In situ X-ray absorption study of copper films in ground water solutions

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Abstract

This study illustrates how the damage from copper corrosion can be reduced by modifying the chemistry of the copper surface environment. The surface modification of oxidized copper films induced by chemical reaction with Cl⁻/CO₃⁻ and HCO₃⁻/CO₃⁻ in aqueous solutions was monitored by in situ X-ray absorption spectroscopy. The results show that corrosion of copper can be significantly reduced by adding even a small amount of sodium bicarbonate. The studied copper films corroded quickly in chloride solutions, whereas the same solution containing 1.1 mM HCO₃⁻ prevented or slowed down the corrosion processes.

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Copper and copper alloys have been known to many for a very long time and have played a significant part in the history of mankind. The corrosion and passivation of copper have also been studied extensively [1]. There are many Letters on specific corrosion problems [2–4] or about detecting corrosion processes [5,6].

Copper is not an inherently reactive metal and the corrosion rate in aqueous solutions is usually low even without films of insoluble corrosion products. The composition of the aqueous phase, however, will influence the stability of the surface films on the copper and, thus, the corrosion rate. The purpose of this Letter is to study the influence of ordinary groundwater components on the nature of the surface films and, also, their ability to suppress or inhibit the corrosion.

It is commonly considered that the corrosion product layer formed on a copper surface consists of an inner layer of Cu₂O and an outer layer of Cu(II) oxides or other Cu(II) compounds, depending on the composition of aqueous solution in contact with the copper. X-ray absorption spectroscopy (XAS) can be used to determine the oxidation state for different type of copper compounds [7–9] and can, therefore, be a suitable technique for studying the corrosion processes. The corrosion progress can be determined by monitoring the Cu(I) and Cu(II) signals.

In this study, Cu 2p XAS was employed to study, in situ, the chemical reactions of 100 Å thick Cu films with groundwater and aqueous solutions of chloride and bicarbonate. All solutions were prepared from analytical grade chemicals and ultra-pure deionized water (MQ). The composition of the synthetic groundwater we used is given in Table 1. This water mimics a typical low ionic strength granitic groundwater from the Fenno-Scandian shield. The other solutions we studied were 1.4 mmol/L of Cl⁻, 1.1 mmol/L of HCO₃⁻ and 1.5 mol/L Cl⁻ (i.e., seawater concentration) with Na⁺ as the cation.

For this study, we used specially designed liquid cells. A schematic picture of the cell is shown in Fig. 1. The cells are made of PEEK polymer and are about 20 mm in diameter and 4 mm thick. They hold approximately 4 μL of liquid. The X-rays penetrate through a 100 nm thick silicon nitride (Si₃N₄) membrane window. The size of the membrane is...
1 mm × 1 mm and it is held by a 10 mm × 10 mm Si frame, which is attached to the cell. On the inside of the Si3N4 windows 100 Å thick copper films were deposited. These films were in direct contact with the aqueous solutions and the chemical reactions between the copper and the various solutions could be studied in situ. The spectral shape of the Cu 2p absorption edge and the chemical shift of the main absorption line served as a tool in monitoring the changes during the reaction. The Cu 2p absorption spectra were measured on beam-line 7.0 [10] at the advanced light source (ALS) at Lawrence Berkeley National Laboratory using a spherical grating monochromator, which gave a resolution of 200 meV at the Cu 2p3/2 peak of CuO (931.9 eV). The X-ray absorption spectra were recorded in total fluorescence yield (TFY) mode under high vacuum conditions (∼10⁻¹⁰ torr).

First, we examined the 100 Å copper thin film deposited on the Si3N4 window ‘as received’ by XAS. It is evident from Fig. 2 that both oxidized and metallic copper are present in the film on the window membrane. Cu2O has predominantly d¹⁰ configuration with a small mixture of d⁹ character and only the final state 2p⁵3d¹⁰⁴s¹ can be reached, which gives rise to the main peak at 933.3 eV. There is also a small peak at ∼930.8 eV, which shows the presence of Cu²⁺ impurities and, thus, indicates that further oxidation of copper has taken place. Metallic copper is represented by characteristic satellite structures in the 938–942 eV range and a higher background.

All clean copper surfaces begin to oxidize as soon as they come into contact with air. In dry air, a very thin layer of copper oxides forms on the copper surface. This process is sometimes referred to as ‘toning’ and it usually protects the surface from further oxidation [4]. At higher moisture levels, however, or in moist or wet environments the corrosion may progress further and not stop with toning. This is especially the case for objects buried in soil or submerged in water, where acids and salts present in the soil and in the water can aggravate the attack on the metal. Copper is a near noble metal and its corrosion in aqueous environments, such as groundwater, is controlled by the availability of oxygen [15,16]. The final corrosion product will be controlled by the composition of the groundwater contacting the copper surface. In general, copper metal corrosion in soil and in groundwater can lead to products such as cuprous chloride (CuCl), cupric chloride (CuCl₂), cuprous oxide (Cu₂O), and the green- and blue-colored cupric carbonates, malachite (Cu₂(OH)₂CO₃), and azurite (Cu₃(OH)₂(CO₃)₂) [11]. The most damaging corrosion occurs at high chloride concentrations and, unfortunately, chloride is a common anion in some groundwaters and in marine environments. During these conditions basic cupric chlorides such as paratacamite and atacamite (both structural modifications of Cu₂(OH)₃Cl) may form.

First, we investigated the corrosion behavior of copper in the synthetic groundwater. The Cu 2p XA spectrum of the copper film exposed to the synthetic groundwater solution, the 1.4 mM Cl⁻ in ultra-pure deionized water (MQ) and the 1.1 mM HCO₃⁻ solution in MQ water. pH for all solutions was adjusted to 8.5.
liquid cell with 1.4 mM Cl\textsuperscript{−} ion solution. For this solution we dissolved 8.18 mg of NaCl in powder form in 100 mL of MQ water and adjusted pH to 8.5, the pH in the groundwater, using sodium hydroxide NaOH. The resulting Cl\textsuperscript{−} ion is the same as in the synthetic groundwater (see Table 1). Fig. 2 shows the XA spectrum of the film exposed for 1 h to this chloride solution. The main line of the spectrum is at energy ~933.3 eV and corresponds to monovalent copper species. The peak at ~930.8 eV is due to Cu\textsuperscript{2+} contribution. Fig. 2 also shows Cu 2p XAS taken from the copper film in the liquid cell containing 1.1 mM HCO\textsubscript{3}−. For this solution we dissolved 9.24 mg of sodium bicarbonate (NaHCO\textsubscript{3}) in 100 mL MQ water. The resulting HCO\textsubscript{3}− concentration is the same as in the synthetic groundwater. In this case, the pH was adjusted to 8.5 using hydrochloric acid HCl. In the XA spectrum at the Cu 2p edge, recorded after 1 h exposure of the Cu film to the solution, one can see that the peak at lower energy corresponding to the divalent copper species is almost absent. The first step in the electrochemical corrosion of copper and copper alloys in chloride solutions is the production of cuprous ions. These ions are then combined with the chloride ions in solutions to form cuprous chloride as a major component of the corrosion layer:

\[
\text{Cu} \rightarrow \text{Cu}^+ + \text{e} \\
\text{Cu}^+ + \text{Cl}^− \rightarrow \text{CuCl}
\]

Cuprous chloride CuCl is unstable in water and the copper will continue to corrode chemically by reaction between cuprous chloride and oxygen to form hydrochloric acid and basic cupric chloride [12]

\[
4\text{CuCl} + 4\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{CuCl}_2 \cdot 3\text{Cu(OH)}_2 + 2\text{HCl}
\]

These reactions may continue until no metal remains. This chemical corrosion process was confirmed here by XAS. We prepared a liquid cell with 1.5 M of Cl\textsuperscript{−}, which is close to the Cl\textsuperscript{−} concentration in a marine environment. Fig. 3 shows the presence of divalent copper species on the investigated copper film. The ground state of divalent copper in oxide can be described as a mixture of 3d\textsuperscript{9} and 3d\textsuperscript{10}L character [7], where L stands for a hole in the O 2p band. The main peak at 930.8 eV in the XA spectrum corresponds to the 2p\textsuperscript{3}d\textsuperscript{10} final state. This state gives a single line without multiplet splittings because the d shell is full. Our data indicate that in solutions with Cl\textsuperscript{−} content approaching that of sea water, the copper was fully corroded due to the high Cl\textsuperscript{−} concentration.

By comparing spectra for the two chloride concentrations in Fig. 3 we conclude that a strong complex formation of Cu(II) chloride species occurs on the copper surface at the higher Cl\textsuperscript{−} concentration. We believe that the difference between seawater (Fig. 3) and groundwater (Fig. 2) is caused by the differences in Cl\textsuperscript{−} concentrations, pH values [13,14] and the presence of carbonate in groundwater solution.

The pH value of the solution also influences the corrosion process. The stability of divalent copper species, compared to monovalent, increases for pH higher than 8.5 [3,13]. This effect is illustrated in Fig. 4, which shows the Cu 2p XA spectrum from a copper film exposed to a 1.4 mM Cl\textsuperscript{−} solution in the liquid cell for 1 h. The pH value of the solution was adjusted to 10 by adding a small amount of sodium hydroxide NaOH. The spectrum shows almost fully corroded copper in this case.

We suggest that the presence of carbonate ions may lead to a passivation with a decreased amount of divalent copper in accordance with previous observations [15]. Adeloju and Duan [16] suggest that the increased protectiveness is a consequence of pH buffering by HCO\textsubscript{3}−, which stabilizes the oxide film rather than leading to the formation of basic cupric carbonate species. This is illustrated in Fig. 4, where 1.1 mM HCO\textsubscript{3}− (i.e., the same concentration as in the synthetic groundwater) was added to the 1.4 mM Cl\textsuperscript{−}, pH 10.0

![Fig. 3. Cu 2p X-ray absorption spectra of the copper film in the liquid cell after 1 h exposure to 1.5 M Cl\textsuperscript{−} and with 1.4 mM Cl\textsuperscript{−} solution in MQ water, respectively.](image)

![Fig. 4. Cu 2p X-ray absorption spectrum of the copper film (top) in the liquid cell exposed for 1 h to a 1.4 mM Cl\textsuperscript{−} solution in MQ water with pH adjusted to 10 with NaOH. Cu 2p X-ray absorption spectrum of the copper film (bottom) exposed to the same solution, but with an addition of 1.1 mM HCO\textsubscript{3}−.](image)
solution. The bicarbonate buffers the pH to a near neutral value and improves the passivity of the copper. The Cu 2p XA spectrum displays this sensitivity to the presence of carbonate ions. The monovalent copper signal is clearly observed in this spectrum, which indicates that the copper film was not corroded in the presence of 1.1 mM HCO₃⁻.

Our results are not surprising since the sodium sesquicarbonate (equal amount of Na₂CO₃ and NaHCO₃) treatment has been the standard chemical treatment used by antiquaries in order to clean cuprous chloride formed on copper surfaces [12,17]. There are three different treatments available to clean chloride contaminations: sodium sesquicarbonate, sodium carbonate and benzotriazole [17–19]. These three alternatives can remove cuprous chlorides, but these chemical techniques do not strip the corrosion layer. The sodium sesquicarbonate treatment seems to be ideal for the antiquaries, since they do not want to remove the outer green patina layers while the cuprous chloride is removed. The normal concentration for this chemical treatment is a 5% solution of sodium sesquicarbonate [19], which is higher than what we used for sodium bicarbonate.

The in situ analysis of liquid cells showed corrosion of copper at pH 8.5 for high Cl⁻ concentration and at pH 10 for low Cl⁻ concentration. Small amount of bicarbonate in corrosive solutions can improve the corrosion resistance of copper in aqueous environments. This is due to the ability of bicarbonate ions to stabilize the passivity of copper and to their pH buffering capacity. The groundwater composition was considered as 'non-corrosive' due to the presence of carbonate ions and near neutral pH value. In the present experiments, we also showed that the corrosion damage can be reduced if a small amount of bicarbonate is introduced into a solution.

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