Copper corrosion in bentonite/saline groundwater solution: Effects of solution and bentonite chemistry

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Copper corrosion has been studied in simulated groundwater with and without added bentonite clay using different electrochemical techniques. The corroded surfaces were characterised by SEM/EDS, Raman spectroscopy and Auger depth profiling. In both environments small amounts of sulphide (0.005 mM) control the early corrosion behaviour. Under aerated conditions an initially formed Cu2S film is rapidly converted to a non-protective layer of cuprite and corrosion proceeds with the deposition of an outer layer of atacamite. In the presence of bentonite corrosion proceeds slowly under O2 transport control. No atacamite is observed and the Cu surface appears slightly pitted.

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1. Introduction

Both the Scandinavian and Canadian high-level radioactive waste disposal programs propose to place spent nuclear fuel in tightly sealed copper canisters in a geologic repository backfilled with compacted bentonite clay [1,2]. By supplementing engineered barriers with naturally occurring materials, it is hoped to closely imitate nature [3]. Since the Cu container is the only absolute barrier to the release of radionuclides, its corrosion has been studied extensively [2,3–14].

The initial rate of Cu corrosion will be determined by factors such as moisture, temperature, and the presence of aggressive groundwater species like chlorides, nitrates and sulphates [1]. In the longer term the corrosion process will evolve towards steady state at a rate depending on the corrosive environment (chemical composition, pH, resistivity), and the metallurgical properties of the container.

When exposed to humid air, Cu oxidises to Cu2O, which protects it from further corrosion [15]. However, in the presence of aggressive species, secondary corrosion processes occur. In the fields of atmospheric and archaeological corrosion the resulting film is referred to as a patina [16,17]. The structure of natural patinas grown on artefacts exposed for long periods of time depends on whether exposure was to soil, atmosphere, water or seawater. For atmospheric corrosion, the rates over a 20-year exposure period were reported to be 1 μm/year, 0.8 μm/year and 0.5 μm/year for industrial, marine and rural atmospheres, respectively [17]. Cu is also resistant to corrosion in seawater [17].

The design lifetime of the Cu container is >10⁶ years [2]. On sealing, a limited amount of air will be trapped in the repository in the low permeability groundwater-saturated bentonite surrounding the container [1]. This O2 will be consumed by reactions with minerals and organic material in the rock and the bentonite as well as container corrosion. Once this O2 has been consumed, further corrosion is most likely to be sustained by a supply of dissolved SH− to the copper surface [1]. Consequently, extensive study of Cu corrosion in sulphide systems under anoxic conditions has been undertaken [9–13]. However, it is likely that small amounts of sulphide could also influence corrosion during the early oxic repository period.

The influence of sulphide in chloride environments has been investigated under different conditions, especially on Cu–Ni alloy corrosion in seawater polluted by SH− [18–24], including studies in the presence of inhibitors [20–22,24]. Small concentrations of SH− have been shown to accelerate the anodic reaction in the overall corrosion process [23], and it has been suggested that SH− ions compete with BTAH inhibitor molecules for adsorption on a Cu surface [21].

Our previous studies on Cu corrosion under oxic conditions in the presence of bentonite saturated with groundwater yielded a corrosion rate around 1 μm/year after 3.5 years of exposure [14,24]. In that study, Cu corrosion sensors and impedance spectroscopy were used to evaluate the corrosion rate, but many
questions remained unanswered, including the effects of solution chemistry in the presence of bentonite. The focus of this paper is on a comparison of the initial corrosion behaviour of Cu in oxic saline groundwater with and without bentonite. A range of electrochemical techniques including electrochemical impedance spectroscopy (EIS) has been used and supplemented by spectroscopic analyses using Raman and Auger spectroscopy and FIB/SEM analysis.

2. Experimental

2.1. Electrode preparation and solutions

Discs, 16 mm in diameter, were cut from 2 mm thick oxygen free high conductivity (OHPC) Cu (99.99%) foil (Goodfellow Cambridge Ltd., UK). A Cu wire was attached to the back side of the disc, and the sides and the back of the electrode protected with epoxy paint. This assembly was embedded in a Teflon holder leaving a single exposed face with a surface area of 0.785 cm². Prior to measurements, the electrode was abraded with 1200-grit emery paper, polished to a mirror finish with 0.15 µm Al₂O₃ powder, ultrasonically treated in acetone for 3 min, and then dried. A saturated calomel reference electrode (SCE) and a Pt-grid counter electrode were used to fit and analyse the impedance spectra. Resistive measurements were performed three times.

For potentiodynamic and voltammetric experiments, an Autolab PGStat 100 (floating version expanded with Nova software 1.8) was used. The electrode was first held at E_corr for 1 h followed by a potentiodynamic scan from −0.25 V (vs. E_corr) to more positive potentials at a scan rate of 1 mV/s. The scan was reversed when a maximum current of 1 mA/cm² was reached. Cathodic stripping voltammograms (CSV) were performed at a scan rate of 10 mV/s from 0 V (vs. SCE) to −1.4 V (vs. SCE). Measurements were performed three times.

2.2. EIS measurements

EIS measurements were performed using a Solartron 1287 electrochemical interface and a Solartron 1255B frequency response analyser. The validity of impedance data was checked using the Kramers–Kronig transform. All measurements were performed at room temperature with the potential held at the value of the corrosion potential (E_corr) using a perturbation voltage signal of 5 mV (rms) applied over the frequency range from 10⁶ to 10⁻³ Hz. Eleven data points per decade were recorded. The corrosion potential was recorded prior to each EIS measurement. Zview 3.1c software was used to fit and analyse the impedance spectra.

2.3. Potentiodynamic and voltammetric experiments

For potentiodynamic and voltammetric experiments, an Autolab PGStat 100 (floating version expanded with Nova software 1.8) was used. The electrode was first held at E_corr for 1 h followed by a potentiodynamic scan from −0.25 V (vs. E_corr) to more positive potentials at a scan rate of 1 mV/s. The scan was reversed when a maximum current of 1 mA/cm² was reached. Cathodic stripping voltammograms (CSV) were performed at a scan rate of 10 mV/s from 0 V (vs. SCE) to −1.4 V (vs. SCE). Measurements were performed three times.

2.4. Spectroscopic measurements

2.4.1. SEM/FIB analysis

The surface and cross-sectional morphologies of corroded specimens were observed using a Leo 1540 focused ion beam (FIB) scanning electron microscope (SEM, Zeiss Nano Technology systems Division, Germany) and elementally analysed using an energy dispersive X-ray analyser (Inca Oxford Instruments) with an accelerating voltage of 20 keV.

2.4.2. Auger depth profiles

Auger data was obtained using a PHI 660 Auger electron spectrometer (AES) with an excitation energy of 5 keV. A 5 keV electron beam (650 nA current) was rastered over a 100 × 100 µm area. Sputtering was performed using a 3 keV Ar⁺ ion beam rastered over a 1 × 1 mm area of the surface. The sputtering rate under these conditions was determined to be 62 nm/min for a SiO₂ layer on Si. For each sample, a survey scan was acquired prior to depth profiling. The intensities for the elements Cu, O, Cl, S, and C were measured as a function of sputtering time. Time profiles were converted into depth profiles using a sputter rate determined by the depth profiling of a reference sample under identical conditions.

2.4.3. Raman spectroscopy

Raman spectra were recorded on a Renishaw model 2000 Raman spectrometer using a 632 nm laser excitation line. The power of the Melles Griot HeNe laser (3.5 mW) was set to 10% and focused on the sample by an Olympus microscope with a 50 × long working distance objective. Different integration times were used. The spectra are presented without baseline correction.

3. Results and discussion

3.1. Potentiodynamic polarization scans

Fig. 1 shows polarization curves (CP) recorded in a Cl⁻ solution, the simulated groundwater, and the bentonite slurry. The E_corr is ~−0.21V (vs. SCE) in the chloride solution, but ~40 to 60 mV lower in the simulated groundwater and the slurry both of which contain SH⁻. A similar decrease in E_corr in Cl⁻ solutions containing SH⁻ was observed by Rahmouni et al. [22]. At potentials negative to E_corr, the cathodic current is due to O₂ reduction, and H₂O reduction at more negative potentials. In the Cl⁻ solution, at potentials positive to E_corr the current is low until E > −0.14 V (vs. SCE). At potentials <−0.14 V (vs. SCE) formation of a passivating CuCl/Cu₂O layer
occurring, while above this potential the rapid increase in current has been attributed to the dissolution of Cu²⁺ [25]. Since the current continues to rise as the potential increases there is no indication that the anodic process is suppressed by the accumulation of CuI/Cu²⁺ corrosion product deposits. On the reverse scan the current rapidly switches to cathodic indicating that any corrosion products formed anodically are readily reducible and/or capable of catalysing O₂ reduction.

In the simulated groundwater containing SH⁻ an apparent small active to passive transition is observed at \( E > E_{\text{corr}} \). Since the constituent of the groundwater likely to influence Cu reactivity at these potentials is SH⁻, this can be taken as an indication that even at these small concentrations SH⁻ can influence the anodic process with the current peak being assigned to the formation of Cu₂S which retards active dissolution but only partially passivates the surface. At more positive potentials, and on the reverse scan, the behaviour is very similar to that observed in the Cl⁻ solution. At more positive potentials, and on the reverse scan, the behaviour is very similar to that observed in the Cl⁻ solution. In the bentonite slurry the cathodic current is significantly suppressed suggesting some O₂ may have been consumed by oxidizable species in the clay. At potentials positive to \( E_{\text{corr}} \), the current is significantly increased compared to the other two solutions, especially within the potential range \((-0.24 \text{ to } -0.28 \text{ V (vs. SCE)}\) where the active to passive transition is observed in the simulated groundwater. This very large increase in anodic current suggests a very significant anodic activation of the surface both in the CuI (\( E_{\text{corr}} \) to \(-0.14 \text{ V (vs. SCE)}\)) and Cu²⁺ (>\(-0.14 \text{ V (vs. SCE)}\)) regions.

### 3.2. Short-term corrosion experiments

Cathodic stripping voltammograms (CSV) were performed at a scan rate of 10 mV/s after various periods of corrosion (1 h, 4 h, 24 h) in aerated chloride solutions (0.181 M) with and without a low concentration of SH⁻ (0.005 mM). In the absence of SH⁻ cathodic reduction peaks are observed, Fig. 2a. The first peak can be attributed to the formation of an adherent corrosion film since it is fully formed within the first hour of exposure. The second peak is insignificant after 1 h of exposure but becomes the dominant reduction process after 24 h of exposure. Over the longer exposure period the initially formed layer thins slightly, or develops porosity, as indicated by the slight decrease in peak height. Other authors have noted this initially formed base layer becomes porous [22]. These features are consistent with the rapid formation of an adherent base layer followed by the accumulation of a thicker outer deposited layer.

Fig. 2b shows the CSVs recorded in a solution containing a similar [Cl⁻] plus 0.005 mM SH⁻. An apparently similar sequence of film formation processes is observed: a thin layer reduced at \(-0.1 \text{ V (vs. SCE)}\) and a thicker layer reduced at \(-1.1 \text{ V (vs. SCE)}\). The reduction peak 1 \((-0.1 \text{ V (vs. SCE)}\) is considerably smaller than that in the absence of SH⁻ and occurs at a less negative potential. This indicates the involvement of SH⁻ in the corrosion process, suggesting Cu reacts readily with SH⁻, as would be expected thermodynamically. This is consistent with the polarization curve, Fig. 1, which indicates a slight passivation of the surface occurred when SH⁻ was present. Previous experiments [9] in anaerobic SH⁻ solutions showed that the Cu₂S film formed at low [SH⁻] is porous and film growth controlled by the transport of SH⁻ in solution. However, as will be discussed below, SH⁻ is chemically unstable in aerated solutions. The observation of a reduction peak at \(-0.1 \text{ V (vs. SCE)}\) indicates small amounts of Cu₂O are also formed under these conditions. The reduction of Cu₂S would not occur until much more negative potentials [12]. Whether or not this Cu₂O is formed directly by the reaction of Cu with O₂ or involves the partial conversion of the initially formed Cu₂S is unresolved. The eventual observation of the much larger peak at \(-1.1 \text{ V (vs. SCE)}\) confirms that the initially formed Cu₂S/Cu₂O layer is not passive and allows the more extensive growth of the outer deposited layer. While this outer layer is most likely CuI/Cu²⁺ deposits, the Cu₂S film would also be reduced in this potential region [12].

Calculation of the thickness (\( d \)) of these layers, using the relationship \( d = QV/2Fr \) and assuming the film is predominantly Cu₂O in the absence of SH⁻ or Cu₂S/Cu₂O in the presence of SH⁻ (see below), confirms these observations. In this relationship \( Q (\text{C cm}^{-2}) \) is the charge per unit area obtained by integration of the peaks in Fig. 2, \( V \) is the molar volume (23.9 cm³ mol⁻¹ for Cu₂O, 28.2 cm³ mol⁻¹ for Cu₂S and \( r \) is a surface roughness factor taken to be 1. Based on these calculations the film formed after 24 h in Cl⁻ solution without SH⁻ is \( \sim 320 \text{ nm thick} \) and that in the presence of SH⁻, \( \sim 440 \text{ nm thick} \). This comparison should be considered only semi-quantitative since it includes the charges under both peaks in the CSV and assumes that both layers are distributed uniformly which is uncertain. Irrespective of this uncertainty it is clear from the relative peak heights that corrosion is initially (after 1 h) inhibited by the presence of SH⁻, partially due to a rapid initial partial passivation. However, the presence of Cu₂S eventually enhances the formation of the deposited layer [26]. This can best be appreciated from a calculation of the charge associated with the reduction peak at \( \sim 1.2 \text{ V (vs. SCE)} \) after 24 h: \( \sim 1.8 \text{ mC} \) in the absence of SH⁻ and \( \sim 2.9 \text{ mC} \) when SH⁻ is present. These results are consistent with those of Payer et al. [27] who observed that a thick tarnish film developed on Cu when humid vapour mixed with sulphur-containing gases condensed to form a corrosive electrolyte. They also observed that any protective layer already present became non-protective.

To confirm whether or not Cu₂S is rapidly formed in the early stages of corrosion, Raman spectra were recorded after similar exposure periods in the simulated groundwater with/without 0.005 mM SH⁻, Fig. 3. In both sets of spectra the presence of Cu₂O is demonstrated by the broad doublet in the range 490–650 cm⁻¹, although exact peak positions vary between studies [28–34]. Using surface-enhanced Raman, Chan et al. [33,34] observed this doublet at 525 cm⁻¹ and 625 cm⁻¹ which is close to the dominant peak positions in the spectra in Fig. 3. However, an unequivocal assignment of these peak to Cu₂O alone is
complicated by the fact Raman peaks for atacamite, a possible CuII corrosion product (Cu\textsubscript{2}(OH)\textsubscript{3}Cl) are also expected in this wavenumber region. Based on spectra recorded on mineral specimens [35,36] and corrosion patinas [37,38] the peaks at 147 cm\(^{-1}\) and 408 cm\(^{-1}\) could be attributed to this phase. In addition the Raman response around 520 cm\(^{-1}\) could also contain a contribution from this phase. In the SH\(^{-}\) containing solution the presence of Cu\textsubscript{2}S is confirmed by the peak at 294 cm\(^{-1}\) although bands at 328 cm\(^{-1}\) and 611 cm\(^{-1}\) are also expected [10]. However, the peak at 338 cm\(^{-1}\) is expected to be weak and that at 611 cm\(^{-1}\) is difficult to identify in the presence of Cu\textsubscript{2}O. The spectra in Fig. 3 confirm the rapid formation of Cu\textsubscript{2}S in coexistence with Cu\textsubscript{2}O.

3.3. Long-term corrosion experiments

3.3.1. \(E_{corr}\) measurements

Fig. 4 shows \(E_{corr}\) measured just prior to each EIS measurement over the 6-week (~1000 h) exposure period. Except for times ≤40 h, the \(E_{corr}\) for Cu immersed in the simulated groundwater is generally higher than that submerged in the bentonite slurry. In both cases, \(E_{corr}\) rises rapidly to a value of ~0.18 V (vs. SCE) within the first day of immersion. This is expected for exposure to an aerated environment. For the electrode in the simulated groundwater solution, \(E_{corr}\) then slowly decreased up to ~500 h before increasing again. This increase may reflect the period over which Cu\textsuperscript{II} corrosion products accumulate on the surface (see below). By contrast, \(E_{corr}\) on the Cu electrode submerged in the slurry falls rapidly to around ~0.26 V (vs. SCE) after ~72 h. It is likely this drop is caused by the consumption of O\textsubscript{2} by reaction with oxidizable minerals and organic matter present in the bentonite. According to published \(E_{corr}\) values recorded as a function of [Cl\(^{-}\)] in compacted clay [2], for a [Cl\(^{-}\)] of 0.181 M at a potential of ~0.32 V (vs. SCE) (i.e., after 6 weeks of exposure), the concentration of O\textsubscript{2} in bentonite is predicted to be 8 ppb. For an \(E_{corr} = ~0.25 V\) (vs. SCE) (i.e., immediately after the initial decrease) the [O\textsubscript{2}] concentration would be ~80 ppb. These results show that the great majority of available O\textsubscript{2} at the corroding surface is scavenged within the first few hours in the bentonite slurry.
3.3.2. Electrochemical impedance spectroscopy (EIS)

The EIS spectra recorded in the simulated groundwater solution and in the bentonite slurry are shown in Figs. 5 and 6, respectively. The lines show the fits to the equivalent circuits discussed below. Measurements were conducted after 1 h, 24 h, 48 h, 72 h, and subsequently every week, over the 6 week exposure period. In the simulated groundwater two time constants are observed in the high to mid frequency range, and at low frequencies a diffusion response is clearly observed to develop with time. This last response may also be present at shorter exposure times (72 h, 1 week), but the data is erratic. The magnitude of the impedance at the low frequency limit, \(|Z|_{f<0.005}\) Hz is of the order of 36 kΩ cm² after 72 h, and after the first week, decreases to ~12 kΩ cm² over the subsequent 5 weeks of exposure. This decrease occurs over the same period (500–1000 h) when \(E_{\text{corr}}\) is increasing, Fig. 4. Over the exposure period 4–6 weeks, when \(E_{\text{corr}}\) re-establishes a steady-state value, the impedance response does not change significantly.

In the bentonite slurry the impedance response is significantly different. A diffusion response is present at short exposure times and the impedance magnitude at the low frequency limit increases with exposure time. The phase angle indicates only one time constant is detected which shifts to lower frequencies with time. The impedance magnitude at the measured low frequency limit, \(|Z|_{f<0.005}\) Hz is of the order of 43 kΩ cm² and 46 kΩ cm² after 72 h and 1 week, respectively, and steadily increases to 200 kΩ cm² over the subsequent exposure period. The exposure period over which this increase occurs correlates with the consumption of O₂ in the bentonite and possibly also the buildup of a partially protective corrosion product deposit.

3.3.3. Analyses of corrosion products

On completion of the 6 week (~1000 h) experiments in the simulated groundwater solution and the slurry, the Cu electrodes were analysed by SEM/FIB and Auger and Raman spectroscopy. The SEM image in Fig. 7(a) shows the deposit formed on exposure to the simulated groundwater is composed of well-developed crystals (~1 to 5 μm in dimension) and exhibits significant porosity. An image from an area where the deposit is detached shows a dual layer structure with a thin base layer and a thick outer deposited layer, Fig. 7(b). In these images the base layer also exhibits open areas where the layer appears to have been chemically/electrochemically destroyed. The uniformly corroded metal surface at these locations confirms these sites are not the locations of pits grown over the 6 week exposure period.

EDS analyses of the base layer indicates the presence of C (8.0 at.%), O (27.5 at.%), Cl (1.5 at.%) and Cu (63 at.%). The Cu/O ratio and low Cl content suggest this layer is Cu₂O and that if CuCl is initially formed over short exposure periods it is hydrolysed to Cu₂O over the longer exposure period, as suggested by King et al. [1]. EDS analyses of the outer deposit (~30 μm thick) shows the film contains C (13.4 at.%), O (41.6 at.%), Cl (16.8 at.%) and Cu (28.2 at.%). These elemental ratios and the green colour (observed optically) suggest this layer is, or contains, significant amounts of atacamite/paratacamite (Cu₂(OH)₃Cl).

The film formed in the bentonite slurry possesses a very different morphology and structure (Fig. 7(c) and (d)). Two distinct regions were observed. One region is covered with fine rounded crystals with many pores (Fig. 7(c)). EDS analyses indicate the presence of C (8.6 at.%), O (25 at.%), Si (1.6 at.%), S (1.7 at.%) and Cu (63.1 at.%), suggesting a Si/S containing Cu₂O. The second layer (Fig. 7(d)) appears to be residual bentonite with an elemental composition of C (18.3 at.%), O (52.5 at.%) and Cu (29.2 at.%). The high Cu content indicates the transport of dissolved Cu (as CuClₓ) in saline solution) and its absorption (as Cu²⁺), after oxidation by O₂, by cation exchange within the clay, as discussed by King et al. [1].

The FIB/SEM cross sections of the films on the two electrodes, Fig. 8, show very different corroded interfaces. For the specimen corroded in simulated groundwater solution, Fig. 8(a), the base layer is compact and ~800 nm thick suggesting the presence of a partially-protective film. The metal/film interface is slightly roughened but generally uniformly corroded. The absence of pits indi-
cates a generally uniform reactivity with the corrosion rate at film covered areas and open areas (Fig. 7(b)) being effectively the same. For the specimen corroded in the slurry, Fig. 8(b), the film is considerably thinner (~300 nm) and apparently porous. As indicated by the arrows, some areas of the surface were more deeply corroded than others. The EDS analyses indicate the presence of S on these surfaces.

Confirmation of the differences in film thickness and elemental composition for the two solutions was obtained by Auger depth profiling, Fig. 9. The profiles were recorded on areas covered only by the base layer. The profiles are shallow and an approximate value of film thickness was obtained from the depth at which the intensity of the O signal achieves half of its surface value. Based on this estimate the film on the electrode exposed to the solution was ~1.6 μm thick while that on the specimen exposed to the slurry was ~480 nm. These values compare acceptably to those obtained from the SEM/FIB analyses (Fig. 7). For the film grown in the simulated groundwater solution a small amount of Cl is detected throughout the film but more noticeably at the surface of the electrode, suggesting some Cl− absorption within the Cu2O.

![Fig. 6. Impedance spectra recorded in a bentonite slurry at various times over a 6 week exposure period.](image)

![Fig. 7. SEM images of Cu electrodes after exposure to a simulated groundwater solution (a and b) and a bentonite slurry (c and d) for 6 weeks.](image)
or the presence of residual traces of CuCl. No such signal for Cl was observed on the electrode corroded in the slurry but a significant amount of S is observed in the outer ~30 nm of the film. This may reflect the greater stability of SH in the slurry since O2 is rapidly consumed in the presence of the clay and unavailable to react with the SH (see the discussion below).

Raman spectra recorded on the two electrodes are shown in Fig. 10. For the electrode exposed in the slurry the spectrum exhibits two main features (Fig. 10(a)): narrow bands at 144 cm$^{-1}$ and 216 cm$^{-1}$, which are difficult to assign, and three broad peaks at 410 cm$^{-1}$, 531 cm$^{-1}$ and 623 cm$^{-1}$. As discussed above the last two peaks are characteristic of Cu$_2$O. The absence of a significant band at 294 cm$^{-1}$ indicates minimal, if any, Cu$_2$S is present [10,37]. The spectrum recorded on the base layer on the electrode exposed to the simulated groundwater solution also shows Cu$_2$O is the dominant phase, Fig. 10(b). Fig. 10(c) shows the spectrum recorded on the green deposit formed on the electrode exposed to simulated groundwater solution exhibits several bands characteristic of atacamite [34,36,38] in the wave number range 3310–3445 cm$^{-1}$. No atacamite was detected on the electrode exposed to the slurry. This would be consistent with the much lower long term corrosion rate indicated by the EIS measurements and may be attributed to the quick consumption of O$_2$ in the slurry. In addition any Cu$^{2+}$ formed while oxidising conditions still prevailed is most likely to have been transported from the electrode surface and absorbed by cation exchange on the clay particles [1].

3.3.4. Reaction mechanism

The corrosion of Cu in Cl$^-$ solutions is known to be accelerated in aerated solutions [39] and to involve the general reactions

$$\text{Cu} + \text{xCl}^- \rightarrow \text{CuCl}_{(\text{ads})}^{(1-x)-} + e^- \quad \text{(Anodic reaction)} \quad (1)$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad \text{(Cathodic reaction)} \quad (2)$$

In the absence of significant amounts of Cl the anodic reaction proceeds via a (CuOH)$_{ads}$ species leading generally to the formation of the stable corrosion product, Cu$_2$O [39–41]. However, in the neutral chloride solution employed in this study the initial stages of film formation involve a competition between Cl$^-$ and OH$^-$ for surface sites [1,25],

$$\text{CuCl}_{ads} + \text{OH}^- \leftrightarrow \text{Cu(OH)}_{ads} + \text{Cl}^- \quad (3)$$

and Cu$_2$O is subsequently formed

$$2\text{Cu(OH)}_{ads} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (4)$$

The extent of Cu$_2$O formation will depend on the relative Cl$^-$ and OH$^-$ concentrations with higher pH favouring its formation. Since its solubility product is high (1.72 $\times$ 10$^{-7}$) [42], the CuCl is soluble and dissolves via Cl$^-$ complexation, a reaction that can be
fast \cite{40}, to produce CuCl$_{2-(x)}$\(^-\). According to King et al. \cite{1} islands of CuCl in a surface film of Cu$_2$O created local defects which can act as pit initiation sites. The dissolution of such islands could account for the open areas observed in the Cu$_2$O base layer (Fig. 7(b)). The absence of pits is consistent with the observations of King et al. \cite{1} who showed corrosion involves a general surface roughening. The CuCl$_{2-(x)}$\(^-\) is transportable and leads to the deposition of the outer layer by one of two reactions:

(a) Hydrolysis to produce Cu$_2$O \cite{25}

\[
2\text{CuCl}_{2-(x)}^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{Cl}^- \tag{5}
\]

(b) Homogeneous oxidation to produce Cu$^{2+}$ \cite{43} and the deposition of Cu$^{5+}$ solids, of which atacamite is the most likely in Cl$^-$ solutions \cite{40} and the phase observed in this study.

\[
2\text{CuCl}_{2-(x)}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_2\text{Cl} + \text{OH}^- + (2x - 1)\text{Cl}^- \tag{6}
\]

Since the base layer of Cu$_2$O is porous \cite{22} the O$_2$ reduction reaction would be expected to occur on the Cu surface and the formation of Cu$_2$O by reaction (5) would be facilitated in the alkaline conditions produced. Cu$_2$O produced in this manner would account for the outer layer formed over 24 h in the short term corrosion experiment, Fig. 2.

In the later corrosion experiments unhydrolysed CuCl$_{2-(x)}$\(^-\) can be transported out of the O$_2$-depleted pores in the base layer to undergo homogeneous oxidation and deposition as atacamite (reaction (5)) once a significant O$_2$ concentration is encountered at the outer surface of the deposit. The Raman analyses conducted on completion of the long corrosion experiment confirm that these reactions, which lead to such a spatial distribution of corrosion products, do occur.

It is well known that, in the presence of SH$^-$ in Cl$^-$ solutions, the chemisorption of SH$^-$ ions on the Cu surface is very strong \cite{13}, and likely to displace Cl$^-$ leading to the formation of CuSH$_{ads}$. Raman analyses after short-term exposure (i.e., up to 24 h) clearly show that the formation of Cu$_2$S from surface adsorbed CuSH$_{ads}$ occurred initially. It has been claimed that the formation of a CuSH$_{ads}$ complex and/or S-Cu linkages weakens Cu bonding to O and OH and leads to an increase in corrosion rate \cite{26}. This would be consistent with the more negative $E_{corr}$ and higher anodic current density observed in the polarization scan when SH$^-$ is present (Fig. 1). A similar minor influence of small concentrations of SH$^-$ on $E_{corr}$ was observed by Rahmouni et al. \cite{21}. This formation of Cu$_2$S accompanied by Cu$_2$O deposition only partially passivates the Cu surface.

In aerated solution, SH$^-$ is unstable and can be converted via the intermediates SO$_3^{2-}$, S$_2$O$_3^{2-}$, to SO$_4^{2-}$ with elemental S and polysulphides ($S_x^{2-}$) also possible products \cite{44}. This reaction proceeds with a half-life of \approx 20 min \cite{45} in neutral solution and can be catalysed in the presence of Cu$^{2+}$ \cite{44}. Under depleted SH$^-$ conditions, the initially-formed Cu$_2$S would convert to Cu$_2$O but the details of this conversion remain to be investigated.

This formation of a non-protective base layer of Cu$_2$O then leads to a higher corrosion rate, indicated by the formation of a thicker outer layer in the short term corrosion experiment. While the short term experiments clearly demonstrate an influence of SH$^-$ on the corrosion process, an effect is not so readily identifiable in the long term experiments in the simulated groundwater since there is no indication of the presence of Cu$_2$S or S in the Raman, Auger and EDX analyses. By contrast, after 6 weeks exposure to the bentonite slurry, S is detected at the surface of the base layer and there is evidence in the SEM/FIB images that some localised corrosion of the metal surface occurs, Fig. 8(b).

The difference in behaviour can be attributed to the difference in redox conditions in the two solutions. In the simulated groundwater, in which O$_2$ is uniformly present throughout the 6 week exposure period, SH$^-$ oxidation to soluble SO$_4^{2-}$ and the conversion of Cu$_2$S to Cu$_2$O would be expected to occur early in the experiment. By contrast, in the bentonite slurry, when an adherent clay layer appears to accumulate on the Cu surface, the O$_2$ is rapidly consumed by reaction with minerals and organic matter in the clay.
achieving concentrations at the Cu surface of <100 ppb in ~40 min. Under these effectively anoxic conditions two scenarios could arise: (a) a low concentration of SH\textsuperscript{−} survives and a small amount of anoxic corrosion leads to the formation of small amounts of Cu\textsubscript{2}S; (b) a second, more likely possibility is that SH\textsuperscript{−} oxidation is only partially complete and lingering amounts of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} (thiosulphate) are responsible for the interfacial corrosion damage at the Cu/base layer interface (Fig. 8(b)), as previously observed in aerated saline solutions [46].

The other significant differences between the electrodes corroded in the simulated groundwater and the slurry are the dimensions of the base layer (~800 nm in the simulated groundwater; ~300 nm in the slurry) and the considerably thicker outer layer deposit on the electrode corroded in the simulated groundwater solution. While the lingering influence of SH\textsuperscript{−} may have impeded growth of the Cu\textsubscript{2}O base layer, the major reason for the much lower amount of deposit is the absence of a significant O\textsubscript{2} content beyond ~40 h in the experiment conducted in the bentonite slurry. Additionally, as indicated by the EDS analyses of the bentonite in close proximity to the corroding surface, a significant amount of transported Cu (as CuCl\textsubscript{x}) is absorbed into the clay by cation exchange after oxidation to Cu\textsuperscript{2+}.

Evidences to support these claims come also from the EIS analyses. The equivalent circuit shown in Fig. 11(a) was used to fit the spectra obtained in the bentonite slurry, in which $R_\text{s}$ and $R_\text{f}$ are the solution resistance and the Faradaic resistance, respectively, and CPE\textsubscript{dl} is the constant phase element (CPE) adopted to represent the non-ideal behaviour of the double layer capacitance. A Warburg element ($W_{\text{inf}}$) was included to account for the diffusion of $O_2$ through the slurry or possibly through the clay layer which appears to adhere to the Cu surface, Fig. 7(d). Since the film formed on the electrode exposed to the simulated groundwater solution consists of a thin compact film of Cu\textsubscript{2}O with a thick outer porous deposit of Cu\textsubscript{2}O/Cu\textsubscript{2}(OH)\textsubscript{3}Cl, a resistance $R_\text{ox}$ and capacitance, again represented by a CPE to account for non-ideal behaviour, CPE\textsubscript{ox}, were added to the circuit to represent the impedance of the oxide film, Fig. 11(b). In this circuit $W_{\text{inf}}$ is attributed to the contribution of $O_2$ diffusion through the porous oxide.

The CPE is defined by [47]:

$$Z_{\text{CPE}}(\omega) = \left|Y_0(j\omega)^n\right|^{-1} \quad (j^2 = -1)$$

(7)

where $\omega$ is the angular frequency, $Y_0$ the CPE amplitude, and $n$ the CPE exponent. A CPE is usually used to describe non-ideal capacitive behaviour due to uneven current distribution or surface inhomogeneity providing the exponent $n$ is close to unity. In such a case, $Z_{\text{CPE}}$ can be converted to an effective capacitance using either the relationship derived by Brug [48] or that derived by Mansfeld depending on whether a surface or normal time-constant dispersion is assumed [49].

The Warburg element is given by Barsoukov and Macdonald [50]

$$W_{\text{inf}} = \frac{\sigma_w}{\sqrt{\omega}}(1 - j)$$

(8)

where the Warburg coefficient is related to the surface concentration ($c_\text{s}$) and diffusion coefficient ($D$) by the equation

$$\sigma_w = \frac{RT}{n^2F^2c_\text{s}\sqrt{2D}}$$

(9)

in which $R$ is the gas constant (8.314 J mol\textsuperscript{−1} K\textsuperscript{−1}), $T$ temperature in K, $n$ the number of electrons, and $F$ is the Faraday constant (96544 C mol\textsuperscript{−1}).

The fitted parameter values for Cu in the bentonite slurry are presented in Fig. 12. The formula developed by Brug was used to obtain capacitance values on the assumption that the CPE behaviour can be attributed to the dispersion of the surface time constant [49]. The capacitance is effectively constant over the full exposure period, and the large value, 300 μF cm\textsuperscript{−2}, may reflect the rough surface as indicated in the SEM/FIB cross sections, Fig. 8.
The value of $R_t$ increases very rapidly over the first ~40 h, although this is not immediately obvious in the linear plot in Fig. 12. Subsequently, $R_t$ increases more slowly but steadily with time. These features are consistent with the evolution of $E_{corr}$ with exposure time, Fig. 4, and confirm that the O$_2$ content in the vicinity of the Cu surface this environment is rapidly reduced to a low value after ~40 h and then subsequently decreases to an extremely low value.

The increase in the value of the Warburg coefficient ($\sigma_W$) over the course of the experiment can be primarily attributed to the decrease in surface O$_2$ concentration, $c_o$, initially rapidly (over 40 h) to ~80 ppb and subsequently more slowly (40–1000 h) to ~8 ppb, although it is possible the effective diffusion coefficient (D) changes with time as the porous film develops. Under these conditions the corrosion process would be under cathodic control.

The values of the parameters obtained using the equivalent circuit in Fig. 11(b) to fit the spectra recorded in the simulated groundwater are plotted in Fig. 13. Over the first ~200 h, when $E_{corr}$ remains effectively constant, Fig. 4, the slight increase in $R_{ox}$ and accompanying decrease in $R_t$ suggest the formation of a surface film which initially catalyses the interfacial charge transfer process. This would be consistent with the rapid formation of a Cu$_2$S film, as indicated in the short term corrosion experiments and confirmed by Raman spectroscopy, Fig. 3(a)–(c). Since a Cu$_2$S film would be a conductor it would not be expected to significantly influence the value of $C_{dl}$ as shown to be the case, Fig. 13.

The subsequent decrease in $R_{ox}$ would be consistent with the conversion of this Cu$_2$S layer to non-protective Cu$_2$O and the long term low value of $R_{ox}$ supports the claim that the thick layer of Cu$_2$O/Cu$_2$(OH)$_3$Cl which subsequently grows is unprotective. This is further supported by the invariance of $R_{ox}$ and $C_{dl}$ over the duration of the experiment, Fig. 13. The slight increase in $C_{dl}$ may reflect a roughening of the Cu surface as corrosion progresses. The $\sigma_W$ values in the saline groundwater solution containing sulphide are low and remain relatively constant as opposed to that obtained in the bentonite slurry which continues to rise with time. Providing the diffusion coefficient remains relatively constant, this would be consistent with a higher surface concentration of O$_2$ in the groundwater solution, as expected in the groundwater solution.

4. Conclusions

The corrosion of Cu has been studied in a simulated groundwater and in the same groundwater containing bentonite slurry.

The early corrosion behaviour appears to be strongly influenced by the presence of a very small concentration (0.005 mM) of SH$^-$ in the groundwater. Raman spectroscopy shows that a thin layer of Cu$_2$S is rapidly formed. While this layer may initially partially passivate the Cu it is unstable in the presence of dissolved O$_2$ and is at least partially converted to a non-protective layer of Cu$_2$O.

After 6 weeks of exposure to the aerated simulated groundwater, this Cu$_2$S layer is no longer detectable and no S species are detected in the corrosion product layer. This can be attributed to the oxidation of SH$^-$ to soluble SO$_4^{2-}$ in aerated solutions.

In aerated groundwater corrosion continues relatively rapidly leading to the build-up of a surface layer of Cu$_2$O and atacamite (Cu$_2$(OH)$_3$Cl).

In the bentonite slurry the corrosion reaction appears to be similarly accelerated initially by the formation of Cu$_2$S. However, O$_2$ is rapidly depleted at the Cu surface by reaction with organic matter and minerals in the clay and the formation of a deposited clay layer on the Cu surface.

In bentonite slurry the corrosion reaction rate is significantly decreased and the reaction is controlled by O$_2$ transport through the surface layer. No CuII deposit formed on the outer surface of the specimen, and residual traces of unoxidised S are detected in the corrosion product. Some pitting is observed and may indicate the presence, at least temporarily, of incompletely oxidised S species such as S$_2$O$_3^{2-}$ which are known to cause intergranular corrosion of Cu.

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