Atmospheric Corrosion of Ag and Cu with Ozone, UV and NaCl

Dissertation

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Abstract

Ag and Cu are both used for electronics and are susceptible to atmospheric corrosion. They are also good corrosivity monitors used to evaluate the aggressiveness of the environments. Numerous experiments have been carried out in laboratory environment to understand and predict corrosion behavior of Cu in the field, although relatively less on Ag. Unfortunately, laboratory exposure testing does not always represent the field environments very well. Discrepancies between lab and field exposure testing are not uncommon. For example, Ag does not corrode in salt spray exposure during ASTM B117 test, while it corrodes everywhere outdoors. This suggests that a new laboratory exposure test for Ag needs to be designed and studied.

Previous research showed exposures to a lab environment containing humidity, ozone, NaCl and UV light is promising for the study atmospheric corrosion of Ag. So efforts were first put on to further understanding the interaction among all the factors. A full factorial experiment was carried out with three factors: ozone, UV intensity and relative humidity (RH). NaCl was loaded by fast evaporation of NaCl/ethanol solution before exposure. After exposure, corrosion products were identified by XRD and quantified by the galvanostatic reduction technique. Meanwhile, corrosion behavior of
Ag in different field environments was studied to correlate lab and field exposure tests. Advances were made in the galvanostatic reduction of Ag, which makes it more powerful for analysis of Ag corrosion products.

For lab exposure samples, AgCl was identified as the only corrosion product in high RH (87%) environments, while Ag₂O and AgO formed as well during exposures at low RH. This result proved a qualitative prediction for the corrosion behavior of Ag in the field. It predicts that less stable silver compounds such as oxide and sulfate are possible corrosion products in the field even if silver chloride is the predominant corrosion product. This prediction was confirmed by analysis of field exposed Ag samples.

By quantification of corrosion products, UV has found to have two contravening effects on atmospheric corrosion of Ag. In low RH and high ozone environments, UV accelerates Ag corrosion, whereas in high RH environments, UV decreases Ag corrosion rate. In environments with low RH (28%) and low ozone (360ppb), Ag corrosion rate increases and then decreases as the intensity of UV increases. These phenomena are attributed to a combination of photolysis of ozone to generate stronger oxidizing species such as atomic O and photodecomposition of Ag corrosion products by UV radiation.

Using fuzzy analysis of all lab exposure data determines that RH was found to have stronger influence than ozone and UV. All lab exposure data were fitted by Artificial Neural Networks (ANNs) and the model successfully predicts Ag corrosion rate in marine environment.
Following the success in Ag corrosion research, the environment of UV, ozone and NaCl was extended to the study of Cu corrosion. It was determined that UV alone can double the Cu corrosion rate by generation of electron-hole pairs in n-type cuprous oxide. Ozone alone is not as aggressive on Ag as on Cu because protection of naturally formed cuprous oxide. With the addition of NaCl, the corrosion rate of Cu increases dramatically because of the breakdown of the naturally formed cuprous oxide by NaCl. Loading of NaCl is also very critical for formation of Cu$_2$(OH)$_3$Cl. However, deposition of NaCl before exposure does not provide a constant deposition source of NaCl, which impedes kinetic studies.

To mimic corrosion behavior of metals in real field, a new environment chamber that generated constant deposition of NaCl was invented. By bubbling saturated NaCl solution, a constant NaCl aerosol environment was achieved for exposure of Cu. With this novel environment chamber, the kinetics of Cu corrosion with constant deposition of NaCl in synthetic air with high and low CO$_2$ and UV was studied. Cu$_2$O and Cu$_2$(OH)$_3$Cl were both dominant corrosion products after exposure. 0.1 M Na$_2$CO$_3$ instead of 0.1M KCl was used as supporting electrolyte for reduction of Cu$_2$O and Cu$_2$(OH)$_3$Cl, because it can clearly differentiate reduction of Cu$_2$O and Cu$_2$(OH)$_3$Cl. With quantification of Cu$_2$O and Cu$_2$(OH)$_3$Cl respectively, UV was found to have a strong effect on the formation of Cu$_2$O but little effect on Cu$_2$(OH)$_3$Cl. It was also determined that localized corrosion of Cu dominates at the beginning of Cu corrosion and then uniform corrosion takes over.
Dedication

This document is dedicated to my wife, my baby, my parents and my parents-in-law.
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First of all, I would like to thank my advisor, Dr. Gerald Frankel for giving me an opportunity to study corrosion and continuously supporting and mentoring my research. My PhD study could not be accomplished without his valuable teaching and guidance. I am also deeply grateful for his help on my family and career development. Many thanks to Dr. Frankel and his wife Ms. June Frankel for their efforts in improving my English too. I would also like to thank Dr. Rudolph Buchheit, Dr. Hendrik Verweij and Dr. Michael Day for being my dissertation committee members and providing valuable comments and suggestions. Special thanks also go to Dr. Christine Lemon, Ms. Erica Ballou Neiser, Dr. Heather Allen, Dr. Robert Kelly and Dr. William Abbott for their assistance on this project. Without collaborating with them, many things could not be achieved.

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Chapter 1  Introduction

Silver is used for electronics because of its outstanding electrical conductivity and relatively low cost compared to gold. Because most electronics are used in indoor environments, previous research mainly focused on indoor field exposure testing and corresponding laboratory exposure studies. Recently, Ag has been used as a corrosivity monitor to evaluate environmental aggressiveness. A strong correlation between the corrosion rates of Ag and carbon steel was reported [1]. This result encouraged the study of the corrosion behavior of Ag in outdoor environments. In contrast to indoor exposure tests, AgCl instead of Ag$_2$S is the most dominant Ag corrosion product in outdoor exposure [1-2]. Although the amount of AgCl formed in the field is known to depend on the amount of atmospheric chlorides, the mechanism of formation of AgCl is not well understood.

Since AgCl is not a common corrosion product in indoor environments, studies of the formation of AgCl in the laboratory have not been performed until very recently. It is surprising that no AgCl is found on Ag after exposure for several weeks in an ASTM B117 salt spray chamber test. Ag remains shiny after exposure. This is probably because oxygen alone is not aggressive enough to attack Ag. Therefore, a stronger oxidant is
usually necessary for laboratory study of AgCl formation. Ozone is more aggressive than oxygen and its concentration is about 20 to 100 ppb in real atmospheres. A combination of ozone, UV and NaCl has been proven to be a promising laboratory environment for the formation of AgCl and the study of Ag corrosion [3]. So a goal of this dissertation is to study the effects of ozone, UV and NaCl on atmospheric corrosion of Ag and the corrosion behavior of Ag in different field environment. Another goal is to correlate lab and field exposure studies and to predict the corrosion behavior of Ag in the field.

Because ASTM B117 is not suitable for Ag accelerated testing and the combination of ozone and UV appears promising, it has been suggested that ozone and UV should be included into a modified B117 test [4]. A successful lab accelerated test should be universal rather than specific for only one metal. Therefore, it is very interesting and worthwhile to study effects of ozone, UV and NaCl on corrosion of other metals, especially Cu, another commonly used corrosivity monitor. Atmospheric corrosion behavior of Cu has been extensively studied by field and lab exposure, and NaCl, UV and ozone all have been found to have significant influence on atmospheric corrosion of Cu separately [5-7]. Therefore, it is very interesting to study combined effects of all of these factors, which is the other goal of this work.

To achieve these goals, this dissertation includes four subtopics, which are addressed in separate chapters. First, the effects of ozone, UV and relative humidity/NaCl on Ag corrosion are studied by a full factorial experiment with UV, ozone and relative humidity. UV was found to have opposing effects on Ag corrosion. A numerical equation
was obtained by fitting lab exposure data and it successfully predicts Ag corrosion rate in marine environment.

Second, Ag corrosion behavior in different field environments is studied. AgCl and Ag\textsubscript{2}S were confirmed to be the dominant corrosion products in field. Furthermore, results from laboratory studies explain the environmental conditions required to form Ag\textsubscript{2}O and Ag\textsubscript{2}SO\textsubscript{4} in the field. Advances were made in the galvanostatic reduction of Ag, which makes it a more powerful for analysis Ag corrosion products.

The third topic involves the study of the effects of ozone, UV and NaCl on Cu corrosion. It is confirmed that UV alone can accelerate Cu corrosion by interaction between photons and cuprite. While the effect of ozone on Cu corrosion is not as significant as on Ag corrosion, NaCl is much more critical on Cu corrosion than on Ag. A constant NaCl source is necessary to study the kinetics of Cu corrosion.

In the fourth part of this dissertation, a novel environmental chamber that provides constant deposition of NaCl is described. Effects of UV and CO\textsubscript{2} on kinetics of formation of cuprite, tenorite and paratacamite were investigated.

Each of the chapters is written as a stand alone paper with separate sections for introductions, experimental details, results and discussions. Preceding these chapters is a literature review.
References:


Chapter 2  Literature Review

2.1 Introduction

The Earth’s atmosphere is a mixture of gaseous, liquid and particulate species. When a solid metal surface is exposed in the atmosphere, water molecules adsorb onto it almost immediately. As the relative humidity (RH) increases, the adsorbed moisture layer increases, reaching about 10 monolayers of water as the RH approaches 100% [1-2]. The moisture layer containing more than 3 monolayers can behave similarly to bulk water [2]. This moisture layer is necessary for electrochemical reactions during atmospheric corrosion. Besides adsorption of water, deposition of gases and particulate on metal surfaces is another important process during atmospheric corrosion. Sulfates and sea salts are the most common and dominant aerosol particles [2]. They are usually soluble and hydroscopic. Although they are usually not oxidizing species, they have important effects on the chemistry of the moisture layer. For example, ammonium sulfate can increase acidity and also result in formation of ammonium complexes with certain metals [3].

Deposition and absorption of gaseous corrodents provides oxidants as well as surface electrochemical activity. Although the most dominant oxidant is oxygen, the gases listed in Table 2.1 are usually of most interest. The concentrations of these gases in...
the gaseous phase determines their partial pressure and concentration in the moisture layer, which usually affects both thermodynamics and kinetics of the cathodic reaction directly. In summary, adsorption of water, deposition of aerosol particles and gaseous corrodents generate a surface environment containing surface electrolyte and oxidants, which are essentials for an electrochemical redox process. As long as the surface electrolyte is active enough and the oxidants are aggressive enough, corrosion of metals occurs.

The effects of sunlight/photons on atmospheric corrosion have attracted interest recently [9]. The ultraviolet region, which spans from 100 to 400 nm in the sunlight spectrum, is of the most interest because photons within this span have the proper energy to interact with corrosion products, usually oxides, as well with photosensitive gases, e.g. ozone and NO₂ [10].

It has been proven that UV light has strong influence on aqueous corrosion of many metals [11-14]. For example, the pitting corrosion resistance of stainless steel in sulfuric acid or chloride solution was increased by UV illumination, because of the enrichment of Cr in the oxide and extra cathodic photocurrent [11-14].

Besides steel, Zn, Ti and Cu are all photosensitive too [15-17]. Corrosion rate of Zn can be increased by a factor of 3.5 under UV illumination because interaction between photons and n-type ZnO generates extra anodic current [17]. Photocorrosion behavior of Cu will be discussed in detail later.
It is well known that UV results in fast photolysis of ozone and NO$_2$ to generate very aggressive atomic oxygen [10, 18] as equation 2.1 and 2.2 present. The atomic oxygen O may react with water vapor to generate similarly aggressive OH radical (Equation 2.3) or oxidize metals directly [19-20]. Atomic oxygen and OH radical both enhance environment corrosivity and can result in significant acceleration of atmospheric corrosion.

\[
\text{O}_3 + h\nu (\lambda<370\text{nm}) \rightarrow \text{O} + \text{O}_2 \quad (2.1)
\]
\[
\text{NO}_3 + h\nu (\lambda<397\text{nm}) \rightarrow \text{O} + \text{NO} \quad (2.2)
\]
\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad (2.3)
\]

Overall, the study of atmospheric corrosion usually focuses on effect of these factors: RH, gaseous corrodents, aerosols and, more recently, photons. The rest of this chapter reviews the effects of these environmental factors, on the atmospheric corrosion of Ag and Cu. At the end, some common experimental instruments and methodologies are also briefly reviewed.

2.2 Atmospheric corrosion of Ag

2.2.1 Indoor exposure and corresponded lab exposure of Ag

In contrast to other less-noble metals, the Ag corrosion products are usually basic chemicals: Ag$_2$S and AgCl [21-24]. Besides them, silver oxide and silver sulfate can also form, but the presence of these compounds is usually proven only by the presence of corresponding anions. There has not been strong evidence to support formation of oxide,
and sulfate in field exposures. Other compounds, such as nitrates and carbonates, are less soluble or thermodynamic stable than sulfide and chloride.

In indoor environments, Ag$_2$S is usually much more dominant than AgCl and vice versa in the outdoors [21-24]. This is probably because Ag components have more access to reduced sulfur indoors, while chlorine and seasalt particles are more accessible outdoors [22, 25]. A strong correlation between Ag corrosion rate and concentration of reduced sulfur during indoor exposure has been found [22].

Common corrosive atmospheric constituents include oxygen, ozone, nitrogen dioxide, sulfur dioxide, carbon dioxide, hydrogen chloride, hydrogen sulfide, ammonia, ammonium sulfates and sodium chloride and so on [2]. Depending on the climate and the degree of pollution, the concentration of these species varies a lot. Therefore, it is really difficult to determine the real corrosion mechanism. The basic philosophy of laboratory exposure research is to try to reduce uncontrolled variables and expose metals in a well-controlled lab environment with specific corrosive species as a means to discover the corrosion mechanism in real atmospheres. For Ag corrosion, since Ag$_2$S is so dominant, many laboratory exposures have involved different types of reduced sulfur to understand Ag sulfidation, such as hydrogen sulfide [25-30], organic sulfide/COS [26-27, 31-32] and elemental sulfur, S$_8$ [33]. Generally, the sulfidation effect of hydrogen sulfide is stronger than COS and elemental sulfur. The sulfidation rate of Ag can be higher than 1 nm/ppm*h [26].

There has been no agreement on the effect of RH on Ag sulfidation with various corrodents. In the presence of H$_2$S only, RH shows a positive acceleration effect on
sulfidation rate, especially when RH is higher than 70% [26-27]. But when H₂S is mixed with other gases, the effect of RH becomes complicated. It was reported that in a mixture of O₃, H₂S, SO₂, NO₂ and Cl₂, the Ag sulfidation rate is independent of RH [25]. It is not clear why the effect of RH becomes insignificant when H₂S is mixed with other gases yet. It is possible that the sulfidation mechanism might change as other gases are involved, although mechanisms of sulfidation in either condition are not clear yet.

With only H₂S, it is usually considered that the overall reaction 2.4 occurs during sulfidation [28]. However, this reaction suggests that reduction of hydrogen is the dominant cathodic reduction, which is likely not true, since equilibrium reduction potential of Ag is 0.799 V SHE [34], much higher than reduction potential of hydrogen. Hence reduction of oxygen (equation 2.5) was suggested [35].

\[
2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H}_2 \quad (2.4)
\]

\[
4\text{Ag} + 2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{Ag}_2\text{S} + 2\text{H}_2\text{O} \quad (2.5)
\]

Although reduction of oxygen provides much larger driving force, oxygen is not very aggressive for Ag. It was reported that molecular oxygen (O₂) is not aggressive enough to oxidize Ag even at temperatures as high as 310 °C [19]. In a humid environment, the acceleration effect of different corrodents on Ag sulfidation is in the order Cl₂ > NO₂ > SO₂ > O₂ [29].

The acceleration effect of Cl₂, NO₂ and O₃ were all proven by different research groups [7, 25, 27-28, 36], while the effect of SO₂ was generally found to be negligible [28]. So when H₂S is mixed with these gases, they are the dominant oxidizing species.
rather than oxygen. It is likely that RH does not have a significant effect on the oxidation of Ag by these oxidants, so the effect of RH on sulfidation of Ag with a gas mixture containing H₂S becomes less significant. For example, the acceleration effect of O₃ on oxidation of Ag is independent of RH [20]. Another possible reaction pathway is oxidation of H₂S to get elemental sulfur by those strong oxidants and then reaction of silver with S, because RH has very little effect on sulfidation of Ag by elemental sulfur [32].

Since Ag₂S formed on Ag is usually porous, the kinetics of sulfidation are always linear [28, 32, 37] during atmospheric corrosion. This is different than sulfidation of Ag at 300 °C, which exhibits classical parabolic kinetics [38].

Not much study on the effect of UV illumination on Ag sulfidation has been carried out. But UV was found to react with photosensitive organic sulfur and change the sulfidation kinetics from linear at high RH to nonlinear at low RH [32].

Recently, sulfidation of Ag nanoparticles drew some interest too [39-41]. Ag nanoparticles have outstanding antimicrobial properties. However, Ag nanoparticles corrode at a fast rate [40]. The dominant corrosion product is still Ag₂S, which significantly reduces the antibacterial performance of Ag nanoparticles [39]. Currently, it is not clear how to increase the corrosion resistance of Ag particles without losing the antimicrobial performance.

2.2.2 Outdoor exposure and corresponding lab exposure of Ag
Due to the limited use of Ag outdoors, outdoor exposure of Ag is not often reported. AgCl instead of Ag\textsubscript{2}S is the most abundant corrosion product [21, 42-43], unless Ag is exposed close to a source of H\textsubscript{2}S, e.g. a volcanic environment [44]. The formation mechanism of AgCl in outdoor environments is not yet clear, especially considering that the typical concentration of chlorine gas is extremely low (see Table 2.1). Deposition of chloride is likely to play an important role in the formation of AgCl. In marine environments, deposition of NaCl is usually between 15 mg to 1500 mg/cm\textsuperscript{2}d [45], while typical indoor chloride deposition rate is less than 1 \(\mu\text{g/m}^2\text{d}\) [23]. Field exposure also indicates that the amount of AgCl on Ag exposed at the coast is largely influenced by wind direction, which is important for transport and deposition of seasalts.

However, it is reported that Ag corrodes extremely slowly in salt spray chamber during ASTM B117 test [20, 46]. It is believed that the combination of oxygen and sodium chloride is not aggressive enough to attack Ag. This is different than the effect of oxygen and hydrogen sulfide on Ag sulfidation. To study formation of AgCl in the lab, a stronger oxidant is necessary. Ozone has been proven to be a promising oxidant surrogate because it is present in the real atmosphere at a reasonable level and it is much more aggressive than oxygen. Laboratory exposure of Ag with ozone and UV has been reported, which was an important contribution to understand formation of AgCl in the field atmosphere environment [47]. With ozone alone, Ag corrodes extremely slowly. But with the addition of UV illumination, because of formation of atomic oxygen, the Ag corrosion increases several orders of magnitude by the formation of Ag\textsubscript{2}O [47]. Since
AgCl is more thermodynamically stable, Ag₂O gets converted into AgCl immediately in NaCl solution [47-48].

Oxidation of Ag by atomic oxygen occurs by surface adsorption first and then proceeds at a fast rate [49-51]. Therefore, surface coverage of oxygen is critical for silver oxidation [52-53]. Formation of silver oxide is only favored when the surface coverage is high enough [53]. It was proposed that Ag actually can be further oxidized to higher oxidation states to Ag⁶⁺ (AgO₃) at room temperature [54], although no AgO₃ has been reported after field exposure. Oxidation of Ag₂O to AgO has been confirmed by different reports [19, 55].

The kinetics of oxidation of Ag by atomic oxygen are linear [54, 56], because it is believed that atomic oxygen can penetrate through silver oxide film to react with Ag [54]. The linear kinetics are the same as Ag sulfidation and corrosion in outdoor environments [43].

Atomic oxygen usually is generated by photolysis of ozone by UV (equation 2.1), so it has been suggested to include ozone and UV in a salt spray chamber for Ag lab exposure study [20, 57]. Ag corrodes in a modified salt spray chamber containing UV and only AgCl forms after exposure [57]. As for field-exposed samples, the kinetics of formation of AgCl are linear in the modified salt spray chamber because of the porous structure of AgCl. The surface morphology of lab-exposed samples is similar to field-exposed samples.
The effects of ozone, UV, NaCl and RH were carefully studied in a home-built well-defined environment chamber [20]. Chemical reactions in this system are far more complicated than oxidation of Ag by ozone or atomic oxygen directly. Four pathways for formation of AgCl were proposed [20] including formation of chlorine as an important intermediate. As equation 2.3 indicates, water vapor is easily oxidized by atomic oxygen to generate OH radical, which is also a very aggressive oxidizing species [58-59]. OH can oxidize seasalt particles to generate molecular chlorine [10, 59-60], which accelerates Ag sulfidation as mentioned before. Chlorine can be generated by oxidation of Cl\(^-\) by ozone [61] by this equation as well:

\[ 6\text{Cl}^- + \text{O}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Cl}_2 + 6\text{OH}^- \]  

(2.6)

Although this reaction is very slow in neutral or alkaline environments, and no Cl\(_2\) can be detected in a neutral seasalt solution with ozone [58], it can be catalyzed by certain metal ions, e.g. Cu\(^{2+}\) and Fe\(^{3+}\) [62-63]. CO\(_2\) in the ambient environment can also accelerate this reaction by increase the acidity of NaCl solution [64]. Therefore, formation of chlorine in an atmospheric environment with ozone and chloride is highly likely and important for formation of AgCl. However, it is surprising that the presence of NaCl decreases in Ag corrosion rate with ozone and UV because of protection of the surface against exposure to atomic oxygen by the NaCl aqueous layer. So the pathway that Ag gets oxidized by atomic oxygen or ozone should be more critical for AgCl formation.

An important influence of UV on AgCl formation has not been discussed in the literature. It is well known that AgCl is very photosensitive. UV or even sunlight can
result in photodecomposition of AgCl to generate metallic Ag and chlorine gas [65] following reaction 2.7.

\[ 2\text{AgCl} + hv \rightarrow 2\text{Ag} + \text{Cl}_2 \]  \hspace{1cm} (2.7)

Overall, the corrosion behavior of Ag in an environment containing ozone, UV and NaCl is very similar to field-exposed Ag. This proves that a combination of UV, ozone and NaCl is a promising environment for study of atmospheric corrosion behavior of Ag in the lab. It also highlights the importance of oxidants stronger than oxygen in atmospheric corrosion study of Ag.

It has been stated that the corrosion rate of Ag in outdoor environment is on the same order as Ag exposed indoors [22]. This may not be correct, because UV intensity and chloride deposition rate are much higher outdoors. Field exposure tests also indicate a big variation of corrosion rate of Ag exposed in different outdoor environments [20-21, 43-44, 57]. Corrosion rate of silver coupons exposed at Daytona Beach even exceed 1.5 μm/year, which is similar to the corrosion rate of Cu exposed in marine environments [66].

Formation of silver oxide and silver sulfate is speculated during indoor exposure because of detection of corresponding anions by infrared spectroscopy (IR) or x-ray photoelectron spectroscopy (XPS) [23]. Formation of silver sulfate and silver oxide is possible during outdoor exposure, because oxidation of Ag by ozone or atomic oxygen is so critical for Ag corrosion. Furthermore, it was recently confirmed by time of flight secondary ion mass spectrometry that Ag₂SO₃ can form on Ag during exposure to
environments containing SO$_2$ [67-68]. This can very likely lead to formation of sulfate, which is more thermodynamically stable.

This dissertation advances the study of ozone, UV and NaCl effects on Ag corrosion, especially focusing on the effect of UV, which has not been discussed in the atmospheric corrosion scenario. The corrosion behavior of Ag in different field environments is further studied to achieve a deeper understanding of Ag corrosion in field, including formation of silver oxide and silver sulfate.

2.3 Atmospheric corrosion of Cu

Many field exposure studies have been performed to understand the corrosion mechanisms of copper. Conclusions from these field observations provide targets and references for lab research. Cuprous oxide (Cu$_2$O) is the initial first corrosion product formed in the field. Then posnjakite (Cu$_4$(OH)$_6$SO$_4$.H$_2$O), brochantite (Cu$_4$(OH)$_6$SO$_4$) and antlerite (Cu$_3$(OH)$_4$SO$_4$.H$_2$O) form [66, 69]. Posnjakite might transform to brochantite [70]. In a marine environment, atacamite (Cu$_2$(OH)$_3$Cl) also forms [71-73]. Cuprous sulfide (Cu$_2$S) [70] and gerhardtite (Cu$_2$(OH)$_3$NO$_3$) were occasionally reported as minor corrosion products [22, 74]. The corrosion rate of copper corrosion usually decreases as the amount of corrosion products increases in field and is stable at about 1$\mu$m/yr after several years of exposure [75].

In lab exposure of Cu, the effects of sulfurous species and chlorine-containing species usually are of most interest, because copper sulfates (Cu$_4$(OH)$_y$SO$_4$) and copper
hydroxychloride (Cu$_2$(OH)$_3$Cl) are the most common corrosion products found from field exposure samples [74].

Following is a review of the effects of sulfurous gaseous species, oxidants and corrosive particles on atmospheric corrosion of copper according to laboratory exposure results and an attempt to understand atmospheric corrosion of copper in field based on achievements from lab exposures.

2.3.1 Laboratory exposures of Cu with gaseous corrosive species

Sulfur dioxide and hydrogen sulfide are the most interesting gaseous species for copper. Recently, nitrogen dioxide and ozone also have been of interest, especially in those environments with less content of sulfur dioxide [76]. Various well-controlled lab exposures of Cu have been conducted with these species. Usually, Cu coupons or plates are placed in a flowing humid air environment with some amount of corrosive gas. The concentration of these species is usually controlled under 500 ppb in lab exposure environment because their concentration in real atmosphere is usually less than 100 ppb [77].

2.3.1.1 Corrosion of copper in humid air

In humid air environment, a constant layer of adsorbed water was found to cover the copper surface as the mass of this layer was dependent on RH but not on exposure time [78]. Cuprous oxide immediately formed in humid air but the growth rate decreased abruptly to about 1 Å/day after exposure of 100 minutes [79-80]. The formation rate of cuprous oxide increases as relative humidity increases [78, 80], but the overall thickness
of oxide layers was only on the order of a few nanometers even at high relative humidity. At high relative humidity (RH>70%), it was reported that very little cupric oxide (CuO) can be detected by XPS [81-82]. Its content increases as RH increases. It is worth knowing that cuprous oxide is hydroxylated when it is exposed to humidity. Therefore, on the outmost layer, several complexes such as CuOH and CuOH$^+$ are possible. These complexes can promote copper or copper oxide dissolution [83]. This could be an important intermediate step for the formation of other complex corrosion products.

It is clear that humidity alone is not aggressive enough for copper corrosion, but it plays a vital role in Cu atmospheric corrosion that results in formation of Cu complexes for further dissolution of Cu.

2.3.1.2 Exposure of Cu in humid air with H$_2$S

Many lab-accelerated experiments have been carried out with sulfurous gas such as sulfur dioxide and hydrogen sulfide [84-85]. Sulfides, sulfates and sulfites formed during lab exposure [85-86]. Exposures with sulfurous gases are very important for understanding initial stage of atmospheric corrosion of copper.

Exposure experiments have usually been carried out at RH> 65% with hydrogen sulfide. In this condition, the adhesive water layer is thick enough to behave like bulk acid hydrogen sulfide solution [84].

Cuprous sulfide (Cu$_2$S) as well as cuprous oxide (Cu$_2$O) forms during lab exposure with hydrogen sulfide [84, 85]. Cuprous oxide is always sandwiched between copper and
cuprous sulfide and cuprous sulfide impedes the transport of oxygen, which results in the ratio of Cu₂S to Cu₂O increasing during exposure [85].

When the concentration of hydrogen sulfide is higher than 1ppm, cuprous oxide grows to more than 200 nm in one day [30, 84]. Even with only 50 ppb hydrogen sulfide, the cuprous oxide increased to more than 10 nm in one day [7]. Compared to exposure in pure humid air, the growth rate of cuprous oxide increased about three orders of magnitude. However, the relationship between oxide formation and sulfide formation has not been addressed. Given that cuprous sulfide always formed on top of cuprous oxide, and cuprous oxide is not stable in acid solution [87], it is possible that cuprous oxide reacts with hydrogen sulfide to form cuprous sulfide.

The kinetics of cuprous oxide and sulfide are both linear with more than 1ppm hydrogen sulfide [84]. However, a parabolic relationship is found when Cu is exposed to low concentration hydrogen sulfide [85]. Probably, the corrosion product is initially more compact and crack-free, but cracks form during thickening.

At low hydrogen sulfide concentration, the growth rate of cuprous oxide is relatively slow and it is not thick enough to have cracks. This thin cuprous oxide is a good protective layer and so its kinetics are parabolic. When Cu is exposed to high hydrogen sulfide concentration, cuprous oxide grows to hundreds of nm within relatively short time, and also the acidity of the moisture layer increases [84]. Cracks appear, which makes the corrosion rate linear. Pits were found in the cuprous oxide layer [88] and in the base copper [30].
It is also interesting that a three-layer structure of corrosion products, cuprous oxide with a bilayer cuprous sulfide, formed with high concentration hydrogen sulfide [89]. EDS showed the Cu/S atomic ratio of the outermost layer was much less than 1.5, although no CuS was identified by XRD.

2.3.1.3 Exposure of Cu in humid air with SO₂

As with H₂S, the moisture layer on Cu in the presence of SO₂ is acidic [90] with due to reaction 2.8. Corrosion behavior of copper with SO₂ is also similar to Cu with H₂S but slower.

\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HSO}_3^- \]  \hspace{1cm} (2.8)

Corrosion rate of Cu is about 2 nm/h at 80% RH with 250 ppb SO₂ [91], which is similar to Cu exposed with 50 ppb H₂S [85]. When the SO₂ concentration is less than 50 ppb [92], the corrosion rate is very slow and only trace copper sulfite is detected by XPS after exposure. So sulfur dioxide is generally not as corrosive as hydrogen sulfide.

It is interesting that, similar to H₂S, SO₂ also results in a large number of pits, ranging from 50-100 nm [88]. Corrosion rate of Cu during long term exposure experiments even with high concentration SO₂ is much less than short term [93-95]. This suggests a protective corrosion product layer formed during exposure. The bottom layer of corrosion products formed in sulfur dioxide environment was still cuprous oxide. The morphology of Cu₂O was the same as that formed in pure humid air. A film with round grains completely covered the whole surface [91].
Corrosion products formed on Cu during exposure to SO$_2$ are much more complicated than exposure with H$_2$S. Cupric sulfite (CuSO$_3$.xH$_2$O), instead of cuprous sulfide forms on top of cuprous oxide [91, 94]. At the beginning, the sulfite layer is not uniform. Large aggregates of sulfites are sparsely distributed on the Cu surface and surprisingly no sulfate has been identified for up to 1200 h exposure. However, it is believed that SO$_2$ is critical for formation of all kinds of complicated copper sulfates [85, 95, 96], such as antlerite (Cu$_3$SO$_4$(OH)$_4$) [96]. It is possible that basic copper sulfite is a precursor of antlerite. But the issue is that how S(IV) is oxidized to S(VI). There is no clear explanation yet.

Proton-promoted dissolution was proposed for the formation of sulfites by Stumm [97]. In a high RH environment, the cuprous oxide is hydroxylated immediately. SO$_2$ dissolves into adsorbed water on the copper surface and reacts with water to produce protons (H$^+$) and ligands (HSO$_3^-$). Both protons and ligands are able to bond with surface Cu ions in cuprous oxide layer, which can weaken bonds between Cu ions and the matrix [83]. Therefore, the dissolution of copper ions is promoted. After dissolution starts, sulfite precipitates on the sample surface while new surface copper ions are hydroxylated at the same time. However, the mechanism by which Cu(I) is oxidized to Cu(II) has not been pointed out clearly. The content of Cu(II) is large compared to exposure in pure air even though molecular oxygen is still the only oxidant. It is suspected that sulfur dioxide has some catalytic property to promote oxidation of Cu(I) to Cu(II).

It is interesting that sulfur dioxide does not accelerate the growth rate of cuprous oxide very much, which is different than hydrogen sulfide as mentioned before. The
thickness of preformed cuprous oxide layer almost did not change after samples were exposed in sulfur dioxide environment [91].

Contradictory results were reported on the formation rate of copper sulfite and its relationship with the cuprous oxide layer. Itoh [98] reported that the oxide film had an inhibiting effect on sulfite formation with 16-23 ppm SO$_2$. The thicker the oxide film, the slower was the formation of sulfite. Aastrup [91] reported that the growth rate of sulfite in 250 ppb SO$_2$ environment was independent of the cuprous oxide layer. The difference was probably due to the concentration of sulfur dioxide. With higher SO$_2$, the dissolution of surface copper ions is not the rate-limiting step anymore while the oxidation of copper becomes the rate determination step. The thicker the oxide layer, the slower it grows. Therefore the formation rate of sulfite is lower with thicker oxide layer.

Chawla [88] exposed Cu film in highly corrosive environment with 1000 ppm SO$_2$ at 75% RH. It was reported that Cu$_2$S and Cu$_2$SO$_4$ as well as Cu$_2$O and Cu$_2$SO$_3$ formed at the early stage of copper corrosion by Auger Electron Spectroscopy analysis according to atomic ratio. Sulfide ions and sulfate ions were attributed to the disproportionate reaction of SO$_2$. This mechanism is completely different than for low-concentration exposure. Usually, the concentration of SO$_2$ in the field is less than 1ppm. Therefore, this mechanism is probably unrealistic for field exposure.

Lab exposure experiments are typically carried out at high relative humidity. At lower relative humidity or dry environment, the corrosion mechanism might be different. It has been shown that SO$_2$ can dissociate slowly to S and O on the surface of both Cu and Cu$_2$O in dry condition [99]. Besides this, SO$_2$(ads), SO$_3$(ads) and SO$_4$(ads) are
detected on copper surface in dry environment [99]. These might need to be taken into account when analyzing copper corrosion in dry air with SO₂, which has not been reported yet, but it can certainly occur in the field.

In summary, sulfites rather than sulfates form in lab exposures with less than 1 ppm SO₂. This means SO₂ alone is not responsible for copper corrosion in the field, although it is reported that some amount sulfate formed in high temperature environment [100]. However, sulfites formed with SO₂ could be important precursors for other corrosion products.

2.3.1.4 Exposure of Cu in humid air with NO₂ and HNO₃

In the presence of oxygen molecules, nitrogen dioxide dissolves into and reacts with the moisture layer forming nitric acid and nitrous acid [101]. Besides cuprous oxide, formation of cupric oxide, basic nitrate (Cu(NO₃)₂), nitrite (Cu(NO₂)₂) and probably gerhardtite (Cu₂NO₃(OH)₃) have been reported [81, 100]. These nitrates or nitrites are also on top of cuprous oxide.

The most interesting result associated with exposure experiments with NO₂ is that Cu corrosion rate decreases as RH increases, especially in high NO₂ concentration environment [81], because of an inhibiting effect of nitric acid at high RH.

The solubility of NO₂ in water is 0.01 mol/L*atm, much lower than SO₂ [77]. But the corrosion rate of copper in air with NO₂ was higher than copper with SO₂ [81, 96]. This is probably because HNO₃ is much more aggressive than H₂SO₃.
Similar to SO$_2$, the corrosion rate of Cu exposed with NO$_2$ decreases as corrosion products reach a certain thickness. This was considered as a proof for the protective effect of nitrates [81]. The atmospheric concentrations of SO$_2$ and NO$_2$ have been decreasing recently, which could make other pollutants, such as nitric acid more crucial for copper corrosion in the field [102]. The evident difference of Cu exposed to environments with nitric acid is that much less Cu$_2$O forms than in field exposure samples or samples exposed with SO$_2$ or NO$_2$ in the lab. The percentage of Cu$_2$O also keeps decreasing during exposure [103-104]. This is probably because HNO$_3$ is so aggressive that Cu$_2$O is much less stable.

A critical issue for lab accelerated testing with nitric acid is to control and monitor nitric concentration. The most efficient and accurate method is to use a permeation tube to introduce HNO$_3$ gas and measure the outlet HNO$_3$ by dissolving in water to get the real deposition rate of HNO$_3$ on the sample surface [104-106].

HNO$_3$ is much more aggressive than SO$_2$ and NO$_2$ and its solubility is much higher, $2.1 \times 10^5$ mol/L-atm [77]. Therefore, its deposition velocity is rather high [105]. This makes total flow rate or flow velocity an important parameter, while they are often not taken into account for SO$_2$ and NO$_2$. It was reported that with the low flow velocity of 0.03 cm/s, the weight gain rate of copper samples increased linearly from 3 to 10 $\mu$g/cm$^2$/day [102]. The corrosion rate also increased linearly from 8.1 to 50 $\mu$g/cm$^2$/day as flow velocity increased from 0.03 to 35.4 cm/s with 325 $\mu$g/m$^3$ HNO$_3$ [102]. Compared to sulfur dioxide, the corrosion rate of copper with HNO$_3$ is almost 6 times higher.
However even so, the corrosion rate of field samples exposed before 1990 with high sulfurous pollutants was usually higher than corrosion rate estimated by lab exposure experiments with HNO$_3$ [104]. This means HNO$_3$ was not mainly responsible for copper corrosion when a large amount SO$_2$ was present [106-107].

In contrast to NO$_2$, the corrosion rate of Cu exposed with HNO$_3$ increases as RH increases [108]. This indicates that the corrosion mechanisms of Cu exposed to NO$_2$ might be quite different than for HNO$_3$, although dissolution of NO$_2$ certainly leads to formation of nitric acid.

2.3.1.5 Exposure of Cu in humid air with ozone

Ozone is a very strong oxidant, but the corrosion rate of Cu in environments with less than 250 ppb ozone was very low, almost same as pure air. Only trace Cu$_2$O and Cu(OH)$_2$ formed during exposure [92, 109]. An increase of CuO was reported when copper was exposed for longer than 10 days [92]. The low corrosion rate could be attributed to the protection effect of natural oxide layer on the copper surface. Therefore, usually ozone alone is not considered as corrosive species for copper.

2.3.1.6 Exposure of Cu in humid air with multiple corrosive gases

In real atmospheric environments, many kinds of corrosive species coexist. The combined effect of these species on copper is not a linear sum of the individual effects of all these species. Synergic effects of different combinations of corrosive species have been reported. It was mentioned above that SO$_2$ alone did not result in formation of large amount of sulfates, which was found from samples exposed in field. This can be
attributed to the absence of other corrosive species in a lab exposure. Therefore, combinations of different corrosive species should attract more attention for designing of lab exposure experiments. Furthermore, the corrosion mechanisms with combinations of several species are usually more complicated than for single species.

As mentioned above, low concentration of SO\textsubscript{2} resulted in the formation of CuSO\textsubscript{3}.\textsubscript{xH\textsubscript{2}O} but this is not commonly found in field exposure, probably because of the absence of stronger oxidants in the lab exposure environment. For example, ozone and NO\textsubscript{2}, two strong common oxidants in the field, have the ability to oxidize S(IV) to S(VI) \cite{110}. Therefore, basic copper sulfate (CuSO\textsubscript{4}.xH\textsubscript{2}O) instead of sulfite is the dominant cupric corrosion product for short-term exposures with SO\textsubscript{2}/O\textsubscript{3} or SO\textsubscript{2}/NO\textsubscript{2} \cite{100, 110}. When NO\textsubscript{2} is present, Cu(OH)\textsubscript{2} and gerhardtite (Cu\textsubscript{2}(OH)\textsubscript{3}NO\textsubscript{3}) are also identified \cite{85, 100}.

Surprisingly, although NO\textsubscript{2} is a strong oxidant, it usually does not accelerate the corrosion of Cu exposed to SO\textsubscript{2}. When the content of NO\textsubscript{2} is less than or similar to SO\textsubscript{2}, the corrosion rate is even less than the sum of the corrosion rate of Cu exposed to NO\textsubscript{2} and SO\textsubscript{2} individually \cite{82, 91, 100}. The accelerating effect of NO\textsubscript{2} is only significant when SO\textsubscript{2} is much less than NO\textsubscript{2}. Similar to Cu exposed to NO\textsubscript{2} only, the corrosion rate of Cu exposed with SO\textsubscript{2}/NO\textsubscript{2} decreases as relative humidity increases. Also, it is interesting that gerhardtite is covered by sulfates at high relative humidity (RH=90%), while it covers sulfates at low relative humidity (RH\textless; 70%). Unfortunately, little quantification of the product has been provided. This information could be important in understanding the mechanisms of the accelerating effect.
In contrast to NO\textsubscript{2}, O\textsubscript{3} had a significant accelerating effect on Cu corrosion regardless of whether its concentration was less or more than SO\textsubscript{2}[81, 91]. The corrosion rate was more than 10x higher than the sum of the corrosion rates with individual gases [91, 100]. The formation rates of both oxide and sulfate increased [91] compared to exposures with SO\textsubscript{2} or O\textsubscript{3} separately. Ozone played two roles in this accelerating process: it oxidized S(IV) to S(VI) and second, it promoted formation of Cu\textsubscript{2}O.

As RH increases, the corrosion rate increases a lot in the presence of ozone. The consumption of ozone (below 500 ppb) is determined by the SO\textsubscript{2} concentration, while the consumption of SO\textsubscript{2} is determined by its own concentration as well as that of ozone [111-113]. It is apparent that the corrosion rate increased with an increase of either SO\textsubscript{2} or O\textsubscript{3} or both.

It needs to be pointed out that Cu\textsubscript{2.5}(OH)\textsubscript{5}SO\textsubscript{4}.2H\textsubscript{2}O [109] formed when copper was exposed to SO\textsubscript{2}/O\textsubscript{3}. This sulfate is considered as an intermediate between basic sulfate (CuSO\textsubscript{4}) and posonjaket, which was identified after field exposure. This intermediate does not appear when Cu is exposed to SO\textsubscript{2} only. This indicates that ozone does have an effect on copper corrosion in real atmospheres.

Much less has been reported on other combinations, which could be because other combinations do not have synergistic effects. For example, SO\textsubscript{2} and H\textsubscript{2}S do not show any synergism. The corrosion rate in a mixed gas environment is equal to the sum of the rates with two individual gases [114].
In summary, H₂S, SO₂, NO₂, HNO₃ and O₃, are all corrosive for copper in different ways. However, this does not mean they are all directly responsible for corrosion during field exposure. H₂S might be the reason of Cu₂S forms in the field. SO₂ alone is not responsible for formation of copper sulfates in field. Oxidants such as NO₂ and O₃ are necessary for sulfate formation with SO₂. HNO₃ can result in formation of gerhardtite. Ozone has a significant effect to accelerate Cu corrosion when it is combined with SO₂ but ozone alone is not aggressive for Cu.

2.3.2 Exposure of Cu with pollutant particles

Airborne salinity is considered as another important factor for Cu corrosion. Ammonium sulfate (\((\text{NH}_4)_2\text{SO}_4\)) particles were found to play an even more important role than SO₂ for Cu corrosion [115]. In a marine environment, chloride is the most corrosive species that is responsible for formation of atacamite, Cu₂(OH)₃Cl [116]. Therefore, these airborne particles have to be involved in lab exposure experiments to uncover the mechanisms for copper corrosion in real atmosphere.

Relative humidity becomes more critical when pollutant particles are involved because particles begin to deliquesce when RH reaches a critical value. This usually results in a dramatic increase of surface moisture layer thickness. This special RH can be affected a little by the metal surface, but is usually very close to Critical Relative Humidity (CRH) [117], which is the equilibrium RH of saturated salt solution. The CRH of ammonium sulfate is around 80% [118] and the CRH of NaCl is about 73% [119]. Ammonium bisulfate is a special case in that its threshold RH on copper could be much
lower than the CRH [120].

2.3.2.1 Lab Exposure with Ammonium Sulfate and Ammonium Bisulfate

Ammonium sulfate and ammonium bisulfate are the most common particles in typical urban and indoor environments, especially in industrial zones [121]. For ammonium sulfate, thermophoretic deposition was reported for salt particle generation and deposition on Cu [121-122]. However, ammonium sulfate starts to decompose at 86 °C [123], so the highest experiment temperature is usually set at 80°C. Thus, preformed aerosol particles could not be totally dried during deposition. Filters have to be used to dry and load particles on Cu. A disadvantage of this dry process is that distribution of particles is not uniform and agglomeration of particles cannot be avoided. The size of ammonium sulfate particles has little effect on copper corrosion.

As expected, RH has very strong influence on corrosion process with (NH₄)₂SO₄ in the air. Below the CRH, only Cu₂O is identified by XRD and the corrosion process is essentially the same as in pure air [123] but with a faster corrosion rate. At high relative humidity (RH>88%), antlerite (Cu₃(OH₄)SO₄) formed at high temperature (373 K) and posnjakite formed at room temperature (300K) [123]. At the critical relative humidity, brochantite formed at both temperatures, but at high temperature, antlerite also formed if salt load increased to a large amount [123]. This is in line with a theoretical calculation that also shows initial load is a critical factor to determine corrosion products [124].

These three minerals, posnjakite, brochantite and antlerite are the most common corrosion products found from field samples [69], but they are seldom formed in lab
exposure with sulfurous gaseous species. This indicates that ammonium sulfate plays a vital role in formation of these complex copper sulfates in the field.

Lobnig proposed the formation mechanisms of these corrosion products [3, 118, 120, 123]. Cu(NH$_3$)$_2^+$ and Cu(NH$_3$)$_2^+$ complexes were considered as first intermediates formed according to reactions 2.9 and 2.10

\[
\begin{align*}
\text{Cu} + 2\text{NH}_3 & \rightarrow \text{Cu(NH}_3)_2^+ + e^- \quad (2.9) \\
\text{Cu} + \text{NH}_3 & \rightarrow \text{Cu(NH}_3)_2^+ + e^- \quad (2.10)
\end{align*}
\]

Cu(I) ions could react with water to get cuprous oxide (reaction 2.11), disproportionate or be oxidized to Cu(II) (reactions 2.12 & 2.13).

\[
\begin{align*}
2\text{Cu(NH}_3)_2^+ + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 4\text{NH}_3 \quad (2.11) \\
2\text{Cu}^+ & \rightarrow \text{Cu} + \text{Cu}^{2+} \quad (2.12) \\
4\text{Cu(NH}_3)_2^+ + \text{O}_2^+ + 4\text{H}^+ & \rightarrow 4\text{Cu(NH}_3)_2^{2+} + 2\text{H}_2\text{O} \quad (2.13)
\end{align*}
\]

When large amounts of Cu$^{2+}$ and SO$_4^{2-}$ ions were available, brochantite, antlerite, and posnjakite precipitated according to equations 2.14, 15 and 16 due to their insolubility.

\[
\begin{align*}
4\text{Cu}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} & \rightarrow \text{Cu}_4(\text{SO}_4)(\text{OH})_6 \quad (2.14) \\
3\text{Cu}^{2+} + 4\text{OH}^- + \text{SO}_4^{2-} & \rightarrow \text{Cu}_3(\text{SO}_4)(\text{OH})_4 \quad (2.15) \\
4\text{Cu}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O} \quad (2.16)
\end{align*}
\]

Different formations of corrosion products could be due to their stability in acidic environment. Thermodynamically, brochantite is only stable at pH from 3 to 7 and antlerite is only stable from 2 to 3 [87]. It was noticed that NH$_3$ tends to evaporate during
the corrosion process, which could lower the pH. At high temperature, NH$_3$ evaporates fast and the pH could go down to 1, so antlerite is favored. At low temperature, the pH usually stabilized at around 6, so brochantite is the main corrosion product. Posnjakite formed at high relative humidity and it could lose the hydrated water to transform to brochantite or antlerite at low humidity environment [3].

pH is an important parameter for determination of corrosion products, but probably not the only one. At the CRH, there is a saturated solution layer adsorbed on the copper surface, so the pH should be lower than dilute solution since ammonia is a weak base. However, antlerite formation is usually not reported at the CRH. It seems that the ratio of Cu$^{2+}$ to SO$_4^{2-}$ needs to be taken into account, as well as the effect of pH. With higher loading, the electrolyte layer on copper surface should be thicker so that the ratio of Cu$^{2+}$ ions to SO$_4^{2-}$ would probably be less. This could favor the formation of antlerite and it is consistent with field exposed behavior that antlerite is usually found from samples exposed in highly polluted field locations [66].

Cu$_2$O was another important corrosion product formed both in lab exposures with ammonium sulfates and field exposures [3]. Lobnig proposed that Cu$_2$O formation was due to the reverse disproportionation reaction 2.17:

$$\text{Cu}_4(\text{SO}_4)(\text{OH})_6 + 4\text{Cu} \rightarrow 4\text{Cu}_2\text{O} + 2\text{H}^+ + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (2.17)$$

This reaction could explain why Cu$_2$O is always between outer sulfates and inner metallic copper. But in reality Cu$^{2+}$ instead of Cu$_4$(SO$_4$)(OH)$_6$ probably reacts with metallic copper because of the Cu$_2$O barrier.
Ammonium bisulfate induced the formation of large amount ammonium copper sulfate \((\text{NH}_4)_2\text{Cu}(\text{SO}_4)(\text{OH})_2.x\text{H}_2\text{O})\) [120]. This compound has not been found from field exposures. Therefore the research of ammonium bisulfate is not very meaningful.

2.3.2.2 Lab Exposure with Sodium Chloride

Atacamite (and paratacamite), \(\text{Cu}_2(\text{OH})_3\text{Cl}\), is the main corrosion product formed in marine environment [113]. The formation of this hydroxychloride is attributed to the interaction of chloride with copper [125]. Therefore, it is important to understand the effect of NaCl in lab exposures. Saturated NaCl solution in pure ethanol has been used to load NaCl on copper surfaces [126]. This is convenient for small amounts of NaCl deposition. For loading greater than \(10 \mu\text{g/cm}^2\), ethanol/water solution was used as solvent for NaCl [113]. An advantage of loading with an ethanol/water solution is that the concentration of NaCl is usually specific, so the load of NaCl can be calculated and controlled for a controlled volume of applied solution. The disadvantage is that water might cause some corrosion during evaporation of solvent. Usually, particles precipitated from ethanol solution are in the range of 1 to 10 \(\mu\text{m}\), and clusters larger than 100 \(\mu\text{m}\) are possible [127].

\(\text{Cu}_2\text{O}\) was always the main corrosion product, much more than copper chloride (CuCl) or copper hydroxychloride (Cu\(_2\)(OH)\(_3\)Cl) [69]. However, loading of NaCl and exposure time determines composition of corrosion products. For small loading (about 5 \(\mu\text{g/cm}^2\)) and short time exposure (10 days), only \(\text{Cu}_2\text{O}\) was detectable [126], although trace amount of copper chloride or copper hydroxychloride could not be excluded.
Extending exposure time to 28 days, copper chloride and hydroxochloride were both detectable but less than 1% of the total corrosion product. As loading of NaCl increased, formation of both copper chloride and hydroxochloride was accelerated [113].

It is obvious that relative humidity accelerates corrosion of copper in the presence of NaCl. The corrosion rate of Cu exposed in 95% RH is only about 6 times faster than Cu exposed in 55% RH. As loading of NaCl increases, the effect of RH becomes more significant [126]. As RH increases, corrosion of the whole surface is more uniform. Below CRH (75%), corrosion is limited in extent to under and around NaCl clusters. The edge of clusters corroded most heavily. At or higher then CRH, the whole surface corrodes, but the center of clusters corrodes most heavily. This might be an artifact due to the loading of NaCl particles because the chloride concentration around the particles is higher than the nominal average value.

Although NaCl has large effect on accelerating atmospheric corrosion of copper, it is interesting that chloride and hydroxochloride are just less than 1% of total corrosion products. The dominant corrosion product cuprous oxide could reach to 1.6 mg/cm² with only 26.5μg/cm² NaCl [113]. It is speculated that the role of NaCl is to break through the cuprous oxide film, especially the naturally formed protective oxide, but no specific mechanisms were proposed besides equation 2.18 [113, 128]

\[
\frac{1}{2} \text{Cu}_2\text{O} + 2\text{Cl}^- + \text{H}^+ \rightarrow \text{CuCl}_2^- + \frac{1}{2}\text{H}_2\text{O} \quad (2.18)
\]

The combined effect of NaCl and other corrosive gas species such as SO₂ and O₃ has been studied [86, 112-113, 127]. Addition of 50 ppb SO₂, O₃ and NO₂ individually
did not accelerate copper corrosion with NaCl [77, 129]. With higher concentration (>100 ppb), O₃ and NO₂ increased the Cu corrosion rate about 10%, while SO₂ inhibited Cu corrosion. As mentioned before, SO₂/O₃ and SO₂/NO₂ have synergic effects on copper corrosion. This synergism was not enhanced in the presence of NaCl. Basically, no evident synergistic effect of NaCl with corrosive gases was found.

In summary, although sodium chloride and ammonium sulfate have been successfully involved in accelerated lab experiments, the most evident problem is the method for salt deposition. For both thermophoretic deposition and NaCl/ethanol solution, salts are both preloaded before exposure and no salts are replenished during exposure. In real atmospheres, aerosols are always present and the deposition of corrosive species continues during exposure. The ideal setup for lab experiments should include a continuous and constant deposition of particles. With a constant particle deposition rate, the kinetics of Cu corrosion process can be fully investigated. Another advantage of continuous source is to be able to study kinetics of formation of copper hydroxychlorides, Cu₂(OH)₃Cl, the main corrosion product found on copper exposed in marine environment.

2.3.3 Photocorrosion of Cu

As mentioned above, the effect of UV on Cu corrosion is very significant, because cuprous oxide, the most common Cu corrosion product, is a semiconductor with a band gap of around 2 to 2.4 eV [130-131]. Naturally formed cuprous oxide is p-type. Under UV illumination, an extra cathodic photocurrent can be generated from Cu in sulfuric
acid solution because of interaction between photons and cuprous oxide [16-17]. The extra cathodic current actually increases corrosion resistance of Cu. However, during atmospheric corrosion exposure, UV illumination can increase Cu corrosion rate by a factor of 2 [132], probably because newly formed Cu$_2$O is n-type rather than p-type. The transition of cuprite from p-type to n-type has also been confirmed by anodic potentiodynamic polarization under UV illumination [133-134].

2.4 Corrosion product identification and quantification

A key aspect for atmospheric corrosion research is identification and quantification of corrosion products. Especially for lab exposure experiments, corrosion products are usually on the order of a few $\mu$g. Several techniques and instruments are commonly used for corrosion product analysis. A combination of different analysis methods is necessary since each has both advantages and disadvantages. Mass change measurement, electrochemical analysis and spectroscopy analysis are three kinds of methodologies used for investigating silver and copper corrosion products.

2.4.1 Mass Change Measurement

Ex situ measurement of mass change during exposure only needs a sufficiently accurate balance. Usually for lab-exposure samples, a microbalance with a precision of the order of $\mu$g is needed. Mass gain and mass loss are used to represent corrosion rate. Mass gain is the simple comparison of mass of samples before and after exposure. However, the mass gain for a given amount of Cu oxidation depends on the exact product formed. For example, a sample with Cu$_2$O product might have less mass gain but higher
corrosion rate than another sample with CuSO₄. Mass loss does not have this disadvantage but the measurement is more complicated. All corrosion products should be removed chemically or mechanically, while metallic copper should be retained. ASTM G1 provides a reference for cleaning of copper corrosion products [135]. A control sample usually is needed to estimate the loss of metallic copper so that mass loss can be calibrated [86]. Although no information about the composition of the product can be obtained by mass change measurement, it is still the most accurate quantitative measurement of corrosion rate.

Quartz crystal micro-balance (QCM) is a highly sensitive mass measurement technique [78, 136]. Its accuracy is on the order of ng/cm². The most valuable advantage is that QCM can record mass change in situ during whole exposure time. This is important for study kinetics of initial corrosion during exposure.

2.4.2 Electrochemical analysis

Galvanostatic reduction is the most useful electrochemical method for determination of Ag and Cu corrosion products [20, 137-141]. The reduction potential corresponds to some specific species, so it can be used to identify corrosion products. The reduction potentials of Ag₂O, AgCl and Ag₂S have been reported as -0.15, 0.25, and -1.15 V MSE, respectively [20, 47]. The reduction potentials of Cu₂O and Cu₂S are -0.8 V and -1.00 to -1.15 V SCE, respectively [138]. Reduction charge of each reduction plateau corresponds to the amount of corrosion products, so galvanostatic reduction
technique is able to determine both the nature and amounts of the different corrosion products present.

2.4.3 X-Ray Diffraction (XRD)

XRD can be used to identify crystalline corrosion products. However, the corrosion products layer thickness is usually less than 1 μm and the penetration depth of X rays in copper is much larger than 1 μm. A strong signal from the metallic copper substrate reduces the sensitivity of the analysis. Surface sensitivity is increased by Grazing Incidence XRD (GIXRD), in which the incident angle is fixed at some value between 1° to 5°. This could decrease the penetration depth to less than 1 μm [141].

2.4.4 Infrared and Raman spectroscopy

Infrared (IR) and Raman spectroscopy analysis are applicable for both crystalline and noncrystalline species, though the identification of corrosion products is not as straightforward as for XRD. Standard species are needed for peak identification [142]. Overlapping of peaks associated with different species is normal for corrosion products of copper. For example, the peaks of copper oxide (Cu₂O and CuO) are both only present at low frequency in both IR and Raman spectroscopy [143] and they are overlapped by the peaks of brochantite and posnjakite. IR is insensitive for CuCl, but it usually can be identified by Raman at low frequency (178 cm⁻¹) [144]. The primary advantage of these instruments is that it is relatively easy to combine a lab environment chamber with them to do in situ analysis during exposure [82]. IR and QCM is a good complementary combination that can do in situ qualitative and quantitative analysis [95]. This
combination could record the transformation of corrosion products in situ so that corrosion product can be identified and quantified simultaneously [91].

2.5 Research objectives

As can be seen in this literature review, effects of UV on atmospheric corrosion of both Ag and Cu have not been fully studied, although UV strongly influences corrosion of metals. The work describes in this dissertation advances the understanding of laboratory and field exposure tests of Ag, focusing on the effects of UV for both lab and field exposed Ag samples.

Although many lab exposure results of Cu have been reported, the kinetics of Cu corrosion is not well understood, especially the rates of formation of the complicated hydroxylsulfates and hydroxychlorides. This is mainly because current lab environment chamber cannot provide a constant NaCl deposition rate. Furthermore, accurate identification and quantification of different corrosion products is another issue. Therefore, building a novel environment chamber that provides constant deposition of NaCl and development of a suitable and accurate quantification technique are also goals of this project. With this chamber and the quantification technique, kinetics of Cu corrosion is addressed.
Table 2.1 Typical concentration of aggressive gases in atmosphere. [4-8].

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>50-200</td>
</tr>
<tr>
<td>HCl</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Cl₂</td>
<td>&lt;10</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>SO₂</td>
<td>5-30</td>
</tr>
<tr>
<td>NO₂</td>
<td>10-45</td>
</tr>
<tr>
<td>CO₂</td>
<td>300-600</td>
</tr>
</tbody>
</table>
References:


34. CRC Handbook of Chemistry and Physics 61 ed. 1980, CRC Press.


Chapter 3 Lab exposure of Ag with NaCl, ozone and UV illumination

3.1 Introduction

Ag becomes tarnished after exposure in the field. After indoor exposure of Ag, Ag₂S is the most common corrosion product with much less AgCl formed [1]. Therefore, previous laboratory exposure tests mainly focused on Ag atmospheric corrosion behavior with sulfur-containing pollutants, such as H₂S, OCS and SO₂ [2-5]. Usually H₂S, OCS or elemental sulfur (S₈) results in the formation of an Ag₂S film. Strong oxidants, such as NOx and ozone, accelerate formation of Ag₂S significantly [4-6]. Recently, Ag has been used as a monitor to measure outdoor environment corrosivity. Unlike indoor exposure, AgCl is usually much more dominant than Ag₂S on outdoor corrosion films [7, 8]. However, there is still a lack of understanding regarding the formation of AgCl outdoors.

Different laboratory studies have investigated the formation of AgCl in the field. Muller [9] reported that AgCl formed during exposure of Ag to 1.9 ppb Cl₂, typical concentration of Cl₂ in real atmosphere. But corrosion rate of Ag was less than 3 Å/d,
much less than common corrosion rate of Ag in outdoor environment [7]. The standard laboratory accelerated test ASTM B117 has also been used for Ag. However, Ag surprisingly stays shiny after exposure in ASTM B117 chamber up to 4 weeks. It is believed that ASTM B117 test with molecular oxygen and NaCl is not aggressive enough for Ag, so Ag can survive this test [10, 11]. It was also reported that Ag corrodes relatively quickly during exposure to ozone, ultraviolet (UV) illumination and NaCl [10-12]. An environment with ozone, UV and NaCl seems to be a promising accelerated laboratory test to study the atmospheric corrosion of Ag and to understand formation of AgCl in field. However, the effects of these factors need to be further understood. It is also important to know their significance on Ag corrosion if an environment of ozone, UV and NaCl is used for lab accelerated testing of Ag.

Ozone usually ranges from 20 to 100 ppb in real atmospheres. It is a significant pollutant that accelerates corrosion of several metals other than Ag, such as Cu, Zn and Ni [13-15]. Ozone is a much stronger oxidant than oxygen with an equilibrium reduction potential at pH=7 of 1.1 V SHE [16], 280 mV higher than that of oxygen (Equation 3.1 and Equation 3.2).

\[
\begin{align*}
O_3 + 3 H_2O &\rightarrow 6 OH^- & E^\circ = 1.1 \text{ V (pH=7)} \\
O_2 + 4 H_2O + 4 e^- &\rightarrow 4 OH^- & E^\circ = 0.82 \text{ V (pH=7)}
\end{align*}
\]

Equation 3.1 and Equation 3.2.

Ozone is not only capable of oxidizing metals, but it can also oxidize molecular water to hydrogen peroxide (Equation 3.3), which is also corrosive for metals [17, 18]. In the presence of NaCl, ozone can also generate Cl\(_2\) (by Equation 3.4) [19].

\[
O_3 + 3H_2O \rightarrow 3H_2O_2
\]

Equation 3.3
Besides it being a strong oxidant, ozone is very sensitive to UV illumination. It photodecomposes to generate atomic oxygen (Equation 3.5) [20] in the presence of UV radiation ($\lambda<$370 nm). Atomic oxygen is an extremely aggressive radical and active oxidant. It can even oxidize gold to form fairly thick oxide in an hour [21]. OH radical is another strong oxidizing specie that can be generated by atomic oxygen in the presence of water vapor (Equation 3.6). In the presence of ozone and UV, direct oxidation of Ag by atomic oxygen (Equation 3.7) or OH radicals (Equation 3.8) are two possible reactions for corrosion of Ag.

\[ O_3 + hv (\lambda<370\text{nm}) \rightarrow O + O_2 \]  
\[ O + H_2O \rightarrow 2OH \]  
\[ O + 2Ag \rightarrow Ag_2O \]  
\[ OH + Ag \rightarrow AgOH \]

Meanwhile, it is well known that silver compounds, especially AgCl, are very photosensitive. Incident UV radiation can cause fast photolysis of AgCl (Equation 3.9), especially at wavelength less than 380 nm [22, 23]. But there have been few studies on how photodecomposition of AgCl corrosion product by UV affects atmospheric corrosion of Ag.

\[ 2AgCl + hv \rightarrow 2Ag + Cl_2 \]  

NaCl strongly accelerates the corrosion of almost every common metal, such as steel, aluminum alloy, Cu and Zn. However, it is interesting that NaCl does not
accelerate Ag corrosion in the presence of UV and ozone [10], because protection of an aqueous NaCl layer on Ag surface against atomic oxygen.

The corrosion behavior of Ag in an environment containing ozone, UV and NaCl is complicated and has not been fully studied. This paper describes a full factorial study on the effects of ozone, UV and relative humidity on Ag corrosion. Fuzzy analysis of the lab exposure data is used to determine the significance of each factor on Ag atmospheric corrosion.

3.2 Experimental

3.2.1 Sample preparation

All Ag coupons were 99.9% pure and 17mm x 17mm x 2mm in size. They were ground sequentially with 600, 800 and 1200 grit papers, followed by 6 μm and then 1 μm diamond polishing. After polishing, samples were stored in a desiccator for 24 h before they were loaded with NaCl by fast evaporation of NaCl/ethanol solution. The solution was prepared in two steps. First, NaCl was dissolved in deionized (DI) water to make a 1.67 wt% NaCl solution and then it was diluted with pure ethanol to reach a concentration of 990 μg/ml NaCl. Before exposure, 146 μl NaCl/ethanol solution was transferred onto the sample surface with a pipette, which generated 50 μg/cm² loading of NaCl on the samples, and then coupons were immediately placed in a vacuum pumped dessicator. The solution completely dried within 6 min, but the samples were kept in the evacuated desiccator for 30 min to make sure no ethanol remained on surface.
3.2.2 Laboratory exposure of Ag

A home-built environmental chamber was used for exposure of Ag coupons as shown in Figure 1, which has been described elsewhere [10, 12]. Table 3.1 shows the full factorial experimental design with three levels of ozone, five levels of UV and three levels of relative humidity (RH), resulting in a total of 45 different environments for exposure of Ag. Inert nitrogen was used as the carrier gas for water and ozone. Dry nitrogen, wet nitrogen and ozone were mixed before they flowed into the chamber. Total flow rate was controlled at 830 cc/min. RH was controlled by adjusting the ratio of dry and wet nitrogen flow. Exposure duration was 22 h for every sample. The UV intensity at the quartz window of the exposure chamber was measured with a UV radiometer (UVP LLC.) and adjusted by changing distance between the UV lamp (254 nm) and the quartz window. All experiments were carried out at room temperature and each exposure condition was carried out twice for total of 90 exposures. After exposure, samples were analyzed by X-ray diffraction (XRD) or grazing incidence XRD (GIXRD) with 0.5° incident angle to identify corrosion products. SEM and EDS were used to check morphology and composition of corrosion products after exposure. Finally, the amount of corrosion product was determined by galvanostatic reduction at 0.1mA/cm² constant current in pH 10, 0.1 M Na₂SO₄[12]. The average total reduction charge density is used here as a measure of corrosion rate, since all samples were exposed for the same time.

3.3 Results and discussion
3.3.1 Deposition of NaCl

Figure 3.2 shows SEM images of samples after deposition of NaCl. Cubic NaCl particles precipitated out uniformly. Most particles were about 1 to 10 µm, the same size as typical outdoor aerosol particles. Some submicron particles were also present after deposition. These images also show that no corrosion initiated during loading of NaCl.

3.3.2 Identification of corrosion products

After 22 h exposure of Ag in the chamber, corroded samples were analyzed by XRD or GIXRD. As summarized in Figure 3.3 and Table 3.2, AgCl is the main corrosion product at all three levels of RH. Liang et al. [10] proposed four possible pathways for formation of AgCl with ozone, UV and NaCl. They are either direct formation of AgCl from oxidation of Ag by chlorine-containing oxidants such as Cl₂, or transformation of Ag₂O. Cl₂ is generated by oxidation of NaCl with ozone as Equation 3.4 suggests. Ag₂O is generated by oxidation of Ag with atomic oxygen, hydroxyl radicals or hydrogen peroxide. Because AgCl is more stable than Ag₂O, in the presence of NaCl, Ag₂O gets converted to AgCl [12, 24]. Liang et al. [10] did not list oxidation of Ag by ozone as a potential pathway probably because bare Ag (without deposited NaCl) did not corrode with 630 ppb ozone in the dark (no UV). However, in dark environments with the presence of NaCl, this pathway is important, especially at high RH. Because Ag is more electrochemically active with NaCl on the surface than when the surface is bare, cathodic reduction of ozone (Equation 3.1) is significant. Furthermore, oxidation of Ag is more dominant than oxidation of NaCl.
At 28% and 58% RH, both Ag₂O and AgO formed during exposure. It was proposed that formation of AgO was either due to one step oxidation of Ag generated from photodecomposition of Ag₂O [25] or further oxidation of Ag₂O [26, 27]. It is interesting that Ag₂O and AgO coexisted with NaCl after exposure instead of being converted to AgCl by NaCl. The presence of oxides after exposure in low and medium relative humidity environment indicates that conversion of silver oxide to silver chloride requires sufficient mobile Cl⁻. As Figure 3.4 shows schematically that NaCl starts to deliquesce at RH higher than 75%, the critical deliquescent relative humidity (CRH) [28]. Eventually an aqueous NaCl layer exists on Ag sample surface so that any silver oxide gets converted to silver chloride. At RH lower than 75%, silver gets oxidized and forms silver oxide in between NaCl particles. Due to the lack of mobile Cl⁻ ions, silver oxides are retained.

Confirmation of the presence of silver oxide at 28% and 58% RH is helpful in prediction of the corrosion product in the field. Although AgCl and Ag₂S are the most common Ag corrosion products formed in the field, Ag₂O and Ag₂SO₄ are reported occasionally based on X-ray photoelectron spectroscopy or infrared spectroscopy [1, 29, 30]. There is still a lack of strong evidence to support the presence of Ag₂O and Ag₂SO₄ as Ag corrosion products, especially because their solubilities are much larger than Ag₂S and AgCl. However, since Ag₂O and NaCl can coexist after lab exposure, it is predicted that Ag₂O and Ag₂SO₄ can be corrosion products and can be detected after exposure in field as long the environment does not have enough mobile Cl⁻ to
completely convert Ag₂O and Ag₂SO₄ to AgCl. This kind of environment either is very dry or has low chloride deposition.

3.3.3 Galvanostatic reduction of silver corrosion products

Figure 3.5 shows typical reduction curves, i.e. potential transients under constant cathodic current, of Ag after exposure. An exposed Ag sample usually has one or two reduction plateaus before hydrogen evolution (HER) starts at a low potential. According to previous research, the reduction plateaus in Figure 3.5, -0.15 V and -0.25 V MSE, correspond to reduction of silver oxide and silver chloride, respectively [10, 12]. HER occurs at the last plateau at -1.8 V MSE. The reduction time for each species is determined by the local minimum of the derivative of the reduction curve as shown in Figure 3.5 [31, 32]. Total reduction time is the time from start to the last significant minimum before the HER plateau starts. So for the dashed curve in Figure 3.5, the reduction time of silver oxide is 58 s determined from the first minimum and the total reduction time is 568 s. The product of reduction time and cathodic current density, 0.1 mA/cm², is the total reduction charge density used to represent corrosion rate of Ag in this paper.

Sample A in Figure 3.5, which was reduced directly after exposure, only has a silver chloride reduction plateau, while the XRD results (Figure 3.6) indicate the presence of silver oxides (Ag₂O and AgO) as well as silver chloride after exposure. For sample B, which was exposed in the same environment as sample A but was rinsed with ethanol for 30 s before reduction to remove the remaining NaCl, a reduction plateau for silver oxide can be seen. This suggests that sample A did not have an Ag₂O reduction
plateau because the remaining NaCl converted Ag₂O into AgCl. This probably happened in the sodium sulfate solution used in the galvanostatic measurement. The chloride left on the surface dissolved into the solution and then converted the oxide to chloride. The Ag₂O reduction plateau was preserved on sample B because ethanol rinsing removed the NaCl left after exposure. However, rinsing with ethanol usually cannot completely remove the remaining NaCl, so the actual amount of silver oxide is likely more than what its reduction curve indicates. So the absence of a silver oxide reduction plateau does not prove the absence of silver oxide. This is probably the reason why no oxide formation was reported previously [10].

3.3.4 Effect of relative humidity

Ag has very different corrosion behavior during exposure at different RH in the lab chamber. Figure 3.7 shows the relationships between reduction charge of Ag and RH under different conditions of UV and ozone. With UV illumination, reduction charge decreases as RH increases from 28% to 87% regardless of ozone concentration. In dark environment with 360 and 600 ppb ozone, reduction charge increases as RH increases. But with 2000 ppb ozone in the dark, reduction charge decreases first as RH increases from 28% to 58% and then increases as RH increases.

Surface conditions of Ag samples are completely different at different relative humidity. The adsorbed moisture layer on bare Ag is about one equivalent layer at 28% RH and five equivalent layers at 58% RH [33, 34]. At 28%RH, the adsorbed monolayer of water is not continuous. It actually consists of small clusters of 2 to 3 molecules in thickness and about 10 molecules per cluster [35]. So a large portion of Ag surface is
not covered by any water molecules. There is no strong evidence indicating that the presence of NaCl has an effect on adsorption of water on Ag when RH is lower than its DRH (75%). Thus the surface of Ag loaded with NaCl at low RH is very similar to bare Ag. With UV illumination, atomic oxygen generated from photolysis of ozone oxidizes Ag directly at 28%RH. This leads to fast corrosion of Ag at low RH due to the strong aggressiveness of atomic oxygen. At 58% RH, although only about five equivalent water layers are adsorbed on the Ag surface, so it is likely that continuous and uniform moisture layer forms. A large portion of atomic oxygen reacts with water molecules first to generate hydrogen peroxide and OH radicals, which are less aggressive than atomic oxygen. At this RH, Ag is corroded mainly by OH radicals and hydrogen peroxide as well as by remaining atomic oxygen, so the Ag corrosion rate is slower than at 28% RH. Water molecules behave like inhibitors against atomic oxygen at this RH.

At 87% RH, with the presence of NaCl, a 3 M NaCl liquid solution is formed within 10 min [36] due to the deliquescence of NaCl as mentioned above. The liquid layer thickness can reach up to 2.8 μm at the beginning with a loading of 50 μg/cm² NaCl. This liquid layer reduced the attack of Ag by OH radicals and no atomic oxygen could react with Ag directly. The NaCl layer actually protected the Ag against attack by atomic oxygen, which decreased the corrosion rate and thus the reduction charge. Compared to 58% RH, the thickness of the liquid layer increased several orders of magnitude from about 1 nm (5 layers of water molecules) to 2.8 μm, but the reduction charge only decreased by less than one order. This is because the newly formed NaCl layer also behaves like a reservoir for ozone. Especially with the presence of NaCl,
additional oxidants, such as Cl₂ and ClO⁻ are generated by ozone [10, 19] and they increase the environment aggressiveness for Ag. Previous research actually showed that with 630 ppb ozone, 8 μg/cm² NaCl and UV illumination, the corrosion rate of Ag slightly increased as RH increased from 60 % to 90% [10]. The loading of NaCl was less in that work, so the protection effect of the NaCl liquid layer against OH radicals was not high enough to compete against the increased aggressiveness. Therefore the corrosion rate slightly increased rather than decreased.

In a dark environment, electrochemical oxidation of Ag by reduction of ozone is important, as Equation 3.1 depicts, especially at high RH. So with 360 and 600 ppb ozone, corrosion rate increases as RH increases. At 28% RH, the Ag surface was still very dry, even with NaCl. This limited the electrochemical reduction of ozone dramatically. Plus previous research shows that kinetics of direct oxidation of Ag by ozone molecules is very slow, even though ozone is a stronger oxidant than oxygen [10]. Therefore corrosion of Ag with NaCl is very slow, close to zero, with 360 and 600 ppb ozone at low RH in the dark. As RH increases, Ag surface become more and more electrochemically active, so the corrosion rate increases.

The corrosion rate of Ag increased with RH in the dark environment containing 360 or 600 ppb ozone. But the reason why corrosion rate of Ag exposed to 28% RH with 2000 ppb ozone was much higher than at 58% RH or 87% RH is not clear (Figure 3.7).

Figure 3.8 shows reduction curves of two samples both exposed to 2000 ppb ozone, 28% RH in dark environment. The reduction charge of the one exposed without
NaCl is almost zero, while the reduction charge of the one with NaCl was quite large, about 50 mC/cm². Its reduction curve also shows that about 60% of the corrosion product was silver oxide. The actual amount of silver oxide could be higher because a portion of silver oxide was converted to silver chloride due to the presence of deposited NaCl as mentioned above. The fact that the reduction charge of Ag is almost zero with 360 ppb and 600 ppb ozone at 28% RH in the dark regardless of the presence of NaCl indicates that the presence of NaCl does not have strong effect on increase of the surface electrochemical activity. Furthermore, bare Ag without NaCl almost did not corrode with 2000 ppb ozone at 28% RH in the dark environment. Therefore, fast formation of silver oxide with 2000 ppb ozone and NaCl indicates that there is an unknown combined effect of high concentration ozone and NaCl. It is suspected that atomic oxygen or OH radicals were generated by interaction between ozone and dry NaCl at low RH, though the effect of NaCl here is not clear yet.

Relative humidity is a key factor in atmospheric corrosion. Usually metals corrode more severely at higher RH because of more water existing on the surface. For example the corrosion rate of Cu is significantly accelerated by increased RH [4, 37]. There are controversial reports about effect of RH on Ag corrosion. Graedel et al. [2] found that higher RH significantly enhanced the sulfidation rate of Ag in the presence of H₂S or OCS. Rice et al.[4] reported that RH did not have significant effect on Ag corrosion in an environment with a mixture of H₂S, SO₂, Cl₂, HCl and O₃. This is probably because NO₂, Cl₂ and ozone are all strong oxidants and oxidation of Ag by these oxidants is not sensitive to RH. Overall, the effect of RH on Ag corrosion strongly depends on
environment and the corrosion mechanism. In an environment with ozone and UV, direct oxidation by radicals as well as electrochemical oxidation by the reduction of ozone is important. Therefore, the effect of RH is different in various environments. Generally, the corrosion rate of Ag decreases as RH increases with UV illumination and increases as RH increases in the dark with low ozone. With higher ozone, such as 2000 ppb, effect of RH is more complicated.

3.3.5 Effect of ozone

Obviously, the corrosion rate of Ag increased as ozone increased with or without UV radiation as Figure 3.9 and Figure 3.10 show, respectively. With UV radiation, the reduction charge of Ag increased more than a factor of 10 as ozone concentration increased from 360 ppb to 2000 ppb at 28% RH, yet by only a factor of 2.7 at 58% RH and a factor of 3.9 at 87% RH. So the acceleration effect of ozone is more significant at low RH (28%) than medium (58%) or high RH (87%). This is probably because at lower RH, direct oxidation of Ag by atomic oxygen (Equation 3.7) is more dominant, while at high RH oxidation by OH radicals and hydrogen peroxide (Equation 3.8) is more dominant. Since atomic oxygen is more aggressive than OH radicals, the corrosion rate of Ag increased faster at lower RH.

In dark environments, corrosion rate of Ag was almost zero with 360 ppb or 600 ppb ozone at 28% RH, yet with 2 ppm ozone, it was much larger. As described before, ozone alone at 360 or 600 ppb is not sufficiently aggressive to corrode Ag but with 2000 ppb ozone, a different mechanism likely takes over. At 58% and 87% RH, reduction
charge of Ag increased by a factor of 2 and 2.8, respectively, as ozone increased from 360 ppb to 2000 ppb. These acceleration factors are both about 72% that of Ag exposed to UV because ozone is less aggressive than atomic oxygen and OH radicals. The reason that the acceleration factors at 87% RH with or without UV are both 40% higher than at 58% RH is probably deliquescence of NaCl at 87% RH, which results in stronger interaction between ozone and NaCl.

3.3.6 Effect of UV

UV light has different effects on Ag corrosion. It can stimulate corrosion by generating oxidizing species as shown in Equations 3.5 and 3.6 or it can photo-reduce AgCl. To evaluate whether photodecomposition of Ag corrosion products occurs during exposure, two identical samples were first exposed together at 58% RH with 2 ppm ozone, 3.5 mW/cm² UV for 22 h. They should have had similar amount of corrosion products after this first step exposure. Then sample A was immediately reduced and exposure of sample B was continued in the same environment but with no ozone for 66 h. The reduction curves in Figure 3.11 showed that sample B had less than half of the amount of corrosion products that sample A had. This indicates photodecomposition of silver corrosion products by UV occurred during exposure. Without ozone present in the environment, strongly oxidizing species like atomic oxygen and hydroxyl radical did not form so continued formation of corrosion product was not possible. However, the incident UV could photo-reduce Ag⁺ to metallic Ag according to Equation 3.9 and the reduction charge of sample B decreased after the second step exposure.
Figure 3.12 and Figure 3.13 indicate that at 28% and 58% RH, the reduction charge of Ag exposed to 600 ppb or 2000 ppb ozone increase as UV irradiation intensity increases. In contrast, with 360 ppb ozone, the corrosion rate of Ag first increases and then decreases as UV intensity increases. The fastest corrosion of Ag occurred with UV intensity of 1.1 mW/cm$^2$ at both 28% and 58% RH. At 87% RH, the corrosion of Ag decreases with increasing UV intensity regardless of ozone concentration, Figure 3.14. Overall, UV radiation had both accelerating and decelerating effects on Ag corrosion during exposure.

Figure 3.15 schematically shows how UV radiation has both positive and negative effects on Ag corrosion. The increase in corrosion rate results from photolysis of ozone by UV to form atomic oxygen, which either oxidizes Ag directly (Equation 3.7), or reacts with water to generate hydroxyl radical, which reacts with Ag to form AgOH (Equation 3.8). AgOH is not stable and tends to decompose to Ag$_2$O (Equation 3.10) [38].

$$2\text{AgOH} \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \quad (3.10)$$

Since atomic oxygen and hydroxyl radical are both much more oxidizing than ozone, the corrosion rate of Ag increases with UV illumination. Yet this effect is limited by the ozone concentration. It reaches a maximum at some critical UV intensity and then stops increasing.

The negative effect of UV, or really the reversal of corrosion, is the photodecomposition of AgCl, which was proven by the experiments shown in Figure
3.11. Photodecomposition is not limited by ozone and it increases as UV intensity increases. These two opposite effects happen simultaneously during exposure, therefore measured reduction charges are a combination of the positive and negative effects as represented by the solid lines in Figure 3.15. Depending on ozone concentration and UV intensity, the corrosion rate of Ag might increase continuously with increasing UV intensity, which is likely at high ozone concentration, or increase first and then decrease as UV intensity increases, which is likely at low ozone concentration.

However, at 87% RH, as mentioned before, a 2.8 μm thick liquid layer of 3 M NaCl forms on Ag surface. With the presence of a thick NaCl layer, atomic oxygen tends to react with water to generate hydrogen peroxide. Hydroxyl radical also tends to react with Cl⁻ rather than Ag [39], so the positive effect of UV at this high RH environment becomes much less significant compared to at lower RH. The absorption coefficient of UV in water is on the order of $10^{-3}$ to $10^{-4}$ cm$^{-1}$ [40], so the attenuation of UV by the liquid NaCl layer is negligible. Hence, the negative effect of UV on Ag corrosion dominates at high RH environment. At high RH, the corrosion rate decreases with increasing UV illumination.

3.3.7 Morphology of Ag after exposure

Figure 3.16 shows morphology of samples exposed at different relative humidity. At high (87%) and medium (58%) RH, particulate corrosion products formed, while at low (28%) RH, a porous film formed on the surface. This is consistent with previous reports that Ag tends not to form continuous corrosion products in atmospheric exposure.
such as “round clumps” after exposure in H$_2$S [41]. EDS analysis indicates that Cl is enriched in the particles in Figure 3.16, but not at areas away from the particles on the Ag substrate at 58% and 87% RH. At 28% RH, Ag and O are the dominant elements. This indicates formation of AgCl particles instead of AgCl film during exposure at 58% and 87% RH and a porous silver oxide film formed at 28% RH.

Table 3.3 lists the atomic ratio of oxygen to silver of samples exposed with 2000 ppb ozone, 3.5 mW/cm$^2$ UV and different RH as measured by EDS. The scanning area was larger than 2000 $\mu$m$^2$. Clearly, as RH decreased from 87% to 28%, the ratio of oxygen and silver dramatically increased from 0 to about 0.51. This means formation of oxide increases dramatically as RH decreases, which is consistent with the XRD results that silver oxide formed at 28% and 58% RH.

Figure 3.17 is a typical SEM picture of samples exposed in a dark environment with high RH. Similar to samples exposed with UV shows in Figure 3.16, single crystal particles about 2 $\mu$m in size rather than AgCl film formed during exposure. EDS analysis of the labeled particle on Figure 3.17 A showed that the atomic ratio of Cl to Ag was 20% at the beginning of analysis. The atomic ratio was much less than 1 at the beginning partly because of the strong Ag signal from substrate Ag. However, these particles also exhibit decomposition by the electron beam, as shown by the second scan of the same particle taken 3 min after the first in Figure 3.17 B. The atomic ratio of Cl to Ag of the particle on Figure 3.17 B dropped from 20% to less than 10%. Its original smooth surface became very rough and covered with nanoparticles. The decrease of the
EDS Cl signal suggests that the newly formed nanoparticles are Ag particles formed by decomposition of AgCl.

Figure 3.18 shows high magnification images of the particles in Figure 3.16 A. Different than Ag exposed in a dark environment, the particles are clusters of smaller particles rather than the large single crystals formed under UV illumination. Those small crystals are probably metallic Ag formed from photodecomposition of AgCl during exposure, because they did not decompose after being scanned by the electron beam and they look like the nanoparticles in Figure 3.17 formed by e-beam decomposition. Figure 3.18 C and D show loose single Ag particles appeared after Ag was exposed to the environment with UV but no ozone. This indicates that decomposition by UV and electron beams is similar in nature.

Although UV results in photodecomposition of Ag corrosion products, there are no loose Ag particles appearing after exposure in environments with ozone and UV as Figure 3.16 and Figure 3.18 show. Loose Ag particles only appear after exposure to UV with no ozone. It is reported before that surface of Ag nanoparticles is very sensitive to oxygen and can be oxidized to Ag$^+$ within a short time with oxygen [42, 43]. So it is likely that freshly formed Ag nanoparticles from photodecomposition of AgCl are very active and parts of them tend to be oxidized back to Ag$^+$ in the presence of ozone. This explains why formation of clusters of Ag and AgCl.

3.3.8 Fuzzy analysis on significance of ozone, UV and RH and artificial neural network fitting
The previous discussion showed that UV and RH all have significant effect on corrosion of Ag. However, it is difficult to quantitatively compare the effect of each parameter and determine which is the most significant for Ag corrosion.

Fuzzy analysis has been widely used for determination of significance of each input in systems with multiple inputs and a single output [44-46]. It is used here to analyze the relative significance of three inputs: ozone (x₁), UV intensity (x₂) and RH (x₃) on reduction charge of Ag, which is the single output in this fuzzy system. For each input xᵢ, i=1,2,3, the fuzzy membership function φ is defined by Equation 3.11.

$$\phi_{in}(x_i) = \exp\left(-\left(\frac{x_{in} - x_i}{b}\right)^2\right), \quad n=1,2,3,\ldots, P$$  \hspace{1cm} (3.11)

where xᵢ, n=1,2,3,...,45, is reduction charge value obtained from lab exposure tests and b is 20% of the absolute difference between the maximum and minimum inputs. Therefore b is 328 ppb for ozone (x₁), 0.94 mW/cm² for UV (x₂) and 11.8% for RH (x₃). P is total number of data points. In this paper, it is 45.

Centroid defuzzification (Equation 3.12) is used to generate the fuzzy curve for each input.

$$C_i(x_i) = \frac{\sum_{n=1}^{45} \phi_{in}(x_i) y_n}{\sum_{n=1}^{45} \phi_{in}(x_i)} ,$$  \hspace{1cm} (3.12)

Where yᵢ is the reduction charge value and Cᵢ(xᵢ) is the fuzzy parameter, which is plotted in Figure 3.19. If xᵢ has a strong effect on reduction charge y, the product of its fuzzy
membership function $\phi(x_i)$ and reduction charge $y$ leads to a large range of the fuzzy parameter.

Figure 3.19 shows the three fuzzy curves representing the significance of ozone ($C_1$), UV ($C_2$) and RH ($C_3$) on reduction charge. RH has the largest range of fuzzy parameter, which means RH has the most influence on the reduction charge of Ag. Furthermore, the fuzzy parameter decreases as RH increases, which is different than ozone and UV. This reflects that interaction between atomic oxygen and H$_2$O molecules decreases the corrosion rate of Ag as discussed before.

Fuzzy curves of UV and ozone both show their accelerating effect on Ag corrosion. However, the effect of UV is not significant with intensity higher than 1 mW/cm$^2$ and the effect of ozone actually is not significant in the ranges of 360 to 1200 ppb and 1350 to 2000 ppb. This means a combination of 1 mW/cm$^2$ UV and 360 ppb ozone or 1 mW/cm$^2$ UV and 1350 ppb ozone is probably the most efficient environment in terms of acceleration factor for a lab accelerated test.

Artificial neural networks (ANN) are very powerful in predicting a complicated process and have been used to predict atmospheric corrosion rates of metals in the field by fitting experimental data. For example, the corrosion rate of carbon steel in different atmospheres has been predicted with several key input parameters, such as RH, temperature, chloride deposition rate [47, 48]. The atmospheric corrosion process of Ag is very complex in real field environments and even in the lab with ozone, UV and NaCl. ANN should be a promising tool for prediction of Ag corrosion rate in both lab and field environments.
The JMP 9 software program was used to create a feed-forward ANN model with one hidden layer. Part of the lab exposure data (36 of 45 experiments) were used to train the model and rest of the data were used to validate the model. The number of hidden neurons should follow this rule to arrive at a good model [49]:

\[(N+1) \times M < 0.4 \times T \tag{3.13}\]

where \(N\) is the number of input neurons, \(T\) is the total number of training and validation data, and \(M\) is number of hidden neurons. Here \(N=3\): ozone, UV, RH. This equation indicates that the number of hidden neurons should be less than 4 in this case. Two and three hidden neurons were used to develop the ANN model. Both resulted in good fits and prediction capability, so the simpler one with two hidden neurons was used. Figure 3.20 shows actual and predicted data of all training and validation data used for this ANN model. The correlation coefficients for the training and validation datasets are 0.92 and 0.98, respectively.

Equation 3.14 is the explicit equation that results from the ANN fitting. \(RC\) is reduction charge per day in mC/cm²d, and the units of ozone \((x_1)\), UV \((x_2)\) and RH \((x_3)\) are %, ppb and mW/cm², respectively. \(\mathrm{TanH}\) is the hyperbolic tangent function. With this equation, the corrosion rate of Ag in different environments can be predicted. Table 3.4 lists predictions for two lab exposure tests and field exposure at Daytona Beach and West Jefferson reported previously [10, 11]. Ozone concentration and UV intensity values were values reported in literature [10] and the RH values are typical values for Daytona Beach and West Jefferson in May during the exposure. The prediction of field
exposure at Daytona Beach, a marine environment, is much better than the prediction of the West Jefferson sample by this ANN model. This might be because average temperature at West Jefferson during the exposure is only 16 ºC [50], which is much lower than lab exposure temperature.

\[ RC = 199.4 + 71.8 \times TanH(0.5 \times (-0.765 + 0.000250 \times x_3 + 0.000148 \times x_1 + 0.0213 \times x_2)) + 168.9 \times TanH(0.5 \times (-0.763 - 0.119 \times x_3 + 0.00177 \times x_1 + 0.302 \times x_2)) \]  

(3.14)

3.4 Conclusions

A full factorial experimental matrix of lab exposure of Ag with ozone, UV and NaCl, and RH has been carried out. At high RH, AgCl is the only corrosion product formed. Ag₂O and AgO can only form and be retained after exposures at RH lower than the DRH of NaCl (75%). It can therefore be predicted that silver oxide and silver sulfate are possible end corrosion products after silver is exposed in a dry field environment.

Corrosion mechanisms of Ag exposed to UV and dark ozone-containing environments are different. With UV illumination, direct oxidation of Ag by atomic oxygen and hydroxyl radicals is dominant. In dark environment, oxidation accompanied by cathodic reduction of ozone is the main mechanism. With the different corrosion mechanisms, the effect of RH on corrosion of Ag is different. With UV and ozone, higher RH results in lower corrosion rate of Ag, while in dark environment with relatively low ozone (360 ppb and 600 ppb), RH accelerates Ag corrosion.

UV has two opposite effects simultaneously on atmospheric corrosion of Ag. One is photolysis of ozone, which increases the corrosion rate and the other one is
photodecomposition of corrosion products, which turns results in regeneration of Ag.
The reduction charge of Ag after exposure with UV shows a combination of these two opposite effects.

Generally, RH has the strongest effect on Ag corrosion, which is proven by fuzzy analysis. A combination of ozone, UV and NaCl should be a promising environment for a lab accelerated test of Ag. Lab exposure results can be used predict field exposure test of Ag in field very well by ANN.
### Table 3.1. Full factorial design of lab exposures of Ag

<table>
<thead>
<tr>
<th>Factors</th>
<th>ozone, ppb</th>
<th>UV intensity, mW/cm²</th>
<th>RH, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>360</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>Level 2</td>
<td>600</td>
<td>1.1</td>
<td>58</td>
</tr>
<tr>
<td>Level 3</td>
<td>2000</td>
<td>2.0</td>
<td>87</td>
</tr>
<tr>
<td>Level 4</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level 5</td>
<td>4.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.2 Corrosion products identified by XRD

<table>
<thead>
<tr>
<th>RH</th>
<th>Compounds after exposure by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>87%</td>
<td>AgCl and NaCl</td>
</tr>
<tr>
<td>58%</td>
<td>AgCl, Ag₂O, AgO and NaCl</td>
</tr>
<tr>
<td>28%</td>
<td>AgCl, Ag₂O, AgO and NaCl</td>
</tr>
</tbody>
</table>

### Table 3.3 Atomic ratio of O and Ag by EDS (Scan area > 50x40 μm²) *

<table>
<thead>
<tr>
<th>RH</th>
<th>O/Ag</th>
<th>28%</th>
<th>58%</th>
<th>87%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/Ag</td>
<td>0.51</td>
<td>0.15</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

* samples were exposed with 2 ppm ozone, 3.5 mW/cm² UV

### Table 3.4 Prediction of Ag corrosion rate in different environment by ANN

<table>
<thead>
<tr>
<th>RH</th>
<th>Ozone, ppb</th>
<th>UV, mW/cm²</th>
<th>Experimental reduction charge, mC/cm²d</th>
<th>Predicted by ANN, Equation 3.14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab exposure</td>
<td>28</td>
<td>360</td>
<td>0.7</td>
<td>26.7±3.4 17.3</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>360</td>
<td>3.95</td>
<td>13.0±2.1 9.3</td>
</tr>
<tr>
<td>Daytona Beach</td>
<td>70 to 75</td>
<td>70 [10]</td>
<td>0.018 [10]</td>
<td>4 to 5 [10, 11] 5.28 to 5.30</td>
</tr>
</tbody>
</table>
Figure 3.1. Laboratory environment chamber for exposure of Ag.
Figure 3.2. SEM images of samples after deposition of NaCl.
Figure 3.3. XRD spectra of samples exposed at different relative humidity
Figure 3.4. Schematic picture of deliquescent of NaCl and its effect on silver oxide formation.
Figure 3.5. Reduction curves of Ag exposed to 28% RH, 2.0 mW/cm$^2$ UV and 600 ppb ozone. A: Sample was reduced directly after exposure. B: Sample was rinsed with ethanol and then reduced.
Figure 3.6. XRD spectrum of Ag exposed to 28% RH, 2.0 mW/cm² UV and 600 ppb ozone.
Figure 3.7. Reduction charge of Ag exposed to different relative humidity. With 2.0 mW/cm² UV or in dark; 360, 600 or 2000 ppb ozone. The results of all experiments are shown and multiple data points overlap for many of the conditions.
Figure 3.8. Reduction curves of Ag exposed to 2000 ppb ozone, dark, 28%RH, with or without 50μg/cm² NaCl. The first reduction plateau is reduction of Ag₂O; the second one is reduction of AgCl.
Figure 3.9. Reduction charge increases as ozone increase with UV radiation, 3.5 mW/cm$^2$. The results of all experiments are shown and multiple data points overlap for many of the conditions.

Figure 3.10. Reduction charge increases as ozone increases in dark environment. The results of all experiments are shown and multiple data points overlap for many of the conditions.
Figure 3.11. Reduction curves of sample A and B. A: sample exposed to 58% RH and 2 ppm O₃ with 3.5 mW/cm² UV for 22 h; B: sample exposed with sample A first and then continued exposed to 58% RH with 3.5 mW/cm² UV but without ozone for 66h.
Figure 3.12. Reduction charge of Ag exposed at 28% RH but with different UV intensity and different ozone concentration. The results of all experiments are shown and multiple data points overlap for many of the conditions.
Figure 3.13. Reduction charge of Ag exposed at 58% RH but with different UV intensity and different ozone concentration. The results of all experiments are shown and multiple data points overlap for many of the conditions.

Figure 3.14. Reduction charge of Ag exposed at 87% RH but with different UV intensity and different ozone concentration. The results of all experiments are shown and multiple data points overlap for many of the conditions.
Figure 3.15. Schematic of comprehensive effect of UV on atmospheric corrosion of Ag with ozone and NaCl.
Figure 3.16. SEM pictures and EDS spectra of samples after exposure with 2000 ppb ozone and UV 3.5 mW/cm². A: 87% RH; B: 58% RH; C: 28% RH.
Figure 3.17. SEM pictures of Ag exposed to 2000 ppb ozone, 87%RH, dark environment. A: SEM picture taken at the beginning; B: EDS spectrum of the particle finished one minute later after A; C: SEM picture taken at three minutes later after A; D: EDS spectrum finished four minutes later after A.
Figure 3.18. SEM pictures of a sample after different exposure steps. A and B: 2000 ppb ozone, 87% RH, 3.5 mW/cm² UV, 22 h; C: continued after step A, 0 ppb ozone, 87% RH, 3.5 mW/cm² UV, 50 h; D: continued after step C, 0 ppb ozone, 87% RH, 3.5 mW/cm² UV, 60 h.
Figure 3.19. Fuzzy curves of ozone, UV intensity and RH input variables.

Figure 3.20. Predicted value vs Lab exposure data. Prediction is based on a 2 hidden neural network.
References:


Chapter 4  Aspects of Ag Atmospheric Corrosion and Analysis of Ag Corrosion Products

4.1 Introduction

Ag is used in electronics applications, utensils, and decorative arts. Its corrosion behavior in indoor environments [1-3] and in lab chambers containing sulfur [4-11] has been studied. Ag$_2$S is the main corrosion product and the kinetics of its formation rate usually are linear. The sulfidation rate of Ag increases as H$_2$S and carbonyl sulfide increase. Sulfidation rate stays low as long as the relative humidity (RH) is less than 35% but it increases significantly as RH increases up to 95% [6].

The Ag corrosion rate has a strong correlation with corrosion rate of other metals such as carbon steel or aluminum alloys [12]. Ag has been used as an atmospheric corrosion monitor to measure environmental corrosivity [12], which has recently attracted attention to the corrosion behavior of Ag in the field. Previous research shows that AgCl and Ag$_2$S are the two most common corrosion products in the field, with AgCl usually dominating [13-15] except near a volcano where Ag$_2$S is dominant [16]. This is different than indoor exposure of Ag where Ag$_2$S is more dominant than AgCl [17]. This might be because a higher deposition rate of chloride outdoors. However, the details of
how Ag corrodes in the field are not yet clear. It has been reported that oxygen alone is not aggressive enough to generate AgCl during the ASTM B117 test [13]. Since oxidizing species, such as ozone and NOx, have a strong accelerating effect on sulfidation of Ag indoors [11], they should also be relevant to outdoor Ag corrosion. Therefore, an environment of ozone, NaCl and UV has been used in the development of a lab exposure test to model Ag corrosion behavior in outdoor environments [13].

Previous lab exposure tests indicate that UV and ozone have an accelerating effect on Ag corrosion [13, 14, 18]. The previous chapter concluded that, although UV can result in photo reduction of Ag corrosion products back to metallic Ag, UV is overall an accelerating factor for Ag corrosion. It was also shown that the effect of RH depends on whether UV is present. With UV illumination, the corrosion rate of Ag decreases as RH increases, while it increases as RH increases without UV. A numerical equation to predict corrosion rate of Ag in field was also obtained by Artificial Neural Network (ANN) fitting of corrosion rates of Ag exposed at different lab environment with UV, ozone and NaCl. However, these lab exposure results need to be further examined by field exposure of Ag.

The galvanostatic reduction technique has been widely used to quantify and identify Ag corrosion products [3, 13, 14, 18]. It is generally accepted that AgCl is reduced at -0.28 V MSE and Ag₂S is reduced at -1.15 V MSE. Although the reduction plateau of AgCl is usually the dominant one, EDS of field-exposed samples often shows the presence of a large amount of S and O, even when the reduction plateau of Ag₂S is very small [13]. This might be due to the presence of silver oxide and silver sulfate. However,
oxide and sulfate are not well known as Ag corrosion products [17], probably because their solubility is much higher than AgCl and Ag₂S. The results of the previous chapter can be used to predict that silver oxide and silver sulfate might be corrosion products if the exposure location has low chloride deposition or is dry. It is of interest to verify this prediction by further studying field exposed Ag.

The purpose of this work is to investigate several aspects of Ag atmospheric corrosion. Experiments were performed to better understand the species responsible for certain unknown plateaus sometimes found in the galvanostatic reduction curve measured on field exposed Ag samples. Corrosion product analysis was performed using X-ray Diffraction (XRD) or Grazing Incidence XRD (GIXRD). The morphology of the product formed on exposed samples was examined in detail to understand the relevant corrosion phenomena. Finally, the behavior of samples sprayed intermittently with water or seawater was investigated to evaluate the possibility of AgCl dissolution into aqueous layers during exposure.

4.2 Experimental

Ag coupons exposed in the field were about 12 mm x 75 mm x 0.075 mm in size. They were abraded with 600 grit SiC paper and then rinsed with ethanol before exposure. They were exposed at seven different locations including marine, rural, volcanic and urban environments as listed in Table 4.1. Some exposure locations are very close to each other, which facilitates the comparison of the corrosion behavior of Ag. For example, Thompson Farm and Appledore Island are only 30 miles away from each other in NH.
Average temperature at Thompson Farm was only 1.2 °C higher than at Appledore Island during exposure. But their atmospheres are quite different because Appledore Island is on the coast whereas Thompson Farm is inland. All samples were exposed in a natural environment except for some samples exposed at Daytona Beach that were sprayed with distilled water or seawater for 5 s every hour during exposure. All samples were mounted on plastic racks by nylon screws.

Several different types of exposure racks were used and samples were positioned slightly differently on different racks. Type 1 (Figure 4.1) was for samples exposed at West Jefferson. Ag was placed at the top of the rack, just under a plastic roof. Type 2 (Figure 4.2) was only used for samples that were sprayed during exposure at Daytona Beach. Samples were tilted about 45°. Ag was exposed with other metals in both racks, but Ag was always placed at the top so there was no effect of runoff from other exposed metals. Most samples were exposed in the type of rack shown in Figure 4.3. Half of the samples were sheltered by a roof and side walls the other half was unsheltered. The local UV intensity on sheltered samples was decreased because of absorption by the plastic roof and walls. Comparison between sheltered and unsheltered samples is useful in understanding effect of UV on Ag corrosion as well as washoff from precipitation. All of these field exposures of Ag were facilitated by collaborations with Battelle, University of New Hampshire and University of Hawaii.

After field exposure, samples were analyzed with x-ray photoelectron spectroscopy (XPS) or XRD, observed by secondary electron microscopy (SEM) and then reduced in deaerated 0.1 M Na₂SO₄, pH=10 to quantify the corrosion products [18].
Reduction plateaus of silver sulfate and silver oxide were also calibrated by formation of these products in the homemade exposure chamber described in the previous chapter. To mimic the field exposed Ag, all lab-exposed Ag samples were also abraded with paper to 600 grit, unless specified differently. Most Ag lab exposures here started with preformed Ag₂S on Ag. Ag₂S was formed by polarization of Ag in 0.1 M Na₂S at -0.14 V MSE for different times. Roughness of reduced samples was measured by an optical profilometer. Several locations on each sample were measured.

An Ag foil with a dimension of 100 mm x 100 mm x 0.13 mm (about 13.1 g) was cleaned with acetone and ethanol carefully and then exposed in a salt spray chamber for ASTM B1117 testing for periods up to 1060 h. The foil was weighed before and after exposure by an electronic balance with an accuracy of 0.1 mg. After exposure in the salt spray chamber, Ag was rinsed with deionized water and ethanol, and then fully dried before weight measurement.

4.3 Results and discussion

4.3.1 Understanding galvanostatic reduction measurements

Figure 4.4 shows reduction curves of Ag exposed at West Jefferson (WJ) and Appledore Island. Five common reduction plateaus found in field-exposed samples are evident. Previous research indicated that Ag₂O, AgCl, and Ag₂S are reduced at around -0.15, -0.28, and -1.15 V MSE, respectively [13, 14, 18]. Besides these three plateaus, two reduction plateaus at -0.08 V MSE and -1.55 to -1.6 V MSE are evident, but these plateaus have not been reported in the literature and the species responsible for these two
plateaus are unknown. The plateau at the lower potential always appeared after reduction of Ag$_2$S. Samples that did not exhibit a reduction plateau for Ag$_2$S did not have this unknown plateau.

XRD and GIXRD spectra indicated the presence of silver sulfate on the WJ sample, Figure 4.5. This suggests that the unknown plateau at -0.08 V MSE is due to reduction of silver sulfate.

Table 4.2 lists standard free energy of formation for common Ag compounds and related ions [19, 20]. With these data, standard free energy change of each reduction reaction listed in Table 4.3 can be calculated, as can the standard reversible reduction potential, $E^\circ$, using equation 4.1.

$$E^\circ = \frac{-\Delta G^o}{nF}$$  \hspace{1cm} (4.1)

where $\Delta G^\circ$ is the standard free energy change, n is number of electrons and F is the Faraday constant. The order of reduction plateaus of different silver corrosion products is very consistent with the order of standard reduction potentials. The standard reduction potential and reduction plateau of silver sulfate are both the highest values. The difference between standard reduction potential of two kinds of silver oxides, Ag$_2$O and AgO, is relative small compared to other species, which suggests that their reduction potentials should be similar and if might not be possible to distinguish the two reduction plateaus. This is in fact true as will be shown below.
To further confirm the silver sulfate reduction potential, an Ag$_2$SO$_4$ film was intentionally formed on Ag in the lab. Electrochemical formation of Ag$_2$SO$_4$ is possible by polarization of Ag in sulfuric acid solution. This was confirmed by XPS analysis of a sample after polarization. However, the reduction charge of the polarized sample was zero. This is probably because of the high solubility of Ag$_2$SO$_4$, 0.8 g/L [21]. It is likely that very little Ag$_2$SO$_4$ precipitated during polarization and whatever was on the surface probably dissolved prior to reduction.

Because the electrochemical polarization method is not suitable for formation of silver sulfate film, atmospheric formation was utilized. Ag was first polarized in 0.1 M Na$_2$S at -0.14 V MSE for 40 s to form an Ag$_2$S film. XRD analysis confirmed formation of only acanthite, Ag$_2$S, Figure 4.6. This sample was then exposed to an environment with 5.5 ppm ozone, 3.5 mW/cm$^2$ UV and 90% relative humidity for 68 h. The XRD spectrum of the exposed Ag sample has several new peaks that are not present in the spectrum of the unexposed sample, Figure 4.6. The new peaks at 32.3° and 33° indicate significant formation of AgO and Ag$_2$O. Five new peaks can be attributed to Ag$_2$SO$_4$. Four of those peaks are overlapped by peaks of silver oxides or silver sulfide, but the one new small peak at 28.2° only corresponds to Ag$_2$SO$_4$. Therefore, formation of Ag$_2$SO$_4$ as well as a large amount of AgO and Ag$_2$O is confirmed by XRD analysis after exposure of Ag/Ag$_2$S in this aggressive environment.

Figure 4.7 shows the reduction curve of this lab-prepared sample. According to the XRD spectrum in Figure 4.6, it has four different Ag compounds: Ag$_2$SO$_4$, Ag$_2$O, AgO and Ag$_2$S. However, only three reduction plateaus are evident: -0.08 V, -0.15 V and -1.15
V MSE. It is well known that Ag₂O and Ag₂S are reduced at around -0.15 and -1.15 V MSE, respectively [13, 18]. The XRD spectrum for a bare Ag sample (no deposited NaCl or preformed Ag₂S) exposed to an environment of ozone and UV indicates the presence of AgO and Ag₂O, Figure 4.8. The reduction curve for this sample shown in the inserted figure has only one reduction plateau at -0.15 V MSE. This proves that AgO and Ag₂O are reduced at the same potential in Na₂SO₄. Therefore, for the reduction curve in Figure 4.7 for the sample preformed with Ag₂S and then exposed to ozone, RH and UV, the plateau at -0.08 V MSE must be due to reduction of Ag₂SO₄. This indicates that the unknown plateau at this potential for Ag exposed at West Jefferson corresponds to the reduction of Ag₂SO₄.

The reduction charges of silver oxide (Ag₂O and AgO) and Ag₂S are both about 10x higher than that of Ag₂SO₄ for the lab treated sample as shown in Figure 4.7. This suggests that the rate of Ag oxidation is much faster than the oxidation of S²⁻ to SO₄²⁻. Only a very small portion of Ag₂S is oxidized to Ag₂SO₄ even when it is exposed to 5.5 ppm ozone and strong UV illumination. The oxidation pathway for S²⁻ to SO₄²⁻ in supercritical water (698.2-773.2 K and 22.0 MPa-30.0 MPa) has been found to be S²⁻ → S₂O₃²⁻ → SO₃²⁻ → SO₄²⁻ [22]. Supercritical water is clearly much more aggressive than real field atmospheric environments. So far there has been no evidence to support oxidation of S²⁻ to SO₄²⁻ in the field. However it is very likely that strong oxidizing species, such as O₃, can oxidize SO₂ to SO₄²⁻ [17] which then reacts with Ag ions to form Ag₂SO₄.
Another possible Ag$_2$SO$_4$ formation pathway involves airborne sulfate aerosols [17]. Sulfate particles are more than one fourth of the total aerosol particles in the field [23]. Most sulfate particles are ammonium sulfate, which has much higher solubility than silver sulfate. So it is possible that silver sulfate precipitates out when Ag$^+$ ions are exposed to ammonium sulfate solution. This is one possible pathway for the formation of silver sulfate during the exposure in West Jefferson.

Figure 4.9 shows reduction curves of three Ag/Ag$_2$S samples formed in the lab as described above. Different amounts of Ag$_2$S were formed by varying the formation charge. The reduction charges associated with the Ag$_2$S plateau are all slightly larger than the respective Ag$_2$S formation charges, which means that all Ag$_2$S was completely reduced. Following reduction of Ag$_2$S, samples B and C both exhibit an reduction plateau at around -1.55 V MSE, which is the same potential as the unknown plateau of Appledore Island 2 mo sample in Figure 4.4. XRD analysis indicated that only Ag$_2$S formed during the laboratory procedure described above for the formation of Ag$_2$S so the unknown plateau could not be due to reduction of an Ag compound. This plateau is very likely due to hydrogen reduction as discussed previously.

The Hydrogen Evolution Reaction (HER) on sample A, which had the highest Ag$_2$S formation charge, occurred at -1.5 V MSE, which is slightly higher than the unknown reduction plateau. This indicates that HER is a kinetically possible process at the potential of the unknown plateau. A roughness change might contribute to the increase of HER kinetics on sample A. Figure 4.10 shows the sample morphology before reduction and just after the potential dropped to -1.5 V MSE. The sample surface was relative
smooth. It became much rougher once the potential dropped to -1.5 V MSE before HER started. An increase of roughness results in an increase of apparent exchange current density of HER so as to shift the HER to more positive potential.

$S^{2-}$ and $HS^-$ have been reported to have an electrocatalytic effect on the HER in alkaline solution [24]. Therefore, it is possible that the unknown plateau is HER at a high potential caused by a catalytic effect of $S^{2-}$ or $HS^-$ generated from the reduction of Ag$_2$S. A critical concentration might be needed to maintain HER at this potential, so that the potential of HER drops to lower value for samples B and C in figure 4.9, which had less Ag$_2$S and could not maintain the requisite conditions. This would also explain why this unknown reduction plateau always appeared following reduction of Ag$_2$S.

As shown in Table 3, the free energy change for reduction of Ag$_2$S is +29.62 kcal/mol, which is much higher than for the reduction of other species. There is no reduction of any common silver compound that has higher free energy change than Ag$_2$S. This further indicates that the unknown reduction plateau at around -1.6 V MSE is the result of hydrogen evolution rather than the reduction of some corrosion product. Assuming that this plateau does result from hydrogen evolution, its reduction charge should be excluded when corrosion rate is calculated from reduction charge. Because this HER process is not stable, it will be referred to as metastable HER.

It is interesting that the HER potential eventually increased back to close to the unknown plateau after an initial decrease. The reason for this subsequent increase back to around -1.6 V is not clear yet. However, experiments showed a strong correlation between the final HER potential and the amount of corrosion products or roughness.
Figure 4.11 shows reduction curves of five Ag/Ag₂S samples, which all have the reduction plateau at around -1.58 V MSE associated with metastable HER. The plateaus for three of the curves were on the order of a few seconds to a few tens of seconds, so are not visible on the time scale shown in the figure. After this metastable HER plateau, the potential drops to as low as -1.93 V MSE and then goes back to as high as -1.6 V MSE after a few thousand seconds of HER. After reduction of Ag₂S, the sample surface became much rougher than before as shown in Figure 4.10. Figure 4.12 indicates that the final roughness of samples increases as the original amount of Ag₂S increases. The increase of roughness directly resulted in increase of surface area, which will increase the apparent rate of HER. The increased roughness might also increase the catalytic nature of the surface for HER. In other words, the increased roughness could increase the exchange current by increasing the real area and also increase the exchange current density by increasing the catalytic nature of the surface. The outcome of both would be to shift the lowest and stable potentials of HER towards positive direction as Figure 4.12 indicates.

4.3.2 Analysis of corrosion products on field-exposed samples

After all reduction plateaus are accurately correlated to the reduction of specific corrosion products, the galvanostatic reduction technique combined with XRD analysis can be used to determine the type and amount of product formed on field-exposed samples. In fact, galvanostatic reduction is more sensitive to small amounts of corrosion product formed during short exposures than is XRD. These methods were used to analyze the corrosion product formed on the samples exposed in the environments listed in Table 1 and the results are shown in Table 4.4. AgCl is the most common corrosion product
found in the field, especially in marine and volcanic environments. It has been reported that Ag$_2$S forms preferentially to AgCl for Ag exposed in volcanic environments due to the high concentration of H$_2$S [16]. The formation of AgCl on the sample exposed near a volcano as shown in in Table 4.4 is probably because of hydrogen chloride acid emission gas in this particular volcanic environment.

Confirmation of the presence of silver oxide and silver sulfate by XRD and galvanostatic reduction after exposure is a strong evidence for the presence of oxide and sulfate as Ag corrosion product. Since the solubilities of Ag$_2$O and Ag$_2$SO$_4$ are much higher than those of AgCl and Ag$_2$S, they are usually not considered as stable Ag corrosion products. They formed at West Jefferson, Thompson Farm, and Mauna Loa, but not at marine and volcanic exposure sites. In the last chapter it was shown that silver oxide and sodium chloride can coexist at medium (58%) and low (28%) RH. This observation predicts that silver oxide and silver sulfate are possible corrosion products as long as the chloride deposition rate is not high enough to convert them to silver chloride and the environment is dry enough so that there is little mobile Cl$^-$. In the marine and volcanic environments, heavy deposition of chloride, sea-salts or HCl, could convert any silver oxide and silver sulfate into silver chloride. However, at other exposure locations, silver oxide and silver sulfate could be retained.

Mauna Loa Mountain is on the island of Hawaii and its elevation is about 3900 m. The exposure location was on the north slope at an elevation of about 3400 m. The deposition rate of chloride at this location is very low due to the high elevation and wind direction, even though it is relatively close to the shore. Figure 4.13 shows the reduction
curve of an Ag exposed at Mauna Loa unsheltered for 1 mo. No clear reduction plateau associated with AgCl or Ag₂S is evident, which is consistent with the low deposition rate of chloride at Mauna Loa. Reduction of silver oxide and silver sulfates are dominant. EDX analysis indicates presence of only Ag, S and O, which confirms that silver oxide and silver sulfate are the corrosion products. This is in line with XRD and reduction results.

The sheltered Thompson Farm sample has only a trace amount of AgCl coexisting with a large amount of oxide and sulfate, while the unsheltered sample only has AgCl, as also indicated by their reduction curves, Figure 4.14. This suggests that oxide or sulfate probably did form on the unsheltered sample, but they were converted into chloride during wet deposition of chloride or precipitation of water. As described above, oxide and sulfate should be expected as potential corrosion products as long as there is not sufficient available mobile Cl⁻ to completely convert them into chloride.

Table 4.5 lists average Ag corrosion rate in mC/cm²mo in different locations and the average temperature during the exposure period. Except for Mauna Loa at 3400 m elevation, the rest of exposure locations are all around sea level. Generally, Ag corrodes faster in marine and volcanic environments than in rural and urban environments. This is consistent with previous work [13].

Table 4.5 also indicates that sheltering has a significant effect on Ag corrosion. The corrosion rate of all unsheltered samples is about 40% to 50% higher than that of sheltered samples, except for samples exposed at Mauna Loa. This is probably due to the lack of wet deposition of aggressive species on sheltered samples such as the oxidizing
agents $O_3$ and $NO_2$. That UV light was almost completely blocked by plastic roof could be another important difference between sheltered and unsheltered samples. It has been proven in lab exposure tests that UV has a significant accelerating effect on Ag corrosion by the generation of atomic oxygen and OH radicals from photolysis of ozone [13]. NOx is another major photosensitive oxidizing species present in many field environments. However, the results suggest that the accelerating effect of UV on Ag corrosion in field maybe more significant.

Ag exposed at Mauna Loa corroded much faster than the rest of the samples, even though the temperature was just 8 °C due to its high elevation. The average RH value was 35% during exposure, much less than the RH at other exposure locations. Fuzzy analysis of lab exposure data in the previous chapter indicates that RH has the most significant effect on Ag corrosion and Ag corrodes faster at low RH with UV illumination [13]. This is supported by the field exposure test at Mauna Loa.

Lab exposure tests not only predict the effect of RH qualitatively but also quantitatively. The volcanic exposure location and Mauna Loa are only about 30 miles (48 km) from each other. The average RH and ozone concentrations of the volcanic location and Mauna Loa are 70% and 35% and 16 and 46 ppb, respectively. Assuming a UV intensity of 0 for the sheltered samples, the ANN fitting equation developed from the lab exposure matrix predicts daily Ag corrosion amounts at the volcanic site and Mauna Loa of about 5 and 7.5 mC/cm$^2$, respectively. Although these predicted corrosion rates are about 40% higher than the real corrosion rates, their ratio is almost the same as the ratio of real corrosion rates at these two sites.
4.3.3 Morphology of exposed Ag

The morphology of the corrosion product formed on field exposed Ag strongly depends on the corrosion product composition. Ag exposed at Mauna Loa mainly had silver oxide and silver sulfate and it always was a uniform but porous film, as Figure 4.15a shows. Ag exposed in a marine environment mainly had an AgCl corrosion product after exposure. The SEM image in Figure 4.15b shows particulate corrosion product on the surface. EDS analysis indicates that these particles are AgCl and there was no continuous AgCl film formed during exposure.

These morphological features are very consistent with lab exposure of Ag with ozone, UV and NaCl. At lower relative humidity, silver oxide is the dominant corrosion product. There is also a uniform but porous film formed on the surface as Figure 4.15c shows. This morphology is very similar to the Ag sample exposed at Mauna Loa. As for Ag exposed in lab at higher RH, especially when RH>75%, only AgCl forms during field exposure. Its morphology is similar to Ag exposed in marine environment in that AgCl particles rather than AgCl film formed on Ag.

Higher resolution SEM images in Figure 4.16 indicate that these AgCl particles are clusters of particles and “resin”. EDS analysis on the area labeled in Figure 4.16 indicates that atomic ratio of Cl to Ag of the whole cluster is only 36%, much less than 1. EDS also indicates that the atomic percentage of Ag of the large particles is higher than 97%. Therefore the particles are pure Ag and the resin is AgCl and the whole cluster has more Ag than Cl. The resin is very vulnerable to electron beam damage as it decomposes to
very small particles a few tens of nm in size after e-beam scanning, as Figure 4.16b and c indicate. However, the larger particles do not decompose during scanning. In the previous chapter it was shown that these features are generated by lab exposure of Ag to ozone, UV and NaCl at high RH and that photodecomposition of AgCl under UV illumination is the mechanism for formation of these clusters. Formation of these clusters in the field suggests that photodecomposition of AgCl by UV is also an important process for Ag exposed in the field.

4.3.4 Sprayed Exposure Samples

Six samples were exposed at Daytona Beach with intermittent spraying of solution on some samples. Three samples were pre-polarized in solution before exposure to form a surface film of AgCl (equivalent to 0.18 C/cm²). A pair of samples (one bare and one with pre-formed AgCl) was sprayed with distilled water for 5 s every hour. Another pair was sprayed with seawater for 5 s every hour. The third pair was not sprayed at all.

SEM images of samples after exposure in figure 4.17 show that the morphology of bare samples (without preformed AgCl) that were sprayed with distilled water is very similar to non-sprayed samples in that both have AgCl particles on the surface. The water-sprayed and non-sprayed samples with preformed AgCl also look similar; larger AgCl particles are evident and the particles start to coalesce. Reduction charges of non-sprayed and samples sprayed with distilled water are very close (Table 4.6). This indicates that spraying of distilled water for 5 s every hour does not have a significant effect on Ag corrosion for samples exposed at Daytona Beach.
However, samples sprayed with seawater behaved completely different than other samples. Figure 4.17e and f show that the surfaces of these samples are not apparently covered by a corrosion product. In contrast, the surfaces have many holes after exposure, which indicates a severe corrosion process during exposure. However, there is no reduction charge associated with any corrosion product for both the bare sample and the one with preformed AgCl after exposure at Daytona Beach with intermittent spraying of seawater. As will be discussed below, this is probably because of dissolution of AgCl in the chloride-containing seawater sprayed on the surface.

Even though the solubility of AgCl in pure water is very low, on the order of 10 μM, it increases as the Cl⁻ content increases, reaching 6 mM in 5 M NaCl [25, 26]. Normally insoluble AgCl can form soluble silver chloride complexes, including AgCl₂⁻, AgCl₃²⁻, and AgCl₄⁻³, in the presence of chloride ions in solution. The solubility curve in Figure 4.18 (generated from [25, 26]) describes the relationship between AgCl solubility and NaCl concentration. The solubility of AgCl in seawater, which contains about 0.6 M Cl⁻ is about 0.035 mM. This means that about 300 ml of seawater are needed to completely dissolve 1 C of AgCl. Assuming that the maximum amount of AgCl formed during exposure is 0.25 C/cm², which is the reduction charge of Ag with preformed AgCl exposed with no spraying, and also assuming that a saturated AgCl-seawater solution was reached immediately after seawater was sprayed on Ag, then no AgCl will be left after exposure as long as the amount of sprayed seawater is more than 0.105 ml/cm²h.

The actual concentration of chloride on Ag during exposure could reach saturation because the typical RH at Daytona Beach is around 80% in the morning and 60% in the
afternoon [27]. The equilibrium NaCl concentration at 80% RH is about 5 M [28]. So in the morning, sprayed seawater could develop into a concentrated chloride liquid layer on the sample surface. In that case, the solubility of AgCl would increase dramatically as Figure 4.18 shows and then the amount of sprayed seawater needed to completely dissolve AgCl could be much less than 0.105 ml/cm².

Knowing that deposition of chloride solution can result in loss of AgCl corrosion product by chemical dissolution, the corrosion rate of exposed samples measured by the galvanostatic technique is very likely less than the actual value, especially when Ag is exposed in an environment with strong deposition of chloride and high RH, e.g. marine environments. The measurement error associated with this dissolution phenomenon can be estimated assuming that NaCl is the dominant chloride deposited on Ag by the seawater spray and that the deposited NaCl reaches the equilibrium NaCl concentration immediately when the RH is higher than 75%:

$$R_{\text{diss}} = \frac{nF \times 10^{-10} \times R_{\text{dep}} \times S}{M_{\text{NaCl}} \times C_{eq}}$$  \hspace{1cm} (4.2)

where \( R_{\text{diss}} \) is the rate of chemical dissolution AgCl product into the aqueous surface layer converted into units of C/cm²d, \( R_{\text{dep}} \) is the NaCl deposition rate in mg/m²d, \( C_{eq} \) is the RH-dependent equilibrium NaCl concentration in M, \( S \) is the RH-dependent AgCl solubility in mM, \( n=1 \) is the charge on Ag⁺ in eq/mol, \( F \) is the Faraday constant, and \( M_{\text{NaCl}} \) is the molecular weight of NaCl in g/mol.
$C_{eq}$ and $S$ are plotted in Figure 4.19 as functions of RH using literature data [25, 28]. Also shown in the figure are fitted equations for $C_{eq}(RH)$ and $S(RH)$. At higher RH, NaCl solutions are more diluted so the solubility of AgCl is smaller. When RH is smaller than 75%, NaCl stays dry and loss of AgCl need not be considered.

Figure 4.20 shows the maximum AgCl loss as a function of RH and NaCl deposition rate calculated using the fitted equations for $C_{eq}$ and $S$. Clearly, higher deposition rate of NaCl and relative lower RH can lead to a significant loss of AgCl. If the maximum possible loss of AgCl by dissolution into NaCl solution is on the same order of reduction charge, the reduction charge probably cannot be used to evaluate corrosion rate.

Usually the deposition rate of NaCl by airborne sea salt deposition is less than 1500 mg/m²d [29] even in a marine environment. At this deposition rate, the maximum loss of AgCl is 0.31 mC/cm²d. Compared to the typical corrosion rate of Ag at Daytona Beach determined by galvanostatic reduction, 3.1 to 4 mC/cm²d, the error associated with AgCl dissolution is negligible. Therefore, the galvanostatic reduction technique is suitable for analyzing samples exposed under usual field conditions. However, if there is unusually high deposition rate of NaCl, such as splash or spray of seawater during exposure, the loss of AgCl can be on the same order as the Ag corrosion rate and the charge measured by galvanostatic reduction measurements would not accurately reflect the real corrosion rate.

Figure 4.21 shows weight loss of Ag during ASTM B117 testing. The weight decreased with time indicating that Ag did corrode during exposure, although no AgCl
was detected by galvanostatic reduction analysis [13, 14]. This suggests that AgCl completely dissolved in the NaCl-containing solution during exposure in the salt spray chamber. The AgCl formation rate can be calculated from the weight loss data in figure 4.21 by equation 4.3:

$$R = 0.024 \times W \times \frac{F}{t} \times M$$

(4.3)

where R is formation rate of AgCl in mC/cm²d, W is weight loss of Ag in g/cm², F is the Faraday constant, 96500 C/mol, t is exposure time in h and M is the Ag atomic weight, 108 g/mol. This calculation indicates that the formation rate of AgCl was less than 0.9 mC/cm²d. As mentioned before, formation rate of AgCl in marine environment is usually higher than 3 mC/cm²d, at least a factor of 3 higher than this calculated formation rate of AgCl during the B117 test. This confirms that B117 is not an accelerated corrosion environment for Ag and oxygen is not an aggressive oxidant for Ag.

In the ASTM B117 test, the NaCl deposition rate is quite high, 158 to 316 g/m²d [30]. Considering that the solubility of AgCl in 5 wt % NaCl is 0.1 mM [25], this can result in a AgCl loss as much as of 2.9 to 5.8 mC/cm²d, according to Equation 4.2. This rate of AgCl dissolution is much higher than the formation rate of AgCl calculated for exposure in the salt spray chamber, which is why reduction charge of Ag exposed in salt spray chamber is zero, although Ag does corrode during exposure.

4.4 Conclusions

Ag has been exposed in different environments including marine, volcanic, rural, suburban and alpine. Morphology of exposed samples, corrosion products and corrosion
rate during exposure have been studied by SEM/EDS, XRD and the calibrated galvanostatic reduction technique. The following was concluded:

1. The reduction plateaus of Ag$_2$SO$_4$ and AgO were defined. A commonly observed reduction plateau at -1.55 V MSE was attributed to HER. These assignments enable the coulometric reduction technique to be used as a semi-quantitative analysis tool for Ag.

2. AgCl was the most common corrosion product after exposure, but the presence of silver oxide and silver sulfate was also confirmed by XRD and calibrated reduction technique. Confirmation of the presence of sulfate and oxide also proves previous prediction concluded from lab exposure of Ag with ozone, UV and NaCl.

3. Field exposure of Ag proves that UV has an accelerating effect on Ag corrosion, while RH likely decelerates Ag corrosion. This is consistent with lab exposure of Ag with ozone, UV and NaCl.

4. Clusters of Ag and AgCl are the main morphology of Ag exposed in marine environment. Formation of them is due to photodecomposition of AgCl.

5. Formation of soluble silver chloride complexes rather than insoluble AgCl explains why Ag exposed on the seacoast with intermittent spraying of seawater exhibits no reduction charge. Under conditions of very high NaCl deposition, the coulometric reduction technique may not be able to evaluate the Ag corrosion rate accurately because of loss of the corrosion product.
6. Error of galvanostatic reduction technique for normal field exposure samples is negligible even though some soluble silver chloride complexes might form during exposure tests.
<table>
<thead>
<tr>
<th>Location</th>
<th>Environment</th>
<th>Exposure period</th>
<th>Rack type</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Jefferson, OH</td>
<td>Suburban</td>
<td>1 mo, July 2010</td>
<td>Type 1</td>
</tr>
<tr>
<td>Daytona Beach, FL,</td>
<td>Marine, some sprayed intermittently</td>
<td>1 mo, May 2012</td>
<td>Type 2</td>
</tr>
<tr>
<td>Thompson Farm, NH</td>
<td>Rural</td>
<td>1 to 6 mo, Feb 2011 to Aug 2011</td>
<td>Type 3</td>
</tr>
<tr>
<td>Appledore Island, ME</td>
<td>Marine</td>
<td>1 to 6 mo, Feb 2011 to Aug 2011</td>
<td>Type 3</td>
</tr>
<tr>
<td>Oahu, HI</td>
<td>Marine</td>
<td>1 to 6, Apr 2011 to Oct 2011</td>
<td>Type 3</td>
</tr>
<tr>
<td>Kilauea, HI</td>
<td>Volcanic</td>
<td>1 to 6, Apr 2011 to Oct 2011</td>
<td>Type 3</td>
</tr>
<tr>
<td>Mauna Loa, HI</td>
<td>Highland (3397 m)</td>
<td>1 to 6, Apr 2011 to Oct 2011</td>
<td>Type 3</td>
</tr>
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</table>
Table 4.2. Formation free energy of common silver compounds and related ions [19, 20].

<table>
<thead>
<tr>
<th>Species</th>
<th>Ag₂SO₄</th>
<th>SO₄²⁻</th>
<th>Ag₂O</th>
<th>AgO</th>
<th>AgCl</th>
<th>Cl⁻</th>
<th>Ag₂S</th>
<th>S²⁻</th>
<th>H₂O</th>
<th>OH⁻</th>
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<tbody>
<tr>
<td>Formation free energy, kcal/mol</td>
<td>-147.17</td>
<td>-177.34</td>
<td>-2.59</td>
<td>2.6</td>
<td>-26.22</td>
<td>-31.35</td>
<td>-9.62</td>
<td>20.0</td>
<td>-56.7</td>
<td>-37.6</td>
</tr>
</tbody>
</table>

Table 4.3. Standard reversible potential of reduction and reduction plateau of different silver corrosion products.

<table>
<thead>
<tr>
<th>Reduction reaction</th>
<th>Free energy change ΔG°, kcal/mol</th>
<th>E⁺, V MSE</th>
<th>E_plateau, V MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂SO₄ + 2e → Ag + SO₄²⁻</td>
<td>-30.17</td>
<td>0.01</td>
<td>-0.08</td>
</tr>
<tr>
<td>H₂O + Ag₂O + 2 e → 2Ag + 2OH⁻</td>
<td>-15.92</td>
<td>-0.18</td>
<td>-0.15</td>
</tr>
<tr>
<td>H₂O + AgO + 2 e → 2Ag + 2OH⁻</td>
<td>-21.11</td>
<td>-0.29</td>
<td>-0.15</td>
</tr>
<tr>
<td>AgCl + e → Ag + Cl⁻</td>
<td>-5.13</td>
<td>-0.42</td>
<td>-0.28</td>
</tr>
<tr>
<td>Ag₂S + 2e → 2Ag + S²⁻</td>
<td>29.62</td>
<td>-1.28</td>
<td>-1.15</td>
</tr>
</tbody>
</table>
Table 4.4. Corrosion products of Ag identified by XRD and galvanostatic reduction. Species in parentheses are present in only a trace amount as detected by reduction.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sheltered</th>
<th>Unsheltered</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Jefferson, OH 🇺🇸</td>
<td>Ag₂O, Ag₂S, AgCl, Ag₂SO₄ (Ag₂S)</td>
<td>N/A</td>
</tr>
<tr>
<td>Daytona Beach, FL 🇺🇸</td>
<td>N/A</td>
<td>AgCl, Ag₂S</td>
</tr>
<tr>
<td>Thompson, NH 🇺🇸</td>
<td>Ag₂SO₄, Ag₂O, AgO, (AgCl)</td>
<td>AgCl</td>
</tr>
<tr>
<td>Appledore Island, ME 🇺🇸</td>
<td>AgCl</td>
<td>AgCl</td>
</tr>
<tr>
<td>Oahu, HI 🇺🇸</td>
<td>AgCl, Ag₂S</td>
<td>AgCl, Ag₂S</td>
</tr>
<tr>
<td>Kilauea, HI 🇺🇸</td>
<td>AgCl, Ag₂S</td>
<td>AgCl, Ag₂S</td>
</tr>
<tr>
<td>Mauna Loa, HI 🇺🇸</td>
<td>Ag₂O, AgO, Ag₂SO₄, (AgCl)</td>
<td>Ag₂O, AgO, Ag₂SO₄, (AgCl)</td>
</tr>
</tbody>
</table>
Table 4.5. Conditions and average corrosion rate of Ag in field.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sheltered Corrosion Rate (mC/cm²mo)</th>
<th>Unsheltered Corrosion Rate (mC/cm²mo)</th>
<th>Average Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Jefferson, OH</td>
<td>50.5</td>
<td>N/A</td>
<td>22.7</td>
</tr>
<tr>
<td>Daytona Beach, FL</td>
<td>N/A</td>
<td>122</td>
<td>25</td>
</tr>
<tr>
<td>Thompson, NH</td>
<td>2.7</td>
<td>4</td>
<td>13.8</td>
</tr>
<tr>
<td>Appledore Island, ME</td>
<td>52.3</td>
<td>77.4</td>
<td>12.6</td>
</tr>
<tr>
<td>Oahu, HI</td>
<td>35.7</td>
<td>51.5</td>
<td>26.1</td>
</tr>
<tr>
<td>Kilauea, HI</td>
<td>104.6</td>
<td>144.2</td>
<td>23.0</td>
</tr>
<tr>
<td>Mauna Loa, HI</td>
<td>164.7</td>
<td>322.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>
Table 4.6. Reduction charge and EDS analysis results of samples exposed at Daytona Beach

<table>
<thead>
<tr>
<th></th>
<th>Normal</th>
<th>Distilled water sprayed</th>
<th>Seawater sprayed</th>
<th>Ag + AgCl, no spray</th>
<th>Ag + AgCl, distilled water sprayed</th>
<th>Ag + AgCl, seawater sprayed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction charge, C/cm²</td>
<td>0.093</td>
<td>0.11</td>
<td>0</td>
<td>0.18 + 0.07</td>
<td>0.18 + 0.05</td>
<td>0</td>
</tr>
<tr>
<td>EDS analysis</td>
<td>AgCl</td>
<td>AgCl</td>
<td>Ag only</td>
<td>AgCl</td>
<td>AgCl</td>
<td>Ag only</td>
</tr>
</tbody>
</table>
Figure 4.1. Exposure rack for Ag exposed at West Jefferson, OH.
Figure 4.2. Exposure rack for Ag exposed at Daytona Beach, FL.
Figure 4.3. Exposure Rack for Ag exposed at Thompson Farm, NH; Appledore Island, ME; Mauna Loa, HI; Volcanic Hi; Severe Marine, HI.
Figure 4.4. Reduction of curves of Ag exposed at West Jefferson (WJ) and Appledore Island.
Figure 4.5. XRD and GIXRD spectra of West Jefferson field exposure Ag. Scan rate: 1°/min for XRD and 0.1 °/min for GIXRD.
Figure 4.6. XRD spectra of exposed Ag. “After polarization”: after Ag is polarized in 0.1 M Na₂S for 40 s to get a layer of Ag₂S on Ag; “After exposure”: after polarized Ag/Ag₂S sample exposed to 5.5 ppm ozone, UV and 90% RH for 68 h.
Figure 4.7. Reduction curve of Ag/Ag$_2$S film exposed to 5.5 ppm ozone, 90% RH, 3.5 mW/cm$^2$ UV for 68 h.
Figure 4.8. XRD spectrum of bare Ag exposed to 2 ppm ozone, 90%RH, 3.5 mW/cm² UV for 22 h. Inserted figure is reduction curve of this sample.
Figure 4.9. Reduction curves of three Ag/Ag₂S in 0.1 M Na₂SO₄. Ag₂S was preformed in 0.1 M Na₂S at -0.14 V MSE for different periods. A: formation charge 300.6 mC/cm²; B: formation charge 222.9 mC/cm²; C: formation charges 33.4 mC/cm². The inserted plot is a portion of C from -1.3 to -1.8 V.
Figure 4.10. SEM image of sample A in figure 9. a: before reduction; b: reduced until the potential dropped to -1.5 V MSE, then reduction process was stopped and SEM image was taken.
Figure 4.11. Reduction curves of five Ag/Ag₂S in 0.1 M Na₂SO₄. Ag was polished to 1 μm before formation of Ag₂S.

Figure 4.12. Roughness of Ag after reduction, minimum HER potential and final stable HER potential vs formation charge of Ag₂S.
Figure 4.13. Reduction curve of Ag exposed at Mauna Loa for 1 mo.
Figure 4.14. Reduction curve of Ag exposed at Thompson, NH for 6 mo.
Figure 4.15. SEM images of field and lab exposed Ag. a: Mauna Loa 1 mo, Unsheltered; b: Daytona Beach 1 mo, Unsheltered; c: Lab exposure to 2000 ppb ozone, UV, 28% RH, 50 μg/cm² NaCl; d: Lab exposure to 2000 ppb ozone, UV, 87% RH, 50 μg/cm² NaCl.
Figure 4.16. Clusters of AgCl and Ag. a, b and c: Ag exposed at Daytona Beach for 1 mo. b was taken after a. d: Ag exposed to 2000 ppb ozone, UV at 87% RH.
Figure 4.17. SEM images of Ag exposed at Daytona Beach for 1 mo. a, b, c) Exposure of bare Ag; b, d, f) Exposure of Ag + preformed 0.18 C/cm$^2$; a and b) Normal exposure; c and d) Sprayed with distilled water; e and f) Sprayed with distilled water.
Figure 4.18. Solubility of AgCl in NaCl solution [25] and volume of NaCl solution needed to completely dissolve 1 C AgCl.
Figure 4.19. Equilibrium NaCl concentration ($C_{eq}$) and solubility of AgCl in NaCl ($S$) at different RH.
Figure 4.20. The maximum possible loss of AgCl of Ag exposed to different RH with different deposition rate of NaCl.
Figure 4.21. Weight loss of Ag during ASTM B117 testing.
References:


Chapter 5  Atmospheric corrosion of Cu in the presence of UV, ozone and NaCl

5.1 Introduction

Cu has been widely used for electronic and heat exchange applications due to its high electronic and thermal conductivity. It also has fairly good atmospheric corrosion resistance so it has been frequently used for art works and building construction such as roofs and gutters [1]. Cu is also suggested by ISSO for use as an atmospheric corrosivity monitor [2]. Due to its wide application in atmosphere environments, atmospheric corrosion of Cu has been studied using both field and lab exposures.

Field exposure of Cu has found that cuprite (Cu$_2$O) is one of the most common Cu corrosion products [3]. During outdoor exposure cuprite is also the initial corrosion product formed on top of which other complex Cu compounds can form. In industrial environments, posnjakite (Cu$_4$(OH)$_6$SO$_4$.H$_2$O), brochantite (Cu$_4$(OH)$_6$SO$_4$) and antlerite (Cu$_3$(OH)$_4$SO$_4$.H$_2$O) [3-5] are the most common compounds found on Cu. Greenish atacamite (Cu$_2$(OH)$_3$Cl) and paratacamite (Cu$_2$(OH)$_3$Cl)[3, 5-9] usually appear after several months of marine exposure. The mechanisms of formation of Cu$_2$(OH)$_3$Cl is still not well understood. Cu$_2$(OH)$_3$Cl deposits are usually porous [9], so its formation should
be avoided if Cu is used as structural material. However, for decorative applications, formation of Cu$_2$(OH)$_3$Cl might be desirable because of its natural greenish color.

Ozone, O$_3$, a common pollutant and strong oxidant present in atmosphere, strongly accelerates Cu corrosion during lab exposure [10]. It is well known that ozone is very sensitive to UV, which accelerates photolysis of ozone to create molecular dioxygen and atomic oxygen[11, 12]. A combination of UV and ozone can dramatically increases corrosivity and result in fast corrosion [13, 14]. Furthermore, it has been reported that copper oxide is very sensitive to UV alone [15]. Interaction between photons and naturally formed copper oxide usually improves the passivity of Cu [16, 17]. Therefore, it is of interest to study atmospheric corrosion behavior of Cu in the presence of ozone and UV. This paper reports effects of ozone, UV and NaCl on Cu corrosion and formation of Cu$_2$(OH)$_3$Cl.

5.2 Experimental

Cu was exposed in a chamber that was described elsewhere [13]. Ozone concentration, UV intensity and relative humidity can be accurately controlled in this chamber. The UV light was generated by a mercury UV lamp with primary energy at 254 nm. UV intensity was 3.6 mW/cm$^2$ for all exposures performed under UV illumination. Lab air or nitrogen was used as carrier gas for ozone and the total flow rate was 830 cc/min.

All Cu coupons were 99.99% pure and 17 mm x 17 mm x 1.6 mm in size. They were ground sequentially with 400 and 600 grit sand papers. They were ultrasonically
cleaned in 99.5 wt% ethanol and dried with a fan immediately after each polishing step. As-polished samples were stored in a desiccator for 24 h before exposure. NaCl was loaded on Cu before exposure by fast evaporation of NaCl ethanol solution. Details are described in Chapter 2. Loading of NaCl ranged from 4 to 32 μg/cm².

The morphology of corroded Cu was observed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Corrosion products were identified by X-ray diffraction (XRD) or Grazing Incidence XRD (GIXRD). The galvanostatic reduction technique was used to quantify corrosion products. As suggested by the ASTM B825 standard [18], 0.1 M KCl was used as the electrolyte during galvanostatic reduction. The reduction current density was 0.1 mA/cm² and a saturated calomel electrode (SCE) was used as reference electrode. All potentials in this paper are referred to SCE. The Cu corrosion rate was calculated by equation 5.1, by assuming cuprous ions are the dominant corrosion product.

$$C = \frac{10 \times M \times R}{n \times F \times D \times t}$$  \hspace{1cm} (5.1)

Where C is corrosion rate in μm/d, M is atomic weight of Cu, 64 g/mol, R is total reduction charge in mC/cm², n=1 is the number of electrons transferred, F is the Faraday constant, 96500 C/mol, D is density of Cu, 8.96 g/cm², and t is exposure duration in d.

The accelerating effect of UV was quantified by the acceleration factor (AF), which is defined by equation 5.2:

$$AF = \frac{Q_{uv}}{Q_d}$$  \hspace{1cm} (5.2)
where $Q_{uv}$ is reduction charge of Cu exposed with UV illumination and $Q_d$ is the reduction charge of Cu exposed to the same environment but in the dark.

5.3 Results and discussion

5.3.1 Exposure of Cu without NaCl

Bare Cu (no NaCl) was exposed in dry (RH ~ 0) or humid (RH 90%) lab air or pure nitrogen with different concentrations of ozone for 22 h. Bare Cu stayed shiny after exposure and seemed not to corrode at all (Figure 5.3a). The reduction charge of bare Cu is are much less than reduction charges of bare Ag exposed with 630 ppb ozone for 22 h, as Figure 5.1 shows. It is surprising that corrosion rate of Cu is much slower than Ag even with higher ozone, because Ag is a more noble metal than Cu.

Figure 5.2 shows reduction curves of as-polished Cu and Ag stored in a dessicator for 24 h after polishing. As-polished Cu has a distinct reduction plateau at -0.65 V before hydrogen evolution started. This potential corresponds to reduction of naturally formed Cu$_2$O, although the reduction potential of CuO is also around -0.65 V SCE [19, 20]. It has been confirmed by linear sweep voltammetry that naturally formed Cu$_2$O can be reduced at the same potential as CuO [21], while corrosion-induced Cu$_2$O is reduced at lower potentials ranging from -0.75 to -0.9 V SCE [21-24]. It is not clear that why naturally-formed Cu$_2$O reduces at a higher potential than corrosion-produced Cu$_2$O, but it might be because that naturally formed Cu$_2$O is nonstoichiometric [21].
The thickness of the naturally formed Cu$_2$O is about 2.5 nm by calculation from reduction charge. This is consistent with previous reduction analysis and measurement by XPS depth profile analysis [25-27]. Generally, it is believed that this naturally formed oxide has a bilayer structure [26]. The inner layer is dense Cu$_2$O, which has fairly good protection and outer layer is porous CuO or Cu(OH)$_2$ [26, 27]. The Ag reduction curve does not have a reduction plateau before hydrogen evolution. This means that the naturally formed oxide layer is very thin or does not exist on Ag. This suggests that bare Cu corroded slower than Ag because it was protected by its naturally formed oxide, even though Ag is more noble than Cu.

Figure 5.2 also shows a typical reduction curve of exposed bare Cu. It roughly has two reduction plateaus. The first one is around -0.65 V SCE and the second one is very broad, ranging from -0.8 to -1.1 V SCE. The oxide film formed in the presence of ozone during exposure might be very similar to that formed on Cu exposed in humid air at 60 °C, which has a duplex oxide layer [20]. The outside layer is CuO and the inner one is Cu$_2$O. So the first plateau might be due to one-step reduction of CuO [19, 20] and the second plateau is due to newly formed Cu$_2$O during exposure. This newly formed oxide layer is probably nonstoichiometric since its thickness is only on the order of 2 to 3 nm according to its reduction charge, which results in a broad range of reduction potential. Overall, the oxide layer formed during exposure is only about 5 nm.

5.3.2 Identification of corrosion products of Cu exposed with NaCl

Cu corrosion becomes much more severe when the surface is contaminated with NaCl. Significant brownish patinas appeared after 5 hour exposure with only 4 μg/cm$^2$
NaCl. As loading of NaCl increased up to 16 μg/cm² NaCl, small green spots scattered on the surface and become prevalent as Figure 5.3b shows.

Figure 5.4 shows a typical reduction curve of Cu with NaCl exposed to a humid environment. It only has one big plateau around -0.75 to -0.85 V. Normal XRD analysis, Figure 5.5, indicates that only Cu₂O forms during exposure and usually it coexists with remaining NaCl. Therefore, the big plateau corresponds to reduction of Cu₂O. As shown in Figure 4, the reduction potential of the products on corroded Cu usually starts higher than this big plateau and then decreases to a lower value within a few tens of seconds and then increases back the big plateau. The reduction prior to the big plateau is probably due to reduction of Cu corrosion products with higher oxidation state. For example CuO reduces at around -0.6 V [24]. GIXRD in Figure 5.6 further confirms the presence of Cu₂O after exposure. As the incident angle decreases from 3° to 0.5°, broad peaks near CuO character peaks appear. This indicates the presence of trace amount of CuO at the outermost surface. The decrease and then increase in reduction potential might be associated with the reduction of this small amount of CuO at the outer surface before the thicker Cu₂O layer is reduced.

With an NaCl loading of 16 μg/cm², 250 ppb ozone in 90% RH air for only 22.5 h, formation of paratacamite (Cu₂(OH)₃Cl) as well as cuprite were confirmed by GIXRD analysis. Paratacamite is a common greenish corrosion product formed during field exposure in marine environment [6, 7, 9]. So the green species in Figure 5.3 are paratacamite. SEM and EDS mapping observation also indicate the presence of scattered regions enriched in O and Cl but depleted in Cu on samples exposed with 16 μg/cm² or
more NaCl, as Figure 5.8 shows. This confirms the presence of Cu₂(OH)₃Cl and also proves that no continuous Cu₂(OH)₃Cl film formed during exposure.

5.3.3 Effect of NaCl on Cu corrosion

Figure 5.9 shows reduction charge of Cu exposed with different NaCl loading in different environments. With addition NaCl deposited on the Cu surface, even at the low loading of 4 μg/cm², the reduction charge increases dramatically from almost zero to more than 100 mC/cm² after exposure to 90% air and 250 ppb ozone for 22.5 h. The effect of NaCl on the reduction charge of products formed on Ag, which was reported previously [13], is much less significant than Cu corrosion. The reduction charge of Ag even slightly decreases after addition of 8 μg/cm² NaCl. This is due to protection from NaCl solution on the Ag surface against atomic oxygen [13].

It is been reported that presence of chloride can result in breakdown of the naturally-formed copper oxide layer by formation of CuCl₂⁻ [26, 28, 29], according to;

\[
\frac{1}{2} \text{Cu}_2\text{O} + 2\text{Cl}^- + \text{H}^+ \rightarrow \text{CuCl}_2^- + \frac{1}{2}\text{H}_2\text{O} \quad (5.3)
\]

After breakdown of the naturally formed oxide, normal atmospheric corrosion of Cu starts to proceed. Reduction of oxygen and ozone are the dominant cathodic reactions accompanying the anodic oxidation of copper to cuprous ions. Reduction charge of Cu exposed to 32 μg/cm² NaCl and 250 ppb ozone for 22.5 h is as high as 198 mC/cm², which is equal to a corrosion rate of 0.28 μm/d according to equation 5.1. This is much higher than the normal Cu corrosion rate in the field, which ranges from 0.5 to 3 μm/year.
[4], because the NaCl loading and ozone concentration are much higher than what is typically found in real environments.

Previous research indicates that as NaCl loading increases from 2 to 33.5 μg/cm², corrosion rate of Cu increases linearly [29, 30] for Cu exposed longer than 10 days. This is different than what is shown in Figure 5.9, which indicates that the accelerating effect of NaCl on the initial Cu corrosion decreases as NaCl increases from 4 to 32 μg/cm². In a dark environment, the corrosion rate during 22.5 h exposure period is the same as when NaCl increases from 16 to 32 μg/cm². This is probably because the breakdown of the naturally-formed oxide does not need much NaCl, so the effect of loading of NaCl on the initial corrosion decreases as the loading increases. However, NaCl depletion is more important during long term exposure so loading of NaCl is much more critical for long term exposure.

The SEM image in Figure 5.10a shows appearance of shallow pits at a lightly corroded area. But at a more heavily corroded area, pits are rarely observed in a top view, because pits as well as adjacent area are completely covered by corrosion product, as Figure 5.10b shows.

Owing to the role of H⁺, the conversion from Cu₂O to CuCl₂⁻ (reaction 5.3) tends to occur in acidic solutions. It is likely that, at the beginning, a localized acidic environment forms due to pitting initiation. Increase of acidity results in further breakdown of the naturally-formed oxide layer and then uniform corrosion takes over. This generates the morphology in Figure 5.10b.
Figure 5.11 shows that the kinetics of Cu corrosion with 16 μg/cm² NaCl are close to linear within 45 h. This is different than the parabolic kinetics found for Cu via oxidation by oxygen only and supports the breakdown of naturally-formed oxide due to the presence of NaCl. However, the reported corrosion rate of Cu exposed to 500 ppb ozone and 22 to 33 μg/cm² NaCl for 4 weeks [29] is much less than the short term exposure corrosion rate of Cu reported in this paper. This probably caused by a decrease of Cu corrosion rate from reaction and depletion of NaCl after long exposures.

5.3.4 Effect of UV and Ozone

Figure 5.12 compares reduction curves of Cu exposed to 900 ppb ozone in nitrogen with Cu exposed to pure air. They are on the same order, although the amount of ozone in the nitrogen flow was much less than the 21% of oxygen in air. The corrosivity of 900 ppb ozone in nitrogen is similar to that of air for Cu because ozone is a much stronger oxidant than oxygen. In a dark environment, the main cathodic reactions are the reduction of ozone and oxygen (reactions 5.4 and 5.5). The standard reduction potential of ozone is 280 mV higher than oxygen [31].

In a neural environment, the reversible potential of ozone reduction with 900 ppb ozone is 0.8 V SCE, which is about 230 mV higher than reversible potential of oxygen reduction in ambient air environment (0.57 V SCE), assuming partial pressures of ozone and oxygen are 9 x 10⁻⁷ and 0.21 atm, respectively.

\[
\begin{align*}
O_3 + 3 H_2O + 6 e^- & \rightarrow 6 OH^- & E^o = 1.51 \text{ V} \\
O_2 + 4 H_2O + 4 e^- & \rightarrow 4 OH^- & E^o = 0.99 \text{ V}
\end{align*}
\]
It has been proven that a strong interaction between photons and cuprous oxide has significant effect on Cu aqueous corrosion [16, 17, 32-34]. Since the naturally-formed cuprous oxide is a p-type semiconductor with a band gap of 2.4 eV [35], UV illumination results in a cathodic photocurrent that improves passivity [16, 32]. But the newly formed cuprous oxide in sodium chloride or sodium borate solution is n-type semiconductor with similar band gap [17, 33, 34]. So under illumination of UV, extra anodic photocurrent can be generated, which increases corrosion rate, although it is still not clear why newly formed Cu$_2$O is n-type.

Figure 5.12 indicates that the AF on Cu corrosion is two when Cu is exposed to air without ozone at 90% RH. This is similar to the effect of UV on Cu exposed to H$_2$S [3]. It suggests that newly formed Cu$_2$O during atmospheric corrosion of Cu is also a n-type semiconductor. Interaction between photon and newly formed Cu$_2$O generates extra anodic photocurrent and doubles corrosion rate.

In the presence of ozone and UV radiation, atomic oxygen is generated by photolysis of ozone (reaction 5.6). Atomic oxygen is extremely aggressive and previous research already proved that atomic oxygen has stronger acceleration effect than ozone [13, 14, 36], especially at low RH. But this effect is limited at high RH in the presence of NaCl contamination, because of the protection effect of liquid NaCl solution formed due to deliquescence of NaCl [13]. So at 90% RH, corrosion rate of Cu does not increase because of atomic oxygen generated from photolysis of ozone. This explains why AF on Cu exposed to ozone/nitrogen at 90% RH is almost the same as Cu exposed to air.

\[ \text{O}_3 + \text{hv} (\lambda<370\text{nm}) \rightarrow \text{O} + \text{O}_2 \]  \hspace{1cm} (5.6)
5.3.5 Effect of RH

Figure 5.13 presents reduction charge of Cu exposed at different RH with $4\mu g/cm^2$ NaCl. Corrosion rate of Cu increases as RH increases with or without UV illumination. In a dry environment when RH is close to zero, little moisture layer is present on the Cu surface. The main corrosion mechanism is oxidation of Cu directly by ozone and oxygen. Since the naturally-formed oxide layer is still protective, the corrosion behavior of Cu with NaCl at dry environment is very similar to bare Cu. Therefore reduction charges of Cu in dry environment even with NaCl were close to zero as was the case for bare Cu.

As RH increases, the moisture layer on Cu increases. At 60% RH, adsorption of water can reach to about 5 monolayers, with properties similar to bulk water [37]. Strandberg and Johansson [29] suggested that part of the NaCl dissolves into the moisture layer so the air formed oxide layer can be attacked by Cl$, which results in fast corrosion at 60% RH.

Although water vapor pressure increases linearly as RH increases, corrosion rate of Cu increases nonlinearly as Figure 5.13 shows. At high relative humidity environment, higher than the critical deliquescent relative humidity (CRH) of NaCl, 75%, NaCl starts to deliquesce and eventually a bulk layer of sodium chloride solution is formed [38]. At 90% RH, the equilibrium NaCl concentration is about 2.7 M [39]. Environmental SEM proves that all NaCl particles are completely dissolved within a few minutes [13]. This results in a dramatic increase of surface Cl$ compared to 60% RH and the nonlinear acceleration effect of RH from 60% to 90% RH as Figure 5.13 shows.
Figure 5.13 also indicates that RH influences the effect of UV. At 60% RH, AF is 2.6, and it decreases to 2.2 as RH increases to 90%. This is because the accelerating effect of UV on Cu corrosion includes two mechanisms. The first one is the abovementioned anodic photocurrent due to interaction between photon and cuprous oxide. The second one is generation of atomic oxygen from photolysis of ozone. This effect will be largely limited at high RH as explained before. Therefore the acceleration effect of UV decreases as RH increases.

The AF of UV on Cu exposed to 4 μg/cm² NaCl in Figure 5.13 is slightly higher than Cu exposed to more NaCl in Figure 5.12. It is very likely that surface coverage of NaCl is less than 1 with only 4 μg/cm² NaCl. So atomic oxygen can still attack sample surface to accelerate Cu corrosion, which enhances acceleration effect of UV.

5.3.6 Formation mechanism of Cu₂(OH)₃Cl

Oxidation of CuCl (reaction 5.7) is considered as an important pathway to form Cu₂(OH)₃Cl. [37, 40]. Similarly, oxidation of CuCl₂⁻ was also suggested [29].

\[
4\text{CuCl} + \text{O}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Cu}_2(\text{OH})_3\text{Cl} + 2\text{H}^+ + 2\text{Cl}^- \quad (5.7)
\]

\[
3\text{CuCl}_2^- + 3/4\text{O}_2 + 3/2\text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_3\text{Cl} + \text{Cu}^{2+} + 5\text{Cl}^- \quad (5.8)
\]

CuCl and CuCl₂ are not always reported as Cu corrosion products even for Cu exposed in a marine environment. CuCl and CuCl₂ are often absent after lab exposure with NaCl, especially when ozone is involved during exposure [29, 30, 41]. This suggests another pathway for formation of Cu₂(OH)₃Cl without formation of CuCl. Previous research indicates phase transformation of cuprite powders into atacamite (an isomer of
Cu$_2$(OH)$_3$Cl) in the presence of NaCl in humid air [42]. It is proposed that direct oxidation of Cu$_2$O could be a possible alternative for formation of paratacamite during Cu corrosion.

$$2\text{Cu}_2\text{O} + \text{O}_2 + \text{Cl}^- + 3\text{H}_2\text{O} \rightarrow 2\text{Cu}_2(\text{OH})_3\text{Cl} + \text{OH}^- \quad (5.9)$$

$$2\text{Cu}_2\text{O} + \text{O}_3 + \text{Cl}^- + 3\text{H}_2\text{O} \rightarrow 2\text{Cu}_2(\text{OH})_3\text{Cl} + \text{OH}^- \quad (5.10)$$

Free energies of formation of Cu$_2$(OH)$_3$Cl (paratacamite), Cu$_2$O, Cl$^-$, H$_2$O, O$_3$ and OH$^-$ are –319.8, -34.98, -31.4, -56.7, 34 and -37.6 kcal/mol respectively [40, 43]. So the Gibbs free energy changes of reactions 5.9 and 5.10 are -403 and -437 kcal/mol. Therefore, these reactions are both thermodynamically possible. This mechanism also results in a dramatic increase in volume because density of Cu$_2$(OH)$_3$Cl is only 60% of the density of Cu$_2$O, while its molecular weight is also larger, which results in a loose attachment of Cu$_2$(OH)$_3$Cl on Cu$_2$O. Therefore, it is very easy to strip off the greenish species from the sample surface. Microscopically, it is often to find out that formation of Cu$_2$(OH)$_3$Cl is associated with film rupture of Cu$_2$O, and the surface under Cu$_2$(OH)$_3$Cl usually looks like fresh Cu surface as Figure 5.14 shows. This also supports a transformation from Cu$_2$O to Cu$_2$(OH)$_3$Cl.

According to reactions 5.8 and 5.9, not only ozone can increase formation rate of Cu$_2$(OH)$_3$Cl but also chloride. Even with ozone, no Cu$_2$(OH)$_3$Cl formed during exposure with 8 μg/cm$^2$ or less NaCl. Therefore, it is likely that the kinetics of reactions 5.8 and 5.9 increase dramatically when Cl$^-$ concentration reaches some critical value. Although the nominal chloride concentration depends on RH and not on NaCl loading, local
concentration is possibly much higher than the nominal value, e.g. at local anodes. So the formation of Cu$_2$(OH)$_3$Cl only occurs at some locations, which results in the scattered greenish spots over the sample surface.

5.4 Conclusions

The initial stage of atmospheric corrosion behavior of Cu exposed to ozone, UV and NaCl has been studied. Due to protection of naturally-formed copper oxide, bare Cu corrodes extremely slowly with high ozone and UV illumination, even slower than Ag. With the addition of a trace amount of NaCl, corrosion of Cu becomes much more severe due to breakdown of the naturally-formed oxide by chloride. The acceleration effect of UV includes the generation of aggressive atomic oxygen by photolysis of ozone and anodic photocurrent by interaction between photons and n-type Cu$_2$O. The acceleration effect is more significant at low RH because acceleration effect of atomic oxygen is more evident at low RH.

With enough loading of NaCl (>16μg/cm$^2$) and 250 ppb ozone, formation of Cu$_2$(OH)$_3$Cl was confirmed by GIXRD and SEM/EDS analysis after only 22.5 h exposure. Oxidation of Cu$_2$O to form Cu$_2$(OH)$_3$Cl is proposed as a reaction pathway, which is thermodynamically possible. SEM images also indicate a conversion from Cu$_2$O to Cu$_2$(OH)$_3$Cl.
Figure 5.1. Reduction charge of bare Ag and Cu in air or nitrogen environment with different concentration of ozone. All samples were exposed for 22 h with UV illumination. Ag reduction charges were taken from literature [13] and are shown here for comparison.
Figure 5.2. Reduction curves of as polished Cu, Ag and Cu exposed to 1.5 ppm ozone, 90% RH air, UV for 22h without NaCl.
Figure 5.3. Images of Cu after exposure in 90% RH air. a: 1.5 ppm ozone, UV for 22h without NaCl; b: 250 ppb ozone, no UV for 22.5 h with 16 μg/cm² NaCl; c: 250 ppb ozone, no UV for 22.5 h with 32 μg/cm² NaCl.
Figure 5.4. Reduction curve of Cu exposed to 900 ppb ozone, 90% RH air, UV for 6 h with 9 μg/cm² NaCl.

Figure 5.5. XRD spectrum of Cu exposed to UV, 90% RH air with 900 ppb ozone and 9 μg/cm² NaCl for 6 h. Total reduction charge 150 mC/cm².
Figure 5.6. GIXRD spectra of Cu exposed to UV, 250 ppb ozone, 90% RH air, 4 μg/cm² NaCl for 22.5 h. A: exposed to UV, incident angle 0.5°; B: exposed to dark, incident angle 0.5°; C: exposed to UV, incident angle 3°; D: exposed to dark, incident angle 3°; E: as polished Cu, incident angle 3°
Figure 5.7. GIXRD spectra of Cu exposed to 250 ppb ozone, 90% RH air. Incident angle is 0.5°. A: 32 μg/cm² NaCl with UV; B: 32 μg/cm² NaCl in dark; C: 16 μg/cm² NaCl with UV.
Figure 5.8. SEM and EDX mapping of Cu exposed with 16 μg/cm² NaCl, 250ppb ozone in 90% RH air for 22.5 h.
Figure 5.9. Reduction charge of Cu and Ag exposed with different loading of NaCl. a: Cu was exposed to 90% RH air and 250 ppb ozone, with or without UV illumination for 22.5 h. Cu was exposed to 90% RH air and 250 ppb ozone, with or without UV for 10 h. Exposure results of Ag are from [13] where Ag was exposed to 90% RH, UV and 630 ppb ozone for 22h.
Figure 5.10. SEM image of Cu +16 μg/cm² NaCl in 90%RH air with 250 ppb ozone and UV for 22.5 hr. The leaf-shape feature in the image a is remaining NaCl.
Figure 5.11. Reduction charge of Cu exposed to 16 μg/cm² NaCl, 250 ppb ozone, 90% RH air and UV for 10, 22.5 and 45 h respectively
Figure 5.12. Reduction curves of Cu exposed to 90% RH environment. A and B: 900 ppb ozone + N₂, 9 μg/cm² NaCl, 6 h with or without UV; C and D: no ozone + air, 16 μg/cm² NaCl, 22.5 h with or without UV. The corrosion rates of sample A to D are 0.09 μm/d, 0.17 μm/d, 0.11 μm/d, 0.22 μm/d, respectively.
Figure 5.13. Reduction charge of samples exposed to 250 ppb ozone and NaCl in air, with UV radiation or in dark. Bare Cu means no NaCl was deposited. Loading of NaCl was 4 μg/cm². The dashed lines are extrapolations of the lines from lower RH to facilitate the comparison with the increased charge at high RH.
Figure 5.14. SEM image pictures of Cu exposed to 250 ppb ozone, 90%RH air, 16 μg/cm² NaCl and UV for 22.5 h. a: as exposed; b and c: rinsed with before SEM. (continued on next page)
Figure 5.14. SEM image pictures of Cu exposed to 250 ppb ozone, 90%RH air, 16 μg/cm² NaCl and UV for 22.5 h. a: as exposed; b and c: rinsed with before SEM.
References:


Chapter 6  Atmospheric Corrosion of Cu during Constant Deposition of NaCl

6.1 Introduction

Atmospheric corrosion of Cu in the field and in laboratory chambers has been widely studied because of its use in electronics and architecture [1-6]. NaCl has 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 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 two orders of magnitude for short term 22 h exposure (see Chapter 5) and about one order for 10 days exposure [9].

NaCl has also been shown to be critical for formation of Cu₂(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)$_3$Cl [12]. However, there is a lack of information on the kinetics of Cu$_2$(OH)$_3$Cl formation and how Cu$_2$(OH)$_3$Cl affects the Cu corrosion rate because of difficulties generating a constant deposition rate of NaCl during lab exposure.

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 [9, 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 Cu$_2$(OH)$_3$Cl 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.

UV illumination and CO$_2$ both have strong influence on Cu corrosion in the presence of NaCl or H$_2$S [8, 17] but their influence on Cu corrosion kinetics under those conditions has not been reported.

This paper describes a novel chamber to provide constant deposition of NaCl during atmospheric exposure of Cu. With this chamber, the combination effects of UV illumination and CO$_2$ on Cu atmospheric corrosion kinetics during constant NaCl deposition are studied. An appropriate galvanostatic reduction technique to easily quantify the amounts of Cu$_2$O and Cu$_2$(OH)$_3$Cl is also described.

6.2 Experimental

6.2.1 Sample preparation
All Cu coupons were 99.99% pure and 17mm x 17mm x1.6mm in size. They were ground sequentially with 600, 800 and 1200 grit papers, followed by 6 μm and then 1 μm diamond polishing. After polishing, samples were stored in a desiccator for 24 h before exposure.

6.2.2 Environment chamber design

Figure 6.1 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 [18]. The exposure location of the Cu samples was maintained at a position 35 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 completely 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 CO₂ and the RH during exposure was always close to 100%. Ultra-purified air with less than 1 ppm CO₂ was also used to study the effect of CO₂.
Input 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 Cu to reach steady state conditions in the bubblers and in the chamber. Once exposure of 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 the chamber. The UV intensity was 3.2 mW/cm² 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, input flow A was 830 cc/min and input flow B was not used.

6.2.3 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 a Ag wire and the reference electrode was a saturated mercurous sulfate electrode (MSE). A 0.1 ml aliquot of the AgNO₃ solution was added 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 AgNO₃ volume, as shown in Figure 6.2. The deposition rate of NaCl, D, in mg/cm²h is determined from equation 6.1.

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

(6.1)

Where V is the volume of AgNO₃ at the equivalence point in ml, M is concentration of AgNO₃ in mol/L, t is deposition time in h, and A is area in cm².

6.2.4 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 Na₂CO₃ [19] or 0.1 M KCl [20] as the supporting electrolyte. A constant reduction current density of 0.05 mA/cm² was 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 the potentials mentioned in this chapter are potentials with respect to SCE.

6.2.5 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 H₂SO₄ 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 exposed in the chamber.

6.2.6 Scanning Kelvin Probe (SKP) measurement

Volta potential variation over a droplet of 2 μL saturated NaCl on as polished Cu was measured by SKP in a chamber of 98% RH. A line scan across the droplet was carried out of a scan rate of 0.8 μm/s and 4 μm/step. Details of SKP measurements are described elsewhere [21].

6.3 Results and discussion

6.3.1 Deposition rate of NaCl

The accumulated amount of deposited NaCl per unit area in mg/cm² is plotted in Figure 6.3. For bubbling of 5 wt% NaCl, the rate of NaCl accumulation decreases with time even though a continuous NaCl aerosol is generated. Continuous bubbling in the
solution for 96 h resulted in a decrease in the volume of the solution by about 40 ml with the 830 cc/min flow rate. This change in the conditions in the beaker resulted in a decrease in NaCl deposition rate 0.026 mg/cm²h at the beginning to 0.01mg/cm²h after about 100 h.

When the bubbled beaker in the chamber contained saturated NaCl solution instead of 5 wt.% NaCl, a lower rate of input flow A is needed to get a particular NaCl deposition rate, and so the rate of decrease of solution volume in the beaker decreases. For a flow 15 cc/min, the loss of the solution over the first 24 h is about 1 ml. Even though this change is very small, the deposition rate still decreases during bubbling unless input flow B is added. With the addition of the water-saturated air in flow B, the RH in the chamber can be maintained at very close to 100%. This value is much higher than the equilibrium RH of saturated NaCl (75%), so the saturated solution absorbs water during bubbling. Because the saturated solution contains excess NaCl, the solution stays saturated during bubbling. As long as enough water is absorbed to compensate for the loss due to bubbling, the volume of the solution in the beaker stays constant during bubbling.

The decrease of volume in the saturated solution is 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 6.3 shows that the NaCl deposition rate under these conditions is absolutely constant at 0.1 mg/cm²h.

Unfortunately, the RH in this chamber has to be maintained higher than 75% so that the saturated NaCl solution 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 addition 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 will be an issue.

6.3.2 Calibration of galvanostatic reduction technique

XRD analysis indicates paratacamite and cuprite formed on Cu exposed with 350 ppm CO₂ for longer than 15 h. Figure 6.4a 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 Figure 6.4b indicates. XRD analysis confirmed the presence of paratacamite and cuprite on the exposed sample before reduction, as Figure 6.4c indicates. Reduction of this sample was interrupted when the potential dropped to -0.8 V SCE, as shown in Figure 6.4b. The partially reduced area (within the o-ring) was still reddish-brown but covered by some loose black powder instead of the greenish species, which was the same as for samples that were reduced continuously. The black powder was likely Cu from
reduction of corrosion products and it was 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 left on the sample (Figure 6.4c). 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 6.4c. 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 Cu$_2$O, -0.8 V SCE, is consistent with previously reported values, which indicated reduction potential of Cu$_2$O around -0.75 to -0.9 V SCE in KCl [22, 23], KOH [23] or Na$_2$B$_4$O$_7$ [24]. There are few reports on the coulometric reduction of Cu$_2$(OH)$_3$Cl. Malvault et al. reported a peak reduction potential of paratacamite by linear sweep voltammetry in 0.1 M Na$_2$B$_4$O$_7$ of -0.61 V SCE [24], which is in the range of the first two plateaus in Figure 6.4a. Interestingly, the first two plateaus have almost the same amount of reduction charge. This suggests that reduction of paratacamite in Na$_2$CO$_3$ 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 6.5 shows reduction of Cu exposed in the same environment as the one in Figure 6.4a but for a short time, 23 h, and then reduced in Na$_2$CO$_3$. 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 Cu$_2$O in region II. Here, region I corresponds to the reduction of
paratacamite. Although 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 Figure 6.4a.

Curve A in Figure 6.5 is for another sample that was exposed to the same environment but reduced in 0.1 M KCl as suggested by ASTM B825 [20]. It is quite different, with only one broad plateau ranging form -0.6 to -0.8 V so that the reduction of paratacamite and cuprite cannot be clearly differentiated. Nakayama reports that reduction of CuO and Cu₂O are not be differentiated in neutral KCl but can be differentiated in alkaline solution, e.g. 1 M KOH [23, 25]. Copper hydroxyl oxides (Cu₂(OH)₃Cl and Cu(OH)Cl) are only stable at around pH 3.5 to 5.5 [3, 26], while Cu₂O is more stable in neutral to alkaline environments. 0.1 M Na₂CO₃ is basic with a pH of 11.5, which results in different reduction potentials for paratacamite and cuprite. A clearer distinction between the hydrogen evolution reaction (HER) and reduction of corrosion products is 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 is recommended.

6.3.2 Identification and quantification of corrosion products

Table 6.1 lists corrosion products of Cu exposed to humid air with NaCl deposition rate of 0.1 mg/cm²h determined by XRD. Similar to field-exposed Cu, the initial corrosion product identified by XRD is cuprite and then paratacamite forms later. For Cu exposed less than 4 h, there is 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 forms become much faster. Detection of Cu$_2$(OH)$_3$Cl by XRD was reported after one month exposure [27], while usually it could take several months up to years before Cu$_2$(OH)$_3$Cl is detected by XRD [4, 28] under normal NaCl deposition conditions. A typical deposition rate of NaCl in a marine environment without splash or spray is less than 6.25 μg/cm$^2$h [29], 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/cm$^2$h clearly indicates that formation of paratacamite can be dramatically accelerated by increasing deposition of NaCl.

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

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

(6.2)

where $W$ is total weight loss in g/m$^2$, $Qc$ is reduction charge corresponding to reduction of cuprite in C/cm$^2$, $Qp$ is reduction charge corresponding to reduction of paratacamite in C/cm$^2$, $M$ 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 6.6. The length of each plateau is determined by local minima of the derivative of the reduction
curve [22]. Although no paratacamite was detected by XRD for samples exposed less than 15 h, the reduction charge above cuprite reduction plateau can still be assigned to Qp, since it was due to reduction of Cu$^{2+}$ ions. Besides calculation of total weight loss of Cu, weight loss due to formation of cuprite or paratacamite can also be calculated separately with equations 6.3 and 6.4

$$W_c = \frac{10000 \times Q_c \times M}{F} \quad (6.3)$$

$$W_p = \frac{10000 \times Q_p \times M}{2 \times F} \quad (6.4)$$

where $W_c$ is weight loss due to formation of cuprite and $W_p$ is weight loss due to formation of paratacamite in g/m$^2$.

Figure 6.7a summarizes weight loss data of Cu exposed to humid air with 0.1 mg/cm$^2$ d NaCl deposition rate up to 80 h with UV or in dark environment. Figure 6.7b presents the derivative of each curve in Figure 6.7a, showing the formation rates of cuprite and paratacamite and the total corrosion rate of Cu. Generally, the formation of cuprite is 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 increase significantly, which was likely due to continuous increase of loading of NaCl. Eventually, the rates all became relatively stable.

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. So the increase of total weight loss of Cu exposed to UV was mainly due to an acceleration of cuprite formation. The acceleration effect of UV reported in Figure 6.7 is very similar to Cu exposed with H$_2$S/UV [17].

Naturally formed cuprous oxide is a p-type semiconductor with a band gap of 2.4 eV [30]. Therefore, UV photons ($\lambda < 370$ nm, E $> 3.4$ eV) have enough energy to generate electron-hole pairs. This only leads to cathodic photocurrent, which reduces the passive current and increases corrosion resistance [31]. However cuprite formed during corrosion of Cu in NaCl solution is n-type with a similar band gap of 2 eV, which can lead to anodic photocurrent and increase corrosion rate [32, 33]. Therefore, because Figure 6.7 clearly shows the acceleration effect of UV, it is likely that n-type cuprite formed during exposure of Cu in humid air.

With the presence of n-type cuprite on the anodic area of Cu, an ohmic junction and schottky barrier form as shown schematically in Figure 6.8, which is similar to the model suggested by Gerischer [34] and Burleigh [31, 35] on metals with n-type oxide under anodic polarization. Once a photon with energy larger than band gap hits cuprite, especially on the local anode area, a hole-electron pair forms (Equation 6.5). 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 6.6), while holes move towards the surface. It is proposed that Cu\(^+\) is oxidized to Cu\(^{2+}\) as the result of the formation of hole-electron pairs (Equation 6.7). Reverse disproportionation of Cu\(_4\)(SO\(_4\))(OH)\(_6\) and metallic Cu has been proposed for formation of cuprite in the presence of ammonium sulfate [36]. So a reverse disproportionation reaction of cupric and metallic Cu to generate cuprous ions is also proposed as equation 6.8 suggests. Equation 6.9 is the overall reaction of photon-induced Cu corrosion. Cu(OH) as an intermediate decomposes to form cuprite rapidly according to equation 6.10 [32].

\[
\begin{align*}
4\text{Cu}_2\text{O} + 4 \text{hv} & \rightarrow 4\text{Cu}_2\text{O} + 4\text{e}^- + 4\text{p}^+ & (6.5) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- & (6.6) \\
4\text{Cu}^+ + 4\text{p}^+ & \rightarrow 4\text{Cu}^{2+} & (6.7) \\
4\text{Cu}^{2+} + 4\text{Cu} & \rightarrow 8\text{Cu}^+ & (6.8) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{Cu} + 4 \text{hv} & \rightarrow 4\text{Cu(OH)} & (6.9) \\
2\text{Cu(OH)} & \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} & (6.10)
\end{align*}
\]

Another possible route is formation of oxygen atoms instead of cupric ions as reactions 6.11 and 6.12 suggest:

\[
\begin{align*}
2\text{O}^{2-} + 4\text{p}^+ & \rightarrow 2\text{O} & (6.11) \\
2\text{OH}^- + 2\text{p}^+ & \rightarrow \text{O} + \text{H}_2\text{O} & (6.12)
\end{align*}
\]

\(\text{O}^{2-}\) is oxygen in Cu\(_2\)O and \(\text{OH}^-\) is in NaCl solution adsorbed on sample surface. Gerischer [34] suggests formation of O\(_2\) following reaction 6.11 resulting in dissolution of Zn into ambient solution under UV illumination. Since the formation rate of Cu\(_2\)O increases
under UV illumination, it is more likely that atomic oxygen O atoms diffuse through oxygen vacancies towards the Cu/oxide interface and then react with Cu to form oxide. In this situation, the overall reactions are reactions 6.13 and 6.14, corresponding to 6.11 and 6.12 respectively.

\[
\begin{align*}
O_2 + 2H_2O + 2O_2^- + 4Cu + 4hv & \rightarrow 2Cu_2O + 4OH^- \quad (6.13) \\
O_2 + 4Cu + 4hv & \rightarrow 2Cu_2O \quad (6.14)
\end{align*}
\]

Reaction 6.13 can generate oxygen vacancies, which is consistent with characterization of n-type semiconductors.

The proposed reaction paths both indicate that photons have very little effect on the formation of cupric ions, although the first route might generate some less dominant cupric ions because reaction 6.10 is very likely a slow step. Therefore, only a slight increase of Wp with UV illumination compared to Cu exposed in dark was observed as Figure 6.7 shows. This increase is probably because of unreacted cupric ions converting to Cu(OH)$_2$, CuO or some precursor of paratacamite. Actually, a greenish specie 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 specie is likely paratacamite, although XRD could not identify it, maybe because of its limited amount.

6.3.3 Effect of CO$_2$ on Cu corrosion with NaCl

The corrosion behavior of Cu exposed with low CO$_2$ (< 1ppm) is different than Cu exposed with 350 ppm, which is close to the ambient concentration of CO$_2$ in the air.
Figure 6.9 presents pictures of samples exposed with low and high CO$_2$ respectively. The one exposed with low CO$_2$ has a black surface covered with white salts. In contrast, the one exposed with high CO$_2$ has 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 CO$_2$. However no paratacamite (the green species in Figure 6.9b) or other cupric compound was identified by XRD. SEM images of these two samples are also quite different as Figure 6.10 indicates. The corrosion product on Cu exposed with low CO$_2$ is more compact than that formed on Cu exposed with high CO$_2$, although it still has some fine porosity. Cu exposed with high CO$_2$ has a much less dense product layer covered with paratacamite flakes as Figure 6.10 c and d indicate.

Figure 6.11 is a typical reduction curve of Cu exposed with low CO$_2$. In contrast to the curve for Cu exposed to high CO$_2$ in Figure 6.5, the reduction plateau of cuprite at -0.8 V SCE is 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 [23]. The part of the curve above tenorite reduction plateau is always very small and might due to reduction of some other trace cupric compounds. The amounts of Cu$_2$O and CuO formed during exposure with low CO$_2$ can still be quantified with equation 6.5 and 6.6 separately by their reduction charges.
Figure 6.12 compares the equivalent weight loss and corrosion rate of Cu exposed to high and low CO$_2$. Generally, the corrosion rate of Cu exposed to low CO$_2$ (<1 ppm) is relatively constant in contrast to the behavior of Cu exposed to high CO$_2$ (350 ppm). It is interesting to notice that during the first 5 h, Cu exposed to low CO$_2$ corroded faster than Cu exposed to high CO$_2$. This is similar to exposure of Cu with NaCl particles. With low NaCl loading, Cu corroded faster with low CO$_2$ (< 5ppm), while at high NaCl loading, Cu corroded faster with high CO$_2$ (350 ppm) [8, 37]. This was attributed to the fact that NaCl droplets are more spread with low CO$_2$ [8, 37]. So during the first 5 h, before the Cu surface is completely covered with NaCl droplets, with the same loading of NaCl, samples exposed to low CO$_2$ had higher surface coverage of NaCl solution. This explains why Cu corroded faster with low CO$_2$ during the first 5 h. For Cu exposed longer than 5 h, corrosion rate of Cu exposed to low CO$_2$ becomes slower than Cu exposed to high CO$_2$.

Since no Cu$_2$(OH)$_3$Cl formed during exposure of Cu to low CO$_2$, real time loading of NaCl on Cu was actually more than Cu exposed to high CO$_2$. This explains why Figure 6.9 shows white NaCl on the sample exposed to low CO$_2$. However, even with more NaCl, the corrosion rate of Cu exposed to low CO$_2$ is still much less than high CO$_2$. This is mainly due to the presence of CuO, which provides a high degree of corrosion protection. It has been shown that the initially formed Cu$_2$O has a porous structure [38]. CuO forms in the Cu$_2$O pores to block them and increase corrosion resistance [38-40]. Figure 6.10a and b confirm the relatively compact surface morphology of Cu exposed with low CO$_2$. With high CO$_2$, paratacamite is the main cupric compound instead of

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tenorite. Most of the paratacamite is just flakes loosely attached to sample surface as Figure 6.10d shows. They are not as protective as the compact oxide layer formed in low CO\(_2\) environment. On the other hand, after 10 h exposure, almost the whole sample surface is covered with NaCl droplets, so there is no surface coverage difference between Cu exposed to low CO\(_2\) and high CO\(_2\). However different than formation of paratacamite, the formation rate of cuprite was much faster even at the beginning of exposure. Therefore after 5 h exposure, before the whole surface was covered with NaCl solution, corrosion rate of Cu in low CO\(_2\) became slower than Cu exposed to high CO\(_2\).

pH has a strong influence on the formation or stability of Cu\(_2\)O, CuO and Cu\(_2\)(OH)\(_3\)Cl. Cu\(_2\)O forms at pH > 4, while formation of CuO occurs at pH > 6.7 [40]. Cu\(_2\)(OH)\(_3\)Cl is stable between pH 3.8 to 5.5 [3, 26]. Using software from OLI Systems Inc., the equilibrium pH of water with 350 ppm CO\(_2\) was calculated to be about 5.7 and it increases to higher than 6.8 as CO\(_2\) drops to less than 1 ppm. So with low CO\(_2\), CuO is the dominant cupric corrosion product. This also explains why CuO is not the dominant cupric compound in the field because CO\(_2\) is about 300 to 600 ppm in ambient atmosphere [41]. With high CO\(_2\), formation of Cu\(_2\)(OH)\(_3\)Cl is likely to occur at local anode areas where local pH is lower than the bulk aqueous layer. That is probably why dispersed Cu\(_2\)(OH)\(_3\)Cl appears after relative short term exposure.

6.3.4 Morphology and localized corrosion of exposed Cu

The surfaces of samples exposed less than 12 h have significant circular features with a diameter of a few hundred micrometers as Figure 6.13a and b 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 is much more uniform. However, after corrosion products are dissolved in strong acid, circular features are the most dominant feature on the metallic substrate. As shown in Figures 6.13 d-f, attack is localized in the form of small pits at the periphery of these circles with the similar size as the circular features that appeared after exposure. This morphology was even observed for samples exposed for relatively long times and do not have circular features in the corrosion product layer. Although there are some pits occasionally present at the center of a circle, these peripheral pits suggest that oxidation of Cu primarily occurs around the edge of the initially-formed droplets. This 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 [42]. The mechanism of formation of these pits is not known.

Figure 6.14a 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 early stage of the exposure conditions in the home-built chamber. At the beginning, the potential under the droplet is much lower than the surrounding area and a dramatic potential change occurs right outside of the edge of the droplet. This is the same as previous results on Cu with single NaCl droplet in 85% RH, which suggests a thin electrolyte layer surrounding the droplet [37]. Reduction of oxygen is likely to occur within this thin electrolyte area. Probably because insoluble cuprite and the thin
electrolyte layer generate a large ohmic potential drop between the anode and cathode, 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.

Because the NaCl-saturated droplet kept absorbing water during the SKP measurement, the droplet continued to grow. 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 6.14b. 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.

Figure 6.15 summarizes the maximum pit depth from optical profilometry and equivalent weight loss of Cu exposed to different environments. Generally, at the beginning, the pit depth increases much faster than weight loss, and then it slows down. This suggests that corrosion of Cu with constant deposition is more localized at the beginning and then becomes more uniform.

Figure 6.15 also indicates that UV has a significant acceleration effect on localized corrosion of Cu. 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.
6.4 Conclusions

A novel 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.

With 350 ppm CO₂, paratacamite and cuprite are dominant corrosion products like Cu exposed in field. As 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.

It is determined that UV has a strong acceleration effect on formation of cuprite but little effect on formation of paratacamite due to interaction between UV photons and cuprite.

In various environments, during the beginning of exposure, localized corrosion is always dominant, but uniform corrosion becomes dominant later. Therefore, localized corrosion is not a severe concern for long term exposure of Cu.
Table 6.1. Corrosion products of Cu exposed to 0.1 mg/cm²h NaCl and compressed air

<table>
<thead>
<tr>
<th>Exposure duration, h</th>
<th>Corrosion products identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 4</td>
<td>N/A</td>
</tr>
<tr>
<td>8 to 15</td>
<td>Cu₂O</td>
</tr>
<tr>
<td>&gt; 15</td>
<td>Cu₂O and Cu₂(OH)₃Cl</td>
</tr>
</tbody>
</table>
Figure 6.1. Schematic draw of home-built environment chamber with constant deposition of NaCl.
Figure 6.2. Potentiometric measurement of deposition of NaCl with bubbling of 5 wt. % NaCl
Figure 6.3. Accumulated deposition of NaCl vs deposition period. Saturated and 5 wt% NaCl were used respectively.
Figure 6.4. Reduction curves of Cu in 0.1 M Na₂CO₃. Cu was exposed to humid air, 0.1 mg/cm²h NaCl with UV (Figure 6.4a) or in dark (Figure 6.4b); c: XRD spectra of sample Figure 6.4b before reduction and after reduction of the first two plateaus are completed (To be continued).
Figure 6. 4. Reduction curves of Cu in 0.1 M Na$_2$CO$_3$. Cu was exposed to humid air, 0.1 mg/cm$^2$h NaCl with UV (Figure 6. 4a) or in dark (Figure 6. 4b); c: XRD spectra of sample Figure 6. 4b before reduction and after reduction of the first two plateaus are completed.
Figure 6.5. 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/cm²; B: reduced in 0.1 M Na₂CO₃ with -0.05 mA/cm².
Figure 6.6. 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.
Figure 6.7. 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 (dash lines). b: formation rate of cuprite and paratacamite and corrosion rate of Cu, derivative of data showed in Figure 6.7a.
Figure 6.8. Schematic illustration of the interaction between photons and n-type cuprite. “CB”: Conduction band; “VB” Valence band [31, 34].
Figure 6.9. Pictures of Cu exposed to low or high CO₂. a: Cu exposed to humid air with less than 1 ppm CO₂ and 0.1 mg/cm²·h NaCl for 58.5 h. White salts are NaCl; b: Cu exposed to humid air with 350 ppm CO₂ and 0.1 mg/cm²·h NaCl for 33.5 h. Green compounds are paratacamite. White salts around the edge is also NaCl.
Figure 6.10. 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 b is remaining NaCl 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 confirmed by EDS.
Figure 6.11. Reduction curve of Cu exposed to humid air with less than 1 ppm CO₂ and 0.1 mg/cm²h NaCl for 23.5 h with low CO₂. Cu was reduced in 0.1 M Na₂CO₃ with -0.05 mA/cm² current.
Figure 6.12. 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 and Subscript H and dashed line 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: corrosion rate of Cu exposed to
Figure 6.13. Images of Cu exposed to humid air and 0.1 mg/cm$^2$h 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 H$_2$SO$_4$ to remove corrosion products. a and d are samples exposed for 4h; b and e are 12 h and c and f are 23.5 h.
Figure 6.14. 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.
Figure 6.15. Maximum pit depth and equivalent weight loss of Cu exposed in various environments.
References:


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7.1 Conclusions

Ag has been used as a corrosivity monitor exposed in various outdoor environments [1]. Although a strong correlation between the corrosion rate of Ag and carbon steel was found [1], there is a lack of understanding of the corrosion behavior of Ag. Several uncommon corrosion phenomena related to Ag corrosion has been found. For example, Ag corrodes in the field but stays shiny after exposure in a salt spray chamber [2]. Also, no Ag corrosion product is detected if Ag is intermittently sprayed with seawater during exposure at the seacoast.

In this work, the corrosion behavior of Ag in salt spray chamber, various field environments and a laboratory environment with ozone, UV and NaCl was further studied and understood. The following conclusions are made after analysis and correlation of field and lab exposure experiments:

1. Realizing that the solubility of AgCl increases as Cl\textsuperscript{-} concentration increases provided an explanation for why no AgCl remains on Ag intermittently sprayed with seawater during field exposure. A model to estimate loss of AgCl due to dissolution in NaCl solution was developed. The loss of AgCl was found to be
negligible as long as Ag is not exposed to high rates of NaCl deposition, such as during intermittent spray. So the galvanostatic reduction technique is usually a valid approach for evaluating the corrosion rate of Ag samples exposed in the field.

2, The understanding of galvanostatic reduction for Ag corrosion product analysis was improved. The reduction potential of Ag$_2$SO$_4$ and AgO were defined. A commonly observed reduction plateau at -1.55 V MSE was attributed to the hydrogen evolution reaction. These assignments enable the galvanostatic reduction technique to be used as a semi-quantitative analysis tool for Ag. The presence of silver sulfate and silver oxide after field exposure of Ag was confirmed by the improved galvanostatic reduction technique.

3, Weight loss measurement of Ag tested by ASTM B1117 proved that Ag does corrode in a salt spray chamber because dissolution of AgCl into NaCl solution causes the reduction charge of the tested Ag samples to be zero. Although Ag does corrode during B117 test, its corrosion rate is much less than Ag exposed in a marine environment. This confirms that oxygen is not an aggressive oxidant for Ag and that the ASTM B117 salt spray exposure test is not an accelerated test for Ag.

4, The combination of ozone, UV and NaCl has been proven as a promising environment for Ag laboratory accelerated test. Effects of ozone, UV and RH on Ag corrosion have been fully studied. Ozone, a stronger oxidant than oxygen, results in oxidation of Ag and formation of AgCl.
5. RH has a strong effect in determination of Ag corrosion product. Silver oxide as well as silver chloride can form on Ag exposed at relatively low RH. This leads to a prediction that silver oxide can form in field environments that are dry or have low chloride deposition. Field exposure analysis proves this prediction.

6. UV was found to have two opposing effects on atmospheric corrosion of Ag: photolysis of ozone, which increases corrosion rate, and photodecomposition of corrosion products, which reverses corrosion. Measured reduction charges reflect a combination of these two effects.

7. Artificial neural network modeling was used to describe the effects of RH, UV, and ozone on Ag corrosion using lab environments. Although it is a relatively simple model, it is useful in predicting Ag corrosion rate in marine environment. The effects of more parameters, such as temperature, should be added to allow prediction of Ag corrosion rate in different environments.

The test environment containing ozone, UV and NaCl was also used to study the corrosion of Cu, another widely used corrosivity monitor. The following conclusions are made:

1. Generally, the effects of ozone, UV and NaCl on Cu are different than on Ag. NaCl is very aggressive for Cu but not for Ag. In the absence of NaCl, Cu corrodes slower than Ag due to protection of nature formed copper oxide, even though Ag is more noble.
Since NaCl is critical for Cu corrosion, an environment chamber that provides a constant deposition rate of NaCl was successfully constructed. It can be used to study combined effects of NaCl with other corrosive factors. This is very useful in understanding of Cu corrosion behavior in the field. Previous reports have been limited because of the inability to maintain a constant deposition environment.

An Na$_2$CO$_3$ solution was determined to be more suitable than KCl solution for reduction of copper corrosion products, because it allows the reduction plateaus associated with Cu$_2$(OH)$_3$Cl, CuO and Cu$_2$O to be clearly differentiated. Determination of these reduction potentials allowed the formation rate of Cu$_2$(OH)$_3$Cl, CuO and Cu$_2$O in different environments to be studied.

UV illumination dramatically increases Cu corrosion rate, even without ozone, mainly because of interaction between photons and cuprite that increases the formation rate of cuprite.

CO$_2$ was found to be critical for Cu corrosion. High CO$_2$ accelerates formation of paratacamite, a common corrosion product formed in field, while tenorite only forms in CO$_2$ low environment.

Overall, an environment with ozone, UV and NaCl is very useful for conducting laboratory accelerated test for Ag and understanding Ag corrosion behavior. It can also be used for other metals. However effects of ozone, UV and NaCl on other metals are likely to be very different than on Ag.
7.2 Future work

This work has advanced the understanding of the effects of NaCl, ozone, UV and CO2 on Ag and Cu corrosion. The successful correlation of lab exposure and field exposure behavior of Ag is a big advance in the prediction on Ag corrosion behavior in the field. However, in order to fully understand atmospheric corrosion of Ag and Cu and to predict their corrosion behavior in field, there are still some unresolved issues that need to be addressed in the future:

1. Ozone concentration has a strong effect when Ag is exposed in low RH and dark environment with NaCl. A dramatic jump of corrosion rate as ozone increases from 600 ppb to 2000 ppb. This suggests that there is an interaction between ozone and NaCl that results in decomposition of ozone and generation of radicals. This should be addressed further.

2. NOx, similar to ozone, is an aggressive and photosensitive oxidant that should be included for study on Ag and Cu corrosion.

3. The effects of temperature on corrosion behavior Ag and Cu have not been studied. The effect of temperature is important for predicting corrosion rate in field.

4. SO2, which has a very significant effect on Cu corrosion, should be included in studies with constant NaCl deposition rate. The competition between formation of copper hydroxyl chloride and copper hydroxyl sulfate can be studied, which is an important corrosion phenomenon for Cu in marine environments.
Reference:


Bibliography


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