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Abstract

The possibilities for using x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) to probe the Cu oxidation state and changes in the electronic structure during interaction between copper and ground-water solutions were examined. Surface modifications induced by chemical reactions of oxidized 100 Å Cu films with Cl^-, SO_4^{2-} and HCO_3^- ions in aqueous solutions with various concentrations were studied *in situ* using liquid cells. Copper corrosion processes in ground water were monitored for up to nine days. By comparing Cu 2p–3d, 4s transitions for a number of reference substances previously measured, changes in electronic structure of the Cu films were analysed. The XAS and RIXS spectral shape at the Cu edge, the chemical shift of the main line for Cu^{2+}, and the energy positions of the observed satellites served as a tool for monitoring the changes during the reaction. It was found that the pH value and the Cl^- concentration in solutions strongly affect the speed of the corrosion reaction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Copper can corrode in both gaseous and aqueous environments. The atmospheric corrosion of copper has been studied intensively since copper is used in many fields, such as contact and wiring materials in electronic parts and devices [1, 2]. Corrosion of copper in aqueous solutions has also been studied extensively for more than 100 years. It is the most commonly used material for plumbing because of its high corrosion resistance. One reason for copper's high corrosion resistance is the fact that it is a noble metal, in the sense that it is immune to

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corrosion in pure oxygen-free water. This property is the background to Sweden's choice to encapsulate spent nuclear fuel in cast iron canisters that have an outer corrosion shield made of copper for disposal at a depth of 400–700 m in granitic rock, where the ground water will be oxygen-free [3].

The deep ground water is, however, not 'pure' water. Oxygen will have intruded into the waste repository area during the construction phase. Later in the service life of the repository, other corrosive substances, mainly sulfides, may be present in the ground water. All forms of corrosion that might affect the canister must, therefore, be considered. The performance assessment in this case includes the understanding of the behaviour of copper in the geological environment. Therefore, the monitoring of *in situ* corrosion processes becomes an important topic, which is necessary to study by different methods.

The corrosion of a copper canister in the repository is controlled by the availability of corrosive ground-water components. The composition of deep ground water varies considerably from site to site as well as in time [4]. The repository environment will be oxidizing for some time after closure, but oxygen will be consumed through reactions with minerals in the rock and also through microbial activity, and the original oxygen-free conditions will be re-established. It is important to study copper corrosion in the early stages when there are still traces of oxygen present. The development of the original Cu_2O film on the metal surface, formed through oxidation in dry air after contact with ground water with low oxygen content, is important to establish and understand. It is this surface that later will be contacted by oxygen-free ground water that may contain trace amounts of sulfide. It is therefore important to investigate the copper behaviour in essentially oxygen-free conditions.

The surface modifications induced by chemical reactions on 100 Å Cu films with Cl^-, SO_4^{2-} and HCO_3^- ions in aqueous solutions were studied by using soft x-ray absorption spectroscopy (XAS). The simple oxides [5–10], sulfides [8–10], chlorides [7, 8, 10] and carbonates [5, 9, 10] have been studied before using x-ray spectroscopic techniques and theoretical approaches due to their diverse electronic structure. It has been shown that XAS can be used to determine the oxidation state of the copper for different types of compounds [5–10]. The advantage of XAS above other techniques is the reduced surface sensitivities of the samples in the total fluorescence yield mode.

In the present study, Cu 2p XAS was applied to a number of liquid cells with different water compositions. Our results show that the corrosion behaviour of copper in underground repository conditions depends very much on the Cl^- concentration and the pH value in the solution contacting the copper surface. It has been shown before that the formation of monovalent or divalent copper depend on the pH value of the solution [11–13]. However, the corrosion of copper over a broad pH range was further investigated to allow us to obtain a better understanding for the processes involved in the chemical interaction between copper and ground-water components. We also performed long-term corrosion experiments, using XAS for a number of liquid cells with different compositions.

A discussion of whether Cu is monovalent or divalent is relevant, since copper can form compounds with different valences. In ordinary oxygen-containing environments the surface layer is expected to be a duplex Cu_2O/CuO, $Cu(OH)_2$ structure [13]. In that case, XAS is not capable of giving a distinct difference between the different divalent copper compounds. Therefore, it makes sense to look for other techniques that can guide us even when the materials become complex.

We examined the possibility of using the resonant inelastic x-ray scattering (RIXS) technique to probe the electronic structure of copper in the investigated liquid cell with ground-water solution. In the soft x-ray range, this technique has been used to obtained information about the electronic states in copper materials at the Cu L and M edges [14–17]. We
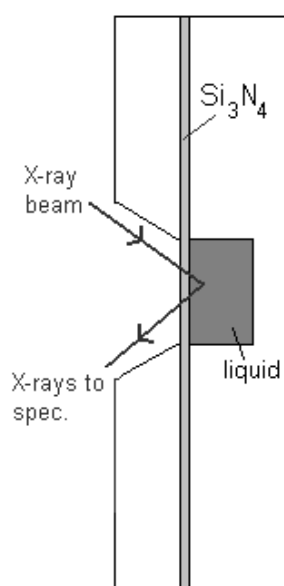
Figure 1. Schematic representation of the liquid cell.

already studied the Cu 2p–3d RIXS spectra of Cu_2O, CuO, $Cu(OH)_2$, $CuCl_2$, $CuSO_4$, malachite $Cu_2(CO_3)_2(OH)_2$, and atacamite $CuCl_2 \cdot 3Cu(OH)_2$ for different excitations energies [10]. In the present paper, we analyse the changes in electronic structure of the Cu film in liquid cells with ground-water solution by comparing copper transitions for a number of reference compounds and we determine which species are present in the liquid cells investigated.

2. Experimental details

Liquid cells with different concentrations of chlorine, sulfate and carbonate ions were used for the *in situ* studies. A schematic picture of the cell is shown in figure 1. The cell was made from PEEK polymer and has a diameter of about 20 mm and is 4 mm thick. X-rays penetrated though a silicon nitride membrane window. The size of the membrane that was used was 1 mm × 1 mm. The membrane was held by a 10 mm × 10 mm Si frame, which was attached to the cell. The volume of the cell is sufficient to hold one drop (approximately 4 μl) of the liquid. On the backside of the 100 nm Si_3N_4 windows a 100 Å copper film was deposited in advanced in order to study the chemical reactions between the copper film and various solutions. Copper film was deposited by dc magnetron sputtering deposition in an ultrahigh-vacuum (UHV) chamber. The pressure before sputter deposition was lower than 10^{-9} Torr. In order to achieve the glow discharge, Ar gas with a purity of 99.9999% at a pressure of 2 mTorr was injected at constant flow directly into the chamber. Fixing the power on the magnetron at 50 W, the resulting growth rate was about 0.85 ± 0.05 Å s^{-1}. The samples were rotated during deposition in order to achieve a homogeneous thickness of copper. After deposition, windows were removed from the chamber and brought to synchrotron facilities under atmospheric conditions.

　　The corrosion behaviour of copper in the ground-water solution was investigated under nearly anoxic conditions. The typical content of different ions in low-salinity ground water is given in table 1. The ground water was deoxygenated by pumping to vacuum and backfilling three times with argon. Through this procedure, we expect to have reduced the oxygen level in
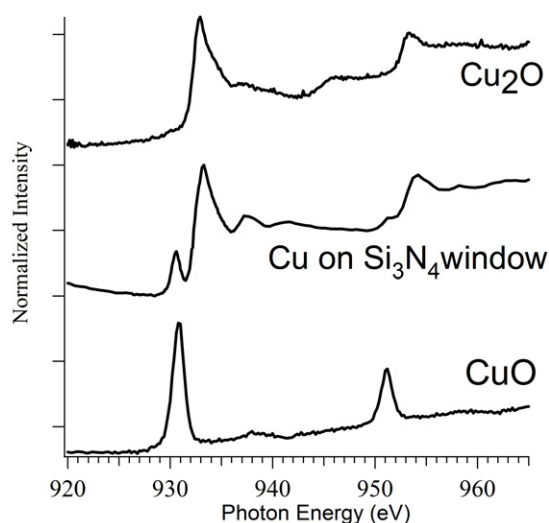
Figure 2. Cu 2p x-ray absorption (XAS) spectra of CuO, Cu_2O, and 100 Å-thick copper film deposited on the 100 nm Si_3N_4 membrane, recorded in the total fluorescence yield (TFY) mode by a photodiode. The main peak at ∼933.3 eV and the small peak at ∼930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

Table 1. Ground-water composition.

Na^+	Ca^{2+}	Mg^{2+}	K^+	SO_4^{2-}	Cl^-	HCO_3^-
52.5 mg l^{-1}	5.1 mg l^{-1}	0.7 mg l^{-1}	3.9 mg l^{-1}	9.6 mg l^{-1}	48.8 mg l^{-1}	65.0 mg l^{-1}

the ground water by about three orders of magnitude. An oxygen concentration in the parts per billion (ppb) range will, however, be sufficient to oxidize the copper film that was investigated to Cu^{2+}. The pH value during the investigation was adjusted using sodium hydroxide (NaOH), in order to increase the value and hydrochloric acid (HCl) in order to decrease the pH value.

The XAS and RIXS measurements were performed on beam-line 7.0 [18] at the Advance Light Source (ALS) of Lawrence Berkeley National Laboratory using a spherical grating monochromator with energy resolution set to 200 meV at the Cu $2p_{3/2}$ peak of CuO (∼931 eV). The XAS spectra were recorded in the total fluorescence yield (TFY) mode under high-vacuum conditions. The RIXS spectra were recorded using a high-resolution grazing incidence grating spectrometer [19], which has an adjustable slit, MCP detector and three gratings covering three energy intervals (figure 1). RIXS spectra were detected with a resolution of 500 meV, using a high-energy grating which has a radius of 5 m and 1200 lines mm^{-1}. The incident angle of the photon beam was approximately 45° from the liquid cell surface and the spectrometer was placed in the horizontal plane at an angle of 90° with respect to the incident beam.

3. Oxidation reaction of copper

First we examined, by Cu 2p XAS, the 100 Å copper thin film deposited on the inside of the Si_3N_4 window; see figure 2. For comparison, spectra of monovalent and divalent copper oxides are also presented in figure 2. The ground state of CuO can be described as a mixture of $3d^9$ and $3d^{10}\underline{L}$ character [8], where $\underline{L}$ stands for a hole in the O 2p band. The main peak at 930.8 eV in the x-ray absorption (XAS) spectrum of CuO corresponds to the $2p^5 3d^{10}$ final state. This
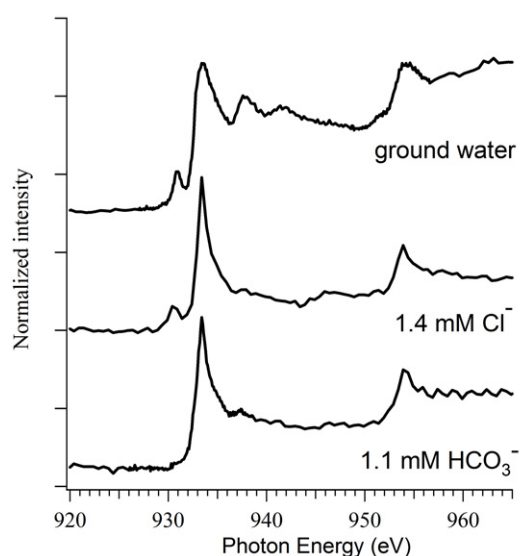
Figure 3. Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells with: ground-water solution and 1.4 mM Cl^- and 1.1 mM HCO_3^- solutions in ultra-pure distilled deionzed (MQ) water. The pH value for all solutions was adjusted to 8.5. The main peak at ∼933.3 eV and the small peak at ∼930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

state gives a single line without multiplet splitting, because the d shell is filled. At ∼20.1 eV above this peak ($2p_{3/2}$), another structure with lower intensity appears ($2p_{1/2}$). This structure is broader due to a shorter core–hole lifetime and interaction with the $2p_{3/2}$ continuum. The XAS spectrum of monovalent copper (figure 2) clearly differs from the Cu^{2+} spectra. The main line of the Cu_2O spectrum is at higher energy (∼933.3 eV) and corresponds to excitations to the empty 4s band.

By comparing the Cu 2p XAS spectra for divalent and monovalent copper, information on the oxidation state can be obtained. We can conclude that the main contribution comes from oxidized copper in the form of Cu_2O on the membrane surface of the Si_3N_4 window (figure 2). This oxide gives rise to the main peak at 933.3 eV. At lower energies, there is also a small peak at ∼930.8 eV, which shows the presence of Cu^{2+} impurities and thus indicates that further oxidation of the copper has taken place.

After the initial analyses of the Cu film, its corrosion behaviour in ground-water solution was investigated. One drop of ground-water solution (∼4 μl) was accommodated in the liquid cell, and 1 h later the XAS spectrum was measured in order to detect the reaction between the copper layer and the ground-water solution. The Cu 2p XAS spectrum (figure 3) shows mainly monovalent copper with small a contribution of divalent copper. It is quite obvious that the intensity of the Cu^{2+} signal for the spectrum of the liquid cell with water of the given composition decreases in comparison with the Cu^{2+} signal for the copper film deposited on the back side of the Si_3N_4 membrane.

We believe that the formation of Cu^{2+} in the ground water will be dominated either by carbonate, chlorine or hydroxide complexes. For that reason, we chose HCO_3^- and Cl^- ions out of the other species in the ground-water solution and investigated independently their influence on the copper film using XAS.

Aqueous solutions containing 1.1 mM carbonate and 1.4 mM chlorine were prepared from 9.24 mg of sodium bicarbonate $NaHCO_3$ and 8.18 mg of NaCl, respectively, and 100 ml of
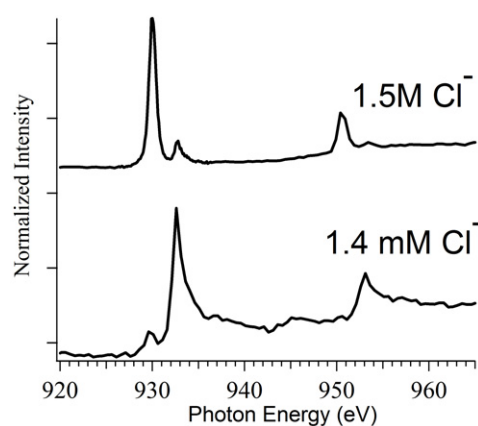
Figure 4. Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells with 1.5 M Cl$^-$ and 1.4 mM Cl$^-$ solutions in MQ water. The peaks at ∼933.3 eV and at ∼930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

ultra-pure distilled deionzed (MQ) water. The pH of the solution was adjusted to 8.5 (as in the ground water) by adding a small amount of sodium hydroxide (NaOH) to the Cl$^-$ solution and hydrochloric acid (HCl) to the carbonate solution in MQ water.

Figure 3 shows the Cu 2p XAS spectrum taken from the copper film in the liquid cell after being in contact with Cl$^-$ solution for 1 h. The main line of the spectrum is at ∼933.3 eV and corresponds to monovalent copper. The presence of the divalent copper species manifests itself in the peak at 930.8 eV. It is, however, unclear what percentage of Cu^{2+} is present in the copper film studied. The spectral intensity of the Cu^{2+} peak was used to evaluate the corrosion rate of copper films in liquid cells containing different water compositions.

Carbonate should form strong complexes with divalent copper [20]. However, the main line of the Cu 2p spectrum indicates the presence of monovalent copper on the copper film exposed for 1 h to the carbonate solution (figure 3). The Cu^{2+} peak is not observed in this spectrum, thus suggesting that carbonate species present in the solution protect the copper film from further corrosion. This is in accordance with previous observations [21]. Adeloju and Duan [22] suggest that an increased protectiveness is a consequence of pH buffering by HCO$_3^-$, which stabilizes the Cu$_2$O phase rather than leading to the formation of basic cupric carbonate species.

It can be seen from figure 3 that the intensity of the divalent copper signal during XAS measurements depends on the composition of the solution used in the liquid cell. We therefore need to investigate the influence of the pH value and Cl$^-$ concentration. There is some evidence that the transformation from Cu^{1+} to Cu^{2+} depends on the pH value and the Cl$^-$ concentration [23].

4. Influence of the Cl$^-$ concentration

We recorded the Cu 2p XAS spectrum from the copper film in the liquid cell with 1 h exposure to the MQ water solution containing 1.5 M of Cl$^-$ (similar to the Cl$^-$ concentration in the marine environment). The spectrum in figure 4 shows the presence of mostly divalent copper in the copper film that was studied. Our data clearly indicate that, in water with chlorine content approaching that of sea water, the copper surface quickly became corroded due to the high chlorine concentration. On the other hand, the divalent copper peak in the Cu 2p XAS
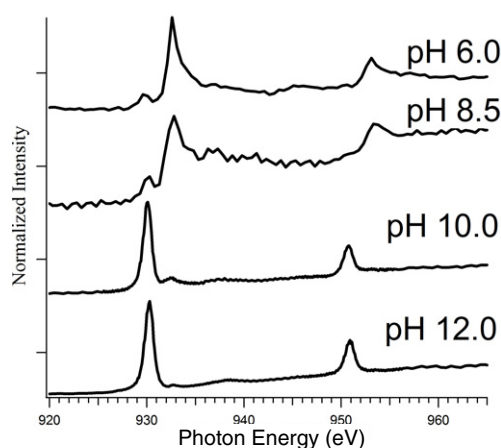
Figure 5. Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells with 1.4 mM Cl$^-$ solution in MQ water with different pHs. The peaks at ~933.3 eV and at ~930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

spectrum of the copper film after being in contact with 1.4 mM Cl$^-$ solution for 1 h has a relatively low intensity. By comparison with the spectra for different concentrations (figure 4) we can conclude that strong Cu^{2+} chloride complexes are formed on the copper surface at high Cl$^-$ concentration.

This finding can be understood on the basis of the next reaction:

$$Cu \rightarrow Cu^+ + e^-.$$

Cuprous chlorine usually formed on the copper film as a major component of the corrosion layer:

$$Cu^+ + Cl^- \rightarrow CuCl.$$

On the other hand, cuprous chloride CuCl is unstable and continues to corrode chemically to form hydrochloric acid and basic cupric chloride [24]:

$$4CuCl + 4H_2O + O_2 \rightarrow CuCl_2 \cdot 3Cu(OH)_2 + 2HCl.$$

This effect has been observed previously for copper after four days exposure to a 0.5 M Cl$^-$ solution [25] and confirmed once more by XAS using a three times higher concentration of sodium chloride in solution. In our case, 100 Å of copper was almost fully corroded after 1 h in contact with 1.5 M Cl$^-$ in aqueous solution.

5. Influence of pH

The pH of the water solution has a quite high influence on the corrosion process. According to a Pourbaix diagram for copper at room temperature [26, 27], Cl$^-$ in small concentrations can form strong complexes with divalent copper at higher pH.

Figure 5 displays Cu 2p XAS spectra obtained for the copper film exposed for 1 h to the 1.4 mM Cl$^-$ solution with different pH values. It is apparent that monovalent copper species are predominantly formed on the copper film at pH 6.0 and 8.5. The signal from divalent copper appears to be particularly strong above pH 8.5. At pH 10.0 and 12.0 (figure 5) divalent copper peaks dominate the spectra. This indicates that the stability of divalent copper over monovalent copper increases with increasing pH. Adeloju and Duan [22] reported the growth
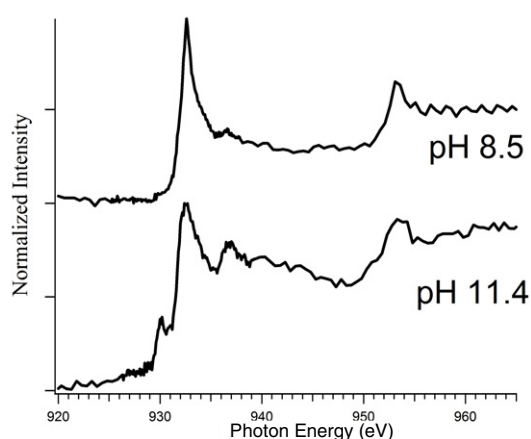
Figure 6. Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells with 1.1 mM HCO_3^- solution in MQ water with different pHs. The main peak at $\sim$933.3 eV and the small peak at $\sim$930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

of corrosion films on copper in aerated solution with pH values between 5 and 13.5. Only Cu_2O was observed after seven days exposure at the lowest pH studied with increasing amounts of CuO reported with increasing pH. The higher concentration of OH^- at higher pH promotes the formation of a passivating Cu^{2+} layer, most likely $Cu(OH)_2$. This is in keeping with the known fact that copper is more corrosion resistant at high pH in an oxygenated solution.

This pH-dependent behaviour is consistent with the Pourbaix diagram, which shows the formation of divalent copper species at a pH higher than 8. It also indicates that the oxidation of copper in the 1.4 mM Cl^- solution is less favourable at a pH of 8.5 than its oxidation to divalent copper at pHs of 10.0 and 12.0. These results are in agreement with Brusic *et al* [28], which shows that a stable oxide of copper can be formed in water solution at a pH of higher than 7.0.

Our results obtained by XAS show that copper corrosion processes in the presence of Cl^- ions are strongly pH dependent. The pH dependence of such processes was also observed for 1.4 mM HCO_3^- solution. Figure 6 shows the pH dependence of Cu 2p XAS spectra obtained for copper film exposed to the 1.1 mM HCO_3^- solution for 1 h. As can be seen from the Cu 2p spectra (figure 6), a monovalent copper signal gives the largest contribution at pH 8.5 and pH 11.4. The divalent copper signal is observed for pH 11.4. It is, however, not as intense as in the case of high pH for the Cl^- solutions. The results for pH 11.4 seem to be contradictory to the observation by Adeloju and Duan [22] that pH buffering by HCO_3^- stabilizes Cu^{1+}.

6. Time dependence

Since the Cu 2p XAS spectra for the copper films in carbonate solution do not show fast corrosion behaviour in high or near-neutral pH, it is of interest to examine their dependence on the exposure time to the solution. Figure 7 shows how the intensity of the divalent copper signal varies with time for the 1.1 mM HCO_3^- solution with pH 8.5. The Cu 2p XAS spectrum for the freshly made liquid cell (recorded after 1 h of exposure time) does not show any divalent copper signal. After 3 days of exposure a small peak appears at the lower energy, indicating the formation of divalent copper species.

Figure 8 shows the time dependence of the corrosion process in a liquid cell containing ground water, which also has pH 8.5. After 5 days exposure time we can clearly see that the
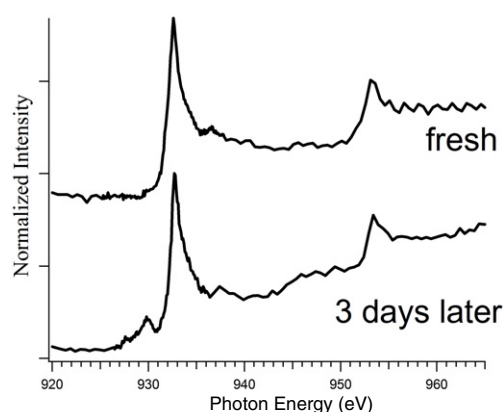
Figure 7. Dependence of Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells on the exposure time to 1.1 mM HCO_3^- solution in MQ water. The main peak at ~933.3 eV and small peak at ~930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.
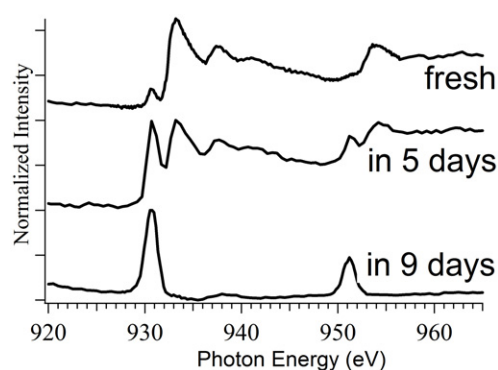

Figure 8. Dependence of Cu 2p XAS spectra of 100 Å-thick copper film in liquid cells on the exposure time to ground-water solution. The peaks at ~933.3 eV and at ~930.8 eV in the XAS spectra correspond to monovalent and divalent copper, respectively.

intensities of the monovalent and the divalent copper are similar, and after 9 days exposure time there is only divalent copper present. The intensity and the shape of the peak after 9 days of exposure time clearly indicate the presence of Cu^{2+} species in the copper film.

Figure 8 indicates that complete oxidation to Cu^{2+} had taken place after 9 days exposure time in the ground water. It is, however, difficult to determine from XAS spectra which kind of Cu^{2+} species are formed. Therefore, the copper film in ground-water solution was additionally analysed by RIXS.

7. Speciation

The species present on a copper surface in contact with aqueous solutions have been investigated before using XPS [13]. It was concluded that mainly a mixture of Cu_2O, CuO or $Cu(OH)_2$ was present on the copper surface after being in contact with a borate buffered solution (pH 7.0). This is in agreement with the current understanding that these three compounds are known to be stable as bulk solids [26, 30]. RIXS spectroscopy can provide
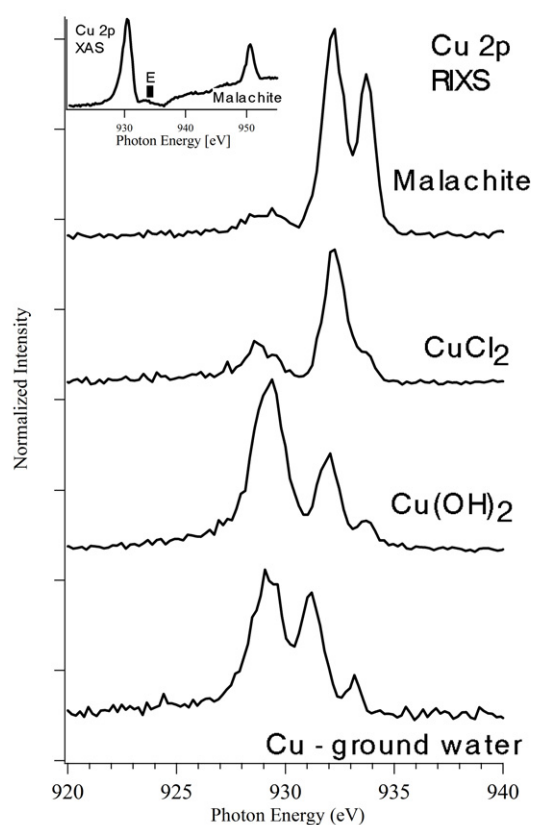
Figure 9. RIXS spectra of CuCl$_2$, Cu(OH)$_2$, malachite Cu$_2$(CO$_3$)$_2$(OH)$_2$ and 100 Å-thick copper film in a liquid cell with ground-water solution recorded at the excitation energy indicated in the top panel of the XAS spectrum.
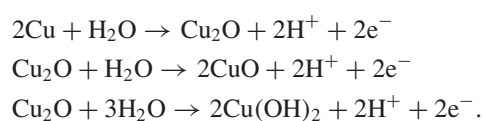
information on the composition of the corroded copper film within the ground-water solution. To do this, we at first monitor by XAS a liquid cell containing ground water until the copper was fully corroded and then we perform the RIXS measurements.

It has been shown that on the Cu 2p–3d resonance, x-ray scattering spectra are mainly composed of two parts: the dd intra-atomic excitations and the structures due to charge transfer excitations from the ligand band to the 3d level [16, 17, 31, 32]. Most RIXS studies were performed by fixing the incident photon energies close to the main XAS peak. We already analysed the Cu 2p–3d RIXS spectra of Cu$_2$O, CuO, Cu(OH)$_2$, CuCl$_2$, CuSO$_4$, malachite Cu$_2$(CO$_3$)$_2$(OH)$_2$, and atacamite CuCl$_2$·3Cu(OH)$_2$ for different excitation energies and found that the RIXS spectra excited at energies in the range of satellite structures in the Cu 2p XAS spectrum are different for the different compounds [10]. It was shown that, using Cu 2p RIXS, the characteristic differences in the chemical bonding between Cu^{2+} and Cl$^-$, SO$_4^{2-}$, OH$^-$ and HCO$_3^-$ ions could be found. This can be used as a fingerprint in the interpretation of complex materials.

In the present study, malachite, copper hydroxide and copper chloride were suggested for use as predominant phases formed on the surface of the corroded copper in the ground-water solution. Figure 9 shows Cu 2p–3d RIXS spectra of CuCl$_2$, Cu(OH)$_2$, and malachite Cu$_2$(CO$_3$)$_2$(OH)$_2$ recorded at the same excitation energy of 933.6 eV. This energy corresponds

to the satellite structure in the XAS spectrum, associated with the $2p^53d^9s$ contribution, the shape of which is defined by the s-density of states in the conduction band. However, in some publications this satellite structure in the XAS spectrum was described as being a result of exciting 'defect states', i.e. the $3d^9 \underline{L}$ initial state leading to the $2p^53d^{10}\underline{L}$ excitations (where $\underline{L}$ stands for a hole in the ligand 2p band) [5]. The differences in shape observed in the RIXS spectra clearly evidenced chemical bonding changes in these compounds. The spectral difference can be taken as an advantage in the identification of corrosion products formed on the copper film in the liquid cell with ground-water solution.

Figure 9 also shows the RIXS spectrum of the fully corroded copper film in contact with the ground-water solution. Due to the experimental difficulties, the spectrum was recorded at an excitation energy lower by 0.6 eV than that for the spectra of reference compounds. This energy is still in the range of the satellite structure in the XAS spectrum and the energy difference is within the total experimental resolution used for RIXS measurements. The shape and the intensities of the RIXS spectrum are similar to those of $Cu(OH)_2$, suggesting the formation of hydroxide species. The process can be described by the following equations [11, 30]:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$$
$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^-$$
$$Cu_2O + 3H_2O \rightarrow 2Cu(OH)_2 + 2H^+ + 2e^-.$$

It is interesting to compare the RIXS results with reports on copper oxidation states in different solution studies by Raman [29, 33] and infrared [34] spectroscopies. The Raman study by Hamilton *et al* [33] was performed using 488 nm laser excitations on copper in a 0.1 M NaOH solution. They showed that initially Cu_2O and then $Cu(OH)_2$ were formed by comparison with the oxide spectra. Melenders *et al* [34] studied *in situ* copper oxidation in alkaline media by infrared spectroscopy using synchrotron radiation. The initially formed corrosion product was identified as Cu_2O with the later formation of CuO or $Cu(OH)_2$. The RIXS spectrum in the present paper provides important information on the chemical composition and confirms unambiguously that hydroxide species were formed on the studied copper film in contact with ground-water solution.

The great sensitivity of the RIXS spectra profile to the type of copper species allows us to better assess the chemical composition of the corroded copper film. RIXS has proven to be a powerful technique for studying the corrosion processes of copper films. The results from our study of the corrosion of copper films are summarized in figure 10.

8. Conclusion

In our experiments, we used different ions for *in situ* studies of liquid cells with synthetic ground water and with de-ionized water with different concentrations of chloride, sulfate and carbonate. It has been shown that XAS can be used to determine the oxidation state of copper for a number of liquid cells with different water compositions. In the present study, Cu 2p XAS was applied to examine the influence of chlorine and carbonate ion concentrations, the pH value of the corrosion processes on oxidized copper films as well as their time dependence. The significance of the pH value for the copper corrosion rate in 1.1 mM HCO_3^- and 1.4 mM Cl^- aqueous solutions was shown.

We found that the corrosion causes the formation of Cu^{2+} species in the copper film in several cases:

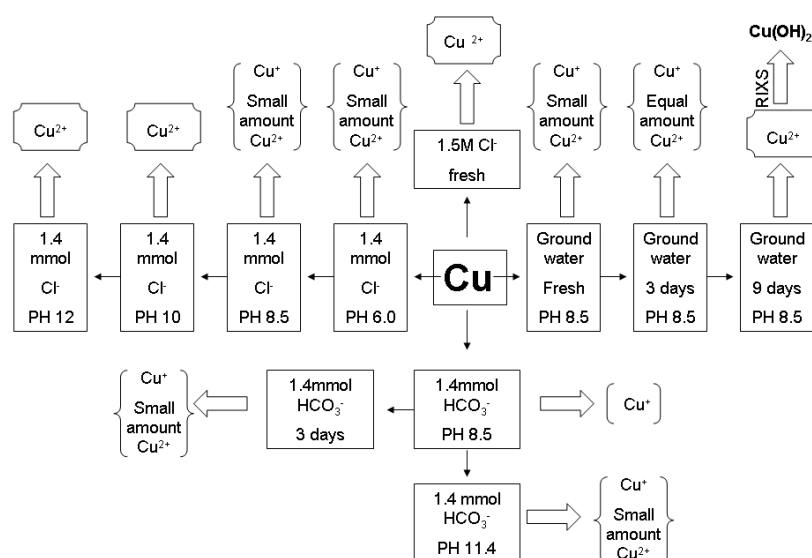- in solution with high Cl^- concentration (1.5 M);

Figure 10. Schematic summary of the copper corrosion processes in different solutions.

- 1.4 mM Cl⁻ solution with pH values higher than 10.0;
- in ground-water solution after 9 days of exposure.

A discussion of whether Cu is monovalent or divalent is found to be relevant for studies of corrosion processes because it is commonly considered that a corrosion product layer formed on the copper surface consists of an inner layer of Cu_2O and an outer layer of Cu(II) oxides or other Cu(II) compounds, depending on the composition of the aqueous solution in contact with the copper. The extent of corrosion can therefore be evaluated from the oxidation state of copper; i.e. from the presence or absence of a divalent copper signal. As shown above, fully corroded copper gives a strong divalent copper signal in the XAS spectrum. It is further shown that the relative intensities of Cu(I) and Cu(II) signals depend very strongly on the nature of species present in the water solutions.

On the other hand, Cu 2p XAS does not show significant differences between different divalent copper compounds. Therefore, Cu 2p–3d RIXS was also employed for determining the chemical composition of the copper corrosion product in a liquid cell containing a copper film with ground-water solution. While in that case the XAS spectrum revealed the presence of divalent copper, RIXS found the formation of hydroxide species. This is a good example where complementary information can be obtained using both XAS and RIXS. The importance of employing spectroscopic techniques in corrosion studies has clearly been demonstrated.

Acknowledgments

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