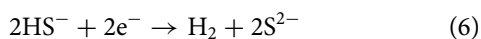
Work is continuing in this area, but two pieces of evidence point in this direction. First, based on mixed-potential theory, E_{CORR} lies close to the equilibrium potential for the cathodic reaction if the anodic reaction is transport limited (and vice versa) [12]. Evidence will be presented below that the anodic reaction is transport limited at E_{CORR}, especially in the restrictive mass-transport conditions in the repository. The equilibrium potential for the H_2O/H_2 reaction at pH 8 and 1 atm H_2 is −0.71 V_{SCE} at 25°C [13,14]. Under the same conditions, the equilibrium potential for Reaction (6) is −0.89 V_{SCE} for an assumed $pK_2 = 16$ (where $K_2 = [H^+][S^{2-}]/[HS^-]$) [13,14]. In comparison, the E_{CORR} of Cu in the presence of HS^- is in the range −0.9 to −1.0 V_{SCE}, depending on the HS^- concentration and the rate of mass transport [9,10,15]. Thus, although the cathodic reduction of both H_2O and HS^- is thermodynamically possible, the observed E_{CORR} is closer to the equilibrium potential for Reaction (6). Second, recently obtained data indicate that Cu_2S films grow in H_2O-free HS^-/glycol solutions at approximately the same rate as in aqueous solutions, consistent with the suggestion that HS^- rather than H_2O is the species being cathodically reduced.

Since the S^{2-} produced by Reaction (6) will readily hydrolyse in water, the overall corrosion reaction obtained by adding Equations (4) and (6) is given by Equation (1). For a corrosion process involving one anodic and one cathodic reaction, the overall rate of corrosion may be either anodically or cathodically limited, both of which may be either kinetically or transport limited (or under mixed-control) (Figure

1). At E_{CORR}, the rates of the anodic and cathodic processes are equal and are equal to the rate of the slowest process, be that the anodic or cathodic interfacial or transport steps. Even if the rate of supply of HS^- is not the overall slowest step, the overall rate of corrosion cannot be faster, in which case prediction of the canister lifetime on the basis of the rate of sulphide transport would be conservative.

Anodic kinetics

Smith and coworkers [8–10] determined the anodic kinetics of copper in sulphide solutions as a function of the $[HS^-]$ and the rate of sulphide supply using a rotating disc electrode (RDE). Using this technique, it is possible to separate the kinetic and transport components of the overall current density based on Equation (5) using Koutecky–Levich (K-L) plots, on the basis of which the reaction mechanism in Equations (2) and (3) was determined. The K-L plots also enable the rate of the interfacial kinetic process to be determined, from which the following relationship was derived [9]

$$i_{kinetic} = nFk[HS^-]_0^2 \exp\left\{\frac{(1+\alpha)F}{RT}E\right\}$$
$$\times \exp\left\{-\frac{F}{RT}(E_2^0 + \alpha E_3^0)\right\} \quad (7)$$

where E is the potential, E_2^0 and E_3^0 are the standard potentials for Equations (2) and (3), respectively, α is the transfer coefficient and n is the number of electrons for the slow electron-transfer step (Equation (3)), $k = k_2k_3/k_{-2}$, $[HS^-]_0$ is the interfacial sulphide concentration and F, R, and T are the Faraday constant, gas constant, and absolute temperature, respectively. Values for k (5.86×10^{-5} cm^4/ mol s), n (1), and α (0.5) can be obtained from analysis of the K-L data given by Smith [8,9]. Values of
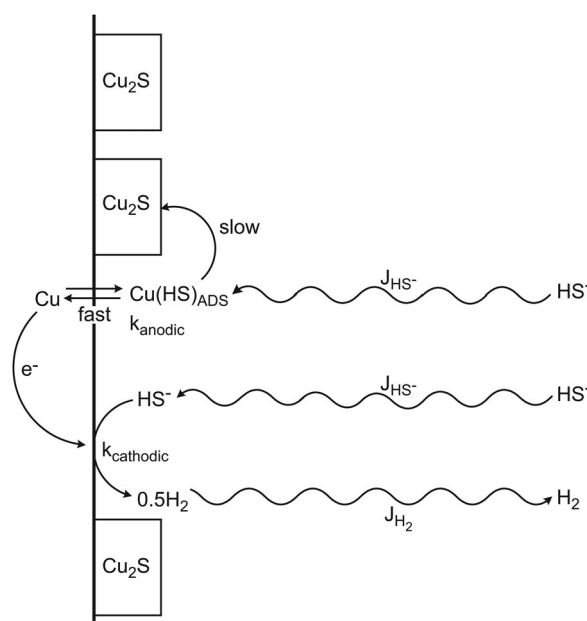

Figure 1. Overall reaction scheme for the corrosion of copper in sulphide solutions. The two interfacial reactions involve the anodic formation of Cu_2S supported by the cathodic reduction of HS^-. Both anodic and cathodic reactions may be limited by the rates of the respective interfacial (kinetic control) or mass-transport steps (transport control), the latter denoted by the wavy lines and the notation J for the flux of reactants or products.

$E_2^0 = -1.63 V_{SCE}$ and $E_3^0 = -0.28 V_{SCE}$ are based on the data in Protopopoff and Marcus [16] (assuming Cu $(HS)_{ADS}$ has the same free energy of formation estimated for CuS_{ADS} in Protopopoff and Marcus [16]).

Cathodic kinetics

There are no data available for the cathodic reduction of HS⁻ on copper. However, Sharifi-Asl and Macdonald [17] have studied the reduction of H_2O on Cu in buffered borate solutions and presented kinetic data in the form of the simplified Butler–Volmer expression

$$i_{cathodic} = -i_0 \exp\left(-\frac{\alpha_c n_c F}{RT}(E - E_{eq})\right) \tag{8}$$

where α_c is the cathodic transfer coefficient, n_c is the number of electrons, E_{eq} is the equilibrium potential, and the exchange current density i_0 is a function of pH, H_2 pressure, and temperature. [17]

Rate-controlling step in laboratory experiments

Evidence from the variation of E_{CORR}

The corrosion potential of copper in sulphide environments has been measured in bulk stagnant solution [9,10] and in experiments in which a 1-mm-thick layer of compacted bentonite was used to separate the copper electrode form the bulk solution [15]. Figure 2 shows the calculated current–potential
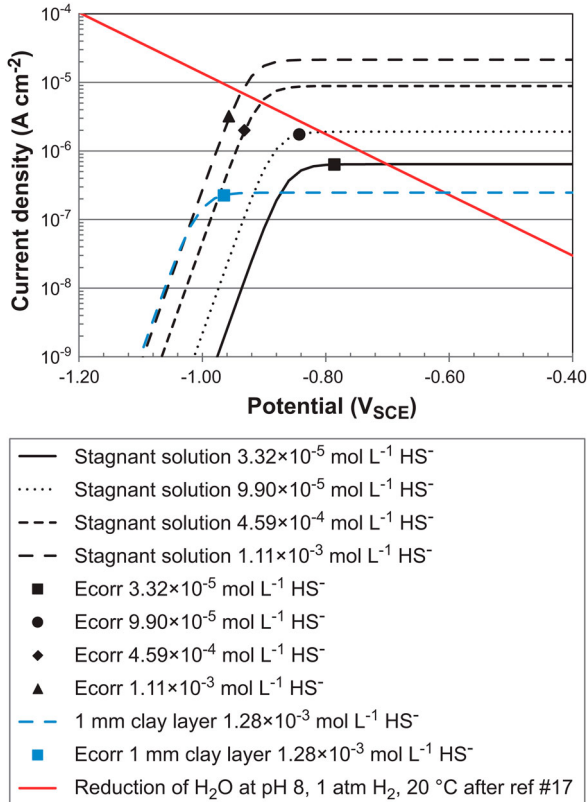

Figure 2. Comparison of the kinetics of the anodic dissolution of copper in sulphide solutions with the value of E_{CORR} measured in separate experiments under similar conditions. Anodic dissolution curves are based on Equation (5) and take into account the effect of kinetic and transport contributions to the net current density. Corrosion potential data are shown for experiments in stagnant solution from Smith [9] and for a clay-covered electrode from King et al. [15]. For comparison, the current–potential curve for the cathodic reduction of H_2O taken from Sharifi-Asl and Macdonald [17] is also shown.

behaviour for the anodic dissolution reaction under the conditions of these experiments, with the measured E_{CORR} values superimposed on the i–E curves. The net anodic current densities are based on Equation (5), with the kinetic component calculated from Equation (7) and the transport-limited current density given by

$$i_{transport} = nF[HS^-]k_M \tag{9}$$

where k_M is the steady-state mass-transfer coefficient given by $k_M = D/\delta$, where D is the diffusion coefficient of HS⁻ and δ is the diffusion layer thickness. For stagnant solution, we estimate a k_M value of approximately 10^{-4} cm/s based on a diffusion coefficient of 10^{-5} cm²/s and an assumed diffusion layer thickness of 0.1 cm. For the 1-mm-clay-covered electrode, we estimate a mass-transfer coefficient of 10^{-6} cm/s because of a reduction of the effective diffusivity of HS⁻ by approximately two orders of magnitude due to the porosity and tortuosity of the network of pores in the compacted bentonite [18]. The potential-independent regions of the curve indicate transport control of the anodic reaction at more-positive potentials and/or lower [HS⁻], with kinetic control at more-negative potentials indicated by the Tafel slope of 40 mV/decade consistent with the reaction mechanism in Equations (2) and (3).

In stagnant solution, the nature of the rate-controlling step for the anodic reaction under freely corroding conditions depends on the sulphide concentration. At the lowest [HS⁻] shown in Figure 2 (3.32×10^{-5} mol/L), the anodic reaction is under transport control at E_{CORR}, as indicated by the location of the corrosion potential in the transport-limited region of the i–E curve. With increasing [HS⁻], the reaction gradually changes to joint kinetic-transport control at intermediate concentrations to complete kinetic control of the anodic reaction at E_{CORR} in 1.11×10^{-3} mol/L sulphide solution. However, transport control of the anodic reaction can be re-established at high [HS⁻] by restricting the rate of mass transport, as in the case for the 1-mm-thick clay-covered electrode in Figure 2. Thus, the anodic reaction is under transport control in the laboratory in stagnant solutions with [HS⁻] of less than approximately 10^{-4} mol/L or in the presence of a 1-mm clay layer at [HS⁻] of 1.28×10^{-3} mol/L HS⁻. The flux of HS⁻ in the repository will be much lower than for the experimental conditions shown in Figure 2. For example, for a ground water sulphide concentration of 1 mg/L (3×10^{-5} mol/L), the estimated HS⁻ flux is of the order of 10^{-16} mol/cm² s for a minimum bentonite thickness of 35 cm. In contrast, the flux of sulphide in stagnant solution in the laboratory experiment for a HS⁻ concentration of 9.90×10^{-5} mol/L (corresponding to the onset of joint transport-kinetic control based on the data in Figure 2) is of the order of 10^{-11} mol/cm² s, approximately five orders of magnitude higher than in the repository.

Also shown in Figure 2, the cathodic current–potential curve based on Equation (8) and the results of Sharifi-Asl and Macdonald [17] at 20°C for pH 8 and 1 atm H_2 pressure. There is generally poor agreement between the theoretical E_{CORR} (as given by the intersection of the anodic and cathodic i–E curves) and the measured values, especially for the clay-covered electrode. This lack of agreement is consistent with our current belief that the cathodic reaction involves electron transfer to HS⁻ rather than to H_2O, although further work is required to clarify this mechanism.
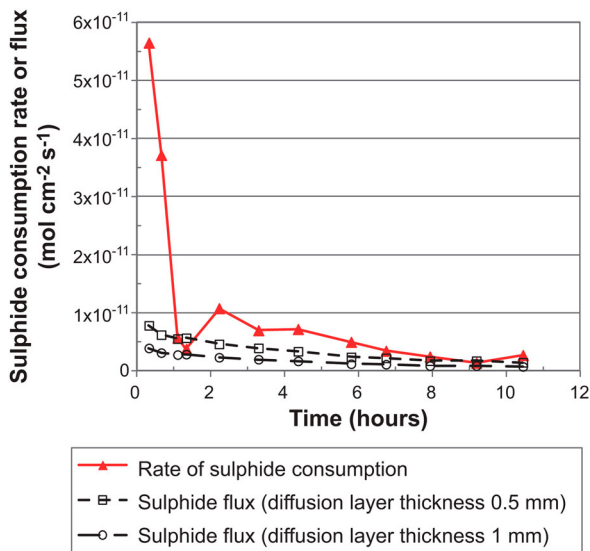
Figure 3. Comparison of the rate of sulphide consumption and the estimated flux to the copper surface for two assumed diffusion layer thicknesses for stagnant solution. Initial sulphide concentration of 5×10^{-5} mol/L in 0.1 mol/L NaCl.

Evidence from sulphide-depletion and Cu$_2$S film-growth studies

There is evidence from the data in Figure 2 for (partial) transport control of the anodic reaction in stagnant solution. With decreasing [HS$^-$] and decreasing rate of mass transport, the extent of transport control of the anodic reaction is expected to increase. Two experiments were conducted to determine the conditions under which, in bulk solution, the overall corrosion reaction becomes transport limited.

First, the rate of sulphide consumption (taken to be a measure of the rate of corrosion) was measured by monitoring the time-dependent decrease in pH due to the depletion of HS$^-$, based on the dissociation of HS$^-$ [19,20]

$$S^{2-} + H_2O = HS^- + OH^- \tag{10}$$

In stagnant 0.1 mol/L NaCl solution containing 5×10^{-5} mol/L HS$^-$, the rate of consumption of HS$^-$ (as determined by the rate of change of pH) was estimated to be the same as the rate of supply of sulphide to the electrode surface (Figure 3), as the consumption rate falls into the same region as the calculated flux (the initial higher rate occurs under transient diffusive conditions). This flux, estimated to be 2×10^{-12} mol/cm^2 s (Figure 3), therefore represents the sulphide flux for which the corrosion reaction is under transport control.

Second, the properties and growth rate of Cu$_2$S films formed under freely corroding conditions were measured as a function of the [HS$^-$] and [Cl$^-$]. It is known that the structure and growth rate of the Cu$_2$S film formed in chloride solutions depend on the [HS$^-$], [Cl$^-$], [Cl$^-$]: [HS$^-$] ratio, as well as the rate of HS$^-$ supply to the copper surface [19]. Three different film structures are observed as a function of the [HS$^-$] and [Cl$^-$] of the solution (Figure 4):

- A porous single-layer Cu$_2$S film formed at relatively low [HS$^-$] which grows at a constant rate, consistent with a porous, non-passive surface layer (denoted P1).
- A compact single-layer Cu$_2$S film formed at high [HS$^-$] that appears more protective and grows with parabolic kinetics (denoted C).
- A porous, columnar Cu$_2$S film formed at high [Cl$^-$]:[HS$^-$] ratio (denoted P2).

The range of [HS$^-$] and [Cl$^-$] in deep Swedish ground waters is also shown in Figure 4. Porous P1-type films would be expected under repository conditions, especially since the interfacial [HS$^-$] would be much lower at the canister surface than at the surface of the electrode in these tests in bulk solution because of the low rate of transport of HS$^-$ through highly compacted bentonite.
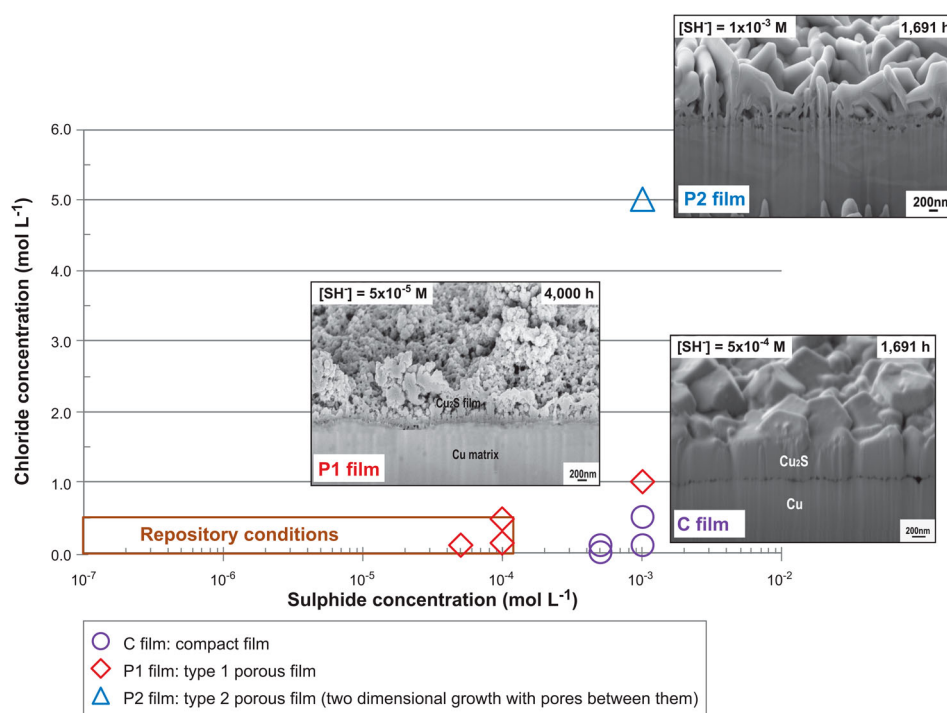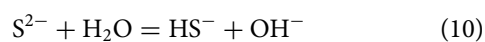

Figure 4. Dependence of the Cu$_2$S film structure on the sulphide and chloride concentration of the solution in which it was formed. The P1 and P2 films are porous, and the C film is compact. The range of sulphide and chloride concentrations in deep Swedish ground waters is also shown.
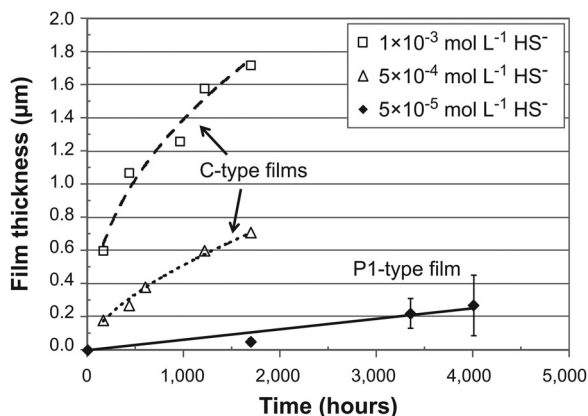
Figure 5. Comparison of the growth kinetics of P1-type and C-type Cu₂S films in 0.1 mol/L NaCl solutions with various concentrations of HS⁻. Further experimental details are given in Chen et al. [19].

Rate-controlling step in repository environments

The flux of sulphide to the canister surface in the repository is several orders of magnitude lower than that in the laboratory experiments. Figure 6 compares the flux of sulphide for a representative sub-set of the conditions in the thousands of deposition holes considered for SR-Site with the threshold flux for sulphide-transport control of the corrosion reaction, based on the sulphide-depletion and linear-film-growth studies described above. Estimated repository fluxes are shown for both the intact and eroded bentonite buffer scenarios [1,2], as well as for steady-state diffusional flux through compacted bentonite. (The intact buffer case flux is lower than the steady-state diffusion due to the transport resistance of solutes going from fractures in the rock into the bentonite.) Also shown in the figure are the estimated corrosion rates for the experiments in stagnant solution in Figure 2, expressed in terms of the corresponding flux of sulphide.

As shown in Figure 6, the vast majority of the repository fluxes are several orders of magnitude below the threshold flux for sulphide-transport control. In the case of intact bentonite, the difference is at least two orders of magnitude. For the case of eroded bentonite, all repository fluxes are at least one order of magnitude lower than the threshold sulphide flux determined from the laboratory sulphide-depletion experiment. Even if we take the lower threshold flux estimated from the linear-film-growth study, all but a few estimated repository sulphide fluxes (those for a combination of the highest sulphide concentration and the highest ground water fluxes from the 50,000 combinations considered) lie below the threshold value.
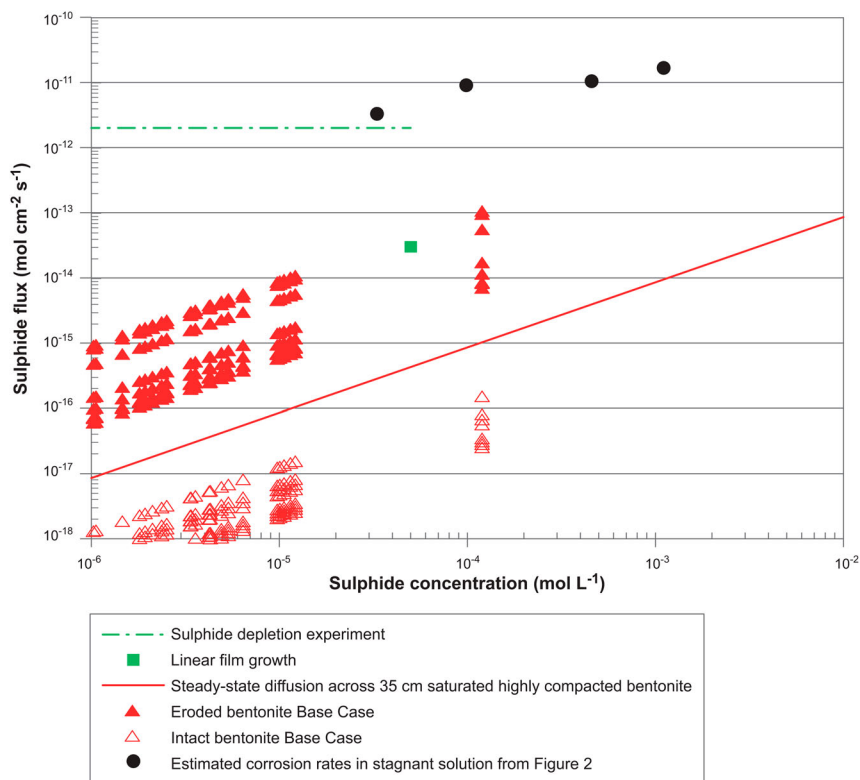
Figure 5 compares the linear-film-growth kinetics for the porous P1-type film with the parabolic kinetics observed for the compact C-type film. The linear kinetics for the P1 film are consistent with a transport-limited process and can be used to estimate the sulphide flux under transport-controlled conditions. For a Cu₂S density of 5.6 g/cm³ [21], a molecular mass of 159.14 g/mol, and an assumed film porosity of 0.5, the flux of HS⁻ corresponding to the linear-film-growth rate in Figure 5 is $3 \pm 2 \times 10^{-14}$ mol/cm² s.

In summary, therefore, at bulk HS⁻ concentrations greater than approximately 5×10^{-4} mol/L, the anodic reaction is kinetically controlled. At lower [HS⁻] and lower rates of mass transport, the overall corrosion reaction becomes limited by the rate of supply of HS⁻.

Sulphide depletion experiment — - · —
Linear film growth ■
Steady-state diffusion across 35 cm saturated highly compacted bentonite ——
Eroded bentonite Base Case ▲
Intact bentonite Base Case △
Estimated corrosion rates in stagnant solution from Figure 2 ●

Figure 6. Comparison of the flux of sulphide to the canister in the repository (red) with the estimated threshold flux for sulphide-transport control (green) of the overall corrosion reaction. Repository fluxes for intact and eroded bentonite are taken from the Base Case analyses performed for SR-Site [2]. Only the 8 deposition positions with the highest fluxes, out of 10,000, are shown. The sulphide flux corresponding to the estimated corrosion rate for experiments in stagnant bulk solution in Figure 2 is also shown (black).

Thus, there is overwhelming evidence in support of the assumption that the corrosion rate of the canister will be determined by the rate of supply of HS^-.

Is the assumption of transport control conservative?

Sulphide sequestration

For the assumed stoichiometry in Equation (1), corrosion rates based on the rate of supply of HS^- will not underestimate the actual rate provided that 1 mol HS^- corrodes no more than 2 mol Cu. Chloride ions increase the solubility of Cu(I) through the formation of cuprous-chloro complex ions, such as $CuCl_2^-$ and $CuCl_3^{2-}$, and will drive the dissolution reaction

$$Cu_2S(cr) + H^+ = 2Cu^+ + HS^- \qquad (11)$$
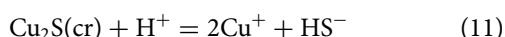
to the right. The solubility product for the dissolution of Cu_2S ($^*K_{sp}^0$) is $10^{-34.02}$ [13]. Similarly, the stability constant of $CuCl_2^-$ (β_2^0)

$$Cu^+ + 2Cl^- = CuCl_2^- \qquad (12)$$
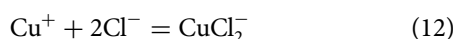
is $10^{5.62}$ [13]. Combining the expressions for $^*K_{sp}^0$ and β_2^0 gives an expression for the concentration of $CuCl_2^-$ in equilibrium with $Cu_2S(cr)$ as a function of $[Cl^-]$, $[HS^-]$, and pH

$$[CuCl_2^-] = \frac{\beta_2^0[Cl^-]^2(^*K_{sp}^0)^{1/2}[H^+]^{1/2}}{[HS^-]^{1/2}} \qquad (13)$$

The dependence of $[CuCl_2^-]$ on $[HS^-]$ is shown in Figure 7 for chloride concentrations of 0.1, 1.0, and 5 mol/L at pH 8. The equilibrium $CuCl_2^-$ concentrations are exceedingly small for the range of $[Cl^-]$ and $[HS^-]$ found in deep Swedish ground waters (up to approximately 0.5 mol/L Cl^- and 10^{-5} mol/L HS^-) and virtually all Cu(I) will exist as precipitated Cu_2S (The results are similar if the higher cuprous-chloro complexes, such as $CuCl_3^{2-}$, are also considered.). Higher dissolved $[CuCl_2^-]$ are possible at high $[Cl^-]$ and/or low $[HS^-]$. Lower $[HS^-]$ might exist at the base of pores in a Cu_2S film where geometrical constraints limit sulphide transport into the pore. Indeed, a mechanism involving the formation of dissolved $CuCl_2^-$ within the pores has been proposed to account for the P2 columnar film structure observed on copper in sulphide solutions in high $[Cl^-]$ shown in Figure 4 [19,20]. However, any dissolved $CuCl_2^-$

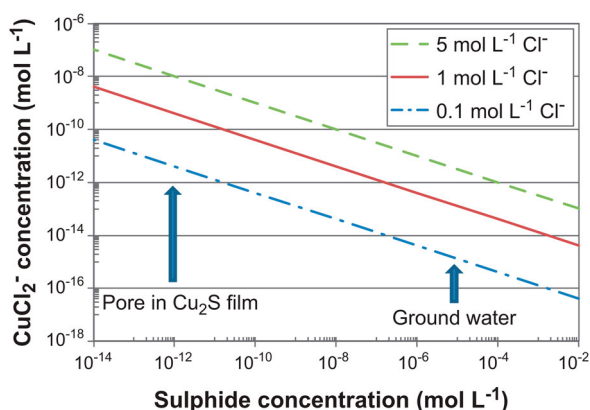exiting the pores would be immediately precipitated as Cu_2S as it encounters the higher $[HS^-]$ in the surrounding environment.

The irreversible sequestration of copper as Cu_2S is supported by the comparison of the oxidation and corresponding reduction charges during cyclic voltammetry in sulphide solutions. The ratio of the cathodic reduction charge Q_C to the anodic oxidation charge Q_A is close to one [10], indicating that all of the oxidised copper remains on the electrode surface as precipitated Cu_2S and is subsequently reduced on the cathodic cycle.

There is no evidence, therefore, that HS^- is not irreversibly sequestered as precipitated Cu_2S during the corrosion of copper in sulphide environments implying that corrosion rates estimated on the basis of sulphide-transport control are conservative.

Catalysis of cathodic reaction by Cu₂S film

Cuprous sulphide films are known to catalyse the oxygen reduction reaction and can lead to accelerated corrosion rates under *aerobic* conditions even when the source of HS^- is removed [6,7]. However, such a catalytic effect, even if it does occur under *anaerobic* conditions, would not invalidate canister corrosion rates based on the assumption of sulphide-transport control.

Catalysis of the cathodic reaction would only lead to accelerated corrosion rates if the overall corrosion reaction was under cathodic kinetic control. There is strong evidence, as discussed above, that the corrosion rate is transport limited for $[HS^-]$ less than approximately 10^{-5} to 10^{-4} mol/L in stagnant solutions. Certainly, for the restrictive mass-transport conditions and the low $[HS^-]$ in the repository, the corrosion rate will be limited by the supply of sulphide and the catalysis of the cathodic reaction would have no impact.

Therefore, we conclude that the catalytic effect of Cu_2S films on the cathodic reaction in aerobic systems will not lead to accelerated corrosion under anaerobic conditions in the repository.

Conclusions

An analysis has been conducted of the rate-controlling processes for the anodic, cathodic, and overall corrosion reactions for copper in sulphide environments. At bulk HS^- concentrations greater than approximately 5×10^{-4} mol/L, the anodic reaction is kinetically controlled. At lower $[HS^-]$ and lower rates of mass transport, the overall corrosion reaction becomes limited by the rate of supply of HS^-, most likely because the anodic reaction becomes transport limited. In laboratory experiments in bulk solution, there is evidence that the corrosion rate is limited by the rate of supply of sulphide for HS^- fluxes below 3×10^{-14} to 2×10^{-12} mol/cm^2 s. In the SR-Site safety assessment, 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} mol/cm^2 s. For the case where the buffer is lost due to erosion, the overwhelming majority of combinations of ground water flow rates at deposition holes and sulphide concentrations also give sulphide fluxes below 10^{-14} mol/cm^2 s. When pessimistically combining the highest sulphide concentrations with the highest ground water

Figure 7. Concentration of $CuCl_2^-$ ions in equilibrium with $Cu_2S(cr)$ as a function of sulphide concentration for various chloride concentrations at pH 8, 25°C.

fluxes from the hydrogeological modelling, sulphide fluxes around 2×10^{-13} mol/cm^2 s are estimated. These highly unlikely fluxes are within the range of critical sulphide fluxes estimated above. However, for intact bentonite and for the majority of cases for the eroded bentonite, the expected HS$^-$ flux in the repository is several orders of magnitude lower than the threshold flux and the corrosion rate of the canister will be determined by the rate of supply of sulphide.

There is no evidence to indicate that the assumption of a transport-limited corrosion rate is non-conservative. All evidence suggest that sulphide is irreversibly sequestered in the form of precipitated Cu$_2$S, with one mole of HS$^-$ leading to the corrosion of 2 moles of copper. Furthermore, catalysis of the cathodic reaction by a Cu$_2$S film, as can occur in aerobic systems, would not lead to accelerated corrosion of the canister under the long-term anaerobic conditions in the repository.

Disclosure statement

Funding

References

[1]   Swedish Nuclear Fuel and Waste Management Company. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project. Swedish Nuclear Fuel and Waste Management Company Report; 2011 (SKB TR 11-01).

[2]   Swedish Nuclear Fuel and Waste Management Company. Corrosion calculations report for the safety assessment SR-Site. Swedish Nuclear Fuel and Waste Management Company Report; 2010 (SKB TR 10-66).

[3]   King F, Lilja C, Pedersen K, et al. An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geologic repository. Swedish Nuclear Fuel and Waste Management Company Report; 2010 (SKB TR 10-67).

[4]   Scully JR, Hicks TW. Initial review phase for SKB's safety assessment SR-Site: corrosion of copper. Strålsäkerhetsmyndigheten technical note; 2012. 2012:21.

[5]   Scully JR, Edwards M, 2013. Review of the NWMO copper corrosion allowance. Nuclear Waste Management Organization, Canada (NWMO TR-2013-04).

[6]   Jacobs S, Edwards M. Sulfide scale catalysis of copper corrosion. Water Res. 2000;34:2798–2808.

[7]   Syrett BC. Accelerated corrosion of copper in flowing pure water contaminated with oxygen and sulfide. Corrosion. 1977;33:257–262.

[8]   Smith J, Qin Z, King F, et al. The electrochemistry of copper in aqueous sulphide solutions. In: Van Iseghem P, editor. Scientific Basis for Nuclear Waste Management XXIX: proceedings of a meeting held in Ghent, Belgium, 12–16 September 2005. Warrendale (PA): Materials Research Society; 2006. p. 869–875. (Materials Research Society Symposium Proceedings 932).

[9]   Smith JM. The corrosion and electrochemistry of copper in aqueous, anoxic sulphide solutions [Ph.D. thesis]. University of Western Ontario; 2007.

[10] Smith J, Qin Z, King F, et al. Sulfide film formation on copper under electrochemical and natural corrosion conditions. Corrosion. 2007;63:135–144.

[11] Lefrou C, Nogueira RP, Huet F, Takenouti H. Electrochemistry. In: Cottis RA, Graham MJ, Lindsay R, Lyon SB, Richardson JA, Scantlebury JD, Stott FH, editors. Shreir's corrosion. 4th ed. Elsevier; 2010. Chapter 1.02, Vol. 1: basic concepts, high temperature corrosion.

[12] Shoesmith DW. Kinetics of aqueous corrosion. In ASM Handbook, Volume 13A, Corrosion: fundamentals, testing and protection. Materials Park (OH): ASM International; 2003. p. 42–51.

[13] Puigdomenech I, Taxén C. Thermodynamic data for copper. Implications for the corrosion of copper under repository conditions. Swedish Nuclear Fuel and Waste Management Company Report; 2000 (SKB TR 00-13).

[14] Macdonald DD, Sharifi-Asl S. Is copper immune to corrosion when in contact with water and aqueous solutions? Swedish Radiation Safety Authority Report; 2011 (SSM 2011:09).

[15] King F, Kolář M, Vähänen M. Reactive-transport modelling of the sulphide-assisted corrosion of copper nuclear waste containers. In Kursten B, Feron D, Druyts F, editors. Sulphur-assisted corrosion in nuclear disposal systems. Leeds, UK: Maney Publishing; 2011. Chapter 9, European Federation of Corrosion, Vol. 59; p. 152–164.

[16] Protopopoff E, Marcus P. Potential–pH diagrams for sulfur and hydroxyl adsorbed on copper surfaces in water containing sulfides, sulfites or thiosulfates. Corros Sci. 2003;45:1191–1201.

[17] Sharifi-Asl S, Macdonald DD. Investigation of the kinetics and mechanism of the hydrogen evolution reaction on copper. J Electrochem Soc. 2013;160:H382–H391.

[18] King F, Kolar M, Shoesmith DW. Modelling the effects of porous and semi-permeable layers on corrosion processes, CORROSION/96. Houston (TX): NACE International; 1996. Paper no. 380.

[19] Chen J, Qin Z, Shoesmith DW. Key parameters determining structure and properties of sulphide films formed on copper corroding in anoxic sulphide solutions. Corros Eng Sci Technol. 2014;49:415–419.

[20] Chen J, Qin Z, Wu L, et al. The influence of sulphide transport on the growth and properties of copper sulphide films on copper. Corros Sci. 2014;87:233–238.

[21] Lide DR, editor. CRC Handbook of Chemistry and Physics, 2003–2004 edition. Boca Raton (FL): CRC Press; 2003.