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The Coordinated Use of Synchrotron Spectroelectrochemistry for Corrosion Studies on Heritage Metals

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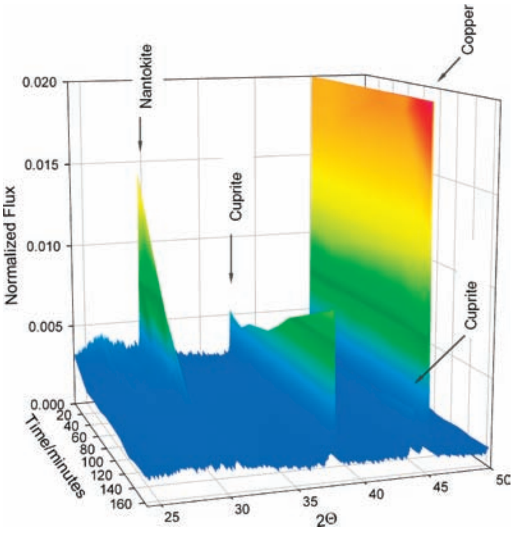

Corrosion is a major source of degradation in heritage metal objects, and any remedial measures are subject to a strong (Western) ethic that favors conservation as opposed to restoration. Accordingly, major scientific challenges exist for developing appropriate treatment methods to stabilize and protect artifacts after they are recovered from an archaeological site, both before and during their display or storage in a museum. Because inappropriate treatments can cause irreversible damage to irreplaceable objects, it is crucial that the chemical processes involved are fully understood and characterized before any preservation work is undertaken.

In this regard, large infrastructural facilities such as synchrotrons, neutron sources, and particle accelerators provide a wealth of analytical possibilities, unavailable in smaller scale laboratories. In general, the intensity of the radiation available allows measurements on a short time scale or with high spatial resolution (or both), so heterogeneous changes induced by a chemical process can be recorded while they occur. The penetrative nature of the radiation (e.g., X-rays, protons, or neutrons) also allows a sample to be studied in air. If necessary, complete artifacts (such as paintings or statuettes) can be examined. In situ analysis in a controlled environment, such as a liquid or corrosive atmosphere, also becomes an exciting possibility. Finally, there are many complementary techniques (local atomic structure or crystal structure determination, macroscopic 3-D imaging (tomographies), imaging chemical analysis, and so on) so the many distinct details of a problem can be thoroughly explored.

In this Account, we discuss the application of this general philosophy to studies of corrosion and its prevention in cultural heritage metals, focusing on our recent work on copper alloys. More specifically, we use synchrotron-based techniques to evaluate the use of corrosion potential measurements as a possible monitoring method for copper-based objects recovered from marine environments. The extraction of chlorides from such artifacts is a process that must take place before the artifacts are put on display or stored, because air exposure of untreated metal will result in severe damage or loss in as little as a few weeks. Chloride is removed by soaking the artifact for up to two years in tap water or dilute sodium sesquicarbonate, with regular solution changes.

Our research supports the effectiveness of this treatment for thin nantokite (copper(I) chloride) layers, but it raises questions for copper hydroxychlorides (atacamite and paratacamite), especially when these minerals are trapped in fissures. Electrochemical parameters such as the corrosion potential are shown to be insensitive to the physical presence of large hydroxychloride coverages if they overlie a cuprite (Cu_2O) layer. X-ray absorption spectroscopy proves to be a good monitor for the chloride in solution over the working electrode, whereas X-ray diffraction offers the potential for real-time measurement of the surface chloride composition. In principle, the two techniques together offer the possibility of monitoring surface and fluid levels simultaneously.

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Introduction

The physical part of our cultural heritage is deteriorating faster than it can be conserved, restored, or studied. Assets are being lost, or are at risk, through natural processes of decay (sometimes accelerated by poor environmental control); environmental disasters (sometimes exacerbated by human activity); direct effects of increased public access (without commensurate conservation measures); conservation/preservation procedures whose long-term effects were damaging; and simple negligence, looting, and war.

While there is a general agreement that action is required to halt or mitigate decline, few people actually realize that high level research and technology play an essential role in protecting our cultural heritage. In fact, advanced analytical methods are an essential prerequisite in this field, as they provide the means to study the structural chemistry of the processes involved. They can, additionally, contribute to the development of simple diagnostic techniques necessary for practical applied conservation, help establish authenticity, and, by identifying materials and processes, allow us to reach back through time and develop a deeper understanding of the craftsmanship and the technology used.

Infrastructural facilities such as synchrotrons, neutron sources, and particle accelerators provide a wealth of analytical possibilities which are unavailable in smaller scale laboratories. In general, the intensity of the radiation available allows measurements on a short time scale or with high spatial resolution, or both, so that heterogeneous changes induced by a chemical process can be recorded while they are happening. Again, the penetrative nature of the radiation (e.g., X-rays, protons, neutrons) allows a sample to be studied in air, and, because there is no need for it to fit within a confined space in an analytical chamber, whole artifacts may sometimes be studied, provided the logistical problems of transporting them to the facility can be solved. The probe intensity also opens up the exciting possibility of analysis in situ in a controlled environment, for example, during immersion in a liquid or while exposed to a corrosive agent. Additionally, there are many complementary techniques available, giving local atomic structure, crystal structure, macroscopic 3-D imaging (tomographies), imaging chemical analysis, and so on, so that the details of a problem can be thoroughly explored.

The use of ion beam analysis (IBA) techniques in the field of cultural heritage goes back for more than 20 years, with particle induced X-ray emission (PIXE) being the most popular fingerprinting technique for trace elements. One of the first proceedings of a workshop on the use of small accelerators in archaeometry was published in 1986 in the journal *Nuclear Instruments and Methods in Physics Research, Section B*.[1] The workshop coincided with the installation of a 2 MV tandem accelerator AGLAE (Accelerateur Grand Louvre pour l'Analyze Elémentaire) in the basement of the Louvre museum in Paris which has since been dedicated exclusively to cultural heritage research.[2] Since 1986, several other proceedings, for example, refs 3 and 4, and individual papers have been published in peer-reviewed journals, all demonstrating the vast interest in using IBA techniques in the area of heritage science. In 1995, COST (one of the EU instruments for funding research networks) dedicated a specific action to the topic. It ran for five years (1995−2000) under the title "COST G1: Application of Ion Beam Analyses to Art and Archaeological Objects" and involved the participation of 12 European countries. The output of this network resulted in ca. 30 joint papers and two monographs.[5,6] Within the sixth and seventh Framework Program of the EU, the EU-ARTECH project and its successor CHARISMA, a consortium among 13 internationally distinguished European infrastructures dedicated to artwork conservation, offer a coherent set of transnational access programs including one to AGLAE.[7]

At the same workshop in 1986, a paper was presented on new possibilities in cultural heritage research using synchrotron facilities,[8] and by 1996 the number of synchrotron-related papers in the field of cultural heritage was increasing rapidly. Today, more than 50 papers per year[9] are published in this area. The main techniques used are X-ray fluorescence (SR-XRF), absorption (XAS), and diffraction (SR-XRD) and infrared spectroscopies. In 2004, an interface dedicated to archeology and cultural heritage was launched at Synchrotron SOLEIL, which aims at facilitating the access of researchers to the synchrotron.[10] Other synchrotron infrastructures also welcome cultural heritage related projects.

The use of neutron imaging techniques is becoming increasingly popular. Paintings (neutron autoradiography) and metallic artifacts such as statuettes (radiography and tomography) are suitable objects of study. Especially with regard to metal or large objects, the advantage of neutron imaging compared to X-ray imaging is the fact that neutrons usually have a much higher range in the material, and in cases where intense X-ray fluxes cause damage, neutrons may not. It is well-known that the attenuation of X-rays increases strongly with higher mass numbers of the investigated material. If heavy metals are to be investigated, a few millimeters are sufficient to shield the X-ray beam completely. At this point, neutrons become valuable due to higher penetration for most of the relevant metals.[11]

In this Account, we will discuss our own experience at synchrotron infrastructures for one specific project, namely, the in situ monitoring of the surface and electrochemical behavior of archeological copper alloys during their storage and stabilization. Artifacts recovered from marine environments or from the ground are typically saturated with chlorides whose attack on the metal will be greatly accelerated upon air exposure. Serious degradation or even loss of the artifact can result. To alleviate this problem, objects are stored in tap water or sodium sesquicarbonate solution for periods of up to several years.[12−14] This is believed both to remove potentially damaging soluble chlorides from the microstructure of the metal and to change various copper chlorides into more benign compounds such as cuprite. A method which has been proposed for monitoring the progress of the treatment and determining its end-point is the measurement of the corrosion potential E_{corr}, the open circuit potential of the electrochemical cell in which, effectively, the artifact is immersed. The storage process in our work was imitated by immersing artificially corroded copper coupons in a 1% (wt/v) sodium sesquicarbonate solution. The possible use of corrosion potential measurements as a monitoring method was evaluated by recording the corrosion potential of the immersed coupons as a function of time while analyzing the surface of the coupon simultaneously using either SR-XRD or XAS. In order to be able to perform these experiments, we developed an electrochemical cell (eCell) which is engineered so as to permit X-rays from a synchrotron beamline to be scattered or absorbed by the surface of a sample while in solution and electrochemical reactions are taking place. X-rays emitted from the surface then carry time-resolved information on the specific reactions as they occur.

Monitoring the Corrosion of Cupreous Artifacts

As with many other metals, copper corrodes once it comes into contact with an aggressive environment, for example, the sea or the atmosphere. In the field of art, copper-based objects are often preferred in the corroded state, not only because of the aesthetically pleasing colors but also because the presence of corrosion products provides evidence of time past and time passing, thereby adding extra value to the object.[12,16] However, corrosion may also become a problem, especially when specific corrosion products (such as cuprous chlorides) are in contact with the metal core. Under certain conditions, the deterioration of the underlying metal will continue and will lead to the destruction of the object.

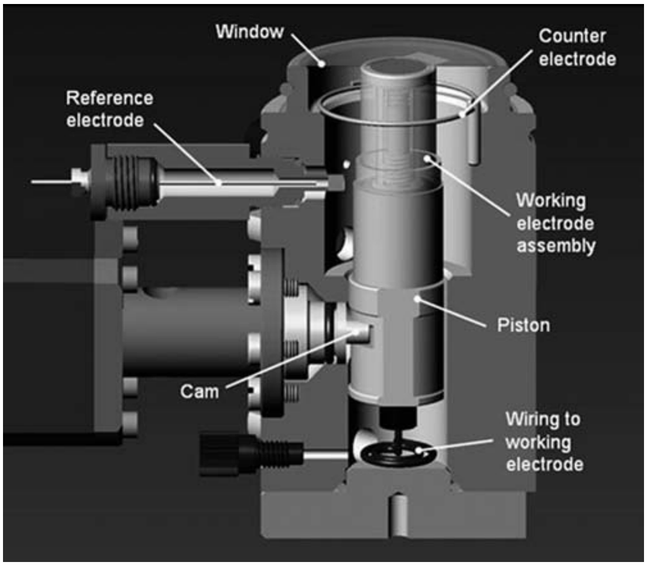

FIGURE 1. Schema of the electrochemical cell used in this work.

Corroded archeological copper and copper alloy artifacts recovered from wet saline environments are particularly susceptible to further corrosion. Studies have shown that, despite storage in tap water and stabilization in sodium sesquicarbonate, corrosion layers can subsequently provoke side effects such as the modification of the natural patina and the development of new active corrosion,[16,17] hence the need for continuous monitoring of the objects under care. During treatment, the chloride concentration in solution can be measured. When this exceeds a predetermined value, the solution is replaced. This procedure is repeated until the chloride concentration remains low enough. The disadvantage of this method is the fact that it is indirect: the conservator has no idea what is happening with the metal surface. Hence, a different monitoring method is needed. In our work, we have evaluated whether E_{corr} measurements may have a role to play. E_{corr} is the open circuit potential of the metal object against a stable reference electrode. The potential obtained depends on the solution (electrolyte) in which the object is immersed (which is known as it was chosen by the conservator) and the composition of the clean or corroded metal surface. The hypothesis is that stable E_{corr} data imply a stable surface chemistry. The method is easy to use, is of relatively low cost, and may therefore be suitable for museum applications.

The Use of eCell

Central to this work is a new environmental cell (eCell), capable of maintaining a controlled liquid, gas, or vapor environment over a sample (Figure 1). The eCell is a second generation of a published design.[18] It can be used as a three electrode electrochemical cell when filled with liquid electrolyte, allowing simultaneous real time analysis of the metal surface using a spectroscopic technique (in our case XRD and XAS).[18,19] To ensure that X-rays can reach the sample surface, and that electrochemical and solution processes can take place undistorted by limited electrolyte volumes, the working electrode can be raised and lowered between "X-ray" and "electrochemistry" positions under remote control. In the former position, about 125 μm of electrolyte remains between the sample surface and an 8 mm thick Kapton X-ray window. In the latter, the electrolyte thickness increases to $\sim$5 mm.

Experiments in this study were carried out on simulated materials; that is, copper coupons were artificially corroded. Four corrosion products commonly found on real copper artifacts were considered:[16] cuprite, nantokite, atacamite, and paratacamite. Cuprite (Cu_2O) is regularly found on copper artifacts and is a stable corrosion product.[20] Among the copper chlorides, nantokite (CuCl), atacamite ($Cu_2(OH)_3Cl$), and a mixture of atacamite and paratacamite (both isomers of $Cu_2(OH)_3Cl$) were selected. Nantokite (CuCl) is considered as the main catalytic agent for active corrosion. The presence of nantokite on the metal surface can jeopardize the long-term stability of an object. In fact, bronze disease or pitting corrosion is usually attributed to this corrosion product.[16,20] 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.[16] Atacamite is the most common of the $Cu_2(OH)_3Cl$ isomers, but it often alters into paratacamite.[20] Conversion between copper hydroxychlorides and their relative stabilities has also been discussed by Pollard et al.[21] The corrosion layers were made on pure copper coupons (ADVENT, purity 99.9%) according to protocols listed in the literature.[19,20]

The corroded coupons were immersed in a sodium sesquicarbonate solution in order to imitate the stabilization treatment. Various concentrations of sodium sesquicarbonate solutions have been used by conservators to stabilize bronze artifacts with lower concentrations currently favored, to limit rinsing steps, and to avoid the potential formation of copper carbonate. For this study, a 1 wt % (wt/v) sodium sesquicarbonate solution was prepared by dissolving 11.89 g/L $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (Sigma) in deionized water (pH = 10).

In addition to the artificial corrosion of the copper coupons, powder samples of Cu_2O (for comparison with cuprite, Fluka, > 99%) and Cu(I)Cl (for comparison with nantokite, Fluka, > 97%) were purchased to serve as reference material. Atacamite powder is not commercially available and was prepared according to an existing protocol.[20]

A first set of simultaneous synchrotron X-ray diffraction (SR-XRD) and electrochemical experiments was carried out at station 2.3 of the Synchrotron Radiation Source, Daresbury Laboratory (U.K.).[22] The amount of data collected as a function of time was limited here by the scan time of the diffractometer (ca. 30 min). Acquisition times of the order of 1 s would, however, would be preferable, so that data for different products can be recorded contemporaneously, fast reactions can be studied, and short-lived byproduct can be observed. Times in this range can be achieved using one- or two-dimensional area detectors which collect a large range of angles in parallel. Parallel collection of spectra also minimizes the X-ray dose; the beam can be off for most of an experiment lasting many hours. Moreover, it is vital to be able to collect the electrochemical data in a mode where the reaction takes place in the bulk of the electrolyte (i.e., allowing the optimization of transport processes in the electrochemical cell), and to raise the working electrode to the cell window for a short time for X-ray analysis. This is not possible with a scanning diffractometer, as spectra must be recorded continuously throughout the experiment. Further sets of SR-XRD experiments were therefore performed at SRS station MPW6.2 and beamline 28 (XMaS) at the ESRF.[23] The advantage of the former beamline lies in the fact that data were acquired using a RAPID II detector system which is one-dimensional and collects all of the in-plane diffraction simultaneously. It allows the acquisition of spectra with a time resolution of under a second.[24] The latter beamline makes use of a 2D Mar CCD 165 detector (Mar USA Inc., Evanston, IL) for the acquisition of surface diffraction patterns. The advantage over a 1-D in-plane detector is that preferential crystallographic orientation shows up immediately as do time dependent changes in crystal orientation. Spectra can be extracted which average over or highlight these effects as one wishes.

XAS measurements were performed at station BM26A (DUBBLE) at the ESRF.[25,26] Cu K-edge (8.979 keV) XAS spectra were recorded as a function of energy. The scan time was 20 min, and measurements were made in fluorescence mode.

Can Corrosion Potential Measurements Be Incorporated in a Trustworthy Sensor?

Figure 2 shows a typical SR-XRD spectrum (gray) of a copper sample initially covered with synthetic nantokite and some cuprite (which is also formed by the protocol). The offset spectrum (black) shows the sample after 10.3 h in the sesquicarbonate. The copper signal increases by a factor 2.4, nantokite disappears, and cuprite diminishes slightly. Figure 3 shows the variation of the SR-XRD peak heights of nantokite and cuprite as a function of time, together with the simultaneously measured E_{corr}.[18] Again, nantokite disappears. This time, however,

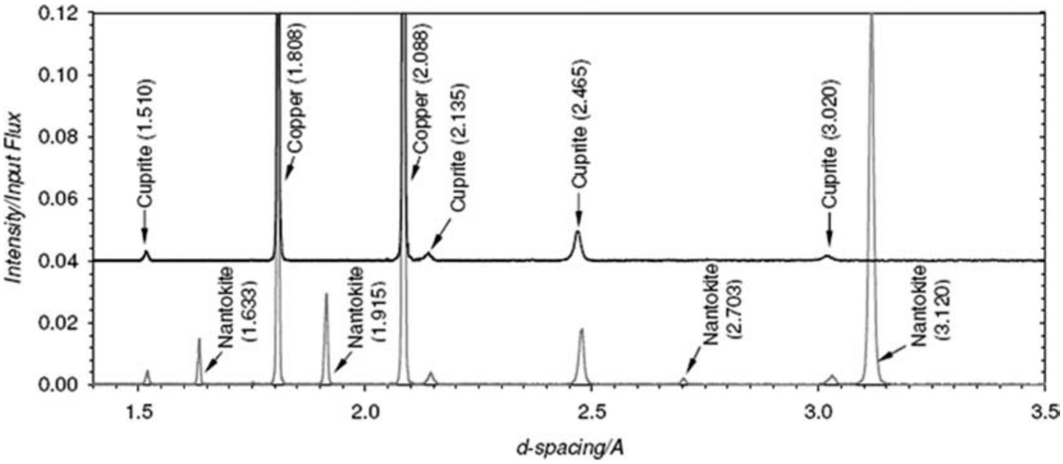

FIGURE 2. Typical spectra from copper coated with nantokite before and after treatment in 1% w/v sodium sesquicarbonate for 10.3 h. In the gray spectrum taken prior to treatment, cuprite and nantokite are evident. After treatment, only cuprite remains. In this experiment, the copper intensity increased by a factor of 2.4.

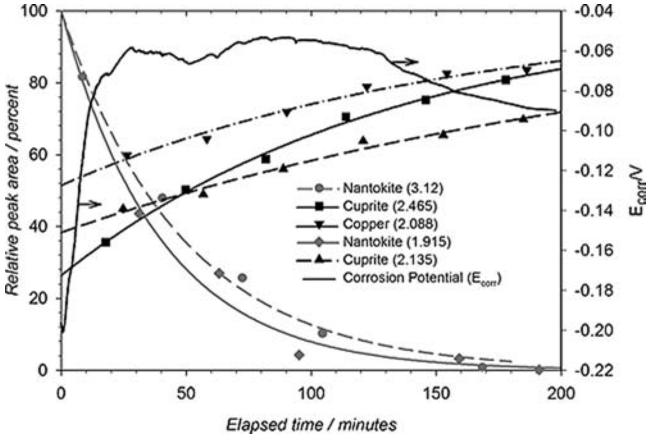

FIGURE 3. Variation of the SR-XRD peak heights of nantokite and cuprite as a function of time, together with the simultaneously measured E_{corr}. The reference electrode was 3 M Ag/AgCl.

the cuprite signal grows by more than a factor of 2.5. Many repeated measurements show behavior between these two extremes, probably dependent on the thickness and morphology of the nantokite, and other factors. The mechanism of cuprite formation remains unclear at this stage, as several routes are possible in the presence of chloride ions. For example, Oddy and Hughes[12] believe that nantokite can react with water to form cuprite through the following reaction:

$$2CuCl + H_2O \rightarrow Cu_2O + 2Cl^- + 2H^+$$

However, cuprite can also be formed through a precipitation reaction.[27]

$$2CuCl_2^- + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^-$$

The increase of the copper signal in Figure 3 may either be due to the fact that the final cuprite layer is thinner than the original nantokite, or, alternatively, give evidence for the precipitation of copper as a superficial layer over the cuprite.[28]

For the open circuit potential (OCP) data, the right-hand *y*-axis gives the corrosion potential. The hypothesis that a stable E_{corr} means a stable surface chemistry is not supported. Although there is a rough correlation between the rise in E_{corr} and the rapid loss of nantokite during the first 30 min, E_{corr} then becomes more or less stable while the surface composition continues to change.

The ongoing processes were studied in further detail using XAS.[25,26] The latter provides an independent means of surface characterization, as the technique is not only sensitive to the presence and evolution of amorphous surface compounds but will also give information on the presence of potential complex ions in the solution. As with the SR-XRD experiments, eCell was filled with a 1% (wt/v) sodium sesquicarbonate solution and XAS data were taken as a function of time.

Overall, the spectra show two significant features:

First, for the thin corrosion layers, such as nantokite and cuprite, the XAS signal is strongly influenced by the presence of the underlying copper, which is less the case for the corrosion layers atacamite and paratacamite. The latter is clearly seen in Figures 4 and 5.[25] Figure 4 shows spectra for the four powder references and a bare copper sample, with an inset to show the details of the edge region. Figure 5, on the other hand, shows the data obtained in fluorescence mode from the corrosion products on the copper surface. The cuprite and nantokite spectra are strongly influenced by the presence of the underlying copper, simply because the layers are thin. Nevertheless, the shoulder in the nantokite at 8985 eV (A) is clearly a relic of the post edge peak in the CuCl, and the spectrum from the cuprite coated sample is modified from its dominant copper shape at (B). The thicker atacamite spectrum

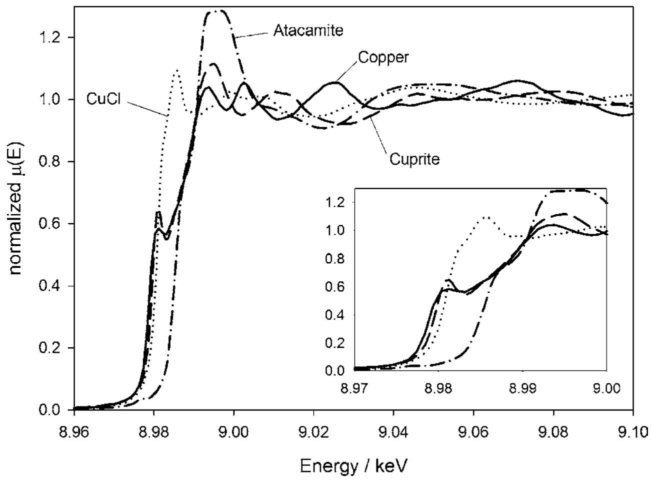

FIGURE 4. XAS spectra for copper, cuprite, CuCl (the analogue for nantokite), and synthesized atacamite. The inset shows the edge region in detail. Reproduced with permission from ref 25. Copyright 2009 The Royal Society of Chemistry (http://dx.doi.org/10.1039/b814181a).

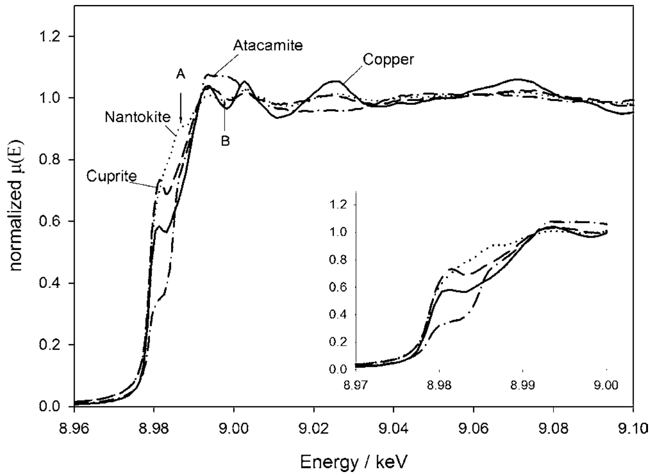

FIGURE 5. XAS spectra for a clean copper electrode and copper electrodes covered with cuprite, nantokite, and atacamite corrosion layers. Reproduced with permission from ref 25. Copyright 2009 The Royal Society of Chemistry (http://dx.doi.org/10.1039/b814181a).

remains distinctive, although it too is clearly influenced somewhat by the underlying copper.

Second, our attention was immediately drawn to the fact that XAS spectra of the corroded copper samples, collected during their immersion in the sesquicarbonate solution, all show increasing signals as a function of time. The increase is observed both at the absorption Cu K edge and in a proportionate increase in the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) modulation, but the shapes of the spectra do not appear to evolve strongly, even though the chemical composition of the surface is undoubtedly changing. The effect is largest for the atacamite layer, as described in what follows. Figure 6 shows the successive XAS spectra recorded for this sample.[26] The copper edge height of the first measurement is set to be equal to 1. All subsequent scans are normalized to the edge height of the first scan. Scan number 8 already shows an increase of 4 times with respect to the copper edge of the first measurement. From the ninth spectrum on, the increase between the different spectra becomes rapidly larger. The obvious change in the XANES or EXAFS intensity of the immersed samples could not be observed for the original dry corrosion layers, monitored over similar times in air (i.e., there is no increase in signal over time for dry samples).

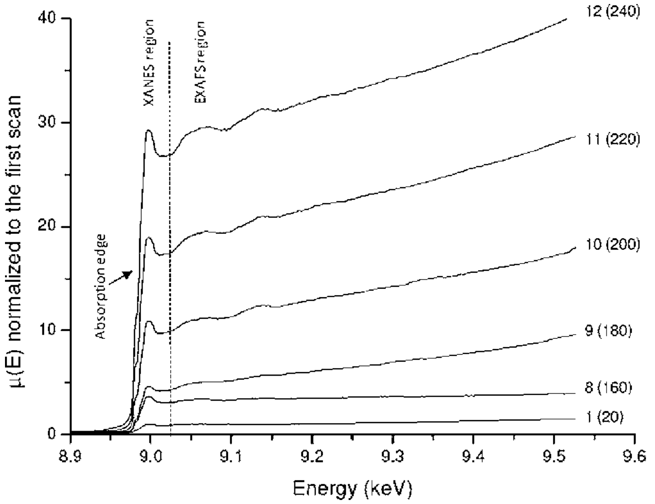

FIGURE 6. Sequential XAS spectra of the copper/atacamite sample in a sodium sesquicarbonate solution. The scan numbers are indicated on the right. The figure in brackets is the elapsed time in minutes at the end of the scan. Reproduced with permission from ref 26. Copyright 2008 Maney Publishing (www.maney.co.uk/journals/sur and www.ingentaconnect.com/content/maney/se).

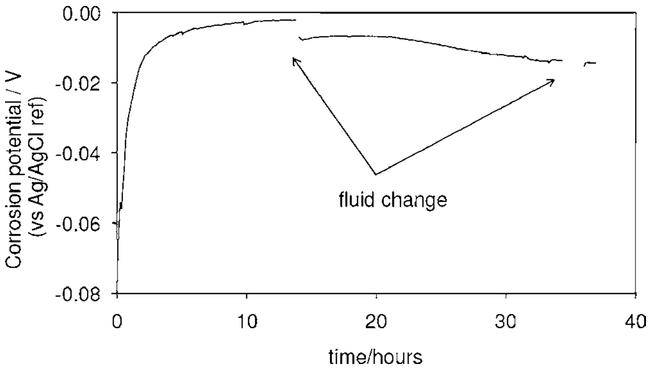

FIGURE 7. E_{corr} data taken simultaneously with each immersion stage of the experiment in Figure 8. The reference electrode was 3 M Ag/AgCl. Reproduced with permission from ref 25. Copyright 2009 The Royal Society of Chemistry (http://dx.doi.org/10.1039/b814181a).

Figure 7 shows the corrosion potential data as a function of time with complete changes of the electrolyte in the cell at 15 and 35 h (imitating typical conservation treatment).[26] Again, these data were collected simultaneously with the XAS

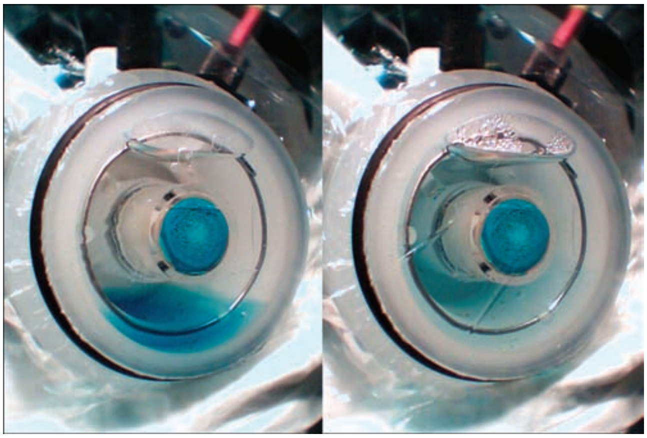

FIGURE 8. Webcam images of the eCell during the sequence in Figures 6 and 7. Left hand plate shows the blue haze flowing off the sample after 20 min immersion. The right-hand plate shows the situation at the end of the first immersion (14 h). Reproduced with permission from ref 25. Copyright 2009 The Royal Society of Chemistry (http://dx.doi.org/10.1039/b814181a).

data mentioned above. The results demonstrate that over a time period of 240 min (4 h) the corrosion potential keeps on changing, implying a continuous change of the surface chemistry. The signal stabilizes after ca. 8 h at which moment the XAS signal is still increasing (not shown). Again, the corrosion potential remains relatively stable after the electrolyte changes, but the XAS data (not shown) indicate further dissolution from the layer.

While the spectra are being recorded and the electrochemistry is in progress, eCell makes a continuous visual record of the process using a webcam. Figure 8 shows two such webcam images recorded after the sample had been immersed for 20 min (left) and 14 h (right).[25] The detachment of material from the atacamite layer is evident as a blue haze which drifts downward as the sample surface is in a vertical plane on DUBBLE. In fact, two sorts of detaching material are clearly visible: relatively large crystalline fragments up to hundreds of micrometers in size and the haze reminiscent of dissolving $CuCl_2$. The sudden increase in signal as of scan number 9 can in this context be explained by the fact that at this stage more of the substance becomes detached. It should be noted, however, that the spectrum remains characteristic of atacamite (or an octahedrally coordinated copper complex ion) throughout this process.

Our very recent work has shown that this behavior is due to a major flaw in the corrosion protocol itself. It produces atacamite only as a minority constituent, and a highly soluble, but as yet unidentified, copper salt in the majority. The soluble component is removed by the soaking process, leaving nearly pure atacamite behind. The solution process as observed in the webcam images is nearly identical to that seen when copper(II) chloride is dissolved in water, although the diffraction pattern of the original corrosion layer has no match with copper(II) chloride. Moreover, although solid copper(II) chloride has a totally different XAS spectrum from that of atacamite, the spectrum of dilute $CuCl_2$ solution is similar to that of solid atacamite and the solution observed here (i.e., the copper becomes octahedrally coordinated in solution). The dissolution of the soluble fraction leaves the atacamite only physically connected to the surface.

Conclusions and Future Perspectives

We have developed an electrochemical cell (eCell) which is engineered so as to permit X-rays from a synchrotron beamline to be scattered or absorbed by the surface of a sample, or by a liquid in which it is immersed, while electrochemical reactions are taking place. X-rays emitted from the system then carry time-resolved information on the specific reactions as they occur. During the analysis, the surface can remain immersed in electrolyte or exposed to air so as to study the process in the most relevant way, and electrochemical data can be measured coincidentally. Although similar in situ cells for the study of idealized (e.g., atomically flat, single crystal) surfaces have been described, this is, so far as we are aware, the first time such experiments have been done on rough (on the 1−100 μm scale), polycrystalline, impure metals typical of real artifacts.

In this work, we have used eCell to evaluate a potential monitoring method for copper-based objects stored in solution. Results have shown that SR-XRD and XAS analyses of a surface with a thin layer of electrolyte above give the possibility of probing both the surface structure and the complex ions or colloidal material in the liquid. The addition of E_{corr} measurements shows that changes in chemistry of the bulk corrosion product are not necessarily linked to this parameter which appears to be dominated by the chemistry of a (semi)conducting interfacial layer of cuprite. Therefore, E_{corr} is not a good indicator of chloride removal; that is, we have not yet found a reliable and straightforward monitoring method (a sensor device) to replace the laborious testing of chloride concentration in solution.

Nevertheless, we will continue our X-ray investigation of the soaking treatment with a view to looking at optical absorption or a more refined electrochemical measurement as the basis for a possible sensor, and more generally to study the details of reactions leading to the formation and removal of corrosion layers, and passivation of copper alloy surfaces. In addition, we will explore the use of X-ray excited optical luminescence (XEOL) to obtain XAS spectra for monitoring corrosion, passivation, and coating in situ. XEOL has a greatly improved surface specificity compared to X-ray diffraction and X-ray fluorescence absorption measurements using beams with energies > 8 keV where the penetration and escape depths exceed the thickness of the layers of interest. It is well-known that the escape depths of optical photons and electrons produced by Auger de-excitation and other processes occurring as a consequence of the X-ray photoionization event are in the range 100s nm to <5 nm (unless the material is transparent to the photons), so that the detection of these, rather than the X-ray fluorescence yield, has the potential to enhance the surface specificity. At SRS, we have pioneered the use of XEOL on corroded metals.[29] We have demonstrated so far that broadband XEOL-XAS spectra from pure copper corrosion products are indistinguishable from those taken with conventional XAS, but those from thin corrosion layers on metal are much more characteristic of the corrosion; that is, one sees an enhanced surface specificity in comparison with conventional XAS. Another significant feature of the technique (complementary to XAS) appears to be that the data do not suffer from self-absorption effects when the radiation escapes through a fluid containing the corrosion product in solution, whereas, in our measurements, XAS data are dominated by the fluid chemistry rather than that of the surface. However, since XEOL relies on detection of visible photons, the data will be optically filtered by colored solutions.

Second, our intention is to design and build derivatives of eCell so that corrosion processes can be studied on a long-term basis, while maintaining an uninterrupted controlled environment around the sample. The new cells will be portable (peCell) while maintaining the sample environment within. Using these devices, controlled environments can be applied months or years in advance of beam time (which is much more realistic timing in terms of actual conservation projects), and the samples re-examined after continuous exposure in successive beam-time allocations. It will be possible to combine continuous monitoring of, for example, the electrochemical parameters of a system over a long time scale with spectroscopic measurements spaced uniformly, but at intervals of months. This is an ideal environment in which to develop and calibrate practical monitoring tools for use by conservators in the field. In addition, it raises the possibility of using complementary techniques at the home institution(s) or at different facilities, but on the same samples. Overall, this work will evolve toward the application of conservation techniques to real artifacts (such as organ pipes, coins, and artifacts recovered from marine environments), and X-ray data will be taken from these as treatment/testing proceeds.

Finally, the failure of the atacamite protocol to produce the target substance led us to examine a large number of protocols for producing copper chlorides in detail. Even those in ref 21 were found to produce far more nantokite than atacamite, botallokite, or paratacamite on the surface of a coupon, although the protocol for precipitating atacamite was found to be reliable. Our future work will therefore also include a search for robust and reproducible protocols suitable for simulating corrosion on heritage copper and its alloys.

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FOOTNOTES

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