Study of corrosion potential measurements as a means to monitor the storage and stabilisation processes of archaeological copper artefacts

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Abstract

Archaeological copper artefacts recovered from wet saline environments are often stored in tap water and stabilized in sodium sesquicarbonate solutions. Modification of the natural patina and development of active corrosion can occur during these processes. This implies that monitoring of storage/stabilisation processes is necessary. The focus of the study consists of examining how corrosion potential (Ecorr) measurements can contribute in providing information on the effectiveness of storage and stabilisation treatments. This paper reports on the Ecorr versus time plots of artificially prepared copper coupons (covered or not with corrosion layers) immersed in tap water and a sodium sesquicarbonate solution. Synchrotron radiation XRD was performed in parallel to understand the reactions that take place during the immersion processes.
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Keywords: corrosion potential measurements, XRD, copper, saline environments, storage, stabilisation, sodium sesquicarbonate, tap water

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1. Introduction

Archaeological copper artefacts recovered from wet saline environments should not be exposed directly to the atmosphere, especially when they contain aggressive chloride species, as the metal will then corrode at an accelerated rate in the oxygen-rich air (Scott 2002, p125). Therefore it is best to store these objects in a solution until a treatment can be applied. The objects are usually stored in tap water or a sodium sesquicarbonate solution (Oddy et al. 1970 and MacLeod 1987a,b). The latter solution has the advantage that stabilization of the artifacts already starts as the chloride ions leach out of the corrosion layer. Nevertheless results often show a certain instability of the artefacts, such as the chemical transformation of the natural patina (for example the formation of tenorite (CuO) (Pollard et al. 1990) or chalconatronite ($Na_2Cu(CuO_3)_2.3H_2O$) (Horie et al. 1982)) and the development of active corrosion. The occurrence of these side effects means that monitoring of the treatments remains necessary.

2. Aims

The objective of this research project is to determine whether corrosion potential (Ecorr) measurements can be used to monitor the behaviour of copper based alloys during their storage and stabilisation processes and to provide early stage information about on-going corrosion processes.

This paper reports on Ecorr versus time plots performed on copper coupons (covered or not with corrosion layers) simulating the behaviour of real copper artefacts immersed in tap water and sodium sesquicarbonate solutions. Synchrotron radiation XRD was performed in parallel to understand the reactions that take place during the immersion processes.

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3. Methods

3.1 Corrosion simulation

Pure corrosion products, commonly found on real artefacts, were artificially prepared on pure copper coupons (ADVENT, purity 99.9%). Five of these corrosion products were selected for the experiments.

Cuprite (Cu_2O) is a stable copper oxide that is regularly found on copper artefacts (Scott 2002; De Ryck 2003). To obtain a cuprite layer, the copper samples were polarized anodically at -360 mV/MSE for 16 hours in a 0.1 M Na_2SO_4 (Fluka) solution (Beldjoudi 1999).

Within the copper chlorides nantokite (CuCl), atacamite and paratacamite (both isomers of $Cu_2(OH)_3Cl$) were selected. Nantokite is considered as the main catalytic agent for active corrosion. The presence of this cuprous chloride as a corrosion product adjacent to the metallic surface can create long-term problems for the stability of an object. Bronze disease or pitting corrosion is usually attributed to this corrosion product (Scott 2002). Copper covered with nantokite is obtained by immersing pure copper samples for one hour in a saturated $CuCl_2.2H_2O$ solution (VWR International). After rinsing with deionised water they were exposed to the atmosphere for a night (Lamy 1997).

Atacamite and paratacamite are two other important chlorides in bronze corrosion. They are often considered as end products and are formed on top of the active corrosion areas. Atacamite is the most common of the $Cu_2(OH)_3Cl$ isomers, but often alters into paratacamite (Scott 2002; De Ryck 2003). In this respect atacamite as well as a mixture of atacamite and paratacamite were prepared in this study. For the atacamite corrosion a solution of 15.07 g $(NH_4)_2CO_3.NH_3$ (Fluka) and 10.02 g NH_4Cl (Aldrich) in 100 ml deionised water was prepared. The copper samples were wetted twice a day with this solution. This procedure was repeated for five days. Between each application the samples were left to dry to the air. After the period of five days the samples were left in the air for another five days without any treatment (Lamy 1997).

The protocol used to obtain a mixture of atacamite and paratacamite was almost the same; only the solution was different: 10.02 g $Cu(NO_3)_2.3H_2O$ (VWR International) and 10.01 g NaCl (Fluka) in 100 ml deionised water was prepared (Lamy 1997).

Chalcocite (Cu_2S) is typical for marine artefacts found in anaerobic environments (Scott 2002). The protocol to form this corrosion product included placing the samples in a closed box for 30 minutes together with a mixture of 4 ml 20 % NH_4S (VWR International) and 20 ml deionised water (Lamy 1997).

Prior to the corrosion simulation, the copper samples were ground first on 1200 grit SiC-emergy paper (Buehler) to obtain a fresh surface. To smoothen the surface they were further polished on a polishing cloth covered with alumina powder of 1 µm particle size. To remove any adherent Al_2O_3 particles the surfaces were rinsed thoroughly with deionised water and cleaned in an ultrasonic bath (Branson 3210).

3.2 Storage / stabilisation treatments

Tap water is often used for the storage of archaeological artefacts recovered from wet saline environments. For this study tap water was artificially prepared according to the composition of tap water of Wageningen (van Meeteren et al. 2000). The artificial tap water was prepared by dissolving 10.76 mg/l $CaSO_4.2H_2O$, 40.66 mg/l $MgCl_2.6H_2O$, 126.01 mg/l $NaHCO_3$ and 1.50 mg/l $CaCO_3$ in deionised water (pH = 7).

Various concentrations of sodium sesquicarbonate solutions are used by conservators for the stabilisation of bronze artefacts. Five to 10 wt% solutions are very common, but due to side effects, such as the formation of chalconatronite ($Na_2Cu(CuO_3)_2.3H_2O$), lower concentrations are now used. For this study a 1 wt% sodium sesquicarbonate solution was prepared by dissolving 11.89 g/l of $Na_2CO_3.NaHCO_3.2H_2O$ (Sigma) in deionised water (pH = 10).

3.3 Electrochemical measurements

For the evaluation of the treatments corrosion potential measurements were recorded in artificial tap water and in a 1 wt% sodium sesquicarbonate solution. The instrumentation was a PC-controlled potentiostat and software package type GPES4.9 (Autolab PGSTAT10, ECO Chemie). A Mercury Sulphate Electrode (MSE, $Hg/Hg_2SO_4,K_2SO_4(sat)$) electrode was used as reference electrode (= 640mV vs. Normal Hydrogen Electrode, NHE). Copper coupon disc electrodes of 6 mm diameter, covered or not with corrosion product, were measured in 150 ml of the electrolyte solution.

3.4 Surface characterization

Synchrotron radiation X-ray diffraction measurements were performed to evaluate the effect of the treatment solutions on the corrosion products. 2D diffraction patterns were acquired using a CCD detector at station 9.6 of the Synchrotron Radiation Source at Daresbury Laboratory (UK). Each of the experiments was performed three times. Powder samples were prepared by scraping the corrosion products off the sample. The powder samples were deposited on tape stretched over thin metal sample holders which were then mounted on the goniometer. Exposure times of 30 s were used in multibunch (250mA) mode. The data were polar transformed and azimuth integrated using the ESRF program FIT2D (Hammersley et al. 1996). The tape gives a background in the spectra, which is more pronounced when a smaller amount of powder is measured or when the corrosion product has a diffracting power (see also the spectrum labelled ‘background’ in Figure 2 and 4).

4. Results

4.1 Artificial tap water

A set of artificially corroded copper coupons was prepared according to the description in subsection 3.1 ‘Corrosion simulation’. The samples were immersed in artificial tap water while corrosion potential measurements were made. In Figure 1 the first 18 hours of the immersion are presented. During the first day the corrosion potentials show the largest variation. For the pure copper samples large potential variations are even seen during the first six hours. Afterwards the potential rises to a steady state value around -0.35 V/MSE where it stays at the same level during at least the next two weeks (not shown). The stabilisation time of copper covered with cuprite is much shorter: after only two hours a more or less stable corrosion potential was achieved. The corrosion potential of copper covered with nantokite shows a strong decrease during the first few hours. Afterwards it rises to a steady state around the same value of the steady state plateau of copper covered with cuprite. The corrosion potentials of the remaining chloride containing corrosion products rise in the first few hours. The corrosion potential of atacamite rises to a steady state, whereas the increase of the corrosion potential of the mixture of atacamite and paratacamite is first followed by a descent before it rises again to its steady state. Finally the corrosion potential curve for chalcocite rises strongly in the first hour to decrease slowly after two hours and stabilise after 10 hours.

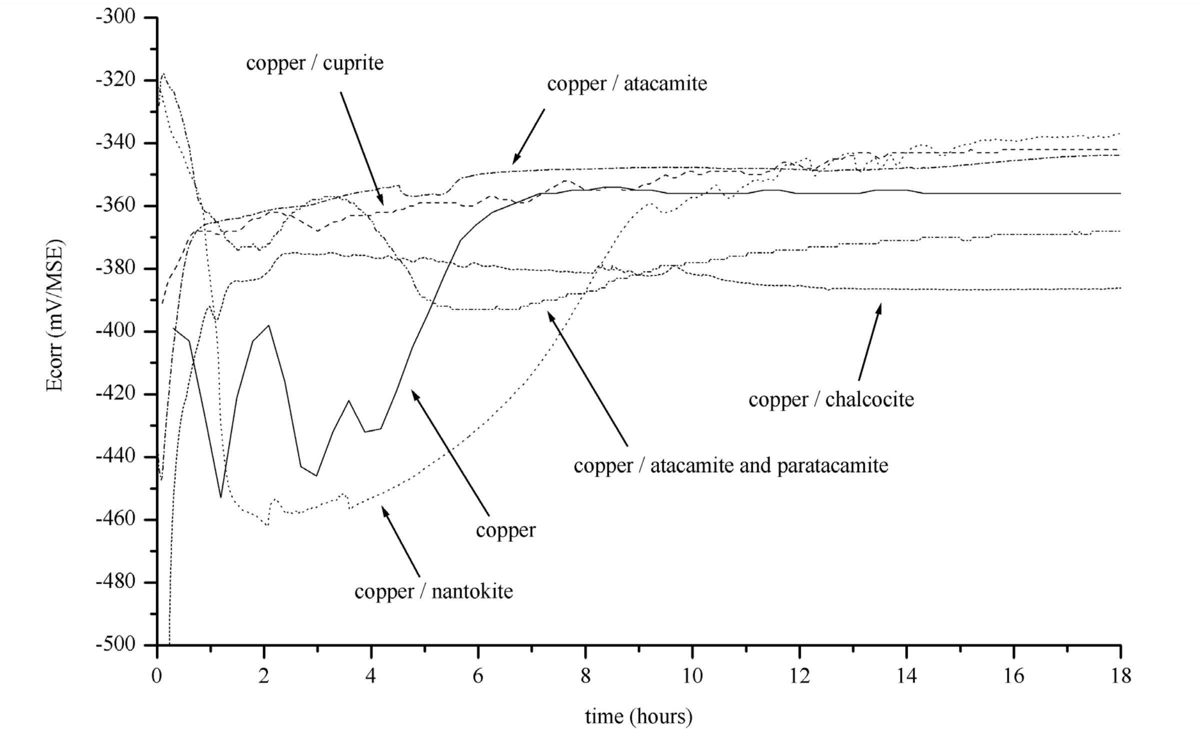


Figure 1. Corrosion potential versus time measurements for pure copper and copper covered with different corrosion products immersed in artificial tap water.

XRD measurements of the copper coupons covered with corrosion products were performed after one day and after 14 days of immersion in the solution. In Figs. 2a to 2e, a representative curve of each of the experiments is given. The XRD diffractograms of cuprite immersed in artificial tap water look the same before and after one day, seven days and 14 days immersion (Figure 2a). (The line basis of the last experiments is changed due to the use of a different tape in the sample holder). Each of the samples clearly shows peaks (Bragg reflections) corresponding to cuprite: 3.020 Å (9%), 2.465 Å (100%) and 2.135 Å (37%) (the relative intensities of the reference spectra are given between brackets). The copper peaks (2.088 Å (100%) and 1.808 Å (46%)) found in the first three diffractograms are most probably due to the sample preparation, as in some cases pure copper was scratched off as well. The XRD spectra show no indication that other corrosion products have formed during immersion.

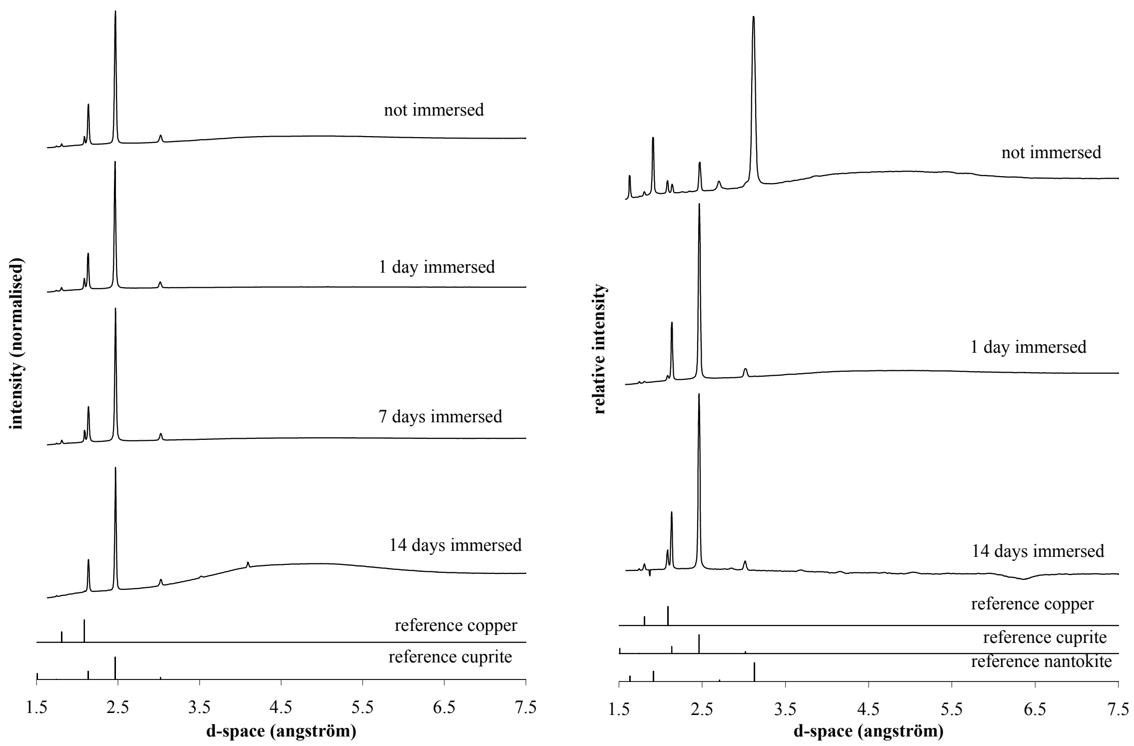
The nantokite samples show more variation as a function of time (Figure 2b). The samples which have not been immersed yet show very clearly the nantokite peaks at 3.117 Å (100%), 2.710 Å (8%), 1.91 Å (55%) and 1.633 Å (30%). Cuprite peaks (2.465 Å and 2.135 Å) and copper peaks (2.088 Å and 1.808 Å) can be seen as well. After one day of immersion the peaks of nantokite have disappeared and only cuprite and some copper remain.

The atacamite samples (Figure 2c) clearly show the presence of atacamite with the largest peaks at 5.485 Å (100%), 5.03 Å (68%), 2.835 Å (51%), 2.78 Å (42%), 2.761 Å (28%), 2.280 Å (29%) and 2.265 Å (41%). These peaks are found in each of the samples, regardless of the time spent in the artificial tap water. The peaks around 4.2 and 6.4 are background and result from the tape used in the sample holder. In addition a few unidentified peaks show up at 3.91 Å, 2.67 Å and 1.96 Å on the samples which had not been immersed. They disappear once the samples have been immersed.

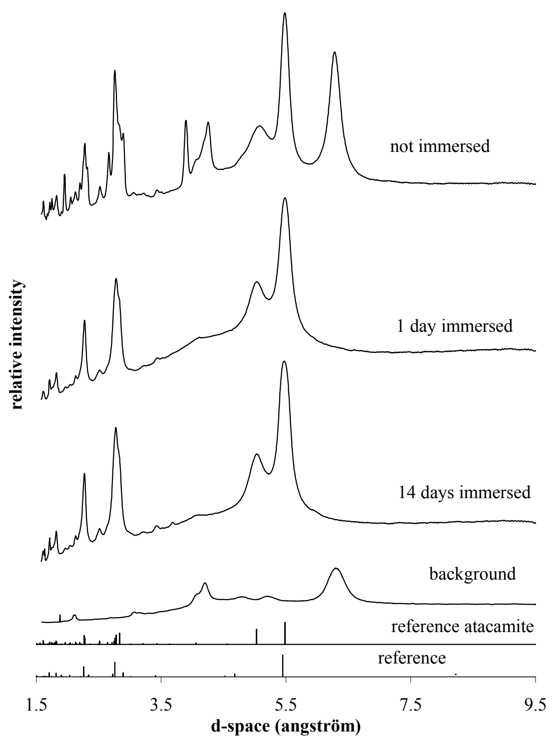
The XRD spectra of the mixture of atacamite and paratacamite are given in Figure 2d. Most of the diffraction lines of atacamite and paratacamite are closely related to each other (paratacamite has main peaks at 5.449 Å (100%), 4.68 Å (14%), 2.893 Å (19%), 2.758 Å (67.2%), 2.724 Å (13%), 2.261 Å (46%), 1.816 Å (17%) and 1.707 Å (19%)). Atacamite has a unique peak at 5.03 Å, where paratacamite has a unique peak at 6.48 Å. Both peaks are present in these spectra. The samples which have not been immersed also show a few unidentified peaks at 1.99 Å and between 3 Å and 3.3 Å. These peaks have not appeared on the immersed sample.

The chalcocite protocol gives a complex diffractogram (Figure 2e). Chalcocite is the principal corrosion product found in this diffractogram with the largest peaks at 3.71 Å (27%), 3.271 Å (36%), 3.162 Å (27%), 2.719 Å (36%), 2.403 Å (55%), 2.398 Å (73%), 2.393 Å (36%), 2.331 Å (27%), 2.192 Å (36%), 1.961 Å (73%), 1.87 Å (73%) and 1.867 Å (100%). After immersion, copper (2.088 Å and 1.808 Å) and cuprite (2.465 Å and 2.135 Å) are the main peaks. Small peaks of chalcocite can also be observed.

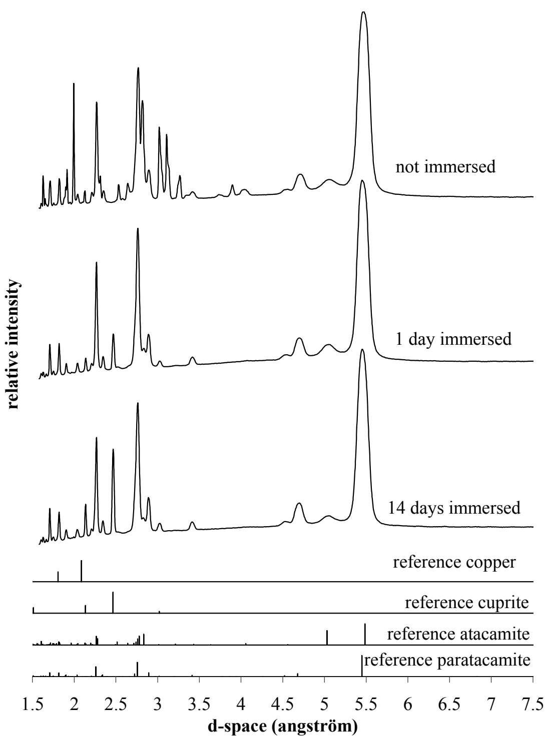
From the diffractograms we can conclude that only nantokite and chalcocite seem to be effected by this short time immersion. The other corrosion products remain stable.


a) cuprite protocol

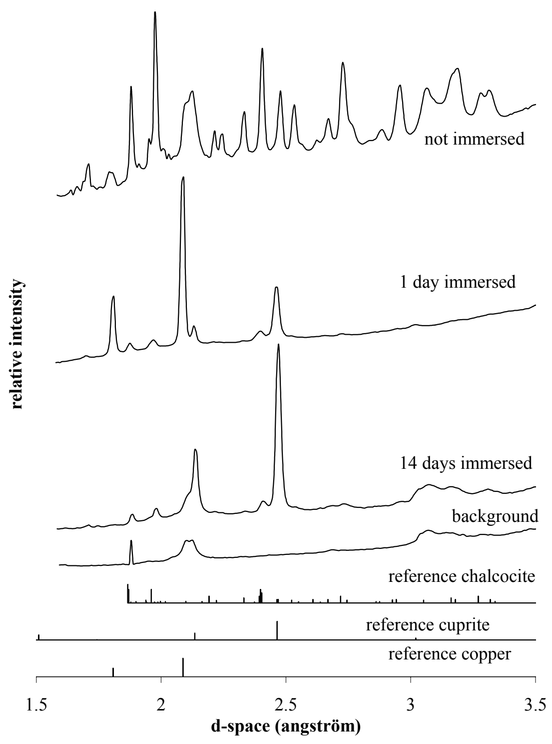
b) nantokite protocol



c) atacamite protocol



d) atacamite/paratacamite protocol



e) chalcocite protocol

Figure 2. SR-XRD measurements of copper coupons covered with corrosion products after different immersion times in artificial tap water. a) cuprite b) nantokite c) atacamite d) atacamite and paratacamite e) chalcocite

4.2 Sodium sesquicarbonate solution

A similar set of coupons were prepared and immersed in a 1 wt% sodium sesquicarbonate solution. Figure 3 shows the corrosion potential measurements during the first 12 days for each of the coupons immersed in the sodium sesquicarbonate solution. It is obvious that the corrosion products in this solution exhibit a different behaviour to tap water. The corrosion potentials of copper and cuprite quickly reach equilibrium. The corrosion potential of nantokite on the other hand shows a quick descent at the beginning, followed by an increase which goes over a maximum to a more or less steady state. After seven days it starts a long rise again. The mixture of paratacamite and atacamite also seems to be unstable; the corrosion potential descending over more than 14 days. The corrosion potential behaviour of pure atacamite on the other hand gives a very slow but steady rise. This indicates the formation of a stable and protective corrosion layer. Finally chalcocite shows a long steady rise to reach a plateau after eight days.

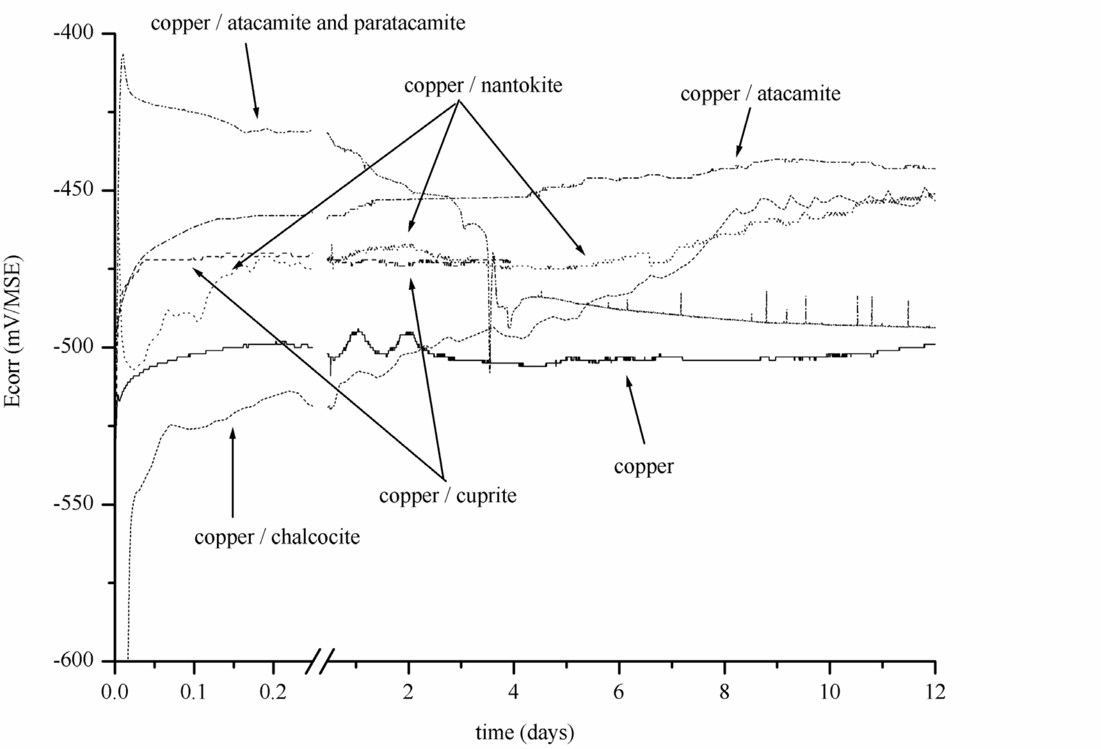


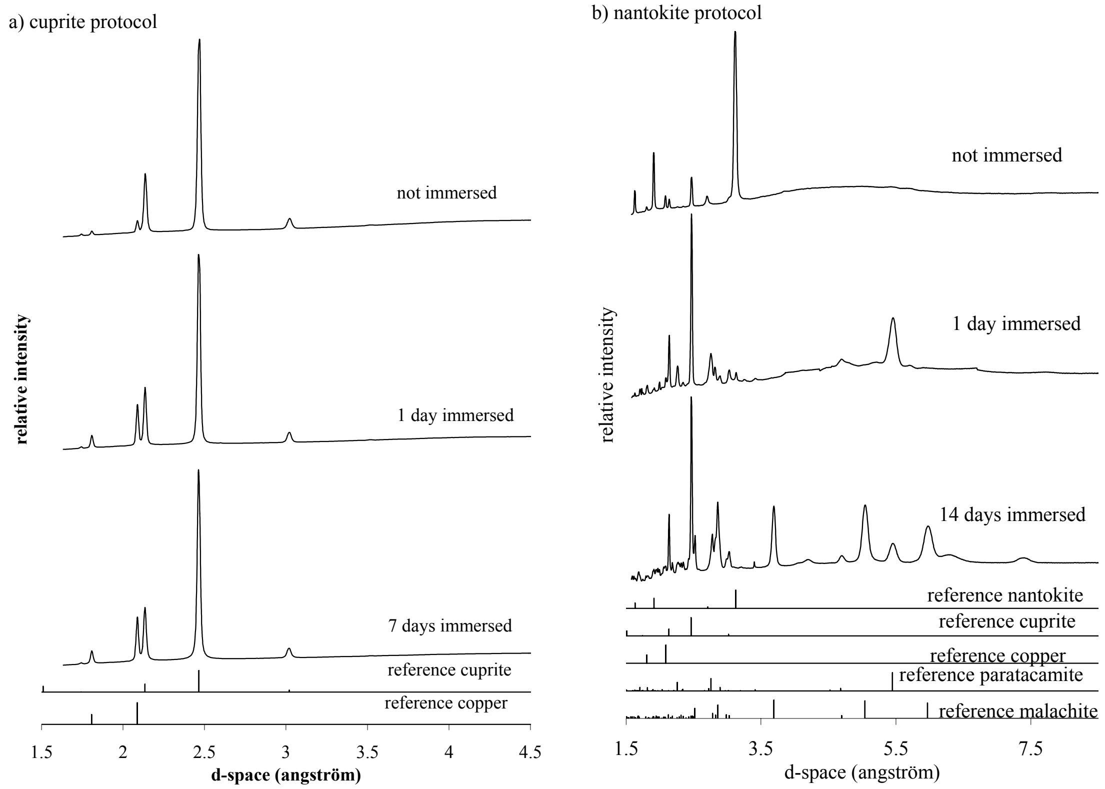
Figure 3. Corrosion potential versus time measurements for pure copper and copper covered with different corrosion products immersed in 1wt% sodium sesquicarbonate.

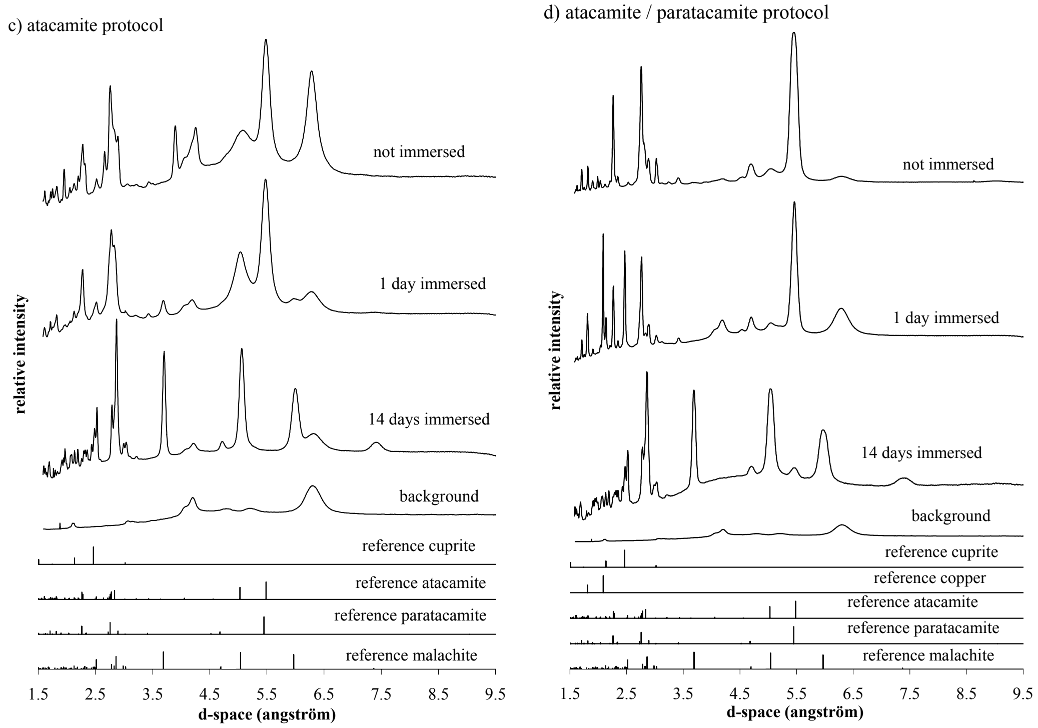
XRD measurements of the copper coupons covered with corrosion products were performed after one day and after 14 days immersion in the solution (Figs. 4a to 4e). The XRD measurements indicate that cuprite does not undergo chemical transformation in the sodium sesquicarbonate solution (Figure 4a.). The XRD spectra before immersion, after 1 day immersion and after seven days immersion in the sodium sesquicarbonate solution all show the presence of cuprite (2.465 Å and 2.135 Å) and copper (2.088 Å and 1.808 Å).

Nantokite on the other hand reacts relatively fast (Figure 4b) in the sodium sesquicarbonate solution. After only one day of immersion the presence of nantokite (3.13 Å, 1.91 Å) is less pronounced and is even missing in some of the samples. Cuprite (2.465 Å and 2.135 Å) and paratacamite (5.44 Å and 4.68 Å) have obviously been formed on the samples. After 14 days in the sodium sesquicarbonate solution nantokite is no longer observed. Cuprite and paratacamite are still present, but also malachite ($CuCO_3.Cu(OH)_2$) has shown up, with mean peaks at 5.970 Å (84%), 5.040 Å (96%), 3.690 Å (100%), 2.985 (20%), 2.861 Å (73%), 2.781 (28%), 2.518 (55%), 2.128 (20%).

The other chloride species, atacamite and paratacamite (Figs. 4c,4d) show a similar behaviour: the chloride products disappear in the XRD spectra in favour of malachite.

Chalcocite on the other hand reveals a special behaviour. Chalcocite can be found as a hexagonal or as an orthorhombic system. The diffractogram in Figure 4e shows the samples which have not been immersed exhibit an orthorhombic structure. For the diffractogram recorded after one day, the pure copper peaks were the most pronounced. To reveal the corrosion layer the copper peaks were truncated in Figure 4e. The diffractogram now reveals the peaks for a hexagonal structure (indicated by arrows in Figure 4e). It is likely that there has been a rearrangement of the crystal structure in the sesquicarbonate solution. After 14 days the layer was too thin to remove and measure. The spectra only reveal pure copper.





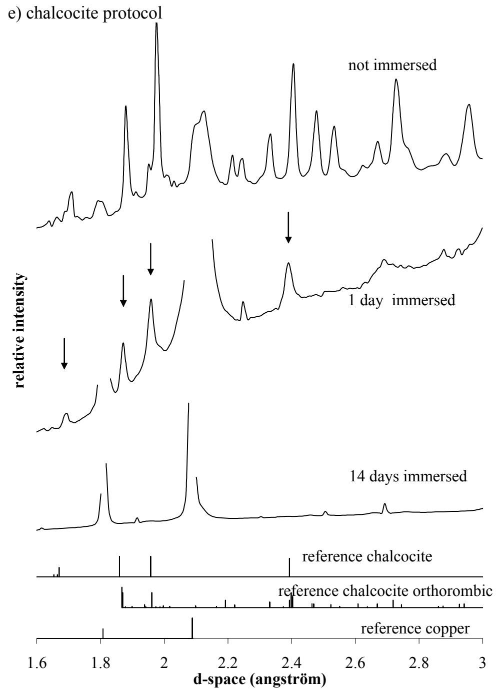


Figure 4. SR-XRD measurements of copper coupons covered with corrosion products after different immersion times in a sodium sesquicarbonate solution. a) cuprite b) nantokite c) atacamite d) atacamite and paratacamite e) chalcocite.

5. Discussion

Chemical and electrochemical transformation of the artificially prepared corrosion products occurring during immersion in tap water and the sodium sesquicarbonate solution were monitored for two weeks. A compilation of the XRD results is given in Tables 1 and 2. Corrosion potentials were recorded in parallel. The corrosion potential of cuprite quickly reached a steady state in both solutions. This is in agreement with the findings in the XRD measurements that cuprite is stable in these solutions. Nevertheless, a transformation at a microscopic level can occur and needs to be investigated.

The preliminary decrease of the corrosion potential for nantokite in the artificial tap water and in the sesquicarbonate solution is characteristic of a transformation process. According to Oddy nantokite can react with water in one of two ways, to give either cuprite or paratacamite by the following reactions (Oddy et al. 1970):

$$2\,\mathrm{CuCl}\ (\text{nantokite}) + \mathrm{H_2O} \rightarrow \mathrm{Cu_2O}\ (\text{cuprite}) + 2\,\mathrm{Cl^-} + 2\,\mathrm{H^+} \quad (1)$$
$$2\,\mathrm{CuCl}\ (\text{nantokite}) + 2\,\mathrm{H_2O} + \mathrm{O_2} \rightarrow \mathrm{Cu_2(OH)_3Cl}\ (\text{paratacamite}) + \mathrm{HCl} \quad (2)$$

In the artificial tap water the XRD spectra clearly indicate the disappearance of nantokite and the formation of cuprite. This can explain why the corrosion potential on copper coupons initially covered with nantokite reaches almost the same steady state value as on cuprite protocol coupons. On the nantokite protocol coupons in the sesquicarbonate solution cuprite as well as paratacamite is formed in the first instance. This is followed by the formation of malachite after a two weeks period. This can be due to the reactions suggested by MacLeod (MacLeod 1987a,b):

$$4\,\mathrm{CuCl} + \mathrm{O_2} + 8\,\mathrm{HCO_3^-} \rightarrow 4\,\mathrm{Cu(CO_3)_2^{2-}} + 4\,\mathrm{H^+} + 4\,\mathrm{Cl^-} + 2\,\mathrm{H_2O} \quad (3)$$
$$\mathrm{Cu_2(OH)_3Cl}\ (\text{paratacamite}) + 4\,\mathrm{CO_3^{2-}} \rightarrow 2\,\mathrm{Cu(CO_3)_2^{2-}} + 3\,\mathrm{OH^-} + \mathrm{Cl^-} \quad (4)$$

The ion $\mathrm{Cu(CO_3)_2^{2-}}$ is supposed to be stable in the presence of bicarbonate ions but Oddy already indicated the precipitation of this compound. In this way a layer of malachite ($\mathrm{CuCO_3.Cu(OH)_2}$) can be formed on the bronze (Oddy et al. 1970). It is probably the formation of the stable malachite that causes the corrosion potential to rise after six days. However, more experiments are needed to clarify how the formation of malachite is reflected in the change of the corrosion potential.

Similar results were obtained with the samples covered with a mixture of atacamite and paratacamite. The red-brown cuprite layer underneath the blue-green atacamite/paratacamite layer was grown in tap water. The relative quick descent of the corrosion potential in the beginning of the immersion can be caused by the decomposition of the copper chloride species. It is probably due to the cuprite layer that the corrosion potential reaches a sort of steady state after a day. In the sodium sesquicarbonate solution the decrease can be slowed down by the formation of a stable malachite (as mentioned in the discussion of nantokite) and cuprite layer. Further measurements are required to explain the behaviour of the corrosion potential in full detail.

The corrosion potential measurements of atacamite in tap water as well as in the sesquicarbonate solution show a quick rise in the beginning of the immersion. A steady state is reached very soon hereafter. Except for the disappearance of a few unknown peaks, the XRD spectra reveal no change of the corrosion products in the artificial tap water. In the sesquicarbonate solution the first malachite peaks can already be seen after one day immersion. The corrosion potential shows little variation after a few hours immersion, probably due to the quick appearance of the malachite.

The XRD spectra indicate that chalcocite is dominated by cuprite after immersion in the artificial tap water. In the sodium sesquicarbonate solution on the other hand no formation of cuprite is indicated and also malachite is not found in this case. As a result it is difficult to explain the large shift of the corrosion potential with time.

Table 1. Compilation of the XRD results before and after 14 days immersion in artificial tap water.

		corrosion products					
corrosion protocols		cuprite (Cu_2O)	nantokite ($CuCl$)	atacamite ($Cu_2(OH)_3Cl$)	paratacamite ($Cu_2(OH)_3Cl$)	chalcocite (Cu_2S)	malachite ($CuCO_3.Cu(OH)_2$)
pure copper	before						
	after	+					
cuprite	before	+					
	after	+					
nantokite	before		+				
	after	+					
atacamite	before			+			
	after	+		+			
atacamite and paratacamite	before			+	+		
	after	+		+	+		
chalcocite	before					+	
	after	+				+	

Table 2. Compilation of the XRD results before and after 14 days immersion in a 1wt% sodium sesquicarbonate solution.

		corrosion products					
corrosion protocols		cuprite (Cu_2O)	nantokite ($CuCl$)	atacamite ($Cu_2(OH)_3Cl$)	paratacamite ($Cu_2(OH)_3Cl$)	chalcocite (Cu_2S)	malachite ($CuCO_3.Cu(OH)_2$)
pure copper	before						
	after	+					
cuprite	before	+					
	after	+					
nantokite	before		+				
	after	+			+		+
atacamite	before			+			
	after	+		+			+
atacamite and paratacamite	before			+	+		
	after	+		+	+		+
chalcocite	before					+	
	after	+				+	

6. Conclusion

Artificially formed patina on copper does not seem to be affected during the immersion in tap water as is shown by both Ecorr and XRD measurements. In the sodium sesquicarbonate solution the decomposition of nantokite favours the stabilisation of artefacts but can change the surface appearance due to the formation of malachite. Monitoring of the corrosion potential with time appears as a very promising and simple technique to record these transformations, particularly when the corrosion layers are made of a single corrosion product. Further research is required as real artefacts are commonly covered with a stratigraphy of different corrosion products, which are all affected separately by the solutions used.

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