Atmospheric Corrosion of Zinc by NaCl, SO$_2$, NH$_3$, O$_3$, and UV Light

THESIS

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By

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Abstract

Zinc (Zn) coatings on steel structures for corrosion protection are by far the greatest use of Zn throughout the world. Numerous experiments have been conducted in laboratory environments to predict and understand the corrosion behavior of Zn coatings in the field. However, many studies have been limited to time of wetness, pH, and chloride (Cl\(^-\)) and sulfur dioxide (SO\(_2\)) concentrations to predict the Zn corrosion rate. The corrosion behavior of Zn exposed to 120 ppb SO\(_2\), 550 ppb ammonia (NH\(_3\)), 650 ppb ozone (O\(_3\)), and ultraviolet (UV) light at 70% RH, with a constant preloading of sodium chloride (NaCl) was investigated in this study. After exposure, corrosion rates were measured using mass loss and corrosion products were identified by x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), and energy dispersive spectroscopy (EDS). UV light and O\(_3\) did not significantly affect the Zn corrosion rate in the absence of Cl\(^-\). However, when NaCl was present, UV light inhibited the Zn corrosion rate below 90% RH and accelerated the Zn corrosion rate at 99% RH. The presence of UV light also increased the formation of zinc hydroxy sulfate and gordaite when exposed to 120 ppb SO\(_2\) and NaCl. The combination of SO\(_2\) and O\(_3\) with the preloading of NaCl increased the corrosion rate of Zn compared to NaCl alone. 550 ppb NH\(_3\) was determined not to have a significant effect on the Zn corrosion rate.
Dedication

This document is dedicated to my mother, Leslie Onye, Father, Chris Onye, and brother, Eric Onye.
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Chapter 1: Introduction

1.1 Background

Zinc (Zn) is the 23rd most abundant element in the earth’s crust, but the 4th most used, produced, and consumed worldwide [1]. Uses include coatings, casting alloys, alloying element in metals such as brass, wrought zinc alloys, zinc oxide, and zinc chemicals production. However, zinc coatings on steel structures for corrosion protection are by far the greatest use of Zn. About half of the Zn produced in the United States is used for coatings. Zn’s low corrosion potential allows for preferential corrosion of Zn when coupled with steel, and Zn’s protective corrosion products result in low self-corrosion rates. For this reason, Zn has been heavily used in automotive and construction industries for auto bodies, housings, and building construction.

Research has shown that the lifetime of Zn coatings is highly dependent on environmental factors such as relative humidity, time of wetness, [Cl\(^-\)], [SO\(_2\)], and pH [2, 3]. However, the atmosphere is composed of other constituents that have not been thoroughly investigated that could also impact the Zn corrosion rate. Some of these constituents include UV light, O\(_3\), and NH\(_3\). UV light has been shown to influence the corrosion behavior of metals such as copper and silver [4]. On silver, UV light can
photoreduce silver corrosion products such as AgCl leading to a lower apparent corrosion rate. In addition, UV light can enhance the silver corrosion rate by producing oxidizing species. UV light also is able to interact with semiconducting corrosion products on materials such as Cu and Zn. Corrosion products formed on Cu such as cuprous oxide are p-type semiconductors. When p-type semiconductors are exposed to UV light, cathodic current may be produced, which promotes passivity. However, ZnO and newly formed Cu$_2$O are both n-type semiconductors and, when exposed, UV light can produce extra anodic current, resulting in an increase in corrosion rate [4, 5].

1.2 Objective

The objective of this work is to understand how the combination of SO$_2$, NH$_3$, UV light, O$_3$, and NaCl, might simultaneously interact with each other and the Zn surface to affect the Zn corrosion rate.
1.3 References


Chapter 2: Literature Review

2.1 Introduction

Understanding the corrosion mechanism for zinc and zinc alloys is important for developing new corrosion resistant steels through the development of corrosion resistant zinc coatings and enhanced passivation systems. It is important to understand what factors control the corrosion rate of zinc in order to accurately model its corrosion and to predict the lifetime of coated steels in a given environment.

The atmosphere is composed of a variety of gases, liquid aerosols, and particulates that could potentially affect the corrosion rate of a metal. The atmospheric corrosion of a metal requires an electrolyte, which is provided by the adsorption of water molecules onto the metal surface and the dissolution of salts or the adsorption of gases into the liquid layer. Electrochemical reactions take place at the metal-electrolyte interface [1]. This electrolyte can easily form outdoors during precipitation or when the temperature of the metal surface is below the dew point. Salt may also be dissolved in the moisture on the metal surface. Salts will become soluble above a critical relative humidity, which is dependent the type of salt and the type of corrosion products found on the metal surface.
Therefore the critical relative humidity depends on the type of metal and pollutants exposed.

Atmospheric pollutants are transported to the metal surface through dry and wet deposition processes [1, 2]. Electrolytes composed of sulfates, nitrates, nitrites, chlorides, carbonates, hydrogen ions, ammonium, metal ions, atmospheric particles and organic compounds are common constituents of surface electrolytes or corrosion products. These result from the deposition of atmospheric constituents or from aqueous phase reactions of deposited gaseous atmospheric constituents.

The link between corrosion products and environmental parameters is not fully understood because of the complexity of the multiphase system which involves chemical reactions, equilibria, and transport phenomena in gaseous, aqueous, and solid phases [2]. The variability of the outside atmosphere creates a tremendous problem when trying to correlate the corrosion rate of a metal to a particular vapor or particulate concentration. Controlled laboratory tests allow the opportunity to study both the effect of each potential corrosion accelerator separately and the effects of a combination of multiple accelerators [3].

For decades, the only factors considered in the atmospheric corrosion of a metal were sulfur dioxide (SO₂) and chloride (Cl⁻). These two pollutants are by far the most studied in atmospheric corrosion. Because of the high solubility of SO₂ in water and its fast oxidation reactions, there is often a relatively high amount of sulfate on surfaces [2]. SO₂ also forms sulfate from reactions involving dissolved nitrogen oxides and their oxyacids [2]. If SO₂ is in the presence of a semiconducting corrosion product,
photochemical reactions can also occur. Oxidizing agents such as ozone and hydrogen peroxide are important reactants for the formation of sulfate.

In response to this understanding, over the past two decades the Environmental Protection Agency has passed regulations that have reduced the allowance of SO\(_2\) released into the atmosphere [2]. Allowable concentrations of other air pollutants such as nitrogen dioxide and ozone have remained the same, and in some cases have increased slightly. This has increased the significance of these pollutants on the corrosion of materials.

2.2 Atmospheric corrosion of zinc (field exposure)

Zinc (Zn) corrodes slowly in pollutant-free dry air because of the formation of a protective oxide film [4]. An amorphous film is produced on the surface, which reaches a thickness of about 10 nm after a few weeks. The film is initially amorphous, but over time the film will become crystalline and more protective. Consequently, the exterior of the oxide film is amorphous while the interior becomes crystalline. When Zn is in contact with moisture from rain, dew or mist, zinc hydroxide is formed by the following reactions [4].

\[
\begin{align*}
Zn + 2OH^- &\rightarrow Zn(OH)_2 + 2e^- \\
2H^+ + 2e^- &\rightarrow H_2 \\
O_2 + 2H_2O + 4e^- &\rightarrow 4OH^- 
\end{align*}
\]

After a few days or weeks, the hydroxide layer will dehydrate or react with carbon dioxide (CO\(_2\)) to form oxide or carbonate corrosion products.

\[
Zn(OH)_2 \rightarrow ZnO + H_2O
\]
The carbonate film allows for more protection against corrosion due to its lower water solubility and greater resistance to chemical dissolution than the oxide film. Although dissolved CO$_2$ can lead to a more protective carbonate layer, if its concentration increases significantly, the pH of the electrolyte will decrease, leading to the dissolution of the protective carbonate film [4].

Field exposure studies have been performed to understand the corrosion mechanisms of Zn and galvanized steels in various environments. A study has been conducted across five countries (Australia, Thailand, Indonesia, Vietnam and The Philippines) in order to better understand the relationship between pollutants and the corrosion of Zn and steel [5]. The Zn corrosion rate was found to be dependent on the exposure environment. In medium polluted atmospheres, zinc carbonate, zinc hydroxide, hydrozincite (Zn$_5$(OH)$_6$(CO$_3$)$_2$) and zinc oxides are formed. Zinc oxide is the most thermodynamically stable corrosion product in the Zn$^{2+}$/H$_2$O-system. In more moderately polluted environments, zinc hydroxy sulfates like Zn$_4$SO$_4$(OH)$_6$·nH$_2$O are found. In marine environments, i.e. in the presence of chlorides, zinc hydroxy chloride forms, which has a low solubility in water [2].

Studies have shown that upon exposure Zn first forms a thin film of zinc hydroxide, which transforms to other corrosion products as exposure continues. Typical corrosion rates of Zn in rural, marine, and urban/industrial environments are shown in Table 2.1.
and Table 2.2 [4, 6, 7]. After the first year of exposure, the corrosion rate of Zn is generally found to be constant. The corrosion rate at a given location can vary year to year due to changing environmental conditions such as pollutant levels and the amount of rainfall [7]. It has been suggested that the primary reason for the differences in corrosion rate in each environment is primarily due to the SO₂ concentration [6, 7]. Many empirical models of corrosion rate have been developed to predict the corrosion rate of Zn in the field, using the most important corrosion rate factors as parameters. Haynie and Upham proposed a relationship between corrosion rate (R), relative humidity (RH) and [SO₂], which is shown below with the corrosion rate given in μm/year [6].

\[ R = 3.92 \times 10^4 \times (RH - 48.8)[SO₂] \]  

(7)

Benarie and Lipfert chose other atmospheric parameters including time of wetness (tₜₜ), chloride deposition rate (Cl⁻), average acidity of precipitation (pH), total time of exposure (t), and SO₂ deposition rate (SO₂) to model the corrosion rate of Zn, which is shown below [6, 8].

\[ M = A \left( \frac{tₜₜ}{t} \right)^b \]  

(8)

\[ A = 4.8 + 0.53 (SO₂) + (Cl⁻) \]  

(9)

\[ b = 1.55 - 0.142 (pH) \]  

(10)

The mechanism of steel protection by Zn is primarily the barrier created by the Zn’s protective corrosion product and secondly cathodic protection[7]. For galvanized steel, Zn covers the majority of the steel surface, and these areas are protected by the
protective Zn corrosion products. When the corrosion product first forms, it loosely adheres to the Zn surface and is not very dense. However, due to the wetting and drying cycles of the weathering process, the corrosion product densifies and becomes more attached to the Zn surface. After the formation of this dense corrosion product layer, further corrosion of the Zn metal can only occur through pores of the corrosion product. The observed corrosion rate, $R$, can be expressed using equation 11 [7].

\[
R = \frac{ra}{A}
\]  

(11)

where $r$ is the actual corrosion rate on an active Zn metal assuming there is no protective corrosion product, $a$ is the area of active Zn surface, and $A$ is the area of the entire surface. Figure 2.1 shows a schematic of Zn corrosion product forming on a Zn surface, reducing the corrosion rate.

2.3 Lab exposure of Zn with NaCl

Sodium chloride (NaCl) is a well-known accelerator of the corrosion of zinc coatings and has been studied thoroughly worldwide. Ionic particles deposited on metal components can damage components and reduce the lifetime of a material. In countries such as Australia with a vast ocean coastline, salt aerosol particles ranging in size from 4-10 µm have been deposited on structures up to 10 km from the coast [9]. As a result, Zn degradation by salt aerosols is a large problem in Australia. The mechanism for salt deposition on surface structures is dependent on climate conditions and the physical and chemical state of the structure.
When the Zn surface is wet enough and there is a significant concentration of salt, Cl\textsuperscript{−} ions penetrate the zinc oxide layer, resulting in further oxidation of Zn. Dissolved oxygen diffuses through the moisture film and is reduced [9, 10]. The mechanism for Zn corrosion has been studied using a micro-particle of salt on a Zn surface. A hemispherical droplet forms when the salt is wetted by the humid air. A secondary spreading effect takes place on the surface, where the alkaline electrolyte extends to a radius 2-3 times greater than the original droplet size in a period of about 90 minutes. A high concentration of sodium ions (Na\textsuperscript{+}) can be found at the perimeters of both the original droplet and the secondary spreading region. The spreading stops when an insoluble carbonate salt forms at the perimeter of the secondary spreading region. The area containing the center of the original drop has a high concentration of Cl\textsuperscript{−}. This is where zinc hydroxychloride forms. The two half-cell reactions taking place inside the hemispherical droplets are the reduction of oxygen and the oxidation of Zn to Zn\textsuperscript{2+}. Due to the higher concentration of oxygen near the surface of the droplet, oxygen reduction takes place near the edges of the droplet while Zn oxidation occurs near the center of the droplet. The reduction and oxidation reactions are shown with the following equations.

\[
\begin{align*}
O_2 + 4e^- + 4H^+ & \rightarrow 2H_2O \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- 
\end{align*}
\]

The corrosion potential represents a mixed potential of both anodic and cathodic reactions [9]. The secondary spreading is the result of instability that occurs at the three phase (air, electrolyte, metal) boundary [11]. The instability is increased by a surface tension gradient, which causes liquid to flow to the instability boundary. High pH near
the droplet edge changes the surface tension of the electrolyte/metal interface, causing the electrolyte to spread outwards from the droplet.

In laboratory studies, the corrosion rate of zinc has been compared to steel in various conditions involving a humid NaCl spray [4]. Conditions that provided high corrosion of steel, but low zinc corrosion rates will receive the most benefit from galvanizing.

2.4 *Lab exposure of Zn with SO₂*

SO₂ is a well-known accelerator of Zn atmospheric corrosion. The exact mechanism for how SO₂ accelerates the corrosion rate for metals such as Zn and copper is not completely understood [12]. There are two theories on how SO₂ affects zinc corrosion. The more accepted theory involves the acidification of the electrolyte through hydration and oxidation of SO₂ to H₂SO₄ and the reduction of H⁺ to enhance Zn corrosion. Equations describing these reactions are shown below [6].

\[
SO₂ + H₂O \rightarrow H^+ + HSO₃^- \quad (14)
\]

\[
2SO₂ + O₂ + 2H₂O \rightarrow 4H^+ + 2SO₄^{2-} \quad (15)
\]

\[
Zn + 2H^+ \rightarrow Zn^{2+} + H₂ \quad (16)
\]

\[
Zn^{2+} + SO₃^{2-} \rightarrow ZnSO₃ \quad (17)
\]

Laboratory data and field exposures show a one-to-one stoichiometric relation between Zn²⁺ and SO₄²⁻ in the solution runoff [6, 13].

Another popular theory suggests that SO₂ acts directly as a cathodic depolarizer, shown by the reactions below [2].
This theory is supported by the observation that the reduction process of SO$_2$ is enhanced when a thin electrolyte layer is present.

It was once believed that the oxidation of SO$_2$ to SO$_4^{2-}$ decreased the local pH and caused the oxide layer to dissolve, leading to an increase in corrosion rate. However, during laboratory exposures, the reaction of SO$_2$ on Zn in the absence of oxidants produced zinc sulfites as the main reaction product, and the oxidation of these zinc sulfite layers to sulfate was slow [12]. The presence of SO$_2$ leads to dissolution of the protective passive layer and the formation of corrosion products with high water solubility [2]. New sulfur-containing corrosion products easily dissolve and do not protect the Zn substrate, leading to higher corrosion rates. SO$_2$ will easily dissolve in water to form H$_2$SO$_3$. If the SO$_2$ concentration in air were 0.1%, the equilibrium H$_2$SO$_3$ concentration would be 1.6 x $10^{-3}$ M resulting in an acidic pH of 2.8 [4].

Ambient atmospheric concentrations of SO$_2$ (in the ppb range) have been studied, showing that the deposition of SO$_2$ is highly dependent on relative humidity and that the four-valent sulfur is relatively stable on the Zn surface [3]. In the presence of NaCl, SO$_2$ is oxidized to SO$_4^{2-}$. Studies show that sulfate forms in electrolyte droplets containing NaCl and that sulfites are dominant in areas outside of the droplet. Oxidation of dissolved SO$_2$ is shown in equation 21 below.
where \( n \) varies from 0-2 depending on the pH of the electrolyte. Additionally, solid surfaces such as ZnO may also act as effective heterogeneous catalysts for sulfite oxidation [12]. However, when just 250 ppb SO\(_2\) is combined with NaCl there is no secondary spreading effect due to the acidification of the electrolyte. Therefore the corrosion rate will initially increase in the presence of SO\(_2\), but over a longer time period the corrosion rate will decrease due to the lack of the secondary spreading effect, which limits surface area for oxygen reduction [12].

2.5 Synergetic effects of O\(_3\) & NO\(_2\) on SO\(_2\)

By itself, nitrogen dioxide (NO\(_2\)) does not affect the corrosion rate of Zn [2]. However, when NO\(_2\) is coupled with SO\(_2\), the corrosion rate increases. In an experiment containing 225 ppb SO\(_2\) and 400 ppb NO\(_2\), the corrosion rate increased more than 4 times compared to SO\(_2\) alone [2]. Likewise, when 225 ppb SO\(_2\) was mixed with 400 ppb ozone (O\(_3\)), the corrosion rate increased by more than 4 times compared to exposure with SO\(_2\) only. The combination of SO\(_2\) and NO\(_2\) produces a higher corrosion rate than the corrosion rate in the corresponding single-pollutant exposures. The combination of SO\(_2\) and O\(_3\) produces even greater acceleration of corrosion. The corrosion rate of Zn samples exposed to the combination of SO\(_2\) and O\(_3\) is more than 3 times greater than in the absence of O\(_3\). However, the synergetic effect of O\(_3\) and NO\(_2\) with SO\(_2\) does not occur at a relative humidity below 70\%. This synergetic effect is attributed to the fact that both O\(_3\) and NO\(_2\) increase the deposition rate of SO\(_2\) and the oxidation of SO\(_2\) on the Zn surface.
Both mass loss and weight gain data show that the synergetic effect of these gases on the corrosion rate of Zn is greater for 95% relative humidity than 70% relative humidity. This is due to the oxidation of IV-valent sulfur (S(IV)) in the electrolyte [2, 3]. These results suggest that NO₂ and O₃ may be important factors in the atmospheric corrosion of Zn.

The accelerated effects of O₃ on the deposition rate of SO₂ on Zn increases as SO₂ concentration decreases. It is suggested that this is due to the positive pH dependence of the oxidation of the S(IV) by ozone to S(VI) [3].

Corrosion products formed from laboratory exposure of Zn with SO₂ and NO₂ include zinc hydroxides, zinc carbonate, zinc oxide, zinc sulfates, and water-soluble nitrates [2]. In the presence of NO₂, nitrates and nitrites were found in the water rinse. It has been depicted that nitrites dominate over nitrates, suggesting that nitrate electrochemically reduces to nitrite. Others believe that dissolved NO₂ only reduces to nitrite in the presence of chlorides [2].

2.6 Lab exposure of Zn with CO₂

Another important gas in the atmosphere to Zn corrosion is CO₂, which has an ambient concentration of about 350 ppm. In the presence of CO₂, Zn₄CO₃(OH)₆ ·H₂O, Na₂CO₃ and hydrozincite (Zn₅(CO₃)₂(OH)₆) will form, but hydrozincite will only form at high concentrations of CO₂ [14]. When NaCl is present, CO₂ decreases the zinc corrosion rate. CO₂ inhibits the NaCl-induced corrosion of Zn by decreasing the rate of the secondary spreading described earlier. Linstrom reported that the secondary spreading on Zn is 3-4 times smaller at 22 °C when ambient CO₂ concentrations are present as opposed to low CO₂ concentrations [12, 15]. On the other hand, Falk showed that when NaCl is
not present, CO₂ enhances the corrosion rate of Zn slightly due to the acidification of the surface electrolyte, which enhances the dissolution of the oxide layer [12, 14]. A schematic of Zn corrosion with low CO₂ and high CO₂ concentrations is shown in Figure 2.2 [8].

2.7 Photocorrosion of zinc

Photons in the ultraviolet region, which spans from 100-400 nm, have energy levels that are able to interact with corrosion products, usually oxides and photosensitive gases such as O₃ and NO₂ [16]. ZnO has been used in the production of paints for its thermal and optical properties, and is used in devices such as varsitors and photocopiers for its unique set of electronic and photoelectronic properties [4]. ZnO has a structure in which oxygen and Zn atoms are arranged in a hexagonal close-packed lattice. When ZnO, in contact with electrolyte, is under illumination, a photocurrent can be measured if the potential is controlled. This photocurrent is the result in a change in the concentration of the electron and holes at the ZnO surface. The concentrations of electrons and holes can be calculated using the equation below [4].

\[ n = n_o \exp\left(\frac{eV}{kT}\right) \]  
\[ p = p_o \exp\left(-\frac{eV}{kT}\right) \]

Where \( n \) and \( p \) are the concentration of electrons and holes respectively, \( n_o \) and \( p_o \) are the initial concentration of electrons and holes respectively, \( eV \) is the energy of the band gap, \( k \) is the Boltzmann Constant, and \( T \) is temperature. Since ZnO is an n-type superconductor, the concentration of the majority carrier, \( n \), will not be much different
from $n_o$ when under illumination because the number of electrons generated will be small compared to $n_o$. On the other hand, the minority carrier, $p$, can increase by orders of magnitude under illumination. This increases the concentration of holes at the surface, increasing the rate of oxidation of Zn.

It has been shown that the measured photocurrent for ZnO in pH 3 solution increases with increasing anodic potential [4]. As the anodic potential increases, the number of holes generated also increases. However, after a critical potential is reached, the current remains constant and does not increase with potential. This is due to the photo-generated holes being consumed by anodic reactions at the surface [4].

It has been shown that UV light has the potential to double the corrosion rate of Zn immersed in a flowing water stream [17, 18]. Burleigh proposed that UV light accelerates the flow of electrons from the surface film to the electrolyte interface and accelerates oxygen reduction, which increases the Zn pitting corrosion rate. Thompson exposed different zinc alloys in flowing running water to UV light for four months and measured the corrosion rate using weight loss and made a correlation between flat band potential and corrosion rate [17, 18]. In these results, UV light increased the corrosion rate of most of the Zn alloys slightly with the greatest increase seen in pure Zn.

2.8 Effect of alloy composition

The effect of alloy composition on the corrosion rate of Zn is of interest in regards to producing better resistant alloy coatings and passivation systems. Some alloying elements may be advantageous in one environment but harmful in another [7]. For example, the addition of 0.82% Cu increased the corrosion resistance by 20% in a two
year exposure to an industrial environment. However, this alloy is more susceptible to pitting corrosion than unalloyed Zn. Small additions of Al (< 0.3%) significantly decrease the atmospheric corrosion resistance of Zn. However, larger Al additions (> 1.0%) increase the corrosion resistance of Zn. This has led to the development of alloys such as Galfan (95Zn-5Al) and Galvalume (55Al-43.5Zn-1.5Si) coatings. Galfan is in general twice as corrosion resistant as galvanized while Galvalume is 2-4 times as corrosion resistant as galvanized, depending on the environment [7].

The drawbacks of pure Zn coatings are inadequate resistance to high temperature and limited lifetime in corrosively aggressive environments [19]. It has been reported that steel coated with 0.3 kg of Zn will rust in less than 6 years in the marine environment of Sandy Hook, NJ, and less than 3 years in the industrial environment of Altoona, PA [19]. Aluminum coated steels provide better passivation than Zn for atmospheric and high temperature application. However, aluminum coatings must be 1 mil thicker than Zn coatings. Drawbacks for aluminum coatings include recrystallization and soft working of steel when exposed to temperatures above the melting point of aluminum. Hot dipped aluminum limits the maximum strength that can be achieved by the steel [19]. The corrosion resistances of hot-dipped aluminum-zinc alloy system have been studied. Using salt spray tests, according to ASTM specifications, it was determined that galvalume coatings have the best corrosion resistance compared to other aluminum-zinc alloys. Galvalume is expected to last 2-4 times as long as galvanized steel in most environments and is more resistant than pure aluminum coatings at rust stain edges. Experiments were carried out in rural, marine, and industrial environments for aluminum-zinc alloys ranging in composition from 0-70 weight percent aluminum [19].
2.9 Experimental methods

Experimental methods for quantifying the corrosion rate of Zn include mass loss and mass gain techniques [3]. Corroded samples were first immersed in water for about 2 minutes to remove water-soluble corrosion products, and the rinse water was analyzed by ion chromatography. The samples were then treated in saturated ammonium acetate solute on for 1 minute. Ultrasonic agitation was used in all steps in the pickling procedure. The metal loss during the corrosion product removal was determined and corrected for by exposing an uncorroded sample to the same procedure.

Corrosion products found in aqueous electrolytes were identified using Fourier transform infra-red (FTIR) microspectroscopy. The spectra obtained from FTIR microspectroscopy were then compared with those obtained from reference compounds in literature. A video camera, along with optical and Scanning Electron Microscope (SEM) images were taken to verify the effect of each gas on secondary spreading [12]. Using a Scanning Kelvin Probe, potential maps have been created showing the secondary spreading effect of NaCl. This technique shows that the secondary spreading produces a potential drop from -450 to -50 mV_{SHE}. The central area of the droplet where zinc hydroxychloride is formed shifts from -550 to -400 mV. The change in potential suggests that significant chemical changes occur in the cathodic region [9].

When Zn is exposed to acidic environments, an optical profilometer can be used to measure the volume loss, which can be used to calculate a corrosion rate. Crystalline corrosion products can be identified with x-ray diffraction (XRD) techniques, and amorphous corrosion products are identified using raman spectroscopy and FTIR. SEM
and energy dispersion spectroscopy (EDS) are used to identify the morphology and elemental analysis of the surface [20].

2.10 Critical unresolved issues

Critical unresolved issues include the effects of NH₃ on the SO₂-induced corrosion of Zn in the presence of UV light and Cl⁻ ions. NH₃ is a basic, highly water soluble atmospheric gas that is produced in natural ecosystems, agricultural industries, synthetic fertilizers, and through the burning of biomass [1]. It has been suggested that NH₃ may negate the accelerating effects of SO₂ due to the production of hydroxide ions. When NH₃ is absorbed into the electrolyte, the solution will become more alkaline and can potentially react with the hydrogen ions produced from the oxidation of SO₂. Thus, the balance between acid and alkali aerosols needs to be considered in estimating the Zn corrosion rate[21]. Ammonia reacts with SO₂ in an aerated environment by the following equations at room temperature [22, 23].

\[ NH_3(g) + SO_2(g) \rightarrow (NH_3 \cdot SO_2)_g \]  \hspace{1cm} (2)

\[ NH_3 \cdot SO_2(g) + NH_3(g) \rightarrow (NH_3)_2SO_2(s) \]  \hspace{1cm} (3)

\[ nNH_3 \cdot SO_2(g) \rightarrow (NH_3 \cdot SO_2)_n(s) \]  \hspace{1cm} (3)

If oxygen and humid air are present, these salts can be oxidized by the reactions below.

\[ (NH_3)_2SO_2(s) + \frac{1}{2}O_2(g) \rightarrow (NH_4)_2SO_3NH_2(s) \]  \hspace{1cm} (4)

\[ (NH_4)_2SO_3NH_2(s) + H_2O(g) \rightarrow (NH_4)_2SO_4(s) \]  \hspace{1cm} (5)
Since oxygen is present it is likely that the final reaction product is an ammonia sulfate salt.

However, when NH$_3$ is exposed to UV light in the presence of Cl$^-$ ions, NH$_3$ can photooxidize, which leads to the production of protons [24]. If this is the case, then the oxidation of NH$_3$ will actually increase the corrosion rate of Zn.

Another area of interest of Zn atmospheric corrosion that has not been thoroughly invested is that of aerosol particulates [1]. Aerosols, small liquid or solid particles suspended in air, can vary in size, with smaller particles less than 1 µm in diameter. These small particles are formed by the condensation of low volatile gases. Ammonium sulfate ((NH$_4$)$_2$SO$_4$) is a common aerosol particle that can form when NH$_3$ interacts with oxidized SO$_2$ in the presence of water vapor. These aerosols can deposit onto the metal surface and dissolve into the aqueous layer on the metal surface forming an aggressive electrolyte. Deposition rate of aerosols varies depending on particle size. Under dry deposition, smaller particles will behave like gases and diffuse to the metal surface, whereas larger particles will be at the mercy of the air and wind direction. During wet deposition, the particles are absorbed by rain or water vapor before depositing onto the metal surface. Once absorbed onto the metal surface, the aerosols such as ammonium sulfate can deliquesce and form a concentrated aqueous solution on the Zn surface [1].

In addition, the effects on Zn exposed to NO$_2$ with ozone and UV light have not been thoroughly investigated. It is possible that this combination of exposures could increase the corrosion rate by producing nitric acid (HNO$_3$). It is known that ozone photodissociated by UV light will produce atomic oxygen. This atomic oxygen can react
with water molecules to produce hydroxyl radicals ($OH \cdot$). These hydroxyl radicals have the potential to react with NO$_2$ in the vapor phase to produce nitric acid (HNO$_3$). Unlike NO$_2$, nitric acid is highly water soluble and has great potential to increase the corrosion rate of Zn [1].
2.11 Tables and figures

Table 2.1 Typical corrosion rates for zinc in a given environment with the middle to lower range being the most probable [4, 6, 7]

<table>
<thead>
<tr>
<th>Environment of Exposure</th>
<th>Corrosion Rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural</td>
<td>0.2-3</td>
</tr>
<tr>
<td>Urban</td>
<td>2-16</td>
</tr>
<tr>
<td>Industrial</td>
<td>2-16</td>
</tr>
<tr>
<td>Marine</td>
<td>0.5-8</td>
</tr>
</tbody>
</table>
Table 2.2 Average corrosion loss in μm/yr of Zn coatings on buildings in various locations and atmospheric environments after 10 years [4].

<table>
<thead>
<tr>
<th>Location</th>
<th>Environment</th>
<th>Roof</th>
<th>Wall</th>
<th>Roof</th>
<th>Wall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zinc</td>
<td>55% Al-Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inland</strong></td>
<td>Rural</td>
<td>0.42</td>
<td>0.17</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>1.48</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>1.4</td>
<td>0.56</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Severe</td>
<td>1.59</td>
<td>0.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inland, shore of lake or marsh</strong></td>
<td>Rural</td>
<td>0.59</td>
<td>0.24</td>
<td>0.20</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>1.97</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>1.4</td>
<td>0.56</td>
<td>0.20</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Severe</td>
<td>2.12</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Coast</strong></td>
<td>Rural</td>
<td>0.74</td>
<td>0.29</td>
<td>0.25</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Urban industrial</td>
<td>2.47</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Severe</td>
<td>2.65</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Seashore</strong></td>
<td>Severe</td>
<td>2.06</td>
<td>0.82</td>
<td>0.46</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.1. Schematic of protective corrosion product formed on Zn coating. Further corrosion can only take place on the active Zn surface, which is the bare Zn surface or through the pores of corrosion product [4].
Figure 2.2. Effect of CO₂ on the secondary spreading effect on Zn in the presence of a droplet of dissolved NaCl [11]. Reprinted from Chen et al with permission from Elsevier.
2.12 References


Chapter 3: Experimental Procedure

3.1 Sample preparation

Chamber 1

Pure Zn foil (99.9+%) containing approximately 11 ppm Cu and 11 ppm Cd from Strem Chemicals was used in all experiments. The samples were cut into 2 cm x 2 cm x 1.5 mm coupons and each side of the coupon was sequentially ground with 320, and 600 grit papers. One of the faces of the each sample was ground with 800 and then 1200 grit paper using an ethanol based lubricant. The samples were then ultrasonicated in ethanol for 5 min, dried with compressed air, and stored in a desiccator until exposure. The samples were then weighed and the dimensions of the samples were measured. Next the samples were loaded with NaCl by fast evaporation of an ethanol/NaCl solution. The solution was prepared using two steps. First NaCl was dissolved in DI water to make a 1.67 wt% NaCl solution, and then it was diluted with pure ethanol to reach a desired concentration of 1333 µg/mL. The solution was then heated to near boiling temperature and 150 µL of the hot NaCl\ethanol solution was transferred onto the sample surface using a micropipette. Heating the NaCl\ethanol solution prior to transfer prevented droplet formation and led to a uniform distribution of NaCl on the surface. If the solution...
volume decreased due to evaporation during the heating process, more ethanol was added to keep the salt concentration constant. The coupons were then immediately placed in a vacuum pump desiccator to remove the ethanol and evenly deposit NaCl onto the surface. This led to 50 µg/cm² NaCl deposited onto the samples as shown by the calculation below.

\[
\frac{\text{Mass}}{\text{Volume}} \times \frac{\text{Volume}}{\text{Surface area}} = \frac{\text{Mass}}{\text{Surface area}}
\]

\[
\frac{1333 \mu g \text{ NaCl}}{L \text{ (solution)}} \times \frac{1 L}{1000 \mu L} \times \frac{150 \mu L}{4 \text{ cm}^2} = \frac{50 \mu g}{\text{cm}^2 \text{NaCl}}
\]

The ethanol solution evaporated after 6 min, but the samples remained in the vacuum desiccator for a total time of 20 min to ensure that the samples were completely dry.

**Chamber 2**

Zn samples were sequentially ground with 320 and 600 grit papers, and were deposited with 50 µg/cm² NaCl using the same method as described earlier. The UV intensity at the top of the quartz window for chamber 2 was measured to be 6.03 mW/cm². The ratio between dry and wet air was adjusted in order to vary the RH from 30 to ~100 % RH.

**3.2 Laboratory exposure of Zn**

Two custom made environmental chambers were used for exposures of polished Zn coupons as shown in Figure 3.1 and Figure 3.2. Table 3.1 shows the experimental test matrix with concentrations of SO₂, NH₃, and O₃ exiting the chamber. Permeation tubes
from VICI Metronics Inc. were used to produce environments containing SO\textsubscript{2} and NH\textsubscript{3}. The sulfur dioxide tube had a specified permeation rate of 518 ng/min ±5 % while the ammonia permeation tube had a specified permeation rate of 209 ng/min ±5 %. The total flowrate entering the test chamber was 450 cc/min. At this flow rate, the measured SO\textsubscript{2} and NH\textsubscript{3} concentrations exiting the chamber were about 120 and 550 ppb, respectively, as shown in Figure 3.3. Dry air was used as the carrier gas for SO\textsubscript{2} and NH\textsubscript{3} entering the test chamber, while ozone was produced using an ozone generator with pure oxygen as the inlet gas and carrier. The ratio of wet to dry air was adjusted to control the RH in the chamber.

For each exposure condition, the samples were exposed for 3 days. The UV intensity at the top of the quartz windows of the exposure chambers was measured with a UV radiometer (UVP LLC.) and found to be 22.6 and 6.03 mW/cm\textsuperscript{2} for chambers 1 and 2, respectively. The two UV lamps used produced their maximum light intensities at 254 nm. Table 3.2 shows a comparison of lab concentrations and intensities to some field data [2, 6, 27, 28]. Figure 3.4 and Figure 3.5 show UV intensities measured by NSF UV Monitoring Network at noon in San Diego, California and Barrow, Alaska [27]. All experiments were carried out at room temperature and each condition was conducted at least twice. After exposure, each sample was rinsed with DI water for 5 seconds to remove any unreacted NaCl, then briefly with rinsed with ethanol, air dried, and stored in a desiccator until removal of corrosion product. After the samples were completely dry, corrosion products were identified with X-ray diffraction (XRD), and infrared absorption
spectroscopy (FTIR). SEM and EDS were used to determine the morphology and composition of corrosion products.

3.3 Corrosion rate quantification

The corrosion rate was determined by measuring the mass of the samples before NaCl deposition and after the removal of corrosion product. The corrosion after exposure was practically uniform due to the uniform deposition of NaCl. The balance used had a precision of 0.01 mg with an accuracy of \( \pm 0.2 \) mg, which allowed corrosion rates as close as 0.02mg/cm\(^2\) to be differentiated. After the exposed samples were analyzed with XRD, SEM, and EDS, the corrosion product was removed using two different methods. The first set of samples was immersed in a 2 M HCl solution with an organic corrosion inhibitor (0.09 wt% acridine orange) for 40 seconds while undergoing ultrasonic agitation. Using this method, about half the total mass loss was due to attack of the Zn metal. Therefore a better method was sought.

The second set of samples was immersed in boiling solution of 0.5 M CrO\(_3\) + 0.06 M AgNO\(_3\) for 5 minutes. Figure 3.6 and Figure 3.7 plot the effects of repetitive cleaning cycles on mass loss using both techniques. The data shows that for the samples immersed in the boiling chromic acid solution, most of the corrosion product is removed after 20 s. After 20 s the mass loss begins to plateau, signifying that the solution is inhibiting attack on the Zn substrate and that the rate of corrosion product removal is much greater than the rate of attack to the Zn metal. On the other hand, Figure 3.6 shows that HCl solution with Acridine Orange is significantly attacking the Zn metal and that a large portion of the mass loss is due to the attack on the Zn and not the removal of corrosion product.
The mass loss of the Zn was accounted for by immersing five unexposed Zn coupons into the acid solutions and recording the mass loss. The average mass loss after 5 min immersion in the chromic acid solution was 0.0132 mg/cm² with a standard deviation of 0.0054 mg/cm², while the average mass loss after 40 s immersion in the HCl solution was 0.597 mg/cm² with a standard deviation of 0.026 mg/cm². These mass losses from unexposed Zn samples were used to correct the corrosion rate obtained after removal of the corroded samples. The corrosion rate was calculated using the equation 1.

\[ R = \frac{(M_{b1}-M_{a1})}{A_1 t} - \frac{(M_{b2}-M_{a2})}{A_2 t} \]  

where R is the corrosion rate, \( M_{a1} \) is the mass after exposure, \( M_{b1} \) is the mass before exposure, \( M_{a2} \) is the mass of an uncorroded Zn sample after immersion into the acid solution, \( M_{b2} \) is the mass of an uncorded sample before being immersed in acid, \( A_1 \) is area of the top face where the corrosion has taking place, \( A_2 \) is the total surface area of the sample, and \( t \) is the duration of the exposure.

### 3.4 Qualitative surface pH analysis

In order to determine the effects of NH₃ and SO₂ on pH of the surface electrolyte, a gel electrolyte with pH indicator was used. The gel was made by bringing a 0.01 M NaCl solution to a boil. 1.5 wt% agar was then dissolved in the boiling salt solution and fully dissolved after 3 minutes. The temperature was reduced and while the solution was hot (not boiling) 15 vol% Fisher Universal pH indicator was added. A micropipette was used to transfer 400 µL of the hot liquid solution onto the Zn surface and onto glass slides where they were allowed to gel for 5 minutes and then were put into the exposure
chamber at 70% RH. After 16 h exposure to 120 ppb SO₂, the gel on the Zn and on the glass turned orange. After 16 h exposure to 550 ppb NH₃, the gel turned dark green with some areas turning bright purple. The gel was then transferred to 4 locations on a glass plate, and buffered pH 4, 6, 8, and 10 solutions were added to the gels to make a color Key. Figure 3.8 shows the gel color key and the gel electrolyte before exposure and after exposure to NH₃ and SO₂.
3.5 Tables and figures

Table 3.1. Experimental test matrix showing concentrations of each constituent in the test chamber after 3 days at 70% RH.

<table>
<thead>
<tr>
<th>Exposure Condition</th>
<th>Dark (50µg/cm²)</th>
<th>UV (254nm)</th>
<th>Ozone (400 ppb) &amp; UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (50µg/cm²)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaCl + SO₂</td>
<td>120 ppb (SO₂)</td>
<td>120 ppb (SO₂)</td>
<td>120 ppb (SO₂)</td>
</tr>
<tr>
<td>NaCl + NH₃</td>
<td>500 ppb (NH₃)</td>
<td>500 ppb (NH₃)</td>
<td>500 ppb (NH₃)</td>
</tr>
<tr>
<td>NaCl + SO₂ + NH₃</td>
<td>100 ppb (SO₂)</td>
<td>100 ppb (SO₂)</td>
<td>100 ppb (SO₂)</td>
</tr>
<tr>
<td></td>
<td>500 ppb (NH₃)</td>
<td>500 ppb (NH₃)</td>
<td>500 ppb (NH₃)</td>
</tr>
</tbody>
</table>

Table 3.2. Comparison of lab vs field exposure constituent concentrations and intensities [2, 6, 27, 28].

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Lab concentration</th>
<th>Typical Peak concentrations</th>
<th>Average concentration</th>
<th>Henry's law const (M/atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>120 ppb</td>
<td>20-200 ppb</td>
<td>1-70 ppb</td>
<td>1.2</td>
</tr>
<tr>
<td>NH₃</td>
<td>500 ppb</td>
<td>-</td>
<td>5-15 ppb</td>
<td>62</td>
</tr>
<tr>
<td>O₃</td>
<td>650 ppb</td>
<td>100-200 ppb</td>
<td>4-40 ppb</td>
<td>0.012</td>
</tr>
<tr>
<td>UV Intensity @ noon (San Diego/Barrow)</td>
<td>22.6 mWcm⁻²</td>
<td>6.4/3.8 mWcm⁻</td>
<td>4.7/1.9 mWcm⁻</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.1. Schematic of homebuilt exposure chamber 1
Figure 3.2. Images of homebuilt exposure chamber 1.
Figure 3.3. Reading of gas detector tubes after exposure to air at 70% RH and a) 550 ppb NH$_3$, and b) 120 ppb SO$_2$. 
Figure 3.4. Power density of UV light (290nm-400nm) measured at noon in San Diego, California from 2019-2014 [27].

UV data from San Diego, California was provided by the NSF UV Monitoring Network, operated by Biospherical Instruments Inc. and funded by the U.S. National Science Foundation's Office of Polar Programs
Figure 3.5. Power density of UV light (290nm-400nm) measured at noon in Barrow, Alaska from 2019-2014 [27].

UV data from Barrow, Alaska was provided by the NSF UV Monitoring Network, operated by Biospherical Instruments Inc. and funded by the U.S. National Science Foundation's Office of Polar Programs.
Figure 3.6. Mass loss of corroded Zn resulting from repetitive cleaning with 2 M HCl and 0.09 wt% Acridine Orange.
Figure 3.7. Mass loss of corroded Zn resulting from repetitive cleaning with a solution of boiling 0.5 M CrO$_3$ and 0.06 M AgNO$_3$. 
Figure 3.8. Top image is the gel electrolyte with pH indicator onto a polished Zn sample, while the bottom image shows the gel electrolyte on glass before exposure.
3.6 References


3. Programs, N.S.F.s.O.o.P., *UV Monitoring Network, operated by Biospherical Instruments Inc. and funded by the U.S. National Science Foundation’s Office of Polar Programs*.

Chapter 4: Results and Discussion

The lifetime of Zn protective coatings is dependent on many environmental factors such as [Cl\textsuperscript{-}], [SO\textsubscript{2}], time of wetness, and pH. However, the atmosphere is composed of other constituents that have not been thoroughly investigated but could impact the Zn corrosion rate. This work addresses the effects of UV light, O\textsubscript{3}, SO\textsubscript{2}, and NH\textsubscript{3} on the Zn corrosion rate.

4.1 Deposition of NaCl

NaCl was deposited onto all samples prior to exposure to accelerate the corrosion rate. Figure 4.1a shows optical images of samples immediately after the deposition of 50 µg/cm\textsuperscript{2} of NaCl. The images show uniform distribution of NaCl particles with sizes around 20-70 µm. Samples deposited with 100 µg/cm\textsuperscript{2} of NaCl, Figure 4.1b produced larger particle sizes on average with some exceeding 100 µm. Figure 4.2 shows that initial corrosion took place on the Zn surface surrounding the NaCl particles. EDS results show that the initial corrosion product that formed surrounding the NaCl particles was predominately composed of Zn and Cl, which is likely ZnCl\textsubscript{2}. 
4.2 Identification of corrosion products

Corrosion products were investigated with XRD, FTIR, SEM and EDS after exposure. Samples were stored in a dedicater over night to ensure that the samples were dry. It is possible that irreversible crystallization of some of the corrosion occurred during the drying process. Pure Zn samples exposed to UV light and O$_3$ at 99% RH for 16 h without the presence of NaCl on the surface produced no visible amount of corrosion product. The polished Zn surface remained shiny. However, Zn exposed to these same conditions for 16 h but with NaCl on the surface formed visible corrosion product, which was analyzed with XRD and FTIR. This analysis showed that, regardless of the presence of SO$_2$, NH$_3$, UV, and/or O$_3$ in addition to NaCl, the type of corrosion product produced on the surface remained the same after 16 h exposure. XRD indicated the presence of crystalline Zn, ZnO, and simonkolleite ($\text{Zn}_5\text{(OH)}_8\text{Cl}_2\cdot\text{H}_2\text{O}$) on the surface following each exposure condition. FTIR identified strong peaks for amorphous hydrozincite ($\text{Zn}_5\text{(CO}_3)_2\text{(OH)}_6$) at 1380 cm$^{-1}$ and 1510 cm$^{-1}$, simonkolleite at 3450 cm$^{-1}$ and weak peaks for zincite (ZnO) between 350-600 cm$^{-1}$.

Because exposure for 16 h at 99% RH revealed the same type of corrosion product regardless of the presence of SO$_2$, NH$_3$, UV, or O$_3$, the experiments were repeated with an increased exposure duration of 3 days and a decrease in RH to 70%. The relative humidity was decreased to increase the SO$_2$ and NH$_3$ equilibrium vapor pressures. The corrosion products were then analyzed as before with XRD, FTIR, SEM, and EDS. Simonkolleite, zinc oxide, and zinc carbonate were present after each exposure condition. However, other products were also observed. After exposure with 120 ppb SO$_2$, NaCl, and
UV, XRD showed the formation of zinc hydroxy sulfate \((\text{Zn}^2\text{O}\text{H}_2\text{O})_3(\text{ZnSO}_4\cdot\text{H}_2\text{O})\), gordaite \((\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl}\cdot6\text{H}_2\text{O})\), and zinc hydroxide nitrate \((\text{Zn}^2\text{O}\text{H})\text{NO}_3\). These sulfate compounds are typically found on zinc components in industrial environments [1-4]. Exposure environments containing 500 ppb NH\(_3\) and NaCl led to additional production of zinc hydroxide nitrate. The combination of SO\(_2\) and NH\(_3\) led to the production of zinc hydroxide nitrate and both sulfates, gordaite and zinc hydroxy sulfate.

The corrosion products that were identified are summarized in Table 4.1 and Table 4.2.

The presence of UV and 650 ppb O\(_3\) did not change the composition of the corrosion products identified after exposure for given conditions of SO\(_2\) and NH\(_3\), but they influenced the relative amounts of the various corrosion products formed on the surface. For samples containing only NaCl, the presence of UV increased the relative amount of simonkolleite formed on the surface, but the addition of ozone led to a decrease in simonkolleite. UV and O\(_3\) both led to an increase in the zinc hydroxy sulfate and gordaite found on the Zn surface when SO\(_2\) was present. Gordaite was only detected with XRD after exposure with UV. UV and O\(_3\) both accelerated the production of Zn corrosion product. Figure 4.3 and Figure 4.4 show that UV light accelerates the formation of crystalline sulfate containing corrosion product.

### 4.3 Effect of NaCl

This study shows that the presence of NaCl had a great influence on zinc corrosion by increasing the Zn corrosion rate, and leading to the formation of simonkolleite. Deposited NaCl also absorbs water from the atmosphere and increases the rate of formation of an electrolyte layer [4]. Dissolved NaCl increases the conductivity of the
electrolyte creating a more aggressive environment for Zn. The anodic and cathodic reactions taking place are the dissolution of Zn and the reduction of oxygen [4, 5].

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O
\]  

(1)

\[
Zn \rightarrow Zn^{2+} + 2e^-
\]  

(2)

Anions such as Cl\(^-\) migrate to anodic sites on the surface while cations like Na\(^+\) migrate to the cathodic sites. The simonkolleite forms by equation 3 at the anodic sites on the surface where the concentrations of Zn\(^{2+}\) and Cl\(^-\) are relatively high [4].

\[
4ZnO + Zn^{2+} + 5H_2O + 2Cl^- \rightarrow Zn_5(OH)_6Cl_2 \cdot H_2O
\]  

(3)

This is in agreement with the stability diagram in Figure 4.5. Here simonkolleite is more thermodynamically stable near neutral pH and high [Cl\(^-\)] [4]. ZnO forms near the cathodic sites on the surface where the pH is high and [Cl\(^-\)] is low. The formation of insoluble products such as ZnO and simonkolleite blocks anodic sites and hinders the diffusion of oxygen to the surface, which lowers the Zn corrosion rate. Figure 4.6 shows an SEM image of simonkolleite formed on the surface after a 3 day exposure to 120 ppb SO\(_2\), and air containing an ambient CO\(_2\) concentration at 70 % RH. Because the RH was controlled at 70%, which is below the deliquescence point for NaCl, simonkolleite primarily formed at the location of the NaCl particle, where [Cl\(^-\)] was the highest. If the RH were controlled above 75 %, a NaCl solution would have formed on the surface increasing the mobility of Cl\(^-\). This likely would have led to more formation of simonkolleite in areas away from the NaCl particles. Sulfate compounds formed in the
areas farther from the NaCl particle where the [Cl\textsuperscript{-}] was low. Figure 4.5 shows how as [Cl\textsuperscript{-}] increases, the stability of sulfates decreases [6, 7].

Although the RH was below the deliquescence RH for NaCl, a small amount of NaCl can dissolve because, even at 70 % RH, an equilibrium water film that is a few nm thick exists on the surface [8]. Part of the NaCl particle will dissolve in this water film until it is saturated. This film allows the mobility of ions on the surface, and thus provides an electrolyte for corrosion to occur.

### 4.4 Effects of relative humidity and UV

Relative humidity has a large impact on the Zn corrosion rate in the presence of NaCl. In general, the Zn corrosion rate was found to increase with increasing RH, but a relatively large increase in corrosion rate was observed at RH values above 70%, as shown in Figure 4.7. This is due to the deliquescence of NaCl, which occurs at the critical humidity of 75.3% [6].

In the presence of 50 µg/cm\textsuperscript{2} of NaCl, UV light (6.03 mW/cm\textsuperscript{2}) increased the average corrosion rate of Zn at RH values above 90% RH, as shown in Figure 4.7. However, the average corrosion rate of Zn decreased in the presence of UV light below 90% RH. This is contrary to what has been shown in bulk solution where UV light accelerates the corrosion rate of Zn [9, 10]. The corrosion product that forms, ZnO, is an n-type semiconductor with a band gap of 3.2 eV [9, 11]. ZnO absorbs light with a wavelength less than 370 nm. The absorbed light creates electron/hole pairs that can diffuse to the surface if they do not recombine first. The generated electron and hole may
diffuse to the surface of the oxide and participate in redox reactions [11]. Equation 2 can be rewritten as:

\[ 
Zn + 2h^+ \rightarrow Zn^{2+} 
\]  

\[ 
2H^+ + 2e^- \rightarrow H_2 
\]

where \( h^+ \) are holes participating in the oxidation of Zn, and the electrons at the surface can participate in the hydrogen and oxygen reduction reactions. Equations 5 and 1 are the hydrogen and oxygen reduction reactions occurring on the surface. Under illumination, the concentration of the minority carrier, holes, will increase by orders of magnitude resulting in an increase of the anodic reaction rate at the surface and an increase in the overall corrosion rate. Figure 4.8 schematically shows that when UV light is absorbed, an electron is excited from the valence band into the conduction band, generating an electron/hole pair. The generated electrons and holes can diffuse to the surface of the oxide to participate in redox reactions if they do not recombine first [11].

Under atmospheric conditions, the adsorbed water layer on the surface plays a critical role in Zn corrosion by changing the surface conditions. At about 30% RH, the adsorbed water layer is not continuous and consists of clusters of about 10 water molecules with a thickness of about 2 to 3 monolayers [3, 12]. Therefore, a large portion of the surface is not covered by electrolyte. On the other hand, at 70% RH, a continuous water film, about 5-6 monolayers of water, covers the surface. In addition, the presence of NaCl particles attracts water vapor from the humid air and assists in the formation of
aqueous water layer surrounding the particles. The electrolyte layer is only about 1-2 nm thick at 70\% RH [12].

The Zn corrosion rate after a 3 day exposure to air at 70 \% RH and NaCl was measured as 0.08 mg/cm$^2$day. This would lead to an effective [Zn$^{2+}$] of 0.028 M on the Zn surface after 1 second of exposure assuming an average electrolyte thickness of 5 nm and if none of the ions reacted further. The high [Zn$^{2+}$] on the surface allows for protective insoluble ZnO and Zn(OH)$_2$ to form by the reaction below.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

The [Zn$^{2+}$] and [OH$^-$] are orders of magnitude higher on a corroding Zn surface at 70\% RH compared to Zn corroding in bulk solution. The high [Zn$^{2+}$] increases the probability of the formation of a protective oxide film. The effect of [Zn$^{2+}$] and [OH$^-$] on the stability diagram of Zn were investigated using OLI aqueous electrolyte solution software. Figure 4.9 shows that for Zn corroding in bulk solution, where the [Zn$^{2+}$] is around 10$^{-6}$ M, aqueous corrosion product will be thermodynamically favorable. However, if the [Zn$^{2+}$] is increased, as is expected for the thin layer expected in atmospheric conditions, an insoluble corrosion product will form that will protect the Zn surface. Therefore UV light inhibits corrosion in atmospheric conditions by accelerating the formation of insoluble protective corrosion product. In both high RH and bulk solution, UV light accelerates the formation of insoluble corrosion product, which increases the measured Zn corrosion rate. Figure 4.9 shows schematically how UV light can inhibit corrosion in thin electrolyte layers and increase the corrosion rate in bulk solution.
RH also affects the aqueous NaCl concentration on the surface. At 80% RH the equilibrium concentration of a NaCl is about 4 M [5, 8]. At about 90% RH, the equilibrium NaCl concentration is reduced to about 3 M and the thickness of the electrolyte reaches up to 3 µm with the loading of 50 µg/cm² [3, 8]. This is 3 orders of magnitude larger than for 70% RH, where the liquid layer thickness is only 1-2 nm. The electrolyte thickness will determine whether UV light will accelerate or inhibit corrosion. If the RH is less than 90% RH, the UV light will promote the growth of a protective oxide because of the high [Zn²⁺], which will inhibit further corrosion. If the RH is greater than 90%, aqueous corrosion product will form because of the low [Zn²⁺] in solution and UV light will accelerate the Zn corrosion rate.

4.5 Effect of NH₃

NH₃ is a basic, highly water-soluble gas that is produced in natural ecosystems, agricultural industries, synthetic fertilizers, and through the burning of biomass [13]. Due to its high solubility, it is a dominant species found in industrial aerosols [6]. Figure 4.11 shows that the addition of 500 ppb NH₃ did not have a significant effect on the NaCl induced corrosion rate over a 3 day period. NH₃ absorbs into electrolyte and forms ammonium and hydroxide ions by the reactions below [6, 13].

\[
\text{NH}_3(g) + H_2O(l) \leftrightarrow NH_3 \cdot H_2O(aq) \tag{7}
\]

\[
NH_3 \cdot H_2O(aq) \leftrightarrow NH_4^+(aq) + OH^-(aq) \tag{8}
\]

The equilibrium pH can be calculated using the Henry’s law and equilibrium constant for NH₃, 62 M/atm, and the dissociation constant, 1.8 x 10⁻⁵ [6, 13].
However, to take into account all the different ionic species in solution from dissolved

gasses that could affect equilibrium concentrations and pH, the Stream Analyzer software

from OLI was used. A saturated NaCl solution was used as the electrolyte in all
calculations to account for the thin electrolyte layer at 70% RH and the deposition of 50
μg/cm² NaCl. Mole fractions of oxygen and CO₂ in the system were

set to initial values of those in air, 0.21 and 3.5e-4, respectively, and the balance was nitrogen. The temperature

and total pressure were kept constant at 25 °C and 1 atm, respectively. Desired

equilibrium vapor pressures were set for SO₂, and NH₃, and the pH and ionic species in

solution were calculated. Table 4.3 shows the results. The equilibrium pH is predicted to

be 8.43 when a vapor pressure of 500 ppb NH₃ is present. The surface pH was also

qualitatively measured using a gel electrolyte containing a pH indicator. A Zn sample

was loaded with a gel electrolyte containing 0.01 M NaCl and exposed to the same

conditions. Figure 4.12 shows that the pH on the Zn surface was about 8 after 16 h

\[
C_{NH_3} = \frac{P_{NH_3}}{H_{NH_3}}
\]

\[
k_{NH_3} = \frac{([NH_4^+][OH^-])}{(NH_3(aq))}
\]

\[
k_{NH_3} = \frac{[x]^2}{[C_{NH_3} - x]}
\]

\[
x = [OH^-]
\]

\[
pH = -\log \left(\frac{10^{-14}}{OH^-}\right)
\]
exposure to air containing 550 ppb NH\textsubscript{3} and 70% RH. However, the gel electrolyte was determined not to be a good method of measuring the pH of the electrolyte because it changed corrosion mechanism. Instead of forming visible corrosion product on the surface, pits were found on the Zn surface underneath the gel.

Assuming ionic concentrations of $10^{-6}$ M, the Pourbaix diagram for Zn predicts the formation of ZnO\textsubscript{(s)} and passive behavior between pH 8.5 and 11.5, as seen in Figure 4.13a. However, as stated earlier, the activity of Zn\textsuperscript{2+} in the thin electrolyte layer was calculated to be 0.028 M, which expands the Zn passive region to between pH 6.3 and 14. At equilibrium, the presence of 500 ppb NH\textsubscript{3} should increase the pH of the electrolyte layer on the Zn surface to 8.4 causing the Zn to passivate. However, this is not reflected in the corrosion rate, because the presence of 500 ppb NH\textsubscript{3} did not decrease the Zn corrosion rate. This is due to the water film on the surface being saturated with NaCl and the buffering capabilities of the formation and dissolution of ZnO and Zn(OH)\textsubscript{2} [14].

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$$ \hspace{1cm} (9)

$$Zn^{2+} + 2OH^- \leftrightarrow ZnO + H_2O$$ \hspace{1cm} (10)

In the OLI simulation there were no Zn\textsuperscript{2+} ions in solution, so the simulation did not consider the how the formation of ZnO and Zn(OH)\textsubscript{2} could lower the electrolyte pH. When 0.03 M ZnCl\textsubscript{2} was added to the same simulation as before, the pH decreased to 7.4. This is attributed to the formation of solid and aqueous Zn(OH)\textsubscript{2} and ZnOH\textsuperscript{+} as seen in Table 4.4. In addition, Figure 4.13b shows that the saturated NaCl solution on the surface decreased the stability of the passive film and reduced the passive region to between pH
7.5 and 14, assuming a $[\text{Zn}^{2+}]$ of 0.028 M. The combination of the presence of NaCl and the formation of ZnO and Zn(OH)$_2$ prevented the passivation of Zn.

4.6 Effect of SO$_2$

Figure 4.11 shows a comparison of the measured corrosion rates by mass loss after 3 day exposures of Zn to NaCl, NaCl +SO$_2$, NaCl +NH$_3$ and NaCl + SO$_2$ + NH$_3$. The effects of UV and ozone were also investigated in each exposure condition. The addition of 120 ppb SO$_2$ led to a decrease in Zn corrosion rate in the presence of NaCl due to the formation of a more protective corrosion product. Protectiveness of oxide films are affected by chemical composition, morphology, and structural form [6]. There are many ways in which corrosion products may inhibit corrosion: i) formation of an oxide film that is resistant to oxygen, charge, or ionic species transfer from the metal surface to the electrolyte ii) lowering the total salt content of the electrolyte which would decrease the electrolyte conductivity iii) decreasing the wettability of the surface [6]. The protectiveness of Zn corrosion products have been compared based on their ability to reduce Cl$^-$ transport through the oxide [6]. It was found that oxides with more negative zeta potentials in neutral or acid pH repel Cl$^-$, while those with positive zeta potentials attract Cl$^-$ and accelerate corrosion. The results are listed below in decreasing order of protectiveness.

Zinc hydroxy carbonate > zinc hydroxy sulfate > zinc hydroxide > zinc hydroxy chloride
Therefore, zinc sulfates such as zinc hydroxy sulfate and gordaite should be more protective than simonkolleite (zinc hydroxy chloride) due to their ability to reduce Cl\textsuperscript{–} transport.

In reality SO\textsubscript{2} has both accelerating and inhibiting effects on the corrosion rate of Zn. SO\textsubscript{2} can accelerate the Zn corrosion rate by the acidification of the electrolyte via reactions below [4].

\begin{align*}
SO\textsubscript{2}(g) & \rightarrow SO\textsubscript{2}(aq) \\
SO\textsubscript{2}(aq) + H\textsubscript{2}O & \rightarrow HSO\textsubscript{3}^{-}(aq) + H\textsubscript{3}^{+}(aq) \\
HSO\textsubscript{3}^{-}(aq) + \frac{1}{2}O\textsubscript{2}(g) & \rightarrow SO\textsubscript{4}^{2-}(aq) + H^{+}(aq) \\
2H^{+} + ZnO(s) + SO\textsubscript{4}^{2-}(aq) + xH\textsubscript{2}O & \rightarrow ZnSO\textsubscript{4} \cdot xH\textsubscript{2}O + H\textsubscript{2}O
\end{align*}

Figure 4.5 shows that many of the Zn corrosion products, such as zinc sulfates, ZnO, Zn(OH)\textsubscript{2}, and simonkolleite are not stable in acid environments and will dissolve. An environment containing 120 ppb SO\textsubscript{2} and 350 ppm CO\textsubscript{2} will have an equilibrium pH of 4.1 according to a calculation using the OLI software.

However, SO\textsubscript{2} can lower the Zn corrosion rate by the formation of insoluble corrosion products if Cl\textsuperscript{–} is present [6]. In an experiment conducted by Svensson and Johansson, in which Zn was exposed to SO\textsubscript{2} at 95% RH with additions of NaCl, SO\textsubscript{2} was found to increase the corrosion rate because of acidification of the electrolyte [6]. However, NaCl deposition greater than 4 mg/cm\textsuperscript{2} led to lower corrosion rates when SO\textsubscript{2}
was present. Svensson and Johansson attributed this to the formation of gordaite, which lowered the solution conductivity and formed a more uniform barrier.

In addition to slightly reducing the corrosion rate, Figure 4.14 shows that exposure to 120 ppb SO$_2$ led to more amorphous zinc carbonates on the surface. When crystalized, these carbonates might form corrosion products that reduce the transport of Cl$^-$ to the surface. Zn$^{2+}$ migrates towards the cathode sites to balance the negative charge associated with OH production by oxygen reduction. The low [Cl$^-$] and the relatively high [Zn$^{2+}$] in the cathodic sites will lead to favorable conditions for the formation of ZnO and zinc hydroxy sulfates, shown by the reaction below[4].

$$Zn^{2+}_{aq} + 3ZnO_{(s)} + SO_4^{2-}_{(aq)} + 6H_2O \rightarrow Zn_4SO_4(OH)_{6(s)}$$ (15)

And of gordaite by:

$$Na^+ + Cl^- + Zn^{2+}_{aq} + 3ZnO_{(s)} + SO_4^{2-}_{(aq)} + 9H_2O \rightarrow NaZn_4SO_4(OH)_{6Cl} \cdot 6H_2O_{(s)}$$ (16)

The formation of zinc sulfates decreases the conductivity of the electrolyte and impedes the migration of Cl$^-$ and the diffusion of O$_2$ to the surface [4, 6]. Figure 4.6 shows the corrosion that takes place on the Zn surface near a deposited NaCl particle in the presence of SO$_2$. The center of the corrosion product, the anodic region, has high chlorine content and is where the simonkolliete forms. The cathodic reaction takes place outside of this area and this is where the oxygen and sulfur content are much higher and where the ZnO and zinc sulfates formed. Figure 4.15 shows images of sulfur containing corrosion products with pores on the order of microns. Mudcracking of the product occurred because of the high level of vacuum in the SEM. However, this corrosion
product might not be very protective due to the large pores, which can allow migration and diffusion of Cl⁻ and O₂ and be a pathway for the electrolyte to reach the Zn surface. Figure 4.16 shows the formation of corrosion product on the surface after exposure with SO₂, UV light and NaCl. The combination of SO₂ and UV light led to the formation of a layered structure high in chlorine, oxygen, zinc and some sulfur, possibly a combination of simonkolliete and gordaite (NaZn₄(SO₄)(OH)₆Cl·6H₂O).

4.7 Effect of SO₂ and NH₃

SO₂ is able to react with NH₃ in the gas phase to produce ammonia sulfate salts [15].

\[
2NH₃(g) + SO₂(g) + H₂O(g) \rightarrow (NH₄)_2SO₃(s)
\]

(17)

\[
NH₃(g) + SO₂(g) + H₂O(g) \rightarrow NH₄HSO₃(s)
\]

(18)

In the presence of O₂, these salts can be oxidized by the reactions below.

\[
(NH₄)_2SO₃(s) + O₂(g) \rightarrow 2(NH₄)_2SO₄(s)
\]

(19)

\[
2(NH₄)_2SO₃(s) + O₂(g) \rightarrow 2NH₄HSO₄(s)
\]

(20)

\[
2NH₄HSO₃(s,aq) + O₂(g) + 2NH₃(g) \rightarrow 2(NH₄)_2SO₄(s,aq)
\]

(21)

When exposed separately, the [SO₂] and [NH₃] measured at the chamber exit were 120 and 550 ppb respectively. The [SO₂] and [NH₃] decreased by about 20 and 50 ppb, respectively, when exposed simultaneously. However, no ammonia sulfates salts were detected with XRD or FTIR on the Zn surface after exposure. It is likely that the salts deposited on the chamber walls and/or in the tubing, where the surface area to volume ratio is high. The RH was controlled at 70%, which is below the deliquescence RH for
(NH₄)₂SO₄ (79.9%) [6]. Therefore the salts should not have dissolved. Figure 4.11 shows that when Zn was deposited with NaCl and exposed simultaneously to both SO₂ and NH₃ it followed a similar corrosion rate trend to Zn deposited with NaCl and exposed to only SO₂. The presence of both SO₂ and NH₃ led to a slight decrease in the Zn corrosion rate when NaCl was present, possibly due to the formation of gordaite and zinc hydroxy sulfate which would lower the solution conductivity and form a more protective barrier [4, 6]. Similar to Zn exposed to SO₂, the presence of O₃ and UV increased the Zn corrosion rate when both SO₂ and NH₃ were present. However, when Zn was exposed to both SO₂ and NH₃ in the presence of UV light, the corrosion rate decreased.

4.8 Effect of UV light and ozone

As discussed earlier, UV light has both negative and positive effects on the Zn corrosion rate. At RH below 90% UV light reduced the Zn corrosion rate, but above 90% RH, UV light increased the Zn corrosion rate.

For exposure conditions containing SO₂, the presence of UV light increased the amount of gordaite and zinc hydroxy sulfate present after exposure, as seen by comparing peak XRD intensities in Figure 4.3 and Figure 4.4 and the FTIR peak intensities in Figure 4.17. This suggests that UV light may affect the reaction kinetics of reactions involving sulfur dioxide species. When ZnO is exposed to air, oxygen is physically adsorbed onto the oxide surface and some of the electrons at the surface become entrapped by the adsorbed oxygen and form negative ions such as O²⁻ [11, 16]. This would lead to an increase in negative charge on the ZnO surface and repel other anions such as SO₄²⁻, decreasing the reaction rate of the formation of zinc hydroxy sulfate and gordaite.
(equations 14 and 15). Under illumination, these O\(^2\) ions on the surface will be desorbed because of the increased concentrations of holes on the surface, allowing SO\(_4^{2−}\) to react more easily with ZnO [11].

Typical concentrations of ozone range from 100-200 ppb in industrial environments [14]. Ozone is a stronger oxidizing agent than O\(_2\) and has a standard reduction potential of 2.08 V vs. SHE, which is 0.85 V higher than the standard reduction potential for oxygen [17].

\[
O_3 + 3H_2O + 6e^- \rightarrow 6OH^- \quad E^\circ = 2.08 \tag{22}
\]

\[
O_2 + 4H_2O + 4e^- \rightarrow 4OH^- \quad E^\circ = 1.23 \tag{23}
\]

However, O\(_3\) alone does not have a significant effect on the Zn corrosion rate. After 24 h exposure to 300 ppb ozone, 99% RH, and UV (no NaCl), the Zn surface remained shiny and there were no signs of visible corrosion product on the surface. These results agree with the work of Svensson and Johansson, where Zn samples were exposed to 400 ppb O\(_3\) for 4 weeks and the presence of O\(_3\) did not accelerate the corrosion rate [14]. It is likely that O\(_3\) cannot penetrate Zn’s protective oxide layer.

Although ozone does not directly react with Zn, it can make the environment more aggressive. O\(_3\) has many ways in which it can catalyze the oxidation of S(IV) to S(VI) increasing the SO\(_2\)-induced corrosion rate [9, 14]. O\(_3\) can react with water to produce hydrogen peroxide, which can quickly oxidize S(IV) to S(VI), and it can oxidize adsorbed S(IV) directly to SO\(_4^{2−}\) by the equations below [14].
\[ O_3 + S(IV) + H_2O \rightarrow SO_4^{2-} + O_2 + 2H^+ \]  \hspace{1cm} (24)

\[ O_3 + 3H_2O \rightarrow 3H_2O_2 \]  \hspace{1cm} (25)

This will lower the \([SO_2(aq)]\) in the electrolyte and shift the reaction below to the right which will allow for more \(SO_2\) to be absorbed.

\[ SO_{2(g)} \leftrightarrow SO_{2(aq)} \]  \hspace{1cm} (26)

The reaction above will still be controlled the equilibrium, but the presence of \(O_3\) effectively increasing the absorption rate of \(SO_2\) into the electrolyte by oxidizing the absorbed \(SO_2\). \(O_3\) is also a photosensitive gas. In the presence of UV light, atomic oxygen and \(OH\) radicals can be generated, which will enhance the aggressiveness of the environment [3, 13].

\[ O_3 + h\nu \ (370nm) \rightarrow O + O_2 \]  \hspace{1cm} (27)

\[ O + H_2O \rightarrow 2OH^- \]  \hspace{1cm} (28)

These hydroxyl radicals are able to react with gaseous \(SO_2\) to produce sulfuric acid, which is extremely corrosive to Zn [13].

\[ SO_2(g) + OH^- \rightarrow HSO_3^- \rightarrow several \ steps \rightarrow H_2SO_4 \]  \hspace{1cm} (26)

Sulfuric acid dissociates readily in water and quickly acidifies the electrolyte. The rapid oxidation of \(S(IV)\) to \(S(VI)\) by \(O_3\) and \(OH^-\) explains why the combination of \(SO_2\), \(O_3\), and UV light produces a more corrosive environment and increased the Zn corrosion rate.
4.9 Discussion

Even though it is known that UV light has a strong influence on the corrosion of metals such as stainless steel, Ti, Cu, and Zn, UV light is often overlooked when developing models to predict corrosion rates of metals [3, 9]. In the case of Zn, many studies have shown that UV light accelerates the corrosion rate [10, 11, 18]. Therefore, it is of interest to discover that, in certain conditions, UV light can also have a slight inhibiting effect on the Zn corrosion rate.

The effects of NH$_3$ on Zn were investigated because of its high water solubility and ability to produce an alkaline electrolyte [13]. It was hypothesized that NH$_3$ would increase the pH of the surface electrolyte causing the Zn to passivate, lowering the corrosion rate. Although it was predicted in OLI that 550 ppb NH$_3$ would produce an equilibrium pH of 8.4 in the electrolyte, which is in the passive range for Zn, the presence of NH$_3$ did not lower the Zn corrosion rate [11]. This was due to the saturated NaCl solution on the surface, which reduced the stability of the passive film and the formation of ZnO and Zn(OH)$_2$, which would lower the equilibrium pH. When the OLI simulation was repeated with the addition of Zn$^{2+}$ ions, zinc hydroxide species formed, and the predicted pH was lowered to 7, which is not in the Zn passive region when exposed to a saturated NaCl solution. It is possible that if NaCl had not been present, the NH$_3$ would have passivated the Zn.

SO$_2$ is a known accelerator of Zn corrosion; however, there have not been sufficient studies involving the combination of SO$_2$, Cl$^-$, UV light, and O$_3$ [4, 13]. The results from this study support the conclusion that SO$_2$ may have a slight inhibiting effect on Zn
corrosion rate when Cl\(^{-}\) is present due to the formation of gordaite and zinc hydroxy sulfate, which form a more protective barrier to Cl\(^{-}\) transport than simonkolleite and reduces the conductivity of the electrolyte [4, 6]. The synergetic effect with O\(_3\) and SO\(_2\) was also observed [14]. The combination of SO\(_2\) with O\(_3\) in the presence of UV and NaCl led to an increase in the corrosion rate due to the oxidation of SO\(_2\) by O\(_3\), resulting in acidification of the electrolyte. Notably, it was also observed that UV increased the formation of crystalline gordaite and zinc hydroxy sulfate after exposure with NaCl and SO\(_2\). This suggests that UV light affects the reaction rates of other species in the environment.
4.10 Tables and figures

Table 4.1. Corrosion products identification using XRD after 3 day of exposure. All samples were preloaded with 50 µg/cm² and air at 70% RH.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Compounds after exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>Zn₅(OH)₆Cl₂.H₂O,</td>
</tr>
<tr>
<td>SO₂</td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>(Zn(OH)₂)₃(ZnSO₄)·H₂O</td>
</tr>
<tr>
<td></td>
<td>NaZn₄(SO₄)₆Cl·6H₂O</td>
</tr>
<tr>
<td>NH₃</td>
<td>ZnO, Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>Zn(OH)(NO₃)₂H₂O,</td>
</tr>
<tr>
<td>SO₂ &amp; NH₃</td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>(Zn(OH)₂)₃(ZnSO₄)·H₂O</td>
</tr>
<tr>
<td></td>
<td>NaZn₄(SO₄)₆Cl·6H₂O</td>
</tr>
</tbody>
</table>

Table 4.2. Corrosion Products identified with FTIR after 3 day of exposure. All samples were preloaded with 50 µg/cm² and air at 70% RH.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Bond</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Zn-Cl,</td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>CO₃,</td>
<td>Zn₅(OH)₆(CO₃)₂ or Zn₄CO₃(OH)₆H₂O</td>
</tr>
<tr>
<td></td>
<td>Zn-O</td>
<td>ZnO</td>
</tr>
<tr>
<td>SO₂</td>
<td>Zn-Cl,</td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>CO₃,</td>
<td>Zn₅(OH)₆(CO₃)₂ or Zn₄CO₃(OH)₆H₂O</td>
</tr>
<tr>
<td></td>
<td>Zn-O</td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>SO₃</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SO₄</td>
<td>(Zn(OH)₂)₃(ZnSO₄)·H₂O &amp; NaZn₄(SO₄)₆Cl·6H₂O</td>
</tr>
<tr>
<td>NH₃</td>
<td>Zn-Cl,</td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>CO₃,</td>
<td>Zn₅(OH)₆(CO₃)₂ or Zn₄CO₃(OH)₆H₂O</td>
</tr>
<tr>
<td></td>
<td>Zn-O</td>
<td>ZnO</td>
</tr>
<tr>
<td>SO₂ &amp; NH₃</td>
<td>Zn-Cl,</td>
<td>Zn₅(OH)₆Cl₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>CO₃,</td>
<td>Zn₅(OH)₆(CO₃)₂ or Zn₄CO₃(OH)₆H₂O</td>
</tr>
<tr>
<td></td>
<td>Zn-O</td>
<td>ZnO</td>
</tr>
<tr>
<td></td>
<td>SO₃</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SO₄</td>
<td>(Zn(OH)₂)₃(ZnSO₄)·H₂O &amp; NaZn₄(SO₄)₆Cl·6H₂O</td>
</tr>
</tbody>
</table>
Table 4.3. Equilibrium pH calculated for saturated NaCl solution based on steady state vapor pressures measured exiting the test chamber. Ionic species with concentrations above $10^{-7}$ M are shown in decreasing order.

<table>
<thead>
<tr>
<th>Species</th>
<th>Equilibrium Vapor Concentration (ppm)</th>
<th>pH</th>
<th>Ionic aqueous species (Na⁺ and Cl⁻ not shown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>350</td>
<td>5.01</td>
<td>H⁺, CHO₃⁻</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.125</td>
<td>4.13</td>
<td>H⁺, HSO₃⁻, SO₃²⁻, CHO₃⁻</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.530</td>
<td>8.43</td>
<td>NH₄⁺, CHO₃⁻, NaCO₂⁺, CO₂⁻, OH⁻</td>
</tr>
</tbody>
</table>

Table 4.4. Equilibrium pH calculated for 5 M NaCl solution with 0.03 M ZnCl solution based on steady state vapor pressures measured exiting the test chamber. Ionic species with concentrations above $10^{-7}$ M are shown in decreasing order.

<table>
<thead>
<tr>
<th>Species</th>
<th>Equilibrium Vapor Concentration (ppm)</th>
<th>pH</th>
<th>Ionic aqueous species (Na⁺,Cl⁻, Zn²⁺, ZnCl⁺, &amp; ZnCl₃ not shown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>350</td>
<td>4.87</td>
<td>H⁺, ZnOH⁺, CHO₃⁻, ZnCHO₃⁺</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.120</td>
<td>4.22</td>
<td>H⁺, HSO₃⁻, SO₃²⁻, CHO₃⁻</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.525</td>
<td>7.40</td>
<td>NH₄⁺, ZnNH₃²⁺, ZnOH⁺, CHO₃⁻, NaCO₂⁺, CO₂⁻</td>
</tr>
</tbody>
</table>
Figure 4.1. Optical images of Zn surface immediately after deposition of a) 50 µg/cm² NaCl and b) 100 µg/cm² NaCl.
Figure 4.2. Optical (A) and SEM (B) images of Zn immediately after the deposition of 50 µg/cm² NaCl. Initial corrosion is seen surrounding the NaCl particle.
Figure 4.3. XRD scans after 3 days exposures to 70 % RH air and 120 ppb SO₂. All samples were loaded with 50 µg/cm² NaCl before exposure.
Figure 4.4. XRD scans after 3 days exposures to 70 % RH air, 120 ppb SO$_2$, and 500 ppb NH$_3$. All samples were loaded with 50 µg/cm$^2$ NaCl before exposure.
Figure 4.5. Stability diagram calculated using Hydra/Medusa chemical equilibrium software, showing the stable regions for solid and soluble zinc compounds at a redox potential of 0.25 V (SHE) and varying pH and chloride concentration. The concentrations of Zn$^{2+}$, SO$_4^{2-}$, and CO$_3^{2-}$, were kept constant at 0.5, 0.1, and 0.001 M, respectively. From Sandberg et al [7]. Reproduced by permission of The Electrochemical Society.
Figure 4.6. SEM image and EDS mapping of simonkolleite formed on the Zn surface after preloading of 50 µg/cm² NaCl and 3 days of exposure to 70% RH air and 120 ppb SO₂.
Figure 4.7. Effect of RH and the presence of UV light (6.03 mW/cm²) on the Zn corrosion rate. All samples were preloaded with 50 µg/cm² NaCl and exposed for 22 h. The results of all experiments are shown and multiple data points overlap for some conditions.
Figure 4.8. Schematic of process controlling the photocurrent yield for ZnO under illumination. Redrawn based on a schematic by X. Zhang [11].
Figure 4.9. Zinc stability diagram calculated using OLI software showing the effects of $[\text{Zn}^{2+}]$ and pH. The lines $C_b$ and $C_i$ represent the $[\text{Zn}^{2+}]$ for Zn corroding in bulk solution and at 70% RH, respectively.
Figure 4.10. Schematic of UV light leading to inhibition of corrosion by the formation of protective corrosion product in thin electrolyte layers while increasing the corrosion rate in bulk solution. Continued.
Figure 4.10: Continued

Zn corroding at 70% RH

Zn + 2h^+ → Zn^{2+}

UV light
Figure 4.11. Effect of 120 ppb SO$_2$, 500 ppb NH$_3$, UV light, and 650 ppb O$_3$ on the Zn corrosion rate after the deposition of 50 µg/cm$^2$ NaCl. All samples were exposed for 3 days to air at 70% RH. The results of all experiments are shown and multiple data points overlap for some conditions.
Figure 4.12 Observed pH exposures using a gel electrolyte containing 0.01 M NaCl and 15 wt% Fisher universal pH indicator. Samples were exposed for 16 h to 70 % RH air and either SO$_2$ or NH$_3$. 
Figure 4.13. Pourbaix diagram calculated using OLI at 25 °C for the a) Zn-water system and b) Zn in a saturated NaCl solution.
Figure 4.14. FTIR scans after 3 days exposures. All samples were loaded with 50 µg/cm² NaCl before exposure and exposed to air at 70% RH. Samples were exposed with SO₂, NH₃, SO₂ and NH₃, or with NaCl only.
Figure 4.15. SEM and EDS image of sulfur containing corrosion product after exposure. Mudcraking due to the high level of vacuum created from the SEM. Zn surface after the preloading of 50 µg/cm² NaCl and exposure to air at 70% RH and 120 ppb SO₂ for 3 days.
Figure 4.16. SEM and EDS image. Zn surface after the preloading of 50 µg/cm² NaCl and exposure to air at 70% RH, 120 ppb SO₂, and UV light for 3 days. Image is possibly a combination gordaite and simonkolleite on the surface.
Figure 4.17. FTIR scans after the preloading of 50 µg/cm² NaCl and exposure to air at 70% RH and 120 ppb SO₂ for 3 days. Samples were exposed in either the dark, with UV light, or with O₃ and UV light.
4.11 References


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Chapter 5: Conclusions and Future work

5.1 Conclusions

A novel environmental chamber with multiple gas inlets was designed and constructed for Zn laboratory exposures. The effects of UV light, O\textsubscript{3}, SO\textsubscript{2}, NH\textsubscript{3}, and RH on the zinc corrosion rate with the constant preloading of NaCl particles on the surface have been investigated in this work. Corrosion products were analyzed with XRD, FTIR, SEM, and EDS after exposure. Corrosion rate was measured using mass loss. The following conclusions were made after analysis.

1. On their own, UV and O\textsubscript{3} do not have a significant effect on the Zn corrosion rate. After 24 h exposure to 99% RH air, UV light and O\textsubscript{3}, the Zn surface reminded shiny and did not corrode.

2. As expected, increasing the RH increased the Zn corrosion rate when NaCl was present. A relatively large increase in corrosion rate is observed at the deliquescence RH for NaCl.

3. Unlike bulk immersion tests for Zn, UV light actually decreased the Zn corrosion rate at RH below about 90% in the presence of NaCl. Below 90% RH, the electrolyte on the surface ranges from a few nm to a few microns, which leads to
a high \([\text{Zn}^{2+}]\) on the surface. UV light accelerated the growth of insoluble corrosion product that protected the Zn from further corrosion and lowered the corrosion rate.

4. SO\(_2\) had both positive and negative effects on the Zn corrosion rate. The oxidation of SO\(_2\) acidifies the surface electrolyte and can dissolve protective corrosion product on the surface. However, SO\(_2\) actually lowered the corrosion rate when NaCl was present by the formation of protective sulfate containing corrosion product such as zinc hydroxy sulfate, \((\text{Zn(OH)}\)\(_2\))\(_3\)(\text{ZnSO}_4) \cdot \text{H}_2\text{O}\), and gordaite, NaZn\(_4\)(SO\(_4\))(OH)\(_6\)Cl\(_2\)·6\text{H}_2\text{O}. These sulfate containing corrosion product reduce Cl\(^-\) and O\(_2\) transport to the Zn surface better than simonkolleite, Zn\(_5\)(OH)\(_8\)Cl\(_2\)·\text{H}_2\text{O}\ [2].

5. UV light also accelerated the SO\(_2\) kinetics in solution. The simultaneous exposure of Zn to SO\(_2\) and UV light with the loading of NaCl led to increased formation of sulfate containing corrosion product. Absorption of UV light by ZnO likely increased the reaction rate for the formation of zinc hydroxy sulfate and gordaite by neutralizing the charge on the ZnO surface. However, the UV light did not affect the SO\(_2\) induced corrosion rate.

6. The combination of SO\(_2\), UV, and O\(_3\) increased the Zn corrosion rate due to the synergetic effect of O\(_3\) and SO\(_2\). O\(_3\) increased the oxidation rate of S(IV) to S(VI) which acidified the electrolyte and allowed for more absorption of SO\(_2\) into the electrolyte.
7. Although ammonia is a highly water soluble gas and can increase the pH of the electrolyte when absorbed, the presence of 550 ppb NH$_3$ did not significantly affect the Zn corrosion rate. This is possibly due to the buffering capabilities of the formation and dissolution of corrosion products, like ZnO and Zn(OH)$_2$, and the presence of a Cl$^-$ on the surface reducing the stability of any potential passive film. The combination of 100 ppb SO$_2$ and 500 ppb NH$_3$ did not produce any ammonium sulfate salts that were detected by XRD or FTIR.

8. The combination of SO$_2$ and NH$_3$ in the presence of NaCl, followed a similar corrosion rate trend to Zn exposed to SO$_2$ and NaCl only, suggesting that NH$_3$ does not play a critical role in controlling the Zn corrosion rate.

### 5.2 Future work

This work has increased the understanding of the effects of UV, ozone, SO$_2$, and NH$_3$ on Zn corrosion in the presence of NaCl. However, correlation of lab exposure with field data is a key component that needs to be addressed. In order to accurately predict the corrosion behavior of Zn coatings and Zn alloys in various environments some steps must be taken:

1. Artificial neural networks have been used to predict atmospheric corrosion rates for metals in different field environments based on key input parameters, such as, RH, temperature, [SO$_2$] and [Cl$^-$]. The experimental data collected should be fit and used to predict the Zn corrosion rate in both lab and field exposures.

2. Vary the Cl$^-$, [SO$_2$], [NO$_2$], [O$_3$], temperature, RH and UV light intensity and measure the Zn corrosion rate. There should be at least 3 levels of each parameter
studied. Fuzzy analysis has been used to determine the significance of multiple inputs with a single output. It should be used here to determine the significance of each parameter on the Zn corrosion rate.

3 Investigate the effects of UV light on the reaction kinetics of SO$_2$ and the formation of Zn corrosion product. UV light accelerated the formation of crystalline Zn sulfates, so it would be interested to determine the actual mechanism of this phenomenon.

4 The effects of temperature on the corrosion behavior of Zn have not been studied in detail. This would be useful for predicting corrosion behavior in the field.
Bibliography

Chapter 1


Chapter 2


Chapter 3


3. Programs, N.S.F.s.O.o.P., *UV Monitoring Network, operated by Biospherical Instruments Inc. and funded by the U.S. National Science Foundation's Office of Polar Programs*.

Chapter 4


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