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Atmospheric Corrosion of Cu during Constant Deposition of NaCl

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A laboratory environment chamber with a constant deposition rate of NaCl was built. With this chamber, the corrosion behavior of Cu during constant NaCl deposition was investigated with different CO₂ concentrations and ultraviolet (UV) illumination. XRD and coulometric reduction techniques were used to identify and quantify the corrosion products. An Na₂CO₃ solution was found to be more suitable than KCl solutions for quantification of Cu corrosion products. Cuprite was always the dominant corrosion product during exposure of Cu in various environments. UV illumination accelerated formation of cuprite significantly but had very little effect on formation of cupric corrosion product. CO₂ in the environment was important in determination of cupric corrosion product. With 350 ppm CO₂, paratacamite was the dominant product, while tenorite was dominant with <1 ppm CO₂. This explains why tenorite is not a common cupric corrosion dominated at later times. The new environment chamber enables the determination of Cu corrosion kinetics in the lab, especially the formation of paratacamite, which provides insight into Cu atmospheric corrosion in the field. © The Author(s) 2013. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.037308jes] All rights reserved.

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Atmospheric corrosion of Cu in the field and in laboratory chambers has been widely studied because of the use of Cu in electronics and architecture.^{1–6} NaCl has a strong accelerating influence on Cu corrosion in the field, especially in marine environments.^{5,6} The effects of NaCl have also been investigated in laboratory-based atmospheric corrosion studies.^{7–12} NaCl has been shown to accelerate the breakdown of the naturally formed and protective copper oxide by the formation of copper chloride complexes,¹¹ especially at high relative humidity (RH). When the RH is higher than the critical relative humidity of NaCl, 75%,¹³ deposition of 4 µg /cm² of NaCl before exposure increases the Cu corrosion rate of Cu by about one order of magnitude during 10 days exposure.⁸

NaCl has also been shown to be critical for formation of $Cu_2(OH)_3Cl$, a common corrosion product found in marine environments.³ In the presence of NaCl, cuprite (Cu₂O) can be readily oxidized to atacamite or paratacamite, which are isomers of $Cu_2(OH)_3Cl$.¹² However, because of difficulties generating a constant deposition rate of NaCl during lab exposure, there is a lack of information on the kinetics of $Cu_2(OH)_3Cl$ formation and how $Cu_2(OH)_3Cl$ affects the Cu corrosion rate.

Methods used to introduce NaCl onto a surface for laboratory study of atmospheric corrosion of Cu and other metals include deposition of NaCl particles before exposure by fast evaporation of ethanolic NaCl solution,^{8,11} thermophoretic deposition^{14,15} or printing.¹⁶ A disadvantage of prior deposition for the study of Cu corrosion kinetics is that the available NaCl in the environment decreases with time due to formation of Cu₂(OH)₃Cl or CuCl during exposure. Furthermore, deposited NaCl particles can alter the form of corrosion because localized attack can initiate at the edge of a particle or under a particle where deliquescence of NaCl occurs first.⁸

Although UV illumination has been found to increase Cu sulfidation by a factor of 1.5 to 2 in the presence of H_2S ,¹⁷ the effect of UV illumination on atmospheric corrosion of Cu has not been widely studied, especially in the presence of chloride. In slightly acidic or alkaline solution (pH 4 to 8), the formation of n-type of Cu₂O was observed and anodic photocurrent was measured when UV illumination was applied.^{18,19} Therefore, it is interesting to study atmospheric corrosion of Cu with UV illumination.

The CO₂ concentration has been shown to have a critical influence on the initial Cu corrosion reaction in the presence of NaCl particles.^{9,20} With lower CO₂, secondary spreading of NaCl is much more significant²⁰ and formation of CuCl is impeded.⁹ Therefore, depending on loading of NaCl, the effects of CO_2 concentration on Cu corrosion can be different.

This paper describes a new chamber to provide constant deposition of NaCl during atmospheric exposure of Cu. With this chamber, the combined effects of UV illumination and CO₂ on Cu atmospheric corrosion kinetics during constant NaCl deposition are studied. An appropriate coulometric reduction technique to easily quantify the amounts of Cu₂O and Cu₂(OH)₃Cl is also described.

Experimental

Sample preparation.— All Cu coupons were 99.99% pure and 17 mm \times 17 mm \times 1.6 mm in size. They were ground sequentially with 600, 800 and 1200 grit papers, followed by 6 μ m and then 1 μ m diamond polishing. After polishing, samples were stored in a desiccator for 24 h before exposure.

Environment chamber design.— Figure 1 is a schematic representation of a home-built environment chamber that can provide a continuous and constant rate of NaCl deposition from an aerosol. A 200-mL beaker of saturated NaCl solution inside the chamber was bubbled with air through a glass frit tip, labeled inlet flow A. The beaker of saturated NaCl solution (6.2 M) contained enough undissolved NaCl particles to maintain saturation during the entire exposure time. Inlet flow A needed to be pre-humidified to avoid blocking of the frit by precipitation of NaCl associated with concentration buildup adjacent to the frit.²¹ The exposure location of the Cu samples was maintained at a position 53 mm away from the frit bubbler.

During exposure, the area of the Cu samples covered by NaCl droplets increased gradually. After approximately 12 h exposure, samples were completed covered by a thin layer of aqueous NaCl solution.

Another flow of air, inlet flow B, was used to maintain the RH around 100% when the saturated solution was used for flow A. Unless otherwise specified, the air used in this work contained 350 ppm CO_2 and the RH during exposure was always close to 100%. Ultra-purified air with less than 1 ppm CO_2 was also used to study the effect of CO_2 . The flow rates of inlet flows A and B were 15 cc/min and 436 cc/min, respectively. Mass flow controllers were used to control the flows accurately. Flow A and flow B were started at least three days before exposure of the Cu to reach steady state conditions in the bubblers and in the chamber. Once exposure of the Cu started, the flows were maintained, even during the periods of sample changes.

The top cover of this chamber was a 4 mm thick quartz glass window, which allowed UV light (254 nm) to penetrate through into

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Figure 1. Schematic drawing of home-built environment chamber with constant deposition of NaCl.

the chamber. The UV intensity was 3.2 mW/cm^2 at the top side of the quartz window. The Cu samples were exposed in the dark unless it is specified that they were exposed under UV illumination.

In some cases, the beaker in the chamber contained 5 wt.% NaCl. Under these conditions, inlet flow A was 830 cc/min and inlet flow B was not used. This is similar to the salt bubble chamber described previously for the study of Ag atmospheric corrosion.²²

Measurement of NaCl deposition rate.— NaCl aerosols were generated in the chamber by flow A. The deposition rate of NaCl was measured by pseudo-wet-candle collection followed by potentiometric titration. NaCl aerosols were collected with a cylindrical thin-wall beaker without a spout (1 mm in thickness and 2.2 cm inside diameter). The beaker was placed in the chamber at a location where its mouth was at the same distance from the frit and the same height as where the samples were exposed. It had 5 mL of deionized (DI) water inside before collection. After exposure, all NaCl droplets on the top and inside of the wall as well as the inside solution were carefully transferred into a large beaker by rinsing with DI water at least three times. The total volume of the final NaCl solution, including all rinsing water, was controlled to 100–120 mL to reduce errors.

This NaCl solution was potentiometrically titrated with AgNO₃. Three concentrations of AgNO₃, 0.1 M, 0.04 M and 0.004 M, were used depending on the amount of NaCl. The working electrode was an Ag wire and the reference electrode was a saturated mercurous sulfate electrode (MSE). A 0.1 mL aliquot of the AgNO₃ solution was added



Figure 2. Potentiometric measurement of NaCl concentration in wet candle.

repeatedly and the solution was stirred with a glass rod for about 5 s after each addition. A steady potential was noted after waiting at least 100 s. The equivalence point was determined by the maximum of the derivative curve of potential vs $AgNO_3$ volume, as shown in Figure 2. The deposition rate of NaCl, D, in mg/cm²h was determined from equation 1.

$$D = \frac{58.5 \times V \times M}{t \times A}$$
[1]

where V is the volume of $AgNO_3$ at the equivalence point in mL, M is concentration of $AgNO_3$ in mol/L, t is deposition time in h, and A is area in cm².

Identification and quantification of corrosion products.— After exposure, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and X-ray diffraction (XRD) were used to characterize the corrosion products. The amount of corrosion product was then quantified by coulometric reduction technique using 0.1 M Na₂CO₃²³ or 0.1 M KCl²⁴ as the supporting electrolyte. A constant reduction current density of 0.05 mA/cm² was used unless specified otherwise. A conventional three electrode flat cell was used to carry out the reduction testing. Saturated calomel electrode (SCE) was used as a reference electrode and a platinum mesh was used as an auxiliary electrode. All potentials mentioned in this paper are respect to SCE unless specified otherwise.

Pit depth measurement.— To determine pit depth, unreduced samples were pickled in 6.5 M HCl for 5 min followed by soaking in 1 M H_2SO_4 for 1 min. They were then rinsed with DI water for less than 30 s, sprayed with ethanol and immediately air dried. Pit depth was measured by optical profilometry. At least 6 spots close to center of samples with area 0.26 to 1.73 mm² were scanned. No pits were generated during acid pickling and drying of a control sample that was not first exposed in the chamber.

Scanning kelvin probe (SKP) measurement.— A 2 μ L droplet of saturated NaCl solution was transferred onto as-polished Cu and the Cu sample was immediately placed in the airtight SKP chamber. The relative humidity in the chamber was kept at 98% by wet air flow (containing ambient CO₂) before loading of the sample. After loading of the sample, the relative humidity increased back to 98% within 10 min. As a result, the droplet did not dry out before or during SKP measurement. A line scan across the droplet was carried out at a scan rate of 0.8 μ m/s and with 4 μ m step size. Details of the SKP measurements are described elsewhere.²⁵

Results and Discussion

Deposition rate of NaCl.— The accumulated amount of deposited NaCl per unit area in mg/cm² is plotted in Figure 3. When the bubbler



Figure 3. Accumulated deposition of NaCl vs deposition period for saturated and 5 wt.% NaCl solutions in the bubbler beaker.

beaker contained 5 wt.% NaCl, the rate of NaCl accumulation, given by the slope of the curve in Figure 3, decreased with time even though a continuous NaCl aerosol was generated. Continuous bubbling in the solution for 96 h at 830 cc/min resulted in a decrease in the volume of the solution by about 40 mL. This change in the conditions in the beaker resulted in a decrease in NaCl deposition rate from 0.026 mg/cm²h at the beginning to 0.01 mg/cm²h after about 96 h.

When the bubbled beaker in the chamber contained saturated NaCl solution instead of 5 wt.% NaCl, a lower rate of input flow A was needed to get a particular NaCl deposition rate. As a result, the rate of decrease of solution volume in the beaker was lower. For a 15 cc/min flow, the loss of the solution over the first 24 h was about 1 mL. Even though this change is very small, the deposition rate still decreased during bubbling unless input flow B was added. With the addition of the water-saturated air in flow B, the RH in the chamber was maintained at very close to 100%. This value is much higher than the equilibrium RH of saturated NaCl (75%), so the saturated solution in the beaker absorbed water during bubbling. Because the saturated solution contained excess NaCl, the solution remained at the saturation concentration during bubbling. As long as enough water was absorbed to compensate for the loss due to bubbling, the volume of the solution in the beaker stayed constant during bubbling. The decrease of volume in the saturated solution was less than 0.4 mL after bubbling the saturated NaCl solution for 120 h, with flows A and B of 15 and 436 cc/min, respectively. Figure 3 shows that the NaCl deposition rate under these conditions was absolutely constant at 0.1 mg/cm²h. All the exposures of Cu mentioned in this paper, except the SKP measurement, were performed with an NaCl deposition rate of 0.1 mg/cm²h. The deposition rate of NaCl associated with the most severe marine environment (e.g. ISO9223, S3 category) is usually less than 0.00625 mg/cm²h.²⁶ Therefore the NaCl deposition rate in the lab chamber is more than an order of magnitude higher than the deposition rate in severe field environments.

The deposition rate of NaCl can be changed by adjusting flow A or using a dispersion frit with different efficiency. However, it would be necessary to adjust flow B as well to maintain a constant deposition rate.

The RH in this chamber has to be maintained higher than 75% so that the saturated NaCl solution in the beaker continues to absorb water from the ambient atmosphere. It should be possible to achieve an RH between 75% and 100% while maintaining a constant NaCl deposition rate using an additional inlet of dry air, but this was not tried. Another limitation is that the NaCl deposition rate depends on the distance from the frit bubbler. Therefore, for accurate comparison of results, all samples must be exposed at the same location and they cannot be too big or else non-uniform corrosion could occur.



Figure 4. Analysis of Cu exposed to humid air, $0.1 \text{ mg/cm}^2\text{h}$ NaCl. a) reduction curve in 0.1 M Na₂CO₃ for sample exposed with UV b) reduction curve in 0.1 M Na₂CO₃ for sample exposed in dark): XRD spectra of sample from b) before reduction and after reduction through the first two plateaus only.

Calibration of coulometric reduction technique.— XRD analysis indicated that paratacamite and cuprite formed on Cu exposed with 350 ppm CO_2 for longer than 15 h. Quantitative determination of the amounts of each was performed using coulometric reduction. Figure 4a shows a typical reduction curve of Cu with paratacamite and cuprite. Four regions can be discerned: -0.35 to -0.65 V, -0.65 to -0.8 V, a big plateau at -0.8 V and then hydrogen evolution at around -1.1 to -1.2 V. The first two regions do not have very well defined plateaus but have very similar amounts of reduction charge. Before reduction, the samples had greenish product interspersed on a reddish-brown corroded surface. The greenish species disappeared at the end of the first two regions.

To identify the species corresponding to each reduction region, another sample exposed for 60 h in the dark with similar amount of corrosion products was reduced in two steps, as shown in Figure 4b. XRD analysis confirmed the presence of paratacamite and cuprite on the exposed sample before reduction, as shown in Figure 4c. Reduction of this sample was interrupted after about 1600 s when the potential dropped to -0.8 V SCE. The partially reduced area (within the o-ring) was still reddish-brown but was covered by some loose black powder instead of the greenish species. The black powder was likely Cu from the reduction of corrosion products and it was easily rinsed off with DI water after the sample was taken out of the cell. The unreduced area (outside of the o-ring) was hand-polished with SiC paper carefully to remove the corrosion products. XRD was then performed on the partially reduced product, and only cuprite was identified on the sample (Figure 4c). This sample was then reassembled into the cell and reduction was continued. Only one plateau at -0.8 V was observed, as shown in Figure 4b. This experiment shows that the plateau at around -0.8 V SCE corresponds to reduction of cuprite and the first two regions or plateaus are likely due to reduction of paratacamite.

The reduction potential of Cu₂O, -0.8 V SCE, is consistent with previously reported values of -0.75 to -0.9 V SCE in KCl,^{27,28} KOH²⁸ or Na₂B₄O₇.²⁹ There are few reports on the coulometric reduction of Cu₂(OH)₃Cl. Malvault et al. reported a peak reduction potential of paratacamite by linear sweep voltammetry in 0.1 M Na₂B₄O₇ of -0.61 V SCE,²⁹ which is in the range of the first two plateaus in Figure 4a. Interestingly, the first two plateaus have almost the same amount of reduction charge. This suggests that reduction of paratacamite in Na₂CO₃ is a two-step process.

The distinction between the first two regions becomes less apparent as the amount of corrosion products decreases. Reduction curve B in Figure 5 shows reduction of Cu exposed in the same environment as the one in Figure 4b but for a short time, 23 h, and then reduced in Na₂CO₃. XRD analysis indicates the presence of cuprite and paratacamite after exposure as well. This reduction curve can be divided into two regions with a flat plateau for reduction of Cu₂O in region II. Here, region I corresponds to the reduction of paratacamite. Although

Figure 5. Reduction curve of two samples exposed to 100% RH humid air, 0.1 mg/cm²h NaCl for 23 h. A: reduced in 0.1 M KCl with -0.05 mA/cm^2 ; B: reduced in 0.1 M Na₂CO₃ with -0.05 mA/cm^2 .

Table I. Corrosion products of Cu exposed to 0.1 mg/cm²h NaCl and humid air.

Exposure duration, h	Corrosion products identified by XRD
1 to 4	N/A
8 to 15	Cu ₂ O
>15	Cu ₂ O and Cu ₂ (OH) ₃ Cl

there is no clear distinction of two reduction plateaus in region I, its shape is similar to the overall shape of the first two plateaus in Figures 4b and 4a.

Curve A in Figure 5 is for another sample that was exposed to the same environment but reduced in 0.1 M KCl as suggested by ASTM B825.²⁴ It is quite different, with only one broad plateau ranging from -0.6 to -0.8 V so that the reduction of paratacamite and cuprite cannot be clearly differentiated. This is the same as reduction of tenorite and cuprite, which cannot be differentiated in neutral KCl but can be in alkaline solution, e.g. 1 M KOH.^{28,30} Copper hydroxyl oxides (Cu₂(OH)₃Cl and Cu(OH)Cl) are only stable at around pH 3.5 to 5.5,^{3,31} while Cu₂O is more stable in neutral to alkaline environments. 0.1 M Na₂CO₃ is basic with a pH of 11.5, which resulted in different reduction potentials for paratacamite and cuprite. A clearer distinction between the hydrogen evolution reaction (HER) and reduction of corrosion products was also found in Na₂CO₃ than in KCl. This increases the accuracy of quantification of corrosion products with the coulometric reduction technique. Therefore reduction of Cu corrosion products in Na₂CO₃ solution rather than KCl is recommended.

Identification and quantification of corrosion products.— Table I lists corrosion products of Cu exposed to humid air with an NaCl deposition rate of 0.1 mg/cm²h as determined by XRD. Similar to field-exposed Cu, the initial corrosion product identified by XRD was cuprite and then paratacamite formed later. For Cu exposed less than 4 h, there was insufficient corrosion product to be detected by XRD, but the reduction curve confirms the presence of cuprite after exposure as Figure 6 indicates. Besides reduction of cuprite, it also shows a reduction plateau around -0.6 to -0.7 V. This is probably due to reduction of trace cupric compounds, although XRD could not identify the presence of a cupric compound after exposure.

As the NaCl deposition rate increases in a marine environment, e.g. by wave splashing, paratacamite formation becomes much faster. Detection of $Cu_2(OH)_3Cl$ by XRD was reported after one month exposure,³² while it usually could take several months up to years

Figure 6. Cu exposed to humid air with 0.1 mg/cm²h NaCl for 3 h. Solid line: Reduction curve. Dashed line: Derivative of the reduction curve. Note that cupric here represents cupric compounds such as paratacamite or atacamite.





before $Cu_2(OH)_3Cl$ is detected by XRD under normal NaCl deposition conditions.^{4,33} A typical deposition rate of NaCl in a marine environment without splash or spray is less than 0.00625 mg/cm²h,²⁶ which is much less than the deposition rate during most lab exposures. In this work, detection of paratacamite by XRD on Cu exposed for only 15 h with an NaCl deposition of 0.1 mg/cm²h clearly indicates that formation of paratacamite can be dramatically accelerated by increasing the NaCl deposition rate.

An equivalent weight loss of Cu can be calculated from reduction curves by the following equation:

$$W = \frac{10000 \times (Qc + 0.5 \times Qp) \times M}{F}$$
[2]

where W is total weight loss in g/m², Qc is reduction charge corresponding to reduction of cuprite in C/cm², Qp is reduction charge corresponding to reduction of paratacamite in C/cm², M is molecular weight of Cu, 64 g/mol, and F is the Faraday constant, 96500 C/mol.

The approach used for determination of Qc and Qp is described in Figure 6. The length of each plateau is determined by local minima of the derivative of the reduction curve.²⁷ Although no paratacamite was detected by XRD for samples exposed less than 15 h, the reduction charge above the cuprite reduction plateau can still be assigned to Qp, since it was due to reduction of Cu^{2+} ions. Besides the calculation of total Cu weight loss, the weight loss due to formation of cuprite or paratacamite can be calculated separately with equations 3 and 4, respectively:

$$Wc = \frac{10000 \times Qc \times M}{F}$$
[3]

$$Wp = \frac{10000 \times Qp \times M}{2 \times F}$$
[4]

where Wc is weight loss due to formation of cuprite and Wp is weight loss due to formation of paratacamite in g/m^2 .

Figure 7a summarizes weight loss data of Cu exposed to humid air with 0.1 mg/cm²h NaCl deposition rate up to 80 h with UV or in a dark environment. Figure 7b presents the derivative of each curve in Figure 7a, showing the formation rates of cuprite and paratacamite and the total corrosion rate of Cu. Generally, the formation of cuprite was much faster than paratacamite and it has the most dominant influence on the Cu corrosion rate. At the beginning, only part of the Cu surface was covered with NaCl droplets. The covered area kept increasing during exposure until the whole sample surface was fully covered with NaCl solution after about 12 h. During this period, the formation rate of cuprite and total corrosion rate were relatively low but kept increasing, while the formation rate of paratacamite stayed close to zero. After the surface was completely covered with NaCl solution, the cuprite and paratacamite formation rates, and thus the Cu corrosion rate, all increased significantly, which was likely due to continuous increase of NaCl loading. Eventually, the rates all became relatively stable. A constant Cu corrosion rate has been found previously for lab exposure of Cu in mixed flowing gas and field exposure of Cu for three years.^{34,35} The corrosion rate of Cu and formation of Cu₂O are both constant when the corrosion product layer is not thick enough. After exposure of Cu in the field for a few tens of years, when the corrosion product layer is thicker than 10 μ m, the corrosion products become protective and corrosion rate decreases.³ Therefore, a decrease of the Cu corrosion rate is very likely if the Cu is exposed in the lab chamber for a longer period.

It is very clear that addition of UV illumination accelerates Cu corrosion significantly, which is mainly because the formation rate of cuprite is accelerated by UV illumination by about a factor of 2 during the whole exposure from 4 to 60 h. The formation rate of paratacamite is just slightly higher than in the dark. The acceleration effect of UV reported in Figure 7 is very similar to the previously reported effect of H_2S/UV on Cu corrosion.¹⁷

Naturally formed cuprous oxide is a p-type semiconductor with a bandgap of 2.4 eV.³⁶ UV photons ($\lambda < 370$ nm, E > 3.4 eV) have



Figure 7. a) Weight loss and loss in thickness of Cu exposed to humid air and 0.1 mg/cm²h NaCl, with UV (solid lines) or in dark (dashed lines). b) formation rate of cuprite and paratacamite and corrosion rate of Cu, derivative of data showed in Figure 7a.

enough energy to generate electron-hole pairs. This only leads to cathodic photocurrent, which reduces the passive current and increases the corrosion resistance.³⁷ N-type cuprite with a similar bandgap of 2 eV usually forms in slightly acidic to alkaline solution during corrosion, which can lead to anodic photocurrent and increase the corrosion rate.^{18,19,38} Therefore, because Figure 7 clearly shows the acceleration effect of UV, it is likely that n-type cuprite formed during exposure of Cu in humid air and was more dominant than p-type cuprite.

With the presence of n-type cuprite on the anodic area of Cu, an ohmic junction and Schottky barrier form at local anodes, as shown schematically in Figure 8, which is similar to the model suggested by Gerischer³⁹ and Burleigh^{37,40} on metals with n-type oxide under anodic polarization. Once a photon with energy larger than bandgap hits cuprite, especially on the local anode area, a hole-electron pair forms (equation 5). Electrons can drift back to the Cu substrate, assuming the ohmic resistance is negligible, and migrate to cathodic areas to support reduction of oxygen (equation 6), while holes move toward the surface.

Three possible pathways are proposed. First, Cu^+ is oxidized to Cu^{2+} (equation 7). Then a reverse disproportionation reaction of cupric and metallic Cu to generate cuprous ions occurs as equation 8 suggests. This is similar to reverse disproportionation of $Cu_4(SO_4)(OH)_6$ and metallic Cu proposed previously for formation of cuprite in the presence of ammonium sulfate.⁴¹ Equation 9 is the overall reaction of the first pathway. Cu(OH) as an intermediate



Figure 8. Schematic illustration of the interaction between photons and n-type cuprite. CB: conduction band; VB: valence band, modeled after.^{37,39}

decomposes to form cuprite rapidly according to equation 10.38

$$4Cu_2O + 4hv \rightarrow 4Cu_2O + 4e^- + 4p^+$$
 [5]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 [6]

$$4Cu^+ + 4p^+ \to 4Cu^{2+}$$
 [7]

$$4\mathrm{Cu}^{2+} + 4\mathrm{Cu} \to 8\mathrm{Cu}^+ \qquad [8]$$

$$O_2 + 2H_2O + 4Cu + 4hv \rightarrow 4Cu(OH)$$
[9]

$$2Cu(OH) \rightarrow Cu_2O + H_2O$$
 [10]

The other two possible routes are formation of oxygen atoms instead of cupric ions by holes with O^{2-} in Cu₂O (equation 11) or by holes with OH⁻ (equation 12):

$$O^{2-} + 2p^+ \to O \tag{[11]}$$

$$2OH^- + 2p^+ \rightarrow O + H_2O$$
 [12]

Gerischer suggests formation of O_2 by a series of reactions between O^{2-} and photons resulting in dissolution of Zn into ambient solution under UV illumination.³⁹ Since the formation rate of Cu₂O increases under UV illumination, it is more likely that atomic O (from equation 11 or 12) diffuses through oxygen vacancies toward the Cu/oxide interface and then react with Cu to form oxide. In this situation, the overall reactions are equations 13 and 14, corresponding to 11 and 12 respectively.

$$O_2 + 2H_2O + 2O^{2-} + 4Cu + 4hv \rightarrow 2Cu_2O + 4OH^{-}$$
 [13]

$$O_2 + 4Cu + 4hv \rightarrow 2Cu_2O$$
 [14]

Reaction 13 can generate oxygen vacancies, which is consistent with characterization of n-type semiconductors.

The proposed reaction paths all indicate that photons have very little effect on the formation of cupric ions, although the first pathway might generate some less dominant cupric ions because reaction 8 is very likely a slow step. This is supported by the small increase of Wp with UV illumination compared to Cu exposed in dark, as Figure 7 shows. This increase is probably because of unreacted cupric ions converting to $Cu(OH)_2$, CuO or some precursor of paratacamite. Actually, a greenish species started to appear after Cu was exposed to UV for 6 h in the environment chamber with constant deposition of NaCl, about two hours earlier than Cu exposed in dark. The greenish species is likely paratacamite, although XRD could not identify it.



Figure 9. SEM images of Cu exposed to low and high CO₂. a) and b) Cu exposed to humid air with less than 1 ppm CO₂ and 0.1 mg/cm²h NaCl for 58.5 h. Broken film in Figure 10b is remaining NaCl as confirmed by EDS. c) and d) Cu exposed to humid air with 350 ppm CO₂ and 0.1 mg/cm²h NaCl for 60.5 h. Flakes in d) are paratacamite as confirmed by EDS.

Effect of CO₂ on Cu corrosion with NaCl.— The corrosion behavior of Cu exposed with low CO_2 (< 1 ppm) is different than that of Cu exposed with 350 ppm, which is close to the ambient concentration of CO₂ in the air. Cu exposed to a low CO₂ atmosphere exhibited a black surface covered with white salt. In contrast, Cu exposed to high CO₂ had a reddish-brown surface with greenish paratacamite interspersed, which is similar to what forms on Cu exposed in the field.⁴ The black color is due to the presence of black compound tenorite (CuO), which became detectable by XRD on Cu exposed longer than 20 h with low CO2. However no paratacamite or other cupric compound was identified by XRD. SEM images of these two samples are also quite different as Figure 9 indicates. The corrosion product on Cu exposed with low CO₂ was more compact than that formed on Cu exposed with high CO₂, although it still had some fine porosity, Figures 9a and 9b. Cu exposed with high CO_2 had a much less dense product layer covered with paratacamite flakes as Figures 9c and 9d indicate.

Figure 10 is a typical reduction curve of Cu exposed with low CO₂. In contrast to the curve for Cu exposed to high CO₂ in Figure 5, the reduction plateau of cuprite at -0.8 V SCE was relatively small. A broad plateau from -0.7 to -0.76 V is due to reduction of tenorite, as it has been shown that reduction of tenorite occurs at a more positive potential than reduction of cuprite in alkaline solution.²⁸ The part of the curve above the tenorite reduction plateau was always very small and might due to reduction of some other trace cupric compounds. The amounts of Cu₂O and CuO formed during exposure with low CO₂ can still be quantified with equations 3 and 4 separately by their reduction charges.

The equivalent weight loss and corrosion rate of Cu exposed to high and low CO₂ is compared in Figure 11. Generally, the corrosion rate of Cu exposed to low CO₂ (<1 ppm) was relatively constant with time in contrast to the behavior of Cu exposed to high CO₂ (350 ppm). It is interesting to notice that during the first 5 h, Cu exposed to low CO₂ corroded faster than Cu exposed to high CO₂. This is similar to exposure of Cu with NaCl particles. With low NaCl loading, Cu corroded faster with low CO₂ (< 5 ppm), while at high NaCl loading, Cu corroded faster with high CO₂ (350 ppm).^{9,20} This was attributed to the fact that NaCl droplets are more spread out with low CO₂.^{9,20} So during the first 5 h, before the Cu surface is completely covered with NaCl droplets, samples exposed to low CO₂ had higher surface coverage of NaCl solution for the same loading of NaCl. This explains why Cu corroded faster with low CO₂ during the first 5 h. For Cu



Figure 10. Reduction curve of Cu exposed to humid air with less than 1 ppm CO_2 and 0.1 mg/cm²h NaCl for 23.5 h. Cu was reduced in 0.1 M Na₂CO₃.



Figure 11. Effect of CO₂ concentration on Cu corrosion. a) equivalent weight loss of Cu exposed to humid air with 350 ppm or < 1 ppm CO₂. NaCl deposition rate is 0.1 mg/cm²h. Subscript L and solid lines are Cu exposed to < 1 ppm CO₂. Subscript H and dashed lines are Cu exposed to 350 ppm CO₂. For Cu exposed to < 1 ppm CO₂, Wp is weight loss due to formation of tenorite instead of paratacamite. b) formation rate of cuprite and paratacamite and corrosion rate of Cu, derivative of data showed in a).

exposed longer than 5 h, the corrosion rate of Cu exposed to low $\rm CO_2$ became slower than for Cu exposed to high $\rm CO_2$.

Since no Cu₂(OH)₃Cl formed during exposure of Cu to low CO₂, the actual loading of NaCl on Cu was more than for Cu exposed to low CO₂. This is supported by the observation that samples exposed to low CO₂ had much more white NaCl remaining on the surface than samples exposed to high CO₂ after they were taken out of the chamber and dried. However, even with more NaCl, the corrosion rate of Cu exposed to low CO2 was still much less than for the Cu exposed to high CO₂. This is mainly due to the presence of CuO, which can provide a high degree of corrosion protection. It has been shown that the initially formed Cu₂O has a porous structure.⁴² CuO forms in the Cu₂O pores to block them and increase corrosion resistance.^{42–44} Figures 9a and 9b confirm the relatively compact surface morphology of Cu exposed with low CO2. With high CO2, paratacamite was the main cupric compound instead of tenorite. Most of the paratacamite was just flakes loosely attached to sample surface as Figure 9d shows. These flakes were not as protective as the compact oxide layer formed in low CO₂ environment. On the other hand, after 10 h exposure, almost the whole sample surface was covered with NaCl droplets, so there was no surface coverage difference between Cu exposed to low CO_2 and high CO_2 . Therefore after 5 h exposure, before the whole surface was covered with NaCl solution, the corrosion rate of Cu in low CO_2 was slower than Cu exposed to high CO_2 .

pH has a strong influence on the formation or stability of Cu₂O, CuO and Cu₂(OH)₃Cl. Cu₂O forms at pH > 4, while formation of CuO occurs at pH > 6.7.⁴⁴ Cu₂(OH)₃Cl is stable between pH 3.8 to 5.5.^{3,31} Using software from OLI Systems Inc., the equilibrium pH of water with 350 ppm CO₂ was calculated to be about 5.7 but as the CO₂ concentration drops to less than 1 ppm, the pH increases above 6.8. So with low CO₂, CuO is the dominant cupric corrosion product. This also explains why CuO is not the dominant cupric compound in the field because the CO₂ concentration in the ambient atmosphere is about 300 to 600 ppm.⁴⁵ With high CO₂, the formation of Cu₂(OH)₃Cl is likely to occur at local anode areas where local pH is lower than the bulk aqueous layer. That is probably why dispersed Cu₂(OH)₃Cl appeared after relative short term exposure.

Morphology and localized corrosion of exposed Cu.- The surfaces of samples exposed to 350 ppm CO₂ for less than 12 h had significant circular features with a diameter of a few hundred micrometers as Figures 12a and 12b show, which suggests a strong effect of the initial droplets formed by the deposited NaCl solution aerosol. For samples exposed longer, the circular features become less evident and the sample surface was much more uniform. However, after corrosion products were dissolved in strong acid, circular features were the dominant feature on the metallic substrate. As shown in Figures 12d–12f, attack was localized in the form of small pits at the periphery of circles with similar size as the circular features that appeared after exposure. This morphology was even observed for samples exposed for relatively long times and did not have circular features in the corrosion product layer. Although some pits were occasionally present at the center of a circle, these peripheral pits suggest that oxidation of Cu primarily occurred around the edge of the initially-formed droplets. The mechanism of formation of these pits is not known. However, it is completely different than the classical Evans droplet model on steel, where oxidation of iron occurs under the center of a droplet of 0.1 M NaCl as an anode and reduction of oxygen occurs under the edge as a cathode because oxygen is more available at the edge of droplet.⁴⁶ For Cu exposed to less than 1 ppm CO₂, the circular features were less significant. More pits were found close to centers of droplets. This suggests that a stronger secondary spreading of droplets with low $CO_2^{9,20}$ can impede formation of the circular features.

Figure 13a presents Volta potential profiles from SKP measured across the surface of Cu exposed with a single saturated NaCl droplet in 98% RH, which simulates the exposure conditions in the homebuilt chamber. At the beginning, the potential under the droplet was much lower than the surrounding area and a dramatic poten-



Figure 12. Images of Cu exposed to humid air (350 ppm CO₂) and 0.1 mg/cm²h in dark. a), b) and c) are samples after exposure. d), e) and f) are exposed samples after soaked in 6.5 M HCl for 5 min and 1 min in 1 M H₂SO₄ to remove corrosion products. a) and d) are samples exposed for 4h; b) and e) are 12 h; c) and f) are samples exposed for 23.5 h.

tial change occurred right outside of the edge of the droplet. This is the same as previous results on Cu with single NaCl droplet in 85% RH,²⁰ which suggests a thin electrolyte layer surrounding the droplet. Reduction of oxygen is likely to occur within this thin elec-



Figure 13. a) profiles of Cu with one droplet of saturated NaCl in 98% RH for 1 h, 23 h and 69 h respectively. Dashed line: geometrical profile of the droplet. Solid line: Volta potential. b) morphology of the same Cu sample after 72 h exposure and remove corrosion product by strong acid.

trolyte area. Probably because of the formation of insoluble cuprite and the thin electrolyte layer, a large ohmic potential drop is generated between the anode and cathode. Therefore, oxidation of Cu takes place very close to the cathode, at the outer periphery of the droplet. This may explain why small pits formed around the periphery of the droplet.

In the 98% RH SKP chamber, the NaCl-saturated droplet kept absorbing water and growing during the measurement. However, the low potential region was always observed around the edge of the droplet. The topography of the sample after exposure for 72 h and removal of the corrosion product shows a sequence of circular rings of pits that probably formed as the droplet grew, Figure 13b. The eventual increase of potential under the droplet is probably due to formation of paratacamite and depletion of NaCl, which results in an inactive region.

The maximum pit depth from optical profilometry and equivalent weight loss calculated from reduction charge of Cu exposed to different environments are presented in Figure 14. Generally, at the beginning, the pit depth increased much faster than weight loss, and then it slowed down. This suggests that corrosion of Cu with constant



Figure 14. Maximum pit depth and equivalent weight loss of Cu exposed in various environments.

deposition was more localized at the beginning and then became more uniform.

The maximum pit depth of Cu exposed to UV is about three times that of Cu exposed in dark environment as Figure 14 shows. This is consistent with the explanation given above, that extra anodic photocurrent is generated due to interaction between UV photons and local anodes. For Cu exposed with low CO₂, localized corrosion is more severe than Cu exposed with high CO₂, although its total corrosion rate is lower. This again supports that the notion that corrosion products formed in low CO₂ environment are more protective.

Conclusions

A new environment chamber with constant deposition of NaCl was designed and used for laboratory exposure of Cu. Corrosion behavior of Cu with UV and CO2 under constant deposition of NaCl was studied.

· The features in Cu coulometric reduction curves were associated with different corrosion products, allowing the coulometric reduction method to be used for quantification of the different products.

 With 350 ppm CO₂, paratacamite and cuprite are the dominant corrosion products like Cu exposed in the field. When CO₂ drops to less than 1 ppm, which increases pH of aqueous layer on Cu, tenorite and cuprite are dominant. Corrosion products formed in low CO2 are much more dense and protective than corrosion products formed in high CO₂. Therefore, CO₂ is very aggressive for Cu corrosion.

 UV has a strong acceleration effect on formation of cuprite due to interactions between UV photons and cuprite but UV has little effect on the formation of paratacamite.

· In various environments with UV illumination or different concentration of CO₂, during the beginning of exposure, localized corrosion is always dominant, but uniform corrosion becomes dominant after exposure of approximately 20 to 30 h. Therefore, localized corrosion is not a severe concern for long term exposure of Cu in these environments.

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