MARINE ATMOSPHERIC CORROSION INITIATION AND CORROSION PRODUCTS CHARACTERIZATION

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Abstract

This work focused on NaCl particle-induced marine atmospheric corrosion of carbon steel. Corrosion does not initiate under deliquescent NaCl droplets smaller than a critical size. The mechanisms of corrosion initiation and propagation were identified. The effects of diverse natural environments on the formation and aging of iron oxide products were identified.

Part I

On carbon steel that were exposed to Hawai‘i’s marine test sites for 30 min, corrosion did not initiate under small seawater droplets (D < ~30 µm) but occurred under larger droplets. Similarly, laboratory study showed that corrosion did not initiate from small NaCl droplets (D < ~45 µm) formed by the deliquescence of pre-deposited NaCl particles upon exposing to high humidity (RH > 80%), while occurred under larger droplets and sometimes propagated in the form of filiform corrosion. In addition, anodic polarization showed the steel passivated under small NaCl droplets and corroded actively under larger droplets.

In situ and ex situ Raman spectra from the rust species that formed during the corrosion process showed that green rust (GR) formed close to the corrosion pit (i.e., anodic site) while lepidocrocite (γ-FeOOH) clusters precipitated in regions outside of the GR region (i.e., cathodic site). Similarly, the rust formed in Evans’ droplet experiments was also identified as GR and lepidocrocite using In situ Raman spectroscopy.
Part II

The corrosion products formed on 1008 steel that were exposed to Hawai‘i’s diverse micro-climates for 1 year period were characterized using micro-Raman analysis, energy dispersive X-ray analysis (EDXA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis.

Lepidocrocite was identified as the major rust in the surface layers on samples exposed to industrial, rainforest, dry and agricultural test sites, while goethite was detected in the inner rust layers. Akaganeite with high concentration of Cl was also found on the face-down sides of samples from dry and agricultural test sites.

In addition to the dominant rust phases – lepidocrocite in the surface rust layers and goethite in the inner rust layers – more akaganeite was detected on samples from marine test sites, both in the surface and inner rust layers, due to high airborne chlorinity.
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Part I

Marine Atmospheric Corrosion Initiation
Chapter 1

Introduction

1.1 Background

Atmospheric corrosion is the environmental degradation of metallic materials causing deterioration of their microstructures and properties due to the interaction with the surrounding atmosphere and its characteristic temperature, humidity, chemistry, and other climatic parameters. Its complexity comes from the numerous processes involved, i.e., chemical, electrochemical and physical processes, in the interfacial domain from the gaseous phase to the liquid phase, and to the solid phase.[1]

Marine atmospheric corrosion is one of the most severe types of corrosion due to the high content of airborne chlorides, mainly NaCl, that are generated either in the open sea or in the surf zone.[2-4] The aerosols are carried by wind reaching structures inland, accelerating their corrosion.

Even since the 1920s (Vernon), atmospheric corrosion had been studied by electrochemists and corrosion engineers. Research includes both outdoor and controlled laboratory experiments. Outdoor experiments represent the corrosion of materials in real environments and aim to predict the corrosion of materials in a given environment, while the accelerated indoor laboratory experiments are designed to simulate exposure in a given field environment.
In this dissertation, both laboratory and outdoor experiments were conducted. Part I mainly focused on laboratory studies of the very initial stages of NaCl particle-induced marine atmospheric corrosion of steel, including characterization of corrosion initiation phenomena, electrochemical tests in droplets and Raman spectroscopic identification of the rust formed. In Part II, we focused on the final stage of marine atmospheric corrosion by characterizing the rust layers grew on carbon steel that were exposed in Hawai‘i’s diverse micro-climates for 1 year period.

1.2 Objectives of Research

The objectives of this research were

– to characterize the marine salt particles that formed from dehydrated seawater droplets that were naturally deposited on metal samples (i.e., carbon steel, pure zinc).
– to characterize the initial stage of corrosion caused by the deposited seawater droplets.
– to observe and characterize the corrosion initiation on steel under NaCl droplets which were formed by deliquescence of pre-deposited NaCl particles.
– to understand the electrochemistry of droplet corrosion.
– to characterize the rust forms in the initial stage of NaCl particle-induced corrosion.
– to identify the corrosion products in classical Evans’ droplet experiments.
Chapter 2

Literature Review

2.1 Field Study of Marine Atmospheric Corrosion

The amount of marine aerosols present in a specific marine atmosphere, known as marine airborne salinity, is usually measured for both atmospheric studies and corrosion studies. For corrosion studies, correlating marine salinity and metallic corrosion is a major focus. By compiling worldwide research on atmospheric corrosion that was conducted in the last 40 years, Morcillo et al. [5] reported that metallic corrosion increases faster when the airborne salinity values are between 100 and 400 mg Cl⁻/m²/d, while slightly increases when the airborne salinity is less than 100 mg Cl⁻/m²/d or more than 400 mg Cl⁻/m²/d as compared to the case when it is in the range of 100 – 400 mg Cl⁻/m²/d.

Studies have also been focused on the behavior of marine aerosols, including their production, transport and deposition.[2, 6, 7] Cole et al. [2] proposed a comprehensive model that requires input of significant amounts of data, while Meira et al. [7] generated a simplified model which depends on aerosol characteristics and has wind velocity and distance from the sea as independent variables. Airborne salinity generally increases with increasing wind velocity, but the effect becomes significant when a critical value is exceeded. A range of values for the critical wind velocity (3 – 7.1 m/s) have been reported in the literature, but a consensus has not
been reached.[8-10] Meira et al. [11] recommended 3 m/s as the critical wind velocity for the significant increase of airborne salinity.

Marine aerosol particles are usually classified by size into two categories: coarse particles with an equivalent aerodynamic diameter larger than 2 µm, and small particles with a diameter smaller than 2 µm.[12] Ambler et al. [13] however classified them as “falling particles” with a diameter larger than 10 µm and “buoyant particles” with a diameter smaller than 10 µm. Ambler et al. also stated that the corrosion of metallic surfaces is only caused by salt particles and saline droplets with sizes larger than 10 µm or the falling type.

Despite the enormous studies on the behavior of marine aerosols, marine salinity and its effects on metallic corrosion, no work has been conducted to characterize the marine aerosol particles that naturally deposit on metal surfaces and the very initial stage of marine atmospheric corrosion. In this dissertation, marine aerosol particles that formed after dehydration of the seawater droplets that deposited on metal samples (i.e., carbon steel, pure zinc) which were exposed to Hawai’i’s diverse marine environments were characterized and the initial stage of corrosion caused by the deposited seawater droplets was discussed.

2.2 Laboratory Study

A number of studies have been conducted to investigate the corrosion of metal surfaces caused by salt droplets formed by deliquescence [14-21] or manually deposited salt-solution droplets [22-24]. Neufeld et al. [14] studied corrosion initiation from salt particles (D = 40 – 120 µm) that formed droplets by deliquescence
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Zhang et al. [15, 16] investigated the formation of secondary micro-droplets around larger droplets formed by different types of salt particles (D = ~50 µm) on various metals (e.g., carbon steel, zinc). They found that the driving force for the formation of the micro-droplets was the current caused by the potential gradient between the central and peripheral area of the main droplet.

Wessenrieder et al. [17] studied filiform corrosion on pure iron with pre-deposited NaCl particles, and proposed that the filiform corrosion was driven by a differential aeration cell, and propagated by mass-transport-limited Cl⁻ movement towards the filament head.

Chen et al. [18-21] studied the effect of NaCl particles, as well as pollutant gases on the atmospheric corrosion of copper. They used either manually-deposited, relatively large (D > 1 mm) NaCl particles or small NaCl particle clusters (4 µg/cm², with single particle size < 10 µm) deposited using a saturated NaCl solution in 99.5% ethanol which was later evaporated. Manually deposited salt-solution droplets on metal surfaces were also used to study atmospheric corrosion.
Tsuru et al. [22] investigated the formation of secondary micro-droplets around manually-deposited macro dilute droplets (i.e., 0.25 M and 0.5 M, D = 0.5 – 5 mm) of various salts on carbon steel, copper and stainless steel surfaces. They attributed this phenomenon to the formation of a highly concentrated alkaline thin film (resulting from oxygen reduction) that absorbs moisture from the droplet and surrounding environment, forming the secondary micro droplets.

Dubuisson et al. [23, 24] studied the corrosion of galvanized steel under dilute salt droplets containing NaCl and Na₂SO₄ (i.e., Na₂SO₄/NaCl = 0.5 mM/50 g l⁻¹ and 3 mM/50 g l⁻¹, D = 1.34 – 3.35 mm) using a micro-cell with small counter and reference electrodes. The results of electrochemical impedance spectroscopy and polarization experiments showed that the corrosion rate of galvanized steel increases with decreasing electrolyte thickness.

In some studies described above, the salt particles as well as the concomitant droplets were usually larger than those naturally formed from airborne salts. In other studies, the deposited salt droplets were more dilute than droplets formed by deliquescence and can not simulate the initial condition of atmospheric corrosion caused by salt particles. In this dissertation, we studied corrosion of steel under relatively small NaCl droplets (D = 20 – 50 µm) that formed by deliquescence, which better represents the very initial stage of marine atmospheric corrosion.

2.3 Small-scale Electrochemistry

Extensive research was conducted on the electrochemistry of thin electrolyte layers on metal surfaces. Stratmann et al. [25-29] investigated corrosion of metal
surfaces that were covered by very thin electrolyte films using the Kelvin probe as the reference electrode. Polarization results [29] obtained on a platinum surface under 1 M Na$_2$SO$_4$ thin electrolyte layers showed that the diffusion-limited, oxygen reduction current density ($i_{\text{lim}}$) was 1) independent of the electrolyte thickness ($\delta$) when $\delta > 100 \ \mu\text{m}$; 2) inversely proportional to $\delta$ when $\delta < 100 \ \mu\text{m}$; and 3) independent of $\delta$ for very thin electrolyte layers, which might be due to the diffusion of oxygen through the electrolyte/gas boundary being the rate determining step (RDS).[29] Similar, but less pronounced effects were found on iron electrodes, which were likely affected by corrosion on the iron surface.

Lyon et al. [30-33] studied the corrosion of metals under thin electrolyte layers up to 50 $\mu\text{m}$ thick using a conventional three-electrode system with a Luggin capillary connecting the reference electrode and counter electrode to the electrolyte films. Thought to be complementary to the Kelvin probe work described, this system may eliminate the convective effects caused by the oscillations of the Kelvin probe and errors from the conversion between Volta potential and corrosion potential.[31] Cathodic polarization measurements showed an inverse relationship between $i_{\text{lim}}$ and $\delta$ for electrolyte layers varying from 100 – 1132 $\mu\text{m}$ thickness on copper, zinc, and iron.[30]

Tsuru et al. [34-38] investigated the electrochemical behavior of metals under thin electrolyte layers using specially designed three-electrode (for polarization measurements) or two-electrode (for electrochemical impedance measurements) electrochemical cells. Cathodic polarization curves obtained on platinum electrodes
covered with thin electrolyte layers (δ = 10 μm – 1000 μm) showed a distinct
limiting current region due to the oxygen reduction.[38] The \( i_{\text{lim}} \) was 1)
independent of \( \delta \) when \( \delta > 1 \text{ mm} \); 2) inversely proportional to \( \delta \) when \( 20 \text{ μm} < \delta < 1 \text{ mm} \); and 3) independent of \( \delta \) when \( \delta < 20 \text{ μm} \). Tsuru et al. [38]
concluded that when the electrolyte film was thick (\( \delta > 20 \text{ μm} \)), oxygen diffusion
through the electrolyte layer was the RDS; and when the electrolyte film was thin (\( \delta < 20 \text{ μm} \)), oxygen dissolution at the air/electrolyte interface is the RDS.

Frankel et al. [39] obtained cathodic and anodic polarization curves for Type
304 stainless steel under 1M NaCl solution layers of different \( \delta \) using a Kelvin
Probe Potentiostat (KPP), similar to that used by Stratmann et al. A distinct limiting
current region due to the diffusion of dissolved oxygen across the thin electrolyte
layer was observed. Also, they found that \( i_{\text{lim}} \) is inversely proportional to \( \delta \) only
over a limited range, which is also similar to previous results.[29, 35] Convection
caused by the vibration of the Kelvin probe was believed to limit the diffusion layer
thickness in thick electrolyte layers, while the transport of oxygen through the
air/electrolyte interface was the RDS for very thin layers, resulting in the
independence of \( i_{\text{lim}} \) on \( \delta \).

Despite extensive researches on droplet corrosion and thin electrolyte
electrochemistry, relatively few studies have been conducted on the electrochemistry
under droplets. Dubuisson et al. [23, 24] studied corrosion of galvanized steel under
both micrometric NaCl and Na₂SO₄ droplets using a microcell with size-reduced
counter and reference electrodes. The results of electrochemical impedance
spectroscopy showed that the corrosion rate and thus the oxygen reduction rate were independent of $\delta$ when $\delta > 800 \, \mu m$, while it increased with decreasing $\delta$ when $\delta < 800 \, \mu m$. The reason for this result was the change from diffusion-limited oxygen reduction for thick electrolytes to diffusion-controlled reduction for thinner electrolytes.

Recently, Jiang et al. \cite{40, 41} studied the effect of the gas/liquid/solid three phase boundary (TPB) zone on the cathodic polarization behavior of metals. One TPB zone studied was the droplet/metal interface under the peripheral region of a salt droplet with a height of less than 100 $\mu m$. By performing cathodic polarization experiments in large 0.1 M NaCl droplets (D = 1.18 cm – 2.67 cm) on a planar A3 steel sample, the researchers found that limiting cathodic current density increased linearly with increasing the TPB length per unit area, which was calculated as $2/r$.

Literature survey showed that many studies have included electrochemical tests under thin electrolyte layers, but none of these studies used electrochemical methods to examine corrosion initiation from droplets formed by deliquesce of salt particles. In this dissertation, novel micro electrodes were employed to study corrosion of steel under NaCl droplets.

### 2.4 Raman Characterization

There has been extensive in situ Raman spectroscopic work conducted on iron passivity,\cite{42} corrosion of iron and steel in bulk solutions,\cite{43-47} and pitting of stainless steel,\cite{48, 49} Johnston \cite{43} studied corroding iron electrodes polarized at certain potentials using in situ Raman spectroscopy. The results revealed that a
passivating layer of goethite ($\alpha$-FeOOH) formed on the iron electrode that was negatively polarized. Lepidocrocite formed only in high pH environments and subsequently reduced to magnetite.

Boucherit et al. [45, 46] used in situ Raman spectroscopy to characterize the passive films and pitting corrosion products grown on iron and an iron-molybdenum alloy in the presence of Cl$^-$ or SO$_4^{2-}$. They obtained Raman spectra of GR for the first time. By potentiostatically polarizing an iron electrode to the pitting potential (+600 mV$_{SCE}$) in 0.05 M NaOH + 0.03 M NaCl solution, they obtained a green gelatinous rust layer on the electrode, which showed Raman bands at 420 and 505 cm$^{-1}$, corresponding to Fe$^{2+}$–OH$^-$ and Fe$^{3+}$–OH$^-$ stretching modes, respectively. This rust layer evolved towards lepidocrocite with reddish-brown color both when kept in the open air and when left in an electrolyte without polarization. Under the GR layer, an inner layer of magnetite with a Raman band at 665 cm$^{-1}$ also developed.

Lanarde et al. [47] studied the corrosion behavior of iron and X70 carbon steel in mineral waters at the open-circuit potential (OCP) as well as under cathodic polarization (CP). For both iron and X70 steel, at both OCP and under CP, pitting initiated from impurities in the metals and developed around sulfides (in carbon steel) and silicates (in iron). In each case, GR with characteristic Raman bands at 420 and 505 cm$^{-1}$ was the first corrosion product formed and did so preferentially in the vicinity of corrosion pits.

This dissertation investigated corrosion initiation from NaCl droplets formed by deliquescence of pre-deposited NaCl particles upon exposure to high humidity
The various rust species formed during the corrosion process were identified using both *in situ* and *ex situ* Raman spectroscopy.

### 2.5 Evans’ Droplet Experiments

As one of the classic experiments in corrosion science, the droplet experiment reported by U. R. Evans in 1926 [50, 51] explained the establishment of local anodes and cathodes due to the formation of aeration differential cells. According to Evans, [51, 52] any geometrical factor that renders a higher concentration of oxygen at one part of a metal surface and a lower concentration (or zero) at another will result in the former becoming the cathode and the latter the anode of the corrosion cell, thus leading to localized corrosion. For the electrolyte droplets on top of steel sample, if we assume that no dissolved oxygen is present initially and mass transfer occurs only by diffusion, it is apparent that the diffusion of oxygen from the atmosphere to the metal surface will occur most rapidly through the thin layer of solution at the periphery of the droplet and most slowly at the center of the droplet. Therefore, the metal substrate under the periphery of the droplet will become the cathode and that under the center of the droplet will become the anode of the differential aeration cell. This classical work of Evans has been discussed in corrosion textbook [53] and several research papers.[54, 55]

Chen et al. [54] obtained for the first time the potential distribution in the classic Evans droplet experiment conducted on steel using the scanning Kelvin probe analysis. They found that the lowest potential values occur in the center of the NaCl droplet. The potential drop was also observed in areas not under but adjacent to the
droplet, possibly due to the formation of a thin layer of moisture. They believed that much of the driving force for the dissolution reaction in the center of the droplet resulted from the rate of the cathodic reaction in the thin electrolyte layers adjacent to the droplet.

Meijers et al. [55] conducted similar work using scanning Kelvin probe, but with also FeCl$_3$ and NaOH droplets besides the NaCl droplets. In both studies, the peripheral cathode with higher pH environment was verified by the color change of the indicator-phenolphthalein to purple.

The rust species formed in the Evans droplet experiment were not identified experimentally. In his original work, Evans [51] mentioned that the central anodic zone and the peripheral cathodic ring was “separated by a ring of rust”. Chen et al. [54] and Meijers et al. [55] also reported the formation of rust ring in Evans droplet experiments, but did not specify the types of rust formed. In reference [53], it was mentioned that rust formed in between the anodic and the cathodic sites was Fe$_2$O$_3$.H$_2$O, which came from rapid oxidization of Fe(OH)$_2$ by the dissolved oxygen in the droplets.

In this dissertation, the rust species formed in the Evans’ droplet experiments were identified using in situ Raman spectroscopy.
Chapter 3

Natural Salt Particle Collection

3.1 Experimental

3.1.1 Sample Preparation

Specimens with dimensions of 10 mm × 10 mm were cut from 1018 steel sheet (3 mm thick) using a low-speed diamond saw, and were then mounted in epoxy resin (Buehler Epoxicure). The samples were subsequently ground with 180, 400, 1200-grit SiC grinding paper; polished with 9.0, 3.0, 1.0 µm METADI SUPREME polycrystalline diamond suspensions (BUEHLER); and finished with a MASTERPOLISHTM polishing suspension (BUEHLER). The specimens were then rinsed with ultrapure water (18.0 MΩ-cm) and reagent alcohol and then dried under warm air. Finally, all samples were kept in a dry box (~1% RH) for 5 days prior to conducting experiments to allow the formation and stabilization of the surface oxide film.

3.1.2 Sample Exposure

Polished samples (i.e., 1018 steel and pure zinc) were exposed to two marine test sites: Kilauea test site located in the National Volcano Park, Big Island, Hawai‘i, and Coconut Island test site in Oahu, Hawai‘i. The specimens were attached to the exposure racks for 30 min. The racks were designed with a 45° angle facing the northeast (into the trade winds). After exposure, the samples were transported back to the laboratory in Petri dishes and with a dessicator to prevent deliquescence of the
salts particles. Then, in the laboratory, the samples were kept in a dry box (~1% RH) prior to scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDXA).

3.1.3 SEM/EDXA Characterization

A Hitachi S-3400N SEM equipped with an Oxford Instruments energy dispersive X-ray analyzer system was used to characterize the samples. Quantitative elemental analysis (fixed-point) was conducted on both sea salt particles and corroded regions on specimens. Elemental mapping was also conducted on the corroded regions.

3.2 Results and Discussion

3.2.1 Natural Salt Particle Deposition on Steel

3.2.1.1 Characterization of Salt Particles

Many salt particles (Figures 1-4) were found on 1018 steel samples that were exposed to the Kilauea (KI) test site for 30 min. Among these salt particles, single cubic crystals with sizes of 2 – 5 µm (Figure 1a-e) were predominant. Notice the circular areas that surround the main salt particles and are slightly darker than other part of the steel substrate, indicating previous presence of seawater droplets. The dark circular regions may be caused by some organic compounds in seawater droplets. This phenomenon indicated that the salt particles likely formed by dehydration of seawater droplets that initially deposited on the steel surface. Smaller salt particles (D < 1 µm) were found either near the primary salt particles (Figure 1a) or along the peripheries of the darker areas (Figure 1b-e). The main salt particles consisted of
only NaCl, as indicated by an EDXA spectrum (Figure 1f1) from the large particle shown in Figure 1e. The smaller salt particles were either NaCl (as marked by black arrows in Figure 1e) or those containing S and Ca (marked by a white arrow in Figure 1e). The existence of S and Ca indicates the deposition of Na₂SO₄ and CaCl₂, which are also major sea salt constituents (Table 1).[56] Two other major sea salt components, i.e., KCl and MgCl₂, were not detected in any of the small salt particles surrounding the big ones in Figure 1 using EDXA, possibly because their amounts in relatively small seawater droplets (D < 20 µm) is below the EDXA detection limit (0.1%). However, MgCl₂ and KCl were found in salt particles resulted from larger seawater droplets (D > 30 µm) (the following sections).

Figure 1. (a)-(e) Cubic NaCl particles found on 1018 steel samples that were exposed to the KI test site for 30 min; (f) EDXA spectra of the salt particles in (e).
Table 1. The composition of sea salt according to ASTM D-1141-52 [56].

<table>
<thead>
<tr>
<th>Salts</th>
<th>NaCl</th>
<th>MgCl₂•6H₂O</th>
<th>Na₂SO₄</th>
<th>CaCl₂</th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Percent</td>
<td>58.49%</td>
<td>26.46%</td>
<td>9.75%</td>
<td>2.77%</td>
<td>1.65%</td>
</tr>
</tbody>
</table>

In addition to the cubic NaCl particles, individual irregular-shaped NaCl particles were also found on 1018 steel samples that were exposed to the KI test site for 30 min (Figure 2). Similar to previous results (Figure 1), the primary NaCl particles (D = ~ 10 µm) generally crystallized in the centers of the original seawater droplet areas, while smaller salt particles (D < 1 µm) formed surrounding the large salt particles (Figure 2a-c). Notice that some of the large, irregular-shaped salt particles also contained a trace of Mg (Figure 2c), which might be one reason for their irregular shape. Most of the smaller salt particles were NaCl particles (as indicated by black arrows in Figure 2b and c), while others contained Ca and S (as marked by white arrows in Figure 2b and c). Unlike the salt particles shown in Figures 1, 2a and b, some small particles in Figure 2c also contained Mg and K (see Figure 2d2), indicating the existence of MgCl₂ and KCl from seawater. It may be that MgCl₂ and KCl were found because of the higher content of Mg and K in the larger original droplet (D = ~ 30 µm) that resulted in salt particles in Figure 2c compared to those (D = ~ 10 µm) that formed salt particles in Figures 1, 2a and b.
Figure 2. (a)-(c) Irregular-shaped NaCl particles found on 1018 steel samples that were exposed to the KI test site for 30 min; (d) EDXA spectra of the salt particles in (c).

Figure 3. (a) A cluster of salt particles found on a 1018 steel sample that were exposed to the KI test site for 30 min; (b) EDXA spectra of (b1) a cubic salt particle and (b2) a rounded salt particle in (a).

Clusters of salt particles were also found on 1018 steel samples that were exposed to the KI test site for 30 min (i.e., Figure 3). Most of the salt particles in this cluster were cubic NaCl particles (Figure 3b1) with sizes of 1 – 5 µm, while some of them were non-cubic salt particles containing all the major sea salt components, i.e., NaCl, MgCl₂, CaCl₂, KCl and Na₂SO₄ (Figure 3b2 and Table 2).
Table 2. Chemical composition of the rounded salt particle in Figure 3a (indicated by an arrow).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>8.58</td>
<td>22.86</td>
<td>8.37</td>
<td>1.21</td>
<td>0.33</td>
<td>9.9</td>
<td>5.42</td>
<td>1.23</td>
<td>7.78</td>
<td>34.32</td>
</tr>
<tr>
<td>Atomic %</td>
<td>18.46</td>
<td>36.91</td>
<td>9.4</td>
<td>1.28</td>
<td>0.31</td>
<td>7.98</td>
<td>3.95</td>
<td>0.81</td>
<td>5.02</td>
<td>15.88</td>
</tr>
</tbody>
</table>

At other regions of the specimen, individual KCl particles were found. A relatively large particle (D = ~5 µm) (Figure 4a) showed cubic structure, while smaller particles (D < 1 µm) (Figure 4b) were round in shape. Finally, CaCO₃ particles (i.e., Figure 4c), which could be sand particles, were also identified.

![Figure 4](image-url)

Figure 4. (a) and (b) KCl particles found on 1018 steel samples that were exposed to the KI test site for 30 min; (c) a CaCO₃ particle found on a 1018 steel sample; (d) EDXA spectra of the particles in (a)-(c).

The above results showed that, in most cases NaCl and sometimes KCl separated from other sea salt components, likely during the dehydration process of the seawater droplets. Since the relative humidity during sample exposure in the KI test site was about 80%, seawater droplets that attached to the steel samples did not dry out in the ambient environment. When the relative humidity was reduced (in the dessicator), various types of salts crystallized from the droplets.
crystals were the type of salt most often found (Figures 1-3), as it is the primary constituent of seawater. When NaCl crystallizes, it leaves behind other ions from which other salts can crystallize. Potassium chloride crystals were also found, but it was not clear why Na₂SO₄ crystals were not observed, especially since it makes up about 10% of sea salt. Individual MgCl₂ and CaCl₂ particles were also not found and might be due to their low critical relative humidity (CRH) values, which cause them to crystallize lastly and encompass other sea salt components, i.e., KCl and Na₂SO₄. Not to be discussed here, dehydration kinetics of seawater droplets has to be investigated for exact explanation of the above results. Notice that since individual NaCl (Figure 1b) and KCl (Figure 4a) particles were found without coexisting with other sea salt components, they may have formed from seawater droplets containing only NaCl and KCl, indicating the separation of sea salt during the formation process of seawater droplets from the ocean. One possibility is that, airborne seawater droplets may partially evaporate leading to the separation of some of its constituent salts. Hence, when they settle on a substrate, some of the constituent salt species may be missing.

Cole et al. [57] also studied the salt particles that crystallized on metal surfaces, but from laboratory-sprayed saturated seawater instead of natural-deposited seawater droplets. They found that the primary crystal was cubic NaCl, while the fine crystals surrounding the main crystal contained either Na, Mg and Cl or (less frequently) Ca and S. Our natural salt particle deposition experiments showed similar results but with some differences. We found that most of the small salt particles that
surrounded the major NaCl particles were primarily pure NaCl instead of the Mg containing particles as they found. Only a few salt particles contained S and Ca, while salt particles containing Mg were scarce. In addition, individual KCl particles, both a large cubic and fine rounded ones, were identified in this study but not in Cole’s work. Lastly, salt particles (D = ~5 µm) that contained various types of salts resulting from the evaporation of larger seawater droplets (D = ~30 µm) were also found (Figure 3). This finding indicates that larger mixed salt particles (D = ~5 µm) can form from larger seawater droplets (D > 30 µm) which have relatively large amounts of other sea salt components besides NaCl. The differences between Cole’s work and this investigation could be caused by 1) variation in the seawater composition (i.e., ASTM vs. natural airborne), and 2) the rate of evaporation that can affect the nucleation and growth of the salt crystals.

3.2.1.2 Effect of Salt Particles on Corrosion Initiation

Some important observations were made regarding the lack of corrosion initiating near Cl-containing particles that originated from droplets < 30 µm (Figures 1-4). In these cases, the salt particles and clusters were generally less than 10 µm in diameter and crystallized from seawater droplets that left residual features on the substrate, indicating that they were less than 30 µm in diameter. This result generally agrees well with our laboratory study [58] on 1018 steel, in which corrosion did not initiate from small NaCl droplets (D < 45 µm) that formed by deliquescence of pre-deposited NaCl particles, but did initiate under larger droplets.
In contrast, corrosion was found to occur under larger seawater droplets (D > 50 µm) (Figure 5a-c). Corrosion products (Fe and O) were detected over the whole original seawater droplet area (Figure 5d). Sea salts, mostly NaCl but also others, i.e., MgCl₂ (in the center), were found coexisting with the corrosion products. The existence of MgCl₂ (Figure 5d1) corroborates previous discussion concluding that MgCl₂ can be found only in larger seawater droplets and the concomitant salt particles.
Figure 5. (a)-(c) Corroded regions found on 1018 steel samples that were exposed to the KI test site for 30 min; (d) EDX A spectra of the corrosion products and salt particles in (c); (e) elemental maps of (e1) Cl and (e2) Na from the corroded area in (c); (f) comparison of elements Cl and Na along the dashed line shown in (c). The data in (f) was obtained by doing line scan reconstruction from the EDX A elemental mapping data.
Previous studies on corrosion under NaCl droplets [14, 58] have revealed that Na\(^+\) and Cl\(^-\) ions migrated to cathodic and anodic sites respectively during corrosion. Our EDXA elemental mapping over the corroded regions also showed ion migration during the 30 min exposure period. Elemental maps of Cl and Na (Figure 5e) show some regions in the center with Cl and no Na (marked by ovals) and others along the perimeter with Na and no Cl (marked by circles), indicating the migration of Na\(^+\) and Cl\(^-\) ions. Quantitative analysis through line scan reconstruction (line (f) in Figure 5c) from the mapping data shows that Cl had higher atomic percent than Na in the center of the original seawater droplet area, while Na had a higher content in the periphery (Figure 5f), confirming that some Na and Cl ions migrated to the perimeter and the center of the corroded area respectively, under the initially deposited seawater droplet.

It is known that [51, 52] any geometrical factor that renders a higher concentration of oxygen at one part of a steel surface and a lower concentration (or zero) at another will result in the former becoming the cathode and the latter the anode of the corrosion cell, thus leading to localized corrosion. For the case of natural seawater droplets that deposited on steel surface, if we assume that no dissolved oxygen is initially present at the metal/droplet interface and mass transfer occurs only by diffusion, it is apparent that the diffusion of oxygen from the atmosphere to the metal surface will occur most rapidly through the thin layer of solution at the periphery of the droplet and most slowly at the center of the droplet. Therefore, the metal substrate under the periphery of the droplet becomes cathode and that under the center of the droplet becomes anode of the differential aeration cell.
The active dissolution of steel in the central anode generates $\text{Fe}^{2+}$ (Equation 1), which then reacts with water (hydrolysis) forming $\text{H}^+$ (Equation 2), which attracts $\text{Cl}^-$ ions to the anode. Similarly, $\text{Na}^+$ ions migrate to the peripheral cathode due to the attraction of $\text{OH}^-$ generated by $\text{O}_2$ reduction (Equation 3).

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)$$

$$\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \quad (2)$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (3)$$

In contrast to the KI test site, less salt particles and corroded areas were found on 1018 steel samples that were exposed to the mild marine test site in Coconut Island (CI), Oahu, Hawai‘i. A possible reason is the relatively low wind velocity, which was about 2.2 m/s during sample exposure and is below the critical value.[11] A few salt particles that were collected (Figure 6) showed that the large salt particles were composed of mainly $\text{NaCl}$, and sometimes also with $\text{S}$, $\text{K}$, $\text{Mg}$ and $\text{Ca}$. The fine salt crystals that scattered over the initial seawater droplet areas were $\text{NaCl}$. Again, noticeable corrosion was not detected in the initial seawater droplet areas.

![Figure 6. Examples of the salt particles found on 1018 steel exposed to the CI test site for 30 min.](image)
3.2.2 Natural Salt Particle Deposition on Pure Zinc

Extensive corrosion occurred under most of the seawater droplets that deposited on pure zinc samples after 30 min exposure in the KI test site (Figure 7), with similar corrosion morphologies as reported by Cole et al.[59] An EDXA spectrum (Figure 7f) from a corroded area (in Figure 7e) shows the presence of corrosion product (Zn and O) together with sea salts, i.e., NaCl, Na₂SO₄, and MgCl₂. Corrosion also propagated out of the relatively large seawater droplet areas (D = ~30 µm) on zinc substrates (Figure 7a, b and e), possibly due to secondary spreading [14] that occurred during corrosion. Small seawater droplets (D < 10 µm) caused corrosion only under the droplets and not in the surrounding areas (Figure 7c and d). In addition, the seawater droplets that attached to the sample surface at different times may cause corrosion to different extents. A droplet that deposited onto a sample earlier in the 30 min exposure period might have caused more corrosion, while a droplet that deposited on the zinc surface later resulted in less corrosion (Figure 7c and d). Sometimes, NaCl particles crystallized on top of the corrosion products (Figure 7d) instead of mixed with them.
Figure 7. (a)-(e) Corroded regions caused by seawater droplets on pure zinc samples that were exposed to the KI test site for 30 min; (f) An EDXA spectrum from the corroded area in (e).

Individual sea salt particles, mainly NaCl (Figure 8d1), that were not mixed with corrosion products were also found on pure zinc samples that were exposed to the KI test site for 30 min (Figure 8a-c). Only few corrosion products (not very visible) were detected on the zinc substrates that were previously covered by seawater droplets (Figure 8d2). Generally, seawater droplets which had stayed on the zinc surface for only a short time during the 30 min exposure caused little or no corrosion. However, unlike the case for steel, corrosion can occur on zinc after exposure to the seawater droplets due to a lack of surface passive layers.
Neither corroded areas caused by seawater droplets nor sea salt particles were found on the pure zinc samples that were exposed to the Cl test site for 30 min, which was likely due to relatively low wind velocities during the sample exposure period.

### 3.3 Conclusion

To study the initial stage of marine atmospheric corrosion, sea salt particles that deposited on metal surfaces and the corrosion caused by them were studied for the first time by exposing samples in marine test sites for only 30 min. The following results were obtained.

On 1018 steel samples that were exposed to the KI test site, both small sea salt particles ($D < 5 \mu m$) and salt particle clusters ($D < 10 \mu m$) that formed after dehydration of relatively small seawater droplets ($D < 30 \mu m$) and corrosion-initiation sites caused by larger seawater droplets ($D > 50 \mu m$) were found. Among all the small salt particles, single cubic NaCl particles ($D < 5 \mu m$) were predominant. Fine particles...
salt particles (D < 1 µm) containing Ca, S and Mg were found scattered around the larger NaCl particles. Individual KCl particles were also found separated from other sea salt components. Corrosion products were not detected near small sea salt particles/clusters, indicating their inability to induce corrosion on steel during the 30 min exposure period. Corrosion that occurred under larger seawater droplets (D > 50 µm) showed typical characteristics of droplet corrosion, with Cl− and Na+ ions migrated to the central anode and peripheral cathode, respectively.

Corrosion occurred on pure zinc samples under almost all the attached seawater droplets. Corrosion products and sea salts usually coexisted, forming a porous structure. A few NaCl crystals that were not mixed with corrosion products were also found, possibly due to the relatively short time they stayed on the sample.

Few or no sea salt particles and the subsequent corroded regions were found on both 1018 steel and pure zinc samples that were exposed to the CI test site due to low wind velocity during sample exposure period.
Chapter 4

NaCl Particle-Induced Marine Atmospheric Corrosion of Steel

4.1 Experimental

4.1.1 Sample Preparation

Similarly as field study (Chapter 3), 1018 carbon steel was used for the study of salt particle-induced marine atmospheric corrosion initiation. The procedure of sample preparation was the same as that shown in Section 3.1.1.

The salt used was analytical grade NaCl.

Two approaches were employed to deposit salt particles onto the sample surfaces. The first approach involved using an ultrasonic humidifier (ETS, model 5462) and a saturated solution made of analytical grade NaCl and ultrapure water (18.0 MΩ-cm). The samples were exposed to the mist produced by the humidifier for 2 seconds, and immediately placed in a dry box (~1% RH). After drying, the salt droplets rendered many minute salt particles (D ≈ 1 – 10 µm) on the samples.

The second approach was the manual deposition of salt particles using a tiny probe (D ≈ 10 µm) and a stereomicroscope. Analytical grade NaCl crystals were first ground in a glass Petri dish. Then single salt particles (D = 2 – 50 µm) were picked and placed on polished sample surfaces using a tiny probe (D = 2 µm) with the assistance of static electricity.
4.1.2 Experimental Setup

The humidity chamber consisted of a modified plastic Petri dish with cover (Figure 9), containing a small reservoir of ultrapure water to maintain the RH above 80%. A thin ($t \approx 0.14$ mm) glass window was installed in the Petri-dish cover to form a 2-cm diameter view port for the microscope. The glass window was secured using an ethyl cyanoacrylate (Super Glue®) adhesive.

![Figure 9. Schematic of the experimental setup used for corrosion initiation experiments.](image)

4.1.3 Experimental Procedures

The sample with pre-deposited NaCl particles was put into the humidity chamber. Images of the salt particles were taken using an optical microscope. Then, ultrapure water (18.0 MΩ-cm) was injected into the reservoir, and the Petri dish was covered immediately. The relative humidity inside the chamber quickly increased from the ambient room humidity (~58%) to 75% (critical relative humidity of NaCl) within 5 min (Figure 10), enabling the solutionization of the NaCl particles.

The formation of the NaCl droplets and corrosion initiation and propagation under the NaCl droplets were observed and recorded using the optical microscope.
4.1.4 SEM/EDXA Characterization

After the specimen was corroded for 6 h, it was kept in the dry box (~1% RH) for subsequent SEM/EDXA characterization. The elemental distribution over the droplet corrosion area was measured using an Oxford Instruments energy-dispersive X-ray analyzer (EDXA) system integrated with a Hitachi S-3400N scanning electron microscopy (SEM). The quantitative information and comparison of some elements along a line was obtained in atomic percent.

4.2 Results and Discussion

4.2.1 Corrosion Initiation at Pre-deposited NaCl Particles

The deposition of salt particles of various sizes on 1018 steel samples resulted in different corrosion morphologies (Figures 11-14).

Salt particles deposited using the ultrasonic humidifier resulted in deliquescent salt particle sizes ranging from approximately 2 to 30 µm (Figure 11). The four images in Figure 11 were taken at the same site but at different times. Figure 11a shows the salt particles on the sample surface before exposure to the humidity.
chamber. Corrosion did not occur during the deposition process, indicating that the ultrasonic humidifier can be effectively used for minute salt particle deposition.

Upon exposing to RH higher than 80%, the salt particles deliquesced within about 5 min (Figure 11b). Figure 11c shows the droplets exposed in the humidity chamber for 6 h at RH > 80%. The droplets were clear and the steel surface was clean, indicating that corrosion did not occur even after 6 h of exposure. When the sample was removed from the humidity chamber, the salt particles recrystallized at the ambient room humidity (~58%) (Figure 11d). No visible corrosion products were observed on the steel surfaces adjacent to the salt particles representing the areas under the original droplets. On the entire 1-cm² sample, only a few corroded areas were observed almost exclusively in the perimeter region of the sample. Defects left by insufficient polishing or inclusions in the steel are possible explanations for the limited corrosion.

**Figure 11.** Sequence of time-lapsed photographs of ultrasonically-deposited NaCl particles on a steel substrate. a) NaCl particles after deposition and before exposing to high humidity, b) NaCl droplets immediately after the full dissolution of the NaCl particles which were exposed to RH > 80% for approximately 5 min, c) NaCl droplets after 6 h in the humidity chamber, d) recrystallized NaCl salt particles from droplets in (c) after removal from humidity chamber. The scale bar applies to all images.
No corrosion was also observed under droplets originating from small manually-deposited NaCl particles on the 1018 steel surface (example shown in Figure 12). In this example, the droplet size was about 41 µm (Figure 12b) when the salt particle (Figure 12a) first dissolved in the humidity chamber, and increased to about 45 µm after 6 h exposure (Figure 12c). Corrosion was not detected under the droplet even after 6 h of exposure, hence, showing behavior consistent with that of salt particles deposited with the ultrasonic humidifier. The image taken after the droplet evaporated (Figure 12d) showed one relatively large and several minute cubic NaCl particles without corrosion products. Additional experiments also showed that corrosion did not initiate under NaCl droplets with diameter smaller than approximately 45 µm.

Figure 12. Sequence of time-lapsed photographs of a manually-deposited NaCl particle on a steel substrate. a) NaCl particle before exposing to high humidity, b) NaCl droplet immediately after full dissolution of the NaCl particle exposed to RH > 80% for approximately 5 min, c) NaCl droplet after 6 h in the humidity chamber, d) recrystallized NaCl salt particle from droplet in (c) after removal from humidity chamber. The scale bar applies to all images.
There are two possible reasons for the lack of corrosion under these small NaCl droplets. First, the small droplet size reduces the chance of containing a slag-based inclusion or an area with defects in surface iron oxide film, which may serve as an effective anodic site. Therefore, the small droplets were actually in contact with surface iron oxide film, which was supposed to be Fe₂O₃ and with a thickness of approximately 2 – 5 nm according to literature. Calculation showed that the iron oxide film could not be dissolved by the droplets on top even it was very thin.

Second, the higher oxygen content in very small droplets may lead to passivation of the substrate. It is known that steel passivates when oxygen concentrations exceed a critical value.[60] Young’s equation for spherical droplets \( \Delta P = P_{inside} - P_{outside} = 2\gamma / R \) states that smaller droplets have larger pressures than those of larger droplets. Larger pressure inside the small droplet renders higher O₂ concentration. Figure 13 shows the O₂ concentration increase in NaCl droplets with sizes increasing from 1 to 100 µm.

![Figure 13. Oxygen concentrations in different sized NaCl droplets on steel.](image-url)
Under larger deliquescent NaCl particles, corrosion initiated quickly with the concomitant formation of smaller satellite droplets around the periphery of the main droplets (examples shown in Figure 14).

![Figure 14. Three examples of corrosion sites under large NaCl droplets after 6-h exposure in the humidity chamber with RH > 80%.](image)

Corrosion generally occurred within approximately 10 min under large NaCl droplets formed by deliquescence. The time of corrosion initiation was also dependent on the size of the droplets or the local microstructure of the steel samples. Initially, the corrosion products that formed in the droplets were yellowish flocculent clusters, which moved in a random pattern, a phenomenon similar to Brownian motion. Corrosion products, which then appeared dark, spread over the entire droplet area. Many tiny secondary droplets with diameters ranging from approximately 1 – 5 µm formed adjacent to the original salt droplets within about 30 min, varying to some extent with each individual experiment. As corrosion proceeded, more secondary droplets formed on the perimeter of the secondary spreading area. Also, some of the secondary droplets adjacent to the original NaCl droplets coalesced forming larger secondary droplets (Figure 14) having diameters greater than 50 µm. The areas covered by the secondary droplets were significantly larger than those of the original NaCl droplets. The excess water in the secondary
droplets may have originated from both the original NaCl droplets and the moisture in the atmosphere.[22]

Corrosion did not occur under any secondary droplet on the steel substrate (Figure 14), which was likely to have been passivated by the formation of hydroxide ions. Evans [51] reported that during droplet corrosion, the center of the droplet serves as the anodic area, and the perimeter of the droplet serves as the cathodic area. Hence, in this case, if oxygen reduction occurs primarily in the region of secondary spreading, alkalinization of those regions will result (Equation 3).[22]

The increase in pH of the secondary spreading area may passivate the steel in those regions. In addition, if the cathodic area is confined to the secondary spreading region, and the anodic area confined to the original central droplet, an electric field will be set up by the accumulation of hydroxide ions at the cathode and protons at the anode (Equations 1-3).

The potential gradient could induce the migration of Na\(^+\) from the central anodic region to the secondary spreading regions, and concentrate Cl\(^-\) in the central anodic region. This result would render the central anodic region more prone to corrosion and the secondary spreading regions less prone to corrosion.

Filiform corrosion was also observed at some large NaCl droplets (example shown in Figure 15). Upon exposure to high humidity (RH > 80%), a relatively large pre-deposited NaCl particle (Figure 15a) deliquesced within about 5 min (Figure 15b). Corrosion initiated under the droplet after approximately 10 min (Figure 15c). Some small corrosion pits and corrosion products appearing as yellowish specks
became visible in the droplet. Secondary spreading occurred after approximately 30 min (Figure 15d). Even after 6 h of exposure, corrosion did not occur under the secondary droplets. As the corrosion in the original central droplet progressed, two small pools of solution leaked from the central droplet, and corrosion initiated within several min in the pools (Figure 15e). In the following three additional hours of exposure, more NaCl solution leaked from the original droplet, resulting in the initiation of filiform corrosion (Figure 15f). This type of corrosion was also observed on iron by other researchers [17] who proposed that filiform corrosion was driven by an aeration cell, where the tip acts as the anodic area due to higher chloride content (leading to lower oxygen solubility) than the original droplet site.

**Figure 15.** Sequence of images showing the initiation of filiform corrosion on a steel substrate originating from a manually-deposited large NaCl particle after deliquescence. a) NaCl particle on steel substrate before deliquescence, b) NaCl droplet immediately after full dissolution of the salt particle exposed to RH > 80% after 5 min, c) corrosion initiating under the NaCl droplets after 10 min in the humidity chamber, d) secondary droplets forming around the original droplet, e) leakage of the solution pools from the original droplet causing filiform corrosion, f) the filiform corrosion area and part of the secondary spreading area after 6 h exposure in the humidity chamber. The 40 µm scale bar applies to images a – e.
4.2.2 Elemental Mapping of Filiform Corrosion Sites

The resultant morphology of one filiform corrosion site (same as in Figure 15f) originating from an NaCl droplet was investigated using SEM/EDXA. At the location of the original droplet (Figure 16), a porous shell was evident, which might have been a mixture of corrosion products and NaCl salt. To the upper left region of the original central droplet, there was evidence of prior solution leakage with a corrosion filament emanating in a random pattern from the side of the original droplet. Since the sample was kept in the dry box after the corrosion initiation experiment, the filament dehydrated, which was evident by cracking of the corrosion products. Notice that the base of the filament close to the original droplet is brighter than the head of the filament as observed in the SEM (Figure 16), which may indicate some compositional differences between those areas. Since the image was taken in the secondary electron mode, the contrast may be related to charging. The compositional differences were investigated using SEM/EDXA (Figure 16).

Figure 16. SEM image showing the initiation of filiform corrosion from an NaCl droplet.
There was a significant difference in the distribution of Cl and Na (Figure 17). In the area where the original droplet was located, both Na and Cl were found. However, in the region where two small pools leaked from the original droplet (top left of the original droplet site), Cl and no Na was detected. The detection limit for EDXA is on the order of 0.1 atomic percent. During corrosion under the original droplet and the growth of secondary droplets around the perimeter, Na$^+$ migrated to the cathodic secondary spreading area. When the two pools of solution leaked from the original droplet, the uncorroded areas under the pools became new active anodic sites since 1) the solution in the original droplet may have become corrosive by Cl$^-$ accumulation and acidification from the formation of protons due to the hydrolysis of Fe$^{2+}$, and 2) the original anodic area (original droplet) was already covered with corrosion products,[17] which may potentially stifle additional corrosion relative to that in the new anodic areas. The newly formed anodic areas under the two pools further became Na depleted and Cl enriched due to the migration of Na$^+$ to the cathodic area and Cl$^-$ to the anodic area.

In the corrosion filament away from the filament base, only Cl was detected; and in the base of the filament, more Na was detected. Since the base of the filament
was connected to the solution pool that leaked from the original droplets, it may have originally contained Cl when it was actively corroding. However, as the filament grew much longer, the base of the filament became cathodic to support more growth in the anodic filament head. The Cl then could have migrated out of the filament base, as shown by the EDXA mapping results. The filament tip had only Cl and no Na due to its anodic characteristics.

In the area outside of the corrosion region (secondary spreading area), varying levels of Na and Cl were found. Comparing the maps of Na and Cl (Figure 17b), more Na than Cl was detected in the secondary spreading area, especially in the region to the left of the original droplet site. Since the secondary spreading areas served as cathodic sites, more Na\(^+\) ions are expected to migrate to those regions.

To study the distribution of Na and Cl in the corroded area with greater detail, a quantitative comparison (Figure 18) was conducted by line-scan reconstruction from the elemental-mapping data. Two lines were drawn on the micrograph (Figure 18a) to indicate the paths along which the line scan reconstructions were conducted. The solid line traverses a straight path cutting through the original droplet (line-scan results in Figure 18b), and the dashed line traverses a curved path along the corrosion filament (line-scan results in Figure 18c).
Figure 18. Quantitative comparison of Na and Cl profiles. a) SEM image showing the paths along which line reconstructions were conducted. b) the concentration profiles of Na and Cl traversing the secondary droplet region, then cutting through the original droplet site, and exiting to another secondary droplet region (solid line in (a)), c) the concentration profiles of Na and Cl traversing along the region where solution leaked from the original droplet, then into the path of filiform corrosion, and finally exiting into the secondary droplet area (dashed line in (a)).

The line scan through the original droplet (Figure 18b) shows a higher content of Na than Cl in both the original droplet site (region C in Figure 18b) and the secondary spreading areas (regions A and D in Figure 18b). In the original droplet site (region C in Figure 18b), the concentration of Na was approximately 10 atomic % (at.%) and that of Cl was approximately 5 at.%. This is a characteristic of a cathodic area in droplet corrosion. Hence, though the original droplet area was initially an anodic site, it later likely served as a cathodic site to the new anodic regions under the two pools after the solution leaked from the original droplet. Sodium ions may have then migrated back to the original droplet and Cl\(^-\) migrated out of the original droplet.
area. In the secondary spreading areas (regions A and D in Figure 18b), Na and Cl were undetectable in some locations, representing places without secondary droplets. In other areas, the atomic percent of Na was approximately 5 at.% and that of Cl was approximately 1 at.%. Generally, therefore, Na had higher content than Cl in the secondary spreading areas, consistent with the characteristic of cathodic areas. Notice that for some points in region B (Figure 18b), Na was undetectable, while the concentration of Cl ranged from 2 at.% to 6 at.%. This area corresponds to the intersection of the solid line and the dashed line (Figure 18a), which is the initiation site of filiform corrosion and connected to the region where solution leaked out of the original droplet. This region, therefore, has characteristics that are similar to that of the regions where solution leakage occurred.

The concentration profiles of Na and Cl along the regions where solution leaked from the original droplet and along the corrosion filament are compared in Figure 18c. Segment A corresponds to the regions where solution leaked from the original droplet. In this segment, Na was largely undetectable, as indicated by the previous elemental mapping results (Figure 17b). In segment B corresponding to the base of the corrosion filament, the concentration of Na (8 at.%) was greater than that of Cl (3 at.%), indicating that the filament base may have transformed from an anodic to a cathodic region, as previously discussed. In segment C, the head of the corrosion filament, the concentration of Cl ranged from 6 to 12 at.% and Na was undetectable. The contrasting distributions of Na and Cl are likely due to the separation of anodic and cathodic sites. During corrosion, Na⁺ migrated to cathodic
regions while Cl' migrated to anodic regions. Given more time for filiform corrosion to propagate, the filament can grow to lengths much longer than that shown in this example. In that case, the cathodic area in the filament will be much longer, leaving only the very tip of the filament as the Cl-enriched anodic area, which was also observed by Weissenrieder et al. [17] Segment D extends beyond the filament head into the cathodic secondary spreading area and, therefore, the concentration of Na spikes to 6 to 14 at.% while that of Cl drops to less than 2 at.%.

Notice the different concentration profiles for Na and Cl in section B in Figure 18b and section B in Figure 18c. Section B corresponds to a location near the original droplet and might have NaCl solution leaked from it. Therefore, Na increased with the increase of Cl. The opposite trends in section B is due the difference between the anodic (sections A and C) and cathodic (section B) regions. Since anodic regions have higher Cl concentration and cathodic regions have higher Na concentration as compared to each other, the transitional region from anodic to cathodic (A to B) shows an increase of Na and a decrease of Cl. The opposite trends also apply to the transitional region from cathodic to anodic (B to C). Notice that in the filament (A, B and C) Na might exist as NaOH while Cl was incorporated in the rust.

4.2.3 Corrosion Initiation Sites at Slag-based Inclusions

It was found that corrosion always initiated in the same pattern under large NaCl droplets, with corrosion pits first forming in a particular area under the droplet and then expanding to a larger area. In order to study the specific area from where
corrosion initiated, short-time exposure experiments were conducted (Figure 19).

One large NaCl particle (Figure 19a) placed on a steel surface transformed into a large droplet by deliquescence after approximately 5 min in the humidity chamber (RH > 80%). Corrosion then quickly initiated on the perimeter of the droplet, with one corrosion pit forming adjacent to the inside region of the perimeter (Figure 19b). The pit grew with time (Figure 19c), and more corrosion products formed away from the pit. After 30 min in the humidity chamber (Figure 19c), the sample was removed and dried, resulting in the crystallization of the NaCl particle on top of the corrosion pit (Figure 19d). The sample was then cleaned using ultrapure water to remove the NaCl particle (Figure 19e and Figure 19f). EDXA showed the existence of Al which may have originated from slag. Hence, corrosion under relatively large NaCl droplets can also initiate from slag-based inclusions.

**Figure 19.** Images showing the stages of corrosion initiation under a manually-deposited large NaCl particle after deliquescence. a) NaCl particle on steel substrate before deliquescence, b) corrosion pit (indicated by arrow) under the NaCl droplet after 5 min with RH > 80%, c) growth of corrosion pit and formation of more corrosion products, d) recrystallized NaCl crystal on top of the corrosion pit after removal from the humidity chamber, e) same site as in (d) after removing NaCl particle using ultrapure water, f) SEM images showing the corroded area under the droplet. The 40 µm scale bar applies to images a – e.
Figure 20. SEM images showing two inclusions in the secondary spreading area. The lighter areas represent recrystallized NaCl particles from the secondary droplets. Notice the lack of corrosion. The 10 µm scale bar applies to both images.

Slag-based inclusions, however, do not always serve as corrosion initiations sites. Inclusions containing Al, Mg, Ca, and S did not induce corrosion when they were located in secondary spreading regions (Figure 20a and b). The high pH in the cathodic secondary spreading regions is likely to suppress corrosion even around these slag-based inclusions.

4.3 Conclusion

Corrosion did not initiate on 1018 steel under deliquescent NaCl particles having diameters less than approximately 45 µm. The small droplets may contain oxygen above a critical level necessary to passivate the steel surface. Corrosion always initiated under larger deliquescent NaCl particles, which were greater than approximately 45 µm in diameter. Secondary droplets also formed around the larger NaCl droplets, and spread out over a region covering an area at least several times that of the original droplet area. The areas under the secondary droplets served as cathodic sites and were free of corrosion. EDXA elemental mapping showed that Cl− migrated to anodic regions and Na+ migrated to cathodic regions. Hence, Na enrichment was observed in the secondary spreading regions.
Sometimes, filiform corrosion initiated from the larger NaCl droplets. The head of the filament was anodic, and hence found to be rich in Cl. The base of the filament and the original droplet region appeared to serve as cathodic sites, and were richer in Na as compared to Cl. Hence, the original droplet site which was initially anodic, transformed to a cathodic site with the emergence of the growing filament.

There was evidence that corrosion initiation inside of larger droplets occurred in regions of slag-based inclusions. These slag-based inclusions, however, did not initiate corrosion when they were in the cathodic secondary spreading regions.
Chapter 5

Droplet Electrochemistry

5.1 Experimental

5.1.1 Sample Preparation

The procedure for the preparation of 1018 steel samples was the same as that shown in Section 3.1.1.

The grinding of analytical grade NaCl was the same as shown in Section 4.1.1.

5.1.2 Experimental Setup

An experimental chamber was fabricated from acrylic plastic (Figure 21). A sliding glass door (1 mm thick) allowed observation into the chamber using a stereomicroscope. Two electrode ports were drilled on top of the chamber for droplet concentration and pH measurements (Figure 21), while polarization measurements required only one port (Figure 23). Plastic bellows were applied to seal the ports to the electrodes so that a stable humidity could be maintained inside of the chamber. The electrodes were mounted to a computer-controlled, 3D manipulator. A small plastic Petri dish containing pure water (18 MΩ-cm) was placed inside the chamber to increase and maintain the relative humidity (RH) (> 80%) after the chamber was sealed. The position of the illuminator and the stereomicroscope are also shown (Figure 21).
5.1.3 Electrode Preparation

Ag/AgCl electrodes are widely used for electrochemical measurements and can be customized according to specific requirements. Herein, for NaCl droplet concentration measurements, an Ag/AgCl electrode with reduced tip size (approximately 2 µm) was used to minimize the disruption of the droplets by the electrode. Figure 22 shows the experimental setup for fabricating the fine-tipped electrodes. An Ag wire (D = 0.5 mm) was electrochemically micro-machined by oxidizing it in a 0.1 M KNO₃ solution.[61] One end of the Ag wire was bent into a “U” shape, the bottom of which was immersed in the solution. The bottom region of the U-shaped Ag wire was allowed to thin down just prior to breaking down completely. The wire was removed from the solution and the two sections were subsequently parted, leaving the fine tip (insert in Figure 22), which was then rinsed with ultrapure water. Silver chloride was then precipitated on the Ag wire surface by chloriding. The fine-tipped Ag wire was connected to the positive terminal (+) of a 9-V DC battery. The negative terminal (-) of the 9-V battery was connected to another clean, bare Ag wire, which served as the cathode. A 1 KΩ resistor was placed in series with the Ag electrodes to limit the current during chloriding. The
Ag electrodes were immersed in a 0.1 M KCl solution for about 10 sec, until a sufficient amount of AgCl had precipitated on the fine-tipped wire, turning it gray in appearance.

![Schematic diagram of the experimental configuration for fabricating fine-tipped Ag wire electrodes. Insert: a fine-tipped Ag wire fabricated.](image)

**Figure 22.** Schematic diagram of the experimental configuration for fabricating fine-tipped Ag wire electrodes. Insert: a fine-tipped Ag wire fabricated.

For electrochemical studies in the microscale (μm), normal electrochemical methods, which are usually in the macroscale (i.e., mm to cm) cannot be used. Instead, specially designed electrodes or cells are required for electrochemical measurements in the microscale. Micro capillaries have been widely used to study local corrosion phenomena at microscale levels (e.g., pit initiation and effect of inclusion).[62-69] This type of electrochemical capillary cell was reviewed by Lohrengel et al.[70, 71] In Suter’s method,[62-65] the micro-capillary cells (D = ~1 – 1000 μm) contained a platinum (Pt) wire counter electrode and a salt bridge connected to a reference electrode. A bead of silicon rubber on the perimeter of the tip of the micro-capillary cell was used to create a seal with the working electrode substrate to prevent electrolyte leakage.[65] Though this method works well for studies of highly local corrosion under immersed conditions, it cannot be used for droplet corrosion, which inherently has a droplet-air interface. However, only a
small modification needs to be made to the micro-capillary cell described above to study droplet electrochemistry.

In this study, micropipettes with fine tips were used to fabricate microelectrodes. Commercial borosilicate glass tubes (WPI) with 1.5 mm/1.12 mm (outer diameter/inner diameter) were pulled using a P-97 micropipette puller (Sutter Instruments) to form fine tips (D = 2 – 5 µm). The micropipettes were silanized using N, N-Dimethyltrimethylsilyamine (Fluka) to make them hydrophobic. The tips of the silanized micropipettes were filled with a gel consisting of 2 wt.% agar dissolved in saturated NaCl solution.[72] A pre-heated gel was sucked into the micropipette under a vacuum from the wide, back end. The wide end of the micropipette was then pressurized to force the gel to the tip of the micropipette until some of the gel was ejected, ensuring that the tip was completely filled. The micropipettes were then back-filled with a saturated NaCl solution from the wide end. Finally, the tips of the micropipettes were immersed in a saturated NaCl solution to avoid the dehydration of the tip. The micropipettes were used for both Ag/AgCl reference electrodes and combination electrodes (as reference electrodes). These micro-capillary cells were used without silicone beading and were pierced directly into the micro droplets.

An Ag wire with diameter of 0.5 mm was cleaned using fine grinding paper (600-grit) and then rinsed using ultrapure water. Then, an AgCl coating was precipitated onto the Ag wire using the same procedure for chloriding described
above. The chlorided Ag wire was inserted into the back-filled end of the micropipette to form an Ag/AgCl reference electrode.

For droplet pH measurements, micropipette based micro-pH electrodes were used. The tip of the silanized micropipettes were filled with a hydrogen ionophore to make micro-pH electrodes. Details of the procedure are covered elsewhere.[73]

To minimize the intrusion into the micro droplets during the polarization experiments, a combination electrode (Figure 23) similar to that manufactured by Lin et al.[74] was used. An Ag/AgCl reference electrode and a counter electrode (Pt wire) were inserted into the body of a large pipette that was necked down and attached to a micropipette and sealed with PARAFILM®. The micropipette was similar to that used for the micro Ag/AgCl reference electrode but was only 3 cm long. The combination electrode was filled with a saturated NaCl solution. The combined electrode was inserted into the experimental chamber through the plastic bellows (Figure 23).

**Figure 23.** Schematic diagram of the electrochemical cell for polarization experiments.
5.1.4 Experimental Procedures

A two-electrode system was used for NaCl droplet concentration and pH measurements (Figure 21). An Ag/AgCl electrode (chlorided Ag wire with fine tip) and an Ag/AgCl reference electrode were used for droplet concentration measurements, while a self-made micro-pH electrode and an Ag/AgCl reference electrode were employed for the pH measurements. These pairs of electrodes were connected to an EG&G model 273A potentiostat for measurements. After an NaCl droplet formed on the steel sample, the electrodes were carefully positioned into the droplet using computer-controlled stages and under the assistance of a stereomicroscope. For each measurement, 1 min was allowed for the stabilization of readings. Then the potential difference between these two electrodes was recorded using the potentiostat. Relatively stable potential values were obtained for later calculation of droplet concentration and pH value.

The combination electrode (reference + counter) was used for polarization experiments (Figure 23). Polarization experiments were conducted using the same EG&G model 273A potentiostat. Three crocodile connectors were connected to a steel working electrode (with a single NaCl particle on top), a Pt counter electrode and an Ag/AgCl reference electrode (both inside the combination electrode) before sealing the chamber. After an NaCl droplet formed, the combination electrode was carefully positioned into the droplet. The steel electrodes were stabilized at OCP for about 2 min before scanning at a rate of 10 mV/sec. After polarization experiments,
images of the droplet area were recorded using a microscope before and after cleaning the droplet solution and corrosion products with pure water.

Before each electrochemical experiment, the potential values of the self-made Ag/AgCl electrodes versus the saturated calomel electrode (SCE) were recorded using the same potentiostat for the conversion of $V_{\text{AgCl}}$ to $V_{\text{SCE}}$. The aim was to correct possible differences between various Ag/AgCl electrodes.

**5.2 Results and Discussion**

5.2.1 Droplet Concentration Measurements

Salt particles absorb moisture from the ambient environment when the humidity exceeds the CRH value. The deliquescence process was observed using stereomicroscopy. It was observed that NaCl particles first dissolved from their perimeter. If the humidity did not exceed the CRH, some salt remained undissolved inside the droplet, which was believed to be a saturated solution. If the humidity increased beyond the CRH, the salt particles wholly dissolved, forming a droplet; and the concentration should also be near saturation. The NaCl concentration in the droplet was measured, and was found to decrease with the increasing time of exposure and growth of the droplet as the solution concentration equilibrated with the chamber RH.

Three different Ag/AgCl electrodes were calibrated against the concentration of NaCl (Figure 24). The calibration showed a good linear relationship between potentials and NaCl concentrations, indicating that the Ag/AgCl electrodes were suitable for the NaCl concentration measurements. The inserts in Figure 24 show
the micro-reference and Ag/AgCl electrodes penetrating the droplet (upper insert) and
a top view of one droplet region (lower insert) after measurement. Sodium chloride
droplets on both steel and glass surfaces were investigated. One measurement (in
Figure 24 denoted by the * and plotted on the calibration curves) indicates that the
concentration of NaCl in the droplet was 5.29 M. Additional concentration
measurements showed that the NaCl droplets had concentrations in the range of 5.1 –
5.4 M, very close to the saturation value of 5.41 M at 20°C.

It took approximately 2 – 3 min to position the electrodes into the droplet, and
1 min was allowed for the stabilization of the readings; hence, the concentration
measurements were taken approximately 3 – 4 min after full dissolution of the salt
particles. The measured concentrations, therefore, could be slightly lower than
saturation due to the continued absorption of moisture from the environment. Since
corrosion occurred within several minutes under most of the large NaCl droplets on
steel,[58] it was believed that corrosion have occurred during the concentration
measurements, see the lower insert in Figure 24. Generally, the concentration
measurements represent the moment when the corrosion initiated under the droplets.
Tsuru et al. [22] also mentioned that for a MgCl₂ particle deposited on steel, the
concentration will be saturated at the beginning of water absorption and at the end of
the dry-up. As a result, the steel substrate is exposed to about 11 M Cl⁻ solution,
which is highly corrosive to the substrate. For NaCl particles, it was found in this
study that the concentration of Cl⁻ was in the range of 5.1 – 5.4 M, also very corrosive
to the steel surface.

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5.2.2 pH Measurements

The pH values of NaCl droplets formed by deliquescence on steel were measured using self-made micro-pH electrodes. One pH measurement together with the calibration results of the micro-pH electrode using pH = 7 and pH = 10 buffer solutions are shown in Figure 25. The performance of this micro-pH electrode in buffer solutions was good since the potential values were relatively stable in the measurement duration (line with symbols ■ and ● in Figure 25). The potential difference (V_{SCE}) of the micro-pH electrode (line with symbol ♦ in Figure 25) in two different buffer solutions stabilized at about 174 mV after 2 min and dropped slightly to 171 mV in the following 12 min. The Nernst factor was in the range of 57 – 58 mV/dec, close to its theoretical value which is 58 mV/dec.[73] The potential values after 5 min in the measurement (data to the right of the vertical dotted line in Figure 25) were used for the following calculation of pH values. As an example, the insert
in Figure 25 shows a live image of the pH measurement with a micro-pH electrode (left) and an Ag/AgCl reference electrode (right) inserted into one small droplet (D = ~50 µm). The response of the micro-pH electrode in the NaCl droplet was very stable during the 13-min measurement duration (line with symbol ▲ in Figure 25). The calculated pH values were approximately 8 (line with symbol ► in Figure 25), indicating the droplet was a little alkaline.

Figure 26 shows the results of pH measurements in one small NaCl droplet (D = ~41 µm) and one relatively large NaCl droplet (D = ~75 µm), together with the OCP measurements. The curves with symbols ■ and ● in Figure 26 indicate the calibration results of a micro-pH electrode using pH = 7 (■) and pH = 10 (●) buffer solutions. The curves marked by ▲ show the potential differences measured between the micro-pH electrode and the Ag/AgCl reference electrode (for pH measurement) and also the potential differences between the steel electrode and the Ag/AgCl reference electrode (for OCP measurement). The simultaneous
measurement of both OCP and pH was achieved by switching one clip of the potentiostat between the micro-pH electrode and the steel electrode, while fixing another clip to the Ag/AgCl reference electrode. The sections corresponding to OCP and pH measurements are indicated in each figure. The spikes between the sections for OCP and pH were likely caused by the noise during switching the clip.

**Figure 26.** pH and OCP measurements of one small NaCl droplet (a) and one large NaCl droplet (b).

Figure 26a indicates that the OCP values (▲) were not stable initially and fluctuated in the range of -0.05 – 0.10 V_{SCE}, which was likely caused by a bad connection between the steel working electrode and the Ag/AgCl reference electrode. After the electrodes were positioned in the droplet, OCP values stabilized in the range of -0.015 – -0.025 V_{SCE}. During the OCP measurements at 17 – 22 and 27 – 31 min, the OCP values stabilized at approximately -0.025 V_{SCE}. The potential differences for pH measurement were stable at approximately -0.035 V_{SCE}. Calculation showed that the pH value of the measured droplet was about 8.17. The OCP for the large droplet (▲ in Figure 26b) varied in the range of -0.33 – -0.44 V_{SCE}, much lower than those for the small droplet (Figure 26a). Actually, a higher OCP indicates the absence of corrosion under the droplets, while a lower OCP indicates it has taken
place. This potential difference between the small droplets and large droplets will be discussed in the following section by showing more OCP measurement results. The potential differences for pH measurements in Figure 26b were in the range of -0.03 – -0.06 V_{SCE}, based on which the calculated pH values were between 7.97 and 8.96. The above results show that both the small and large NaCl droplets were alkaline several minutes after they formed by deliquescence.

In a previous study,[58] it was found that corrosion did not initiate after 6 h under small NaCl droplets with diameters less than approximately 45 µm, while it did occur under larger NaCl droplets. Accordingly, both droplets with diameters smaller than 45 µm and droplets with diameters larger than 45 µm were selected for pH measurements (Figure 26). Since corrosion occurred under larger droplets several min after full dissolution and with the formation of local anodic and cathodic areas in the droplet, the pH varied in different locations under the droplets. We know that the periphery of the droplet usually serves as the cathode during corrosion while the center of the droplet serves as the anode. In the cathodic area, the generation of hydroxide ions by oxygen reduction makes the solution more alkaline. Since the micro-pH electrode was in contact with the peripheral area of the droplets to avoid contact with the steel surface, the measured pH values were larger than 7.

However, the potential difference between the cathode and the anode is actually not as pronounced as that in bulk solutions. In bulk solutions, the ions can diffuse freely from the local anodic area to the surrounding cathodic area, leaving a highly acidic environment in the anodic area. For droplet corrosion, the amount of
solution is so small that it is difficult for generated ions to diffuse away, possibly causing the solution to neutralize in the confined space. The reason why a small droplet also had a pH of 8.17 (Figure 26a) might be also due to some mild, invisible corrosion under the NaCl droplet. The slightly corroded environment may have made the confined space alkaline.

5.2.3 OCP Measurements

The above results (Figure 26) indicated that the OCP values measured in small and large NaCl droplets are different. Additional OCP measurements were conducted (Figure 27). The inserts in Figure 27 present the live images of the droplets during OCP measurements with their sizes indicated. The results show that the OCP values fell in two different ranges, -0.10 – 0.0 $V_{SCE}$ for small droplets and -0.50 – -0.30 $V_{SCE}$ for larger droplets. However, there is no well defined threshold value for the droplet size between these two different OCP ranges. That is, for some exceptional cases, smaller droplets have OCP values in the range of -0.50 – -0.30 $V_{SCE}$, while larger droplets have OCP values in the range of -0.10 – 0.0 $V_{SCE}$.

Figure 27. OCP measurements on different sized droplets. The 50 µm scale bar applies to all the inserts.
A previous study [58] showed that corrosion did not initiate under small NaCl droplets (D < 45 µm) on steel after 6 h exposure, while it did occur under larger NaCl droplets. This phenomenon was believed to be related to the OCP difference between different-sized NaCl droplets. Since corrosion was not occurring under small droplets, the steel substrate was passivated. The droplets were actually in contact with the surface iron oxide films. The OCP values represent the measured results at the interface of the passive iron oxide films and the NaCl droplets. For larger NaCl droplets, corrosion always initiated within several minutes, rendering the steel substrates in contact with the NaCl droplets and thus lowering the OCP values. For some exceptional cases mentioned above, the corrosion susceptible local microstructures, especially inclusions exposed to the surface, might be a possible explanation. Small NaCl droplets, which formed above inclusions, had lower OCP values in the range of -0.50 – -0.30 V_{SCE} possibly due to inclusion-induced corrosion—while larger NaCl droplets, which covered regions with intact iron oxide film, had higher OCP values in the range of -0.10 – 0.0 V_{SCE} because of the absence of corrosion. However, this does not necessarily mean that corrosion would never occur under all these larger NaCl droplets. In some cases, given enough time, the OCP values dropped between -0.50 and -0.30 V_{SCE}, representing the breakdown of the passive oxide film and the occurrence of corrosion. The OCP drops accompanying with passive film breakdown and pit formation were also observed for stainless steel under thin MgCl₂ electrolyte layers after a long time exposure.[75]
In an effort to better understand the relationship between OCP and the iron oxide film, polished steel samples were kept in a dry box (~1% RH) for various time periods, after which the OCP of NaCl droplets on steel was measured (Figure 28). Inserted in Figure 28 are three live images during the OCP measurements. Image A shows an NaCl droplet on a freshly polished steel sample. The droplet is extremely flat with a contact angle of ~18°, indicating good wettability of the fresh polished steel surface. The droplet kept in the dry box for 10 days had a ~53° contact angle while the one isolated for 40 days was ~82°. The above results indicate that the wettability of the steel surface decreased as the storage time increased. Over time the moisture on the surface evaporated and the iron oxide film became thicker, resulting in different OCP profiles (Figure 28). The OCP values of the NaCl droplet on freshly polished sample, remained at -0.45 V_{SCE} ((a) in Figure 28), indicating that corrosion initiated right after the salt droplet formed. Since there was no protective iron oxide film on the freshly polished steel surface, corrosion occurred quickly in the high Cl⁻ content environment. For the second case ((b) in Figure 28), the OCP was initially higher—0.04 V_{SCE}—indicating the absence of corrosion underneath the droplet. However, after 4 min, the OCP dropped to -0.40 V_{SCE}, an indication that corrosion occurred. For the sample kept in the dry box for 40 days ((c) in Figure 28), the OCP profile was similar to that of sample b. The difference is that OCP first maintained at approximately 0.10 V_{SCE} for 74 min, much longer than the second case and then dropped to the range of -0.50 V_{SCE} – -0.30 V_{SCE}. Corrosion occurred only after 74 min under the NaCl droplet on steel surface kept in the dry box for 40 days.
This result indicates that the surface oxide film grew with exposure time and affects microscale electrochemical measurements.

**Figure 28.** OCP measurements in NaCl droplets on steel surface with different surface conditions. Inserts are live images of the NaCl droplets during the OCP measurements. The 100 µm scale bar applies to all three inserts.

5.2.4 Polarization Experiments

5.2.4.1 Anodic Polarization Experiments

The corrosion initiation phenomena and OCP measurements on small NaCl droplets were different from those for the large droplets.[58] To understand the droplet corrosion in more detail, dynamic polarization experiments were conducted on different-sized NaCl droplets, which were formed by the deliquescence of pre-deposited NaCl particles.

Figure 29 shows the anodic polarization result obtained on one small NaCl droplet with diameter of 42 µm. The inserts in Figure 29a show the live images of the small NaCl droplet on a steel surface and the combination electrode inserted into the droplet. The droplet diameter after the full dissolution of NaCl particle was about 42 µm (Figure 29a1). During polarization, the droplet size increased from 42
µm to 45 µm (Figure 29a2) in the potential range of -0.04 V_{SCE} – 0.39 V_{SCE} and from 45 µm to 71 µm (Figure 29a3) in the potential range of 0.39 V_{SCE} – 0.80 V_{SCE}. The droplet size increase, especially after the pitting potential was reached, was likely caused by the pit formation as also observed by Frankel et al.[39] The abrupt increase of the solution concentration upon the formation of corrosion pit is likely the reason for the rapid absorption of water from the humid air, because water activity needs to be balanced. Also, since the droplet was in contact with the combination electrode, part of the solution may have came from the filling of the combination electrode even with the block of the tip-filled agar solution. Since the droplet size increased only 3 µm in the potential range of -0.04 V_{SCE} – 0.39 V_{SCE}, it was neglected and the original droplet area (D = 42 µm) was used for the calculation of corrosion current density.

![Figure 29](image)

**Figure 29.** Polarization result on one small NaCl droplet. a) Anodic polarization curve obtained on the small NaCl droplet with inserts as live images recorded during polarization (the scale bar applies to all images); b) optical microscope image showing the droplet area after polarization; c) droplet area after rinsing off the salt solution and corrosion products using pure water to show the corrosion pit. Images (b) and (c) have the same scale bar.
The polarization curve in Figure 29a indicates that the OCP for this tiny droplet is lower at approximately -0.04 V\textsubscript{SCE}, implying the absence of corrosion under the droplet. In the potential range of -0.04 – 0.39 V\textsubscript{SCE}, the corrosion current density fluctuated around 10e-7 A/cm\(^2\). The extremely low current density indicates that the steel substrate passivated in this region. When the potential exceeded 0.39 V\textsubscript{SCE}, the corrosion current rapidly increased to 10e-2 A/cm\(^2\), suggesting the occurrence of pitting. Then the current density was limited at around 10e-2 A/cm\(^2\), due to the limited diffusion of species inside the small droplet. The droplet was originally 42 µm in diameter and increased to 71 µm during polarization, which was also very small. The confined space inside the droplet made it difficult for the corrosion products to diffuse from the pitting site, resulting in the diffusion limited current regime shown in Figure 29a.

Images of the polarization site recorded after the experiment, before (Figure 29b) and after (Figure 29c) cleaning the remaining droplet solution and corrosion products indicate that there was only one corrosion pit at the edge of the droplet and general corrosion did not occur. This result indicates that corrosion does not occur under small NaCl droplets, a finding that corroborates previous results of corrosion initiation experiments [58] and the OCP measurement results discussed above.

Figure 30 shows the anodic polarization result on a large NaCl droplet with an original diameter of 74 µm. The OCP value was about -0.07 V\textsubscript{SCE}, which was slightly lower than -0.04 V\textsubscript{SCE} for the small droplet (D = 42 µm). During polarization (Figure 30a), the corrosion current density initially increased gradually
and then maintained at about $10^{-5.7}$ A/cm$^2$ in the potential range of $0.05 \text{ V}_{\text{SCE}} - 0.33 \text{ V}_{\text{SCE}}$, indicating the passivation of the substrate. When the potential reached approximately $0.33 \text{ V}_{\text{SCE}}$, pitting occurred, and the corrosion current density increased suddenly to $10^{-0.8}$ A/cm$^2$. Due to the limited diffusion of corrosion products, the corrosion current maintained at this value. The pitting potential was $0.33 \text{ V}_{\text{SCE}}$ compared with the previous $0.39 \text{ V}_{\text{SCE}}$ for the small droplet. The discrepancy indicates that there was a greater tendency for corrosion under the large NaCl droplet, which is consistent with the previous corrosion initiation experiments.[58] The droplet size increased during the polarization process, especially after pitting.

![Figure 30](image.png)

**Figure 30.** Polarization result on one large NaCl droplet. a) Anodic polarization curve obtained on the large NaCl droplet with inserts as live images recorded during polarization (the scale bar applies to all images), b) optical microscope image showing the droplet area after polarization, c) droplet area after rinsing off the salt solution and corrosion products using pure water, showing the corrosion pit and depleted grain boundaries.

Images (Figure 30b-c) taken after the polarization experiments show that the grain boundaries were depleted during the polarization process, indicating uniform and relatively significant corrosion under the droplet. Also shown in these two
images is a corrosion pit (black spot) in the center of the original droplet. The corrosion has increased the volume of the droplet, which were much more significant than they were for the small droplet (inserts in Figure 30a).

Figure 31 shows the anodic polarization result under a larger NaCl droplet, with an initial diameter of about 165 µm. The OCP value was much lower at -0.43 \( V_{SCE} \) compared with the OCP values for the previous two relatively small NaCl droplets, indicating that corrosion occurred under the larger NaCl droplets, same as the findings in the above-mentioned OCP measurements. The anodic polarization curve shows that there was no passivation and pitting process in contrast to the small droplets. Instead, the polarization curve shows an anodic active dissolution of the steel substrate (Figure 31a), similar to the polarization results obtained in bulk solutions.

![Figure 31](image)

**Figure 31.** Anodic polarization result on an even larger (as compared to the droplet in Figure 30) NaCl droplet. a) Anodic polarization curve obtained on the larger NaCl droplet with inserts as live images recorded during polarization (the scale bar on the bottom insert applies to all the inserts in (a)), b) optical microscope image showing the droplet area after polarization, c) the droplet area after rinsing off the salt solution and corrosion products using pure water, showing lot of corrosion products and depleted grain boundaries.
Images (Figure 31b-c) taken after polarization show that there were more corrosion products (black) than there were on the smaller droplets. Serious depletion of the grain boundaries was also observed under the original droplet area.

The above polarization results for three different-sized NaCl droplets show that the corrosion tendency increased as the size of the droplets increased from 42 µm to 74 µm and finally to 165 µm. As the droplet size increased further, the anodic polarization showed similar results as that of the 165 µm droplet.

5.2.4.2 Cathodic Polarization Experiments

Cathodic polarizations were also conducted on different-sized NaCl droplets. Figure 32 shows the cathodic polarization results on two relatively small NaCl droplets with diameter of 58 µm and 111 µm, respectively. The OCP values are in the range of -0.10 – 0.0 V_{SCE} which is similar as discussed in the previous OCP measurement section that small droplets with diameters less than 100 µm had higher OCP values. However, there is not an accurate threshold size between higher OCP (-0.10 – 0.0 V_{SCE}) and lower OCP (-0.50 – 0.30 V_{SCE}) because local microstructure may vary for each measurement. For this relatively large droplet with diameter of about 111 µm, the OCP values were still higher in the range of -0.10 – 0.0 V_{SCE}. We know that if the OCP is high—around 0.0 V_{SCE}—corrosion will not occur under the droplets or the steel substrate is passivated. In this condition, if the sample is cathodically polarized, oxygen reduction will be the cathodic reaction, as indicated by the characteristic oxygen diffusion limiting current density around 10e-4.7 A/cm² in the potential range of -0.20 V_{SCE} – -0.40 V_{SCE} (Figure 32). The reason why the
corrosion current density continued to increase when the potential went more negative from -0.40 V<sub>SCE</sub> might be due to the flattening of the droplet as indicated by the inserted images in Figure 32. Actually, the increase of the droplet size always shifts the cathodic curve to the higher current density direction characterized by abrupt shifts in the original polarization curves. To resolve this problem, the live images after each droplet size increase were recorded and different droplet sizes were applied to the calculation of the corrosion current density. Generally, the modified polarization curves were smooth without any abrupt shift.

![Figure 32](image-url)

**Figure 32.** Cathodic polarization results on NaCl droplets with diameters of 58 µm and 111 µm. The six inserted images along the polarization curves are live images of the droplets during polarization with combination electrode probed into the droplets. The scale bar applies to all images. The insert in the left bottom is an image of the droplet area after polarization, showing the re-crystallized NaCl particles from the original droplet and the secondary droplets around the original droplet. Note that no corrosion was observed under the droplet after polarization.

Also note in Figure 32 that the 111 µm droplet expanded significantly after polarization. The optical image taken after the polarization (left bottom insert) indicates the formation of small droplets around the original large droplet, a
phenomenon called secondary spreading. The effect of cathodic polarization on the formation of these secondary droplets was also reported by Zhang et al. [15, 16] and Tsuru et al. [22]. Tsuru et al. [22] observed the formation and growth of micro-droplets around NaCl droplets (0.5 M, D = 0.5 – 5.0 mm) on stainless steel and platinum plate when polarizing the sample at -0.70 V_{SSE} (-1.35 V_{SCE}). The initiation of micro-droplets followed the increase of the current after several tens of seconds. Our result (Figure 32) shows that the micro-droplets formed even at a lower potential, about -0.8 V_{SCE}. As mentioned by Tsuru et al.,[22] the time needed for the cathodic transient current to increase or the formation of micro-droplets depended on salt concentration, an almost saturated solution used in this study might promote the formation of micro-droplets at a more noble potential (Figure 32). Also, the size of the droplets might affect the formation of those micro droplets, since no secondary spreading was observed for the relatively small droplets (D = 58 µm) (Figure 32). The very small variance between the two results will be discussed in the following section.

Figure 33 shows the cathodic polarization results obtained on relatively large droplets with diameters ranging from 103 – 426 µm. As mentioned earlier in the OCP measurement section, the OCP values for larger droplets were much lower in the range of -0.30 – -0.50 V_{SCE} as compared to the values for small droplets, which were around 0.0 V_{SCE}. This much lower OCP indicates that corrosion occurred under the NaCl droplets before or during polarization, as shown in the insert in Figure 33. Actually, this image shows the common corrosion morphology under larger NaCl
droplets with corrosion initiating from the edge of the droplet (indicated by an arrow) or an inclusion and corrosion products forming around the corrosion pit. This kind of corrosion always occurs within several minutes after the formation of the droplets. Normally, when the polarization starts, the corrosion has already initiated under the droplet. This phenomenon may help explain why the cathodic polarization curves are not exactly vertical to the axis Log i (Figure 33), partially due to the possible reduction of iron oxide. However, generally speaking, the primary cathodic reaction for the corrosion under large droplets is oxygen reduction, indicated by the diffusion-limited oxygen reduction current at around $10^{-4}$ A/cm². Also, the current density increased with decreasing droplets sizes due to the easier diffusion of oxygen to the steel/droplet interface for thinner droplets.

![Figure 33. Cathodic polarization results on NaCl droplets of different sizes. The insert is an optical image showing the droplet area after cathodic polarization.](image-url)
For cathodic polarization conducted on thin electrolyte films or small electrolyte droplets, many researchers have tried to find the relationship between the cathodic limiting oxygen reduction current density and the electrolyte film thickness [29, 35, 38, 39] or the droplet size.[41] Generally, the equation expressing the relationship between the diffusion limiting current density \( i_{\text{lim}} \) and the diffusion layer thickness \( \delta \) (Equation 4) was employed for interpretation of the results.

\[
i_{\text{lim}} = \frac{nFDC}{\delta} \quad (4)
\]

In Equation 4, \( i_{\text{lim}} \) is the limiting current controlled by diffusion of oxygen; \( n \) is the number of the electrons evolved in oxygen reduction, which is 4 here; \( F \) is the Faraday constant; \( D \) is the oxygen diffusivity; \( C \) is oxygen concentration of dissolved oxygen in the thin electrolyte layer; and \( \delta \) is the diffusion layer thickness. Applied to thin electrolyte layers, Equation 4 shows a linear relationship between the oxygen diffusion limiting current \( i_{\text{lim}} \) and the reciprocal value of the electrolyte thickness \( 1/\delta \). However, this relationship only applies to a limited range of electrolyte thickness.

Previous studies [29, 30, 35, 39] on polarization in thin electrolyte films gave similar relationships between \( i_{\text{lim}} \) and \( \delta \), with different threshold values between different regions that might be due to the variation of techniques, salt types or salt concentrations. The reason for \( i_{\text{lim}} \) being independent of \( \delta \) for thick electrolyte layers was likely the excess of \( \delta \) over the static oxygen diffusion layer thickness. \( i_{\text{lim}} \) became inversely proportional to \( \delta \) when \( \delta \) was smaller because the diffusion of dissolved oxygen through the thin electrolyte layer was RDS. When \( \delta \) was
much smaller (< 10 µm or 20 µm), the solvation process of oxygen gas became the RDS of the oxygen reduction, rendering the independence of \( i_{\text{lim}} \) from \( \delta \). For cathodic behavior of A3 carbon steel under 0.1 M NaCl droplets (\( D = \sim 1.18 \text{ cm} - \sim 2.67 \text{ cm} \)), Jiang et al. [41] found a linear relationship between the cathodic limiting current density and the reverse of the droplet radius (\( 2/r \) in the present work).

We know that for cathodic behavior of metals under thin electrolyte films or droplets, there exists a relationship between the diffusion limiting current density (\( i_{\text{lim}} \)) and the characteristic length of the electrolyte films or the droplets, which is thickness (\( \delta \)) for thin electrolyte films and radius (\( r \)) for droplets. It was found that \( i_{\text{lim}} \) is linearly proportional to the reverse of the characteristic length, except for extremely thick and extremely thin electrolyte films. We found similar relationship between \( i_{\text{lim}} \) and the characteristic length of the droplet (droplet diameter, \( D \)). The \( i_{\text{lim}} \) values at three different potentials in Figure 33 were plotted vs. the reverse of the droplet radius (Figure 34). Generally, the results showed a linear relationship between \( i_{\text{lim}} \) and \( 1/D \). To explain this, we need to consider the characteristic geometry of the droplet. Unlike a thin electrolyte film, which has identical paths over the whole surface for oxygen diffusion, a droplet is not uniform. The periphery of a droplet has a shorter diffusion path for oxygen than does the center, so the oxygen flux and thus the oxygen reduction current at the droplet/metal/air interface is higher than at the central region of the droplet. So, the peripheral part of the droplet contributes more to the total cathodic current. As Jiang et al. [41] mentioned, the edge of the droplet acts like a three phase boundary (TPB) zone during corrosion.
under the droplets. According to their calculation, the factor used to characterize the TPB zone (g-TPB length per unit area) is inversely proportional to the radius of the droplets, which is \( \frac{2}{r} \)—findings that are similar to our results.

**Figure 34.** The dependence of the cathodic diffusion limiting current density on the reciprocal of the droplet diameter.

Since the droplets formed (by deliquescence) were found to be near saturation, at least during the initial stage of the droplet corrosion, the electrochemical behaviors of steel in bulk saturated NaCl solutions were also investigated and compared with those in NaCl droplets. Figure 35 shows the three cathodic polarization curves obtained in bulk NaCl solutions with different conditions and two cathodic curves for droplets on steel. Not surprisingly, the cathodic polarization of steel in bulk saturated NaCl solution showed characteristic oxygen diffusion limiting current regime, and the diffusion limiting current density increased with the increase of the oxygen content. The reason oxygen reduction was still seen in the de-aerated saturated NaCl solution might be due to the residual oxygen left in the solution even after a 1 h nitrogen gas purge.
Figure 35. A comparison of the cathodic polarization curves obtained on NaCl droplets and in saturated NaCl bulk solutions with three different conditions: de-aerated, open to air and aerated.

The oxygen diffusion layer thickness can be calculated according to Equation 4 once we know $i_{\text{lim}}$ and $C$. Millero et al. [76] measured the concentration of oxygen in near saturated NaCl (5.9050 molality, 19.95°C) solution to be 69.2 µmol kg H$_2$O$^{-1}$, which is about 61.43 µmol L$^{-1}$. Sherwood et al. [77] found almost the same result for oxygen concentration in a near saturated NaCl solution (250.59‰, 19.4°C), which is 1.805 mg L$^{-1}$ or 56.4 µmol L$^{-1}$. In this work, $C = 56.4$ µmol L$^{-1}$ was used for calculation. This value was obtained after purging the NaCl solution with oxygen for 2 h to achieve the saturation of oxygen. The $i_{\text{lim}}$ value obtained in aerated condition (10e-4.8 A/cm$^2$) was used for the calculation of diffusion layer thickness by assuming that the oxygen content in small droplets is the same as that in aerated NaCl solution since oxygen would have diffused into the micro-droplets much easier. $D$ was taken as 2.1e-5 cm$^2$ s$^{-1}$, an average value from literature for the
diffusivity of oxygen in water.[78] Using the above parameters, the obtained $\delta$ value from Equation 4 is about 288 $\mu$m. Comparing this diffusion layer thickness value with the droplet heights in Figure 33, the maximum of which is about 67 $\mu$m, we know that the droplets investigated in this study were relatively small and within the scale of the diffusion layer in bulk solution. So, we can say that the dependence of the cathodic diffusion limited oxygen reduction current on the droplet size is similar to what has been observed for electrolyte layers with thickness less than the diffusion layer thickness.[29, 35] However, it seems that for corrosion under droplets, there is no such a critical droplet size that can make the cathodic oxygen diffusion limiting current independent of the droplet size, as observed for thin electrolyte films. The reason for this proposition is based on the research of Jiang et al.,[41] who found that the cathodic diffusion limiting current is still dependent on the droplet size even for much larger droplets with diameters in the range of 1.18 cm – 2.67 cm. This phenomenon was thought to be caused by the existence of TPB zone.[41] In addition, Figure 35 informs us that the cathodic corrosion current density for small droplets was higher than for those in bulk solutions, indicating the acceleration of the cathodic oxygen reduction due to the existence of TPB zone.

Stratmann et al. [29] and Tsuru et al. [35] found that when the thickness of the thin electrolyte film was smaller than a certain value (10 – 30 $\mu$m), the cathodic diffusion limiting current density was again independent of the electrolyte thickness. They believed that the transport of oxygen through the electrolyte/gas boundary instead of the diffusion of oxygen was the RDS for cathodic polarization under very
thin electrolyte layers. In this study, it seems that when the droplets became smaller, the cathodic corrosion limiting current did not depend on the droplet size, as shown in Figure 32. The reason for this result might also be due to the dissolution of oxygen through the droplet/air interface being the RDS. In addition, no corrosion occurring underneath the droplet might also have some effects on the polarization results (insert in Figure 32).

Finally, reversible potentials for oxygen reduction (0.037 $V_{SCE}$) and hydrogen evolution (-0.525 $V_{SCE}$) for the droplet corrosion were calculated (Figure 35). The open circuit potentials for both small and large droplets were negative to 0.037 $V_{SCE}$ and positive to -0.525 $V_{SCE}$, indicating that the cathodic reaction under NaCl droplets was oxygen reduction. The reason that the cathodic curves are not exactly vertical might be the slight increase in the droplet size during polarization even though the corrections were carried out after each abrupt increase of the droplets. Also, corrosion occurring under the droplet might also have exerted an influence on the polarization results (insert in Figure 33).

5.3 Conclusion

Electrochemical measurements including salt droplet concentration measurements, salt droplet pH measurements and polarization experiments were conducted in an effort to understand the atmospheric corrosion of 1018 steel under NaCl droplets formed by the deliquescence of pre-deposited NaCl particles.
The NaCl droplets formed by the deliquescence of pre-deposited NaCl particles upon exposing to high humidity (RH > 80%) were found to be almost saturated.

Measurements of pH conducted several minutes after the full dissolution of the pre-deposited NaCl particles showed that small NaCl droplets without corrosion underneath had pH values around 8, while larger droplets with corrosion had pH values in the range of 8 – 9.

The OCP values for small deliquescent NaCl droplets were in the range of \(-0.10 \ V_{SCE} – 0 \ V_{SCE}\), indicating no corrosion under the droplets. Larger droplets had much lower OCP values in the range of \(-0.50 \ V_{SCE} – -0.30 \ V_{SCE}\), with corrosion occurring underneath.

Anodic polarization showed passivation under smaller NaCl droplets and active dissolution under larger droplets. Cathodic polarization indicated the oxygen reduction as the primary cathodic reduction. Cathodic corrosion current density increased as the NaCl droplets size decreased, due to the easier diffusion of oxygen from ambient to the corroding surface for smaller droplets. The cathodic oxygen diffusion limiting current density was found to be inversely proportional to the droplet size in the range of 103 – 426 µm.
Chapter 6

Raman Spectroscopic Characterization of NaCl
Particle-induced Corrosion of Carbon Steel

6.1 Experimental

6.1.1 Sample Preparation

The procedure for the preparation of 1018 steel samples was the same as that shown in Section 3.1.1.

The grinding of NaCl crystals to form fine NaCl particles and the manual deposition of NaCl particles on steel surface were same as described in Section 4.1.1.

6.1.2 Experimental Setup

The same humidity chamber as shown in Section 4.1.2 (Figure 9) was used for the in situ Raman spectroscopic characterization of the corrosion products under NaCl droplets.

6.1.3 Experimental Procedures

Details on the formation of NaCl droplets in high humidity (> 80% RH) were same as that shown in Section 4.1.3.

Corrosion initiation and propagation under NaCl droplets were observed and recorded using the optical microscope. The corrosion products formed at steel substrate/NaCl droplet interface were identified using in situ and ex situ Raman spectroscopy.
6.1.4 Raman Measurements

A Nicolet Almega XR dispersive Raman Spectrometer (Thermo Scientific Corp.) equipped with multiple Olympus objectives and a Peltier-cold charge-coupled device (CCD) detector was used for the experiments. An objective with magnification of 50× with estimated spatial resolutions of 1.6 µm were used. The instrument was operated with laser sources of a green Nd:YAG laser with 532 nm wavelength excitation and an infrared diode laser with 780 nm wavelength excitation. The laser power was always kept low at approximately 1 mW for in situ Raman analysis and 0.5 mW for ex situ Raman analysis in order to avoid sample degradation by laser heating. The laser power was measured at the air-exposed sample. For in situ Raman measurements, the laser power under the droplet could not be measured but was believed to be less than that measured at the air-exposed sample.

The maximum spectra resolution was up to 2.2 – 2.6 cm⁻¹ using 25 µm pinhole or slit, which requires longer acquisition time and produces more noise. To reduce the collecting time in a fast corroding system, an aperture of 100 µm pinhole was used, giving an estimated resolution in the range of 8.4 – 10.2 cm⁻¹. The resulting Raman spectra were also compared to those with low signal/noise ratio obtained using small-sized filters to confirm that they convey same information. The accumulation time was 120 seconds.

6.1.5 SEM Characterization

The same Hitachi S-3400N scanning electron microscopy (SEM) was used to characterize the rust species formed during droplet corrosion as well as the corrosion
pits before and after cleaning the samples. Inclusions found in 1018 steel were also characterized using SEM and energy dispersive X-ray analysis (EDXA) (Oxford Instruments).

6.2 Results and Discussion

Upon exposure in the enclosed Petri dish with high humidity (>80% RH), NaCl droplets formed within 5 min by the deliquescence of pre-deposited NaCl particles. Then, corrosion initiated quickly in about 2 min underneath the NaCl droplets depending on the local microstructural features.

6.2.1 Short-time Exposure (5 min)

Short-time exposure (5 min) experiments representing the initial stages of corrosion showed two types of corrosion initiation phenomena based on microscopic observation and EDXA results: (1) corrosion initiation from droplet perimeters when inclusions were not present and (2) corrosion initiation at inclusions sites, which could be located anywhere under the droplets. Since only a small volume of corrosion products formed during the short initiation period, high-quality in situ Raman spectra could not be obtained through the water medium. Instead, ex situ Raman spectra were obtained soon after the specimens were quickly dried, but representing similar results as those of in situ Raman spectra.

6.2.1.1 No Inclusions

The NaCl particle that was manually deposited on an inclusion-free surface (Figure 36a and b) quickly transformed into a droplet (Figure 36c) by deliquescence. A corrosion pit formed near the edge of the droplet immediately after the formation of
the droplet (arrow in Figure 36c). It took approximately 2 min for the precipitation of yellowish rust particles, which moved around on the substrate surface in a manner consistent with Brownian motions and discussed elsewhere.[58] After approximately 5 min, the corrosion pit became more noticeable and more yellow rust particles accumulated on the surface in scattered clusters in a circular region adjacent to the pit (Figure 36d). In addition, the color of steel substrate in the close vicinity of the pit became light gray, indicating the formation of a thin film of corrosion product. The sample was then removed from the humidity chamber, rendering the evaporation of the droplet solution in ambient environment within 2 min and the crystallization of NaCl salt particles on the perimeter (Figure 36e). The thin layer of corrosion product near the pit became visible (see arrows in Figure 36e).

**Figure 36.** Time sequenced optical microscope images showing (a) a bare steel substrate; (b) an NaCl particle on the steel substrate; (c) an NaCl droplet on the steel substrate after full deliquescence, notice the tiny corrosion pit indicated by the arrow; (d) corrosion pit (indicated by an arrow) and yellowish rust clusters formed 5 min after full deliquescence; and (e) corrosion products and crystallized NaCl particles (on the perimeter) after dehydration. Note the prominent features in the upper right and lower right corners in (a), (b) and (c), verifying that these images were obtained from the same inclusion-free area. The 50 µm scale bar applies to images (a), (b) and (c).
*Ex situ* Raman spectra (Figure 37) were obtained from different locations of the corroded region (see the square areas in the insert).

![Raman Spectra](image)

**Figure 37.** *Ex situ* Raman spectra from different regions of the corroded area. The steel substrate under the droplet was allowed to corrode for 5 min prior to dehydration. (a) corrosion initiation site or the corrosion pit, (b) and (c) thin corrosion film near to the corrosion initiation site, and (d) yellowish rust cluster.

Raman bands of GR (425 cm\(^{-1}\) and 505 cm\(^{-1}\)) [45] (Figure 37a) were identified at the corrosion initiation site. The Raman technique in concurrent with the optical microscope allows collection of spectra on the focal plane beneath the crystallized NaCl particles, which do not generate any Raman bands. Characteristic bands of GR, but with different band intensity ratios (Figure 37b and c) were observed on the thin film of corrosion product near the corrosion initiation site. Characteristic bands of lepidocrocite (247, 377, 526 and 648 cm\(^{-1}\)) [79] (Figure 37d) were obtained from the yellowish rust clusters. A weak band at 430 cm\(^{-1}\) was attributed to the presence of a small amount of GR under the rust cluster (Figure 37d).
6.2.1.2 Inclusions Present

Corrosion always initiated in the form of pits at inclusion sites if they were present.[58] The composition (Table 3, determined by EDXA) of an inclusion found in the 1018 steel surface (Figure 38) shows characteristics of slag, e.g., high content of Al.

![Image](image.png)

**Figure 38.** An inclusion found in the surface of a polished 1018 steel sample.

**Table 3.** The chemical composition of the inclusion shown in Figure 38 using EDXA.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Au(coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>5.19</td>
<td>28.73</td>
<td>2.86</td>
<td>25.04</td>
<td>0.21</td>
<td>2.00</td>
<td>7.66</td>
<td>1.02</td>
<td>23.45</td>
<td>3.84</td>
</tr>
<tr>
<td>Atomic%</td>
<td>10.83</td>
<td>44.97</td>
<td>2.95</td>
<td>23.25</td>
<td>0.18</td>
<td>1.57</td>
<td>4.79</td>
<td>0.47</td>
<td>10.52</td>
<td>0.49</td>
</tr>
</tbody>
</table>

The corrosion morphologies for the cases with and without inclusions were similar, with the exception of the location of the corrosion initiation site. Raman analyses for cases with inclusions were also similar to cases w/o inclusions: GR was formed at and around the vicinity of the corrosion initiation sites and surrounding yellowish rust clusters consisted of lepidocrocite.

6.2.2 Longer Exposure (30 min)

6.2.2.1 In situ Raman Spectroscopy

For longer exposure times (30 min), it was possible to conduct *in situ* Raman analyses due to a greater amount of corrosion products.
The Raman spectrum in the pit of the corrosion initiation site after 30 min corrosion (see insert in Figure 39a) shows a doublet at 245 and 286 cm\(^{-1}\), assigned to FeCl\(_2\) (that can precipitate onto pit wall) and its chlorides ions, such as FeCl\(_4^{2-}\) and/or FeCl\(_3^-\) (see the discussion session). The weak broad bands in the range of 350 – 750 cm\(^{-1}\) (except that at 525 cm\(^{-1}\) due to system ghosts) were possibly caused by FeCl\(_2\).

In the vicinity just outside of the pit, GR was detected with Raman bands at 425 cm\(^{-1}\) and 501 cm\(^{-1}\) (Figure 39b). In the densely populated yellowish rust clusters outside of the GR region, lepidocrocite was detected with three main bands at 246 (shoulder), 377 and 525 cm\(^{-1}\), and a barely discernable broad band at 645 cm\(^{-1}\) (Figure 39d). In the transitional region from GR to lepidocrocite, magnetite (666 cm\(^{-1}\)), GR (425 and 501 cm\(^{-1}\)) and lepidocrocite (247 (shoulder) and 376 cm\(^{-1}\)) were detected (Figure 39c).

The Raman bands at 226, 235 (truncated), and 273 cm\(^{-1}\) in Figure 39b-d and 525 cm\(^{-1}\) in Figure 39a-d (partially for Figure 39c) are ghost bands obtained using the 780 nm laser system.
**Figure 39.** *In situ* Raman spectra from different locations under the droplet after 30 min corrosion: (a) corrosion initiation site or the corrosion pit, (b) regions surrounding the corrosion initiation site, (c) rust cluster formed in the transitional region from GR to lepidocrocite, and (d) yellowish rust cluster that formed far away from the corrosion initiation site.

### 6.2.2.2 Ex situ Raman Spectroscopy

After 30 min of corrosion, the sample was removed from the humidity chamber. The NaCl droplet solution evaporated in ambient humidity (58%) within 5 min, leaving crystallized NaCl particles on top of the droplet corrosion area. Similar to the previous *in situ* Raman analyses, the *ex situ* Raman spectrum from the corrosion pit (Figure 40a) shows the presence of FeCl$_2$ with a Raman band at 250 cm$^{-1}$, but with diminishing intensities for its chloride ions, i.e., the Raman band at 280 cm$^{-1}$. The Raman spectra from regions surrounding the corrosion pit show typical GR bands at 425 and 505 cm$^{-1}$ (Figure 40b and c) also with varied band intensity ratios of the two bands. The Raman spectrum obtained from the yellowish rust
clusters outside of the GR region shows a Raman signal of lepidocrocite with bands at 247, 376, 528 and 645 cm\(^{-1}\) (Figure 40d).

**Figure 40.** *Ex situ* Raman spectra from different locations under the droplet shown in Figure 39, after dehydration: (a) corrosion initiation site, (b) and (c) regions surrounding the corrosion initiation site, and (d) yellowish rust cluster.

6.2.3 Oxidation and Transformation of GR

Green rust is unstable and can be oxidized in air under ambient conditions. The GR in a corroded region rinsed with ultrapure water and dried with compressed nitrogen following 30 min corrosion under a NaCl droplet experienced oxidation and phase transformation in ambient environment (Figure 41). The NaCl particles crystallized on top of the corrosion pit (arrow in Figure 41a) and the surrounding GR region (e.g., rectangular areas in Figure 41a) were cleaned by rinsing with ultrapure water but not the corrosion products. The GR region and the scattered lepidocrocite
clusters (e.g., circular regions in Figure 41a) appeared light gray and yellow respectively under the optical microscope. The color for GR then changed quickly to yellowish within several min (Figure 41b), indicating the transformation of GR into other rust phase(s). The yellowish color became more noticeable after extended exposure (Figure 41c). The transformed GR show Raman bands of lepidocrocite (Figure 43).

Figure 41. Optical microscope images showing the color change during the transformation of GR to other phase(s): (a) immediately after cleaning the NaCl particles that crystallized on top of the corrosion pit (indicated by an arrow) and the GR region (e.g., rectangular regions) by rinsing the sample with ultrapure water, (b) after 6 min exposure in ambient, and (c) after 18 min exposure in ambient. Notice the color change on the perimeter of the corrosion pit (b and c) due to laser heating. The 10 µm scale bar applies to all three images.

Green rust transformation on an un-cleaned sample after 30 min corrosion was also observed when NaCl particles did not crystallize directly on top of the corrosion pit and the GR regions (Figure 42). Before phase transformation, GR (Figure 42a and b, Raman bands at 425 and 502 cm\(^{-1}\)) and sometimes together with Magnetite (Figure 42a, Raman band at 665 cm\(^{-1}\)) were detected in regions surrounding the corrosion pit (see insert in Figure 42). The GR transformed into yellow-colored rust after 24 h storage in a dry box (∼1% RH) (see insert in Figure 43a). The transformed GR shows Raman bands of lepidocrocite at 244 (shoulder) and 375 cm\(^{-1}\) (Figure 43a,
780 nm laser) or 248 and 377 cm\(^{-1}\) (Figure 43b, 532 nm laser). A broad band at 703 cm\(^{-1}\) (Figure 43b) could be due to amorphous FeOOH and/or Fe(OH)\(_3\) (see discussion session). The bands at 222, 230 (truncated), 269 and 524 cm\(^{-1}\) (maybe partially) are all ghost bands of the 780 nm laser system.

**Figure 42.** *Ex situ* Raman spectra from different locations in the GR region surrounding the corrosion pit (indicated by an arrow in the insert).
Figure 43. Ex situ Raman spectra from the transformed GR using (a) 780 nm and (b) 532 nm laser.

6.2.4 SEM characterization

For SEM characterization, a corroded region after 30 min corrosion under a NaCl droplet was dried in ambient, followed by removing the NaCl particle crystallized on top of the corrosion pit and the GR region using a fine-tipped steel wire (Figure 44a). Notice that the GR already suffered phase transformation prior to SEM characterization, but was believed to have maintained its original structure. The transformed GR appeared as a thin (1 µm) porous film surrounding the corrosion pit (Figure 44b), while lepidocrocite randomly scattered as rust clusters outside of the transformed GR region (Figure 44c).
Figure 44. SEM images showing (a) the entire corroded region after removing the NaCl particle crystallized on top of the corrosion pit (marked by an arrow) and the surrounding GR region (to the left bottom of the dashed line), (b) the transformed GR film, and (c) the lepidocrocite clusters.

Corroded regions under NaCl droplets were also rinsed using ultrapure water and wiped with cotton swaps, revealing the corrosion pits with polygonal (Figure 45a) or hemispherical (Figure 45b) shapes. The substrates in the lower left sides of the pits were also dissolved during corrosion. Some corrosion products that could not be removed by cleaning are also seen here.

Figure 45. SEM images showing the corrosion pits in (a) polygonal or (b) hemispherical shapes, grown in the corrosion initiation sites.
6.2.5 Discussion

6.2.5.1 Corrosion Initiation

As mentioned before, corrosion always initiated from the perimeters of the droplets when inclusions were not present, a possible explanation for which is the local microstructural defects in the surface oxide film grown on the polished 1018 carbon steel samples. When the dissolving and growing NaCl droplets formed on inclusion-free steel surfaces approached the defects, corrosion initiated immediately from the defects in the extremely high Cl⁻-content environment. The droplets then grew towards the other side of the droplets, leaving the corrosion initiation sites on one side. The absence of an effective differential aeration cell inside the relatively small droplet space is a possible explanation for corrosion not initiating in the center of the droplets, similar as described by Evans.[51, 52] When the slag-based metallic inclusions (i.e., slag in Figure 38) were present underneath the droplets, corrosion always initiated preferably from the crevices between the steel substrate and the inclusions, which are vulnerable to corrosion in a corrosive media. The corrosion initiation sites could be either at the edge or the center of the droplets.

6.2.5.2 Salt Precipitation inside the Corrosion Pit

After corrosion initiated, the corrosion initiation site served as the anodic site due to active iron dissolution (Figure 46) (Equation 1).

Other areas under the droplet, especially the substrate under the peripheral part of the droplet, served as the cathodic site with the occurrence of oxygen (O₂) reduction and generation of hydroxyl ions (OH⁻) (Equation 3).
The Fe$^{2+}$ ions generated by reaction (1) were released into the solution inside the pit and reacted with Cl$^{-}$ ions that were driven to the anodic site \[80\] by the corrosion current, forming FeCl$_2$\[81]\]

$$\text{Fe}^{2+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2(\text{aq}) \quad (5\text{a})$$

The dissociation of this highly soluble salt is given by reaction (5b)\[81-83\]

$$\text{FeCl}_2(\text{aq}) \leftrightarrow \text{FeCl}_2(\text{s}) \quad (5\text{b})$$

When the concentration of FeCl$_2(\text{aq})$ in the pit solution reached saturation, FeCl$_2(\text{s})$ started to precipitate onto the pit’s interior surface.\[84-86\] The \textit{in situ} Raman spectrum obtained from the pit (Figure 39a) shows a strong band at 245 cm$^{-1}$, indicating the existence of FeCl$_2$. To verify this, Raman spectrum of pure FeCl$_2$ powder (from Sigma-Aldrich) was also obtained and shows a single strong band at 245 cm$^{-1}$ (780 nm laser). Another major band at 286 cm$^{-1}$ was probably due to the existence of FeCl$_3^-$, which has a strong vibration feature at 273 – 292 cm$^{-1}$ according to calculation.\[87, 88\] It is possible that FeCl$_4^{2-}$ was also presenting in the pit electrolyte since it has vibrational frequencies in the range of 200 – 280 cm$^{-1}$ based on calculation.\[88\] These bands were probably hidden under the strong broad band. Another broad feature at 350 – 750 cm$^{-1}$ was possibly due to other weak vibrational
frequencies of FeCl$_2$ and its chloride ions,[88] as an extremely weak broad band at 489 cm$^{-1}$ was observed on pure FeCl$_2$ powder. Note that the ghost band at 525 cm$^{-1}$ in the 780 nm laser system must have contributed to the broad band at 525 cm$^{-1}$ in Figure 39a. The *ex situ* Raman spectrum obtained from the corrosion pit (Figure 40a) also shows the presence of FeCl$_2$ with a Raman band at 246 cm$^{-1}$ but a diminished feature at 286 cm$^{-1}$, possibly due to the disappearing of FeCl$_2$’s chloride ions during the dehydration of the sample.

6.2.5.3 Rust Formation

The Fe$^{2+}$ ions generated in the corrosion pit also diffused into the droplet solution and reacted with OH$^-$ generated by cathodic reaction (Equation 3), forming Fe(OH)$_2$,

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2$$  (6)

Fe(OH)$_2$ can also form inside the corrosion pit due to the hydrolysis of Fe$^{2+}$ ions (Equation 2). However, the accumulation of H$^+$ in the corrosion pit acidified the local environment, rendering the precipitation of Fe(OH)$_2$ impossible. For Fe(OH)$_2$ to precipitate, a higher pH environment is required.[43, 89] Therefore, Fe(OH)$_2$ formed in the cathodic regions outside of the corrosion pit (Figure 46). Being nonstable in oxygenated aqueous media, Fe(OH)$_2$ further reacted to form other iron oxides or oxy-hydroxides, such as Fe(OH)$_3$, γ-, δ-FeOOH, and γ-Fe$_2$O$_3$, as reported by Thomas et al. [90] and Evans et al.[91]

A Pourbaix diagram of the Fe–H$_2$O–Cl$^-$ system adapted from Refait et al. [92] (Figure 47) shows the various types of rust formed in different regions with given
potential and pH values. For corroded steel under a NaCl droplet, the anode had a lower potential than that of the cathode.[54] It follows that, in this study, the corrosion pit and its surrounding areas (anodic) had lower potential than those of other areas under the droplet (cathodic). In addition, the anodic sites had lower pH due to the generation of H\(^+\) inside the pit and migration of H\(^+\) to the surrounding areas, while the cathodic site had higher pH due to the accumulation of OH\(^-\) (Equation 2). Therefore, the anodic and cathodic regions under NaCl droplets can be depicted by A and B respectively in the Pourbaix diagram (Figure 47). Accordingly, GR1(Cl\(^-\)) formed on the anodic site inside the corrosion pit and on the steel substrate surrounding it, while lepidocrocite formed on the cathodic site, as evidenced by Raman spectra shown in Figure 37, 39, 40 and 42.

\[E_h\]

\[\text{GR1(Cl}^-\text{)}\]

\[\gamma-\text{FeOOH}\]

\[\text{Fe(OH)}_2\]

\[\text{Fe}\]

\[\text{pH}\]

**Figure 47.** Pourbaix diagram for the Fe–H\(_2\)O–Cl\(^-\) system.

The formation of GR1(Cl\(^-\)) came after the oxidization of the initially formed Fe(OH\(_2\)). Not intending to propose a GR formula with specific Fe\(^{2+}/\text{Fe}^{3+}\) ratios, a general formula (GR1(Cl\(^-\))) is used for the GR formed in Cl\(^-\)-containing environment,
Fe(OH)$_2$ + Cl$^-$ → GR1(Cl$^-$) + $e^-$  (7)  (adapted from Refait et al.,[92] not balanced)

According to previous studies,[45-47] for the Raman spectrum of GR1(Cl$^-$), the band at 505 cm$^{-1}$ has a higher intensity than that of the band at 425 cm$^{-1}$. In this study, similar results were observed, as shown by both in situ and ex situ Raman spectra in Figures 37a and c, 39b and c, 40b, 42a and b. However, we also obtained ex situ Raman spectra with the band at 425 cm$^{-1}$ showing a higher intensity than that of the band at 505 cm$^{-1}$ (Figures 37b and 40c), mostly from GR regions that were in the close vicinity of the corrosion initiation site. A difference in local chemistry might explain the contrasting results. Since Fe$^{2+}$ ions initially formed in the corrosion initiation site and then migrated outside, rendering a higher concentration of Fe$^{2+}$ ions in regions very close to the corrosion initiation site than regions away from it. The higher concentration of Fe$^{2+}$ ions might have resulted in GR with higher content of Fe$^{2+}$–OH, rendering the band at 425 cm$^{-1}$ for Fe$^{2+}$–OH bonding with higher intensity.

Lepidocrocite that preferably formed on the cathodic site also came from the initially formed Fe(OH)$_2$ after oxidation. The most likely explanation that lepidocrocite formed in the cathodic region is the alkaline environment. Johnston [43] also found the formation of lepidocrocite on iron electrode resting at OCP in an alkaline electrolyte (1 M KOH). He mentioned that it is necessary to raise local pH for lepidocrocite to precipitate.

It is worth to mention that both GR and lepidocrocite are not confined in isolated regions. Actually, they coexisted in the transitional region from GR to
lepidocrocite, as indicated by SEM images that show lepidocrocite clusters precipitated on top of the porous GR layer (Figure 44a). It seems that GR precipitated as a thin film in a relatively large region surrounding the corrosion initiation site. The lepidocrocite clusters that preferably formed on the cathodic site also precipitated in the GR region once its initial locations have been mostly occupied.

Magnetite that formed mostly in the transitional region from GR to lepidocrocite as clusters similar to lepidocrocite clusters (Figure 46) may have come from the reduction of lepidocrocite in the GR region periphery, a relatively acidic local environment. Note that magnetite always coexisted with GR (Figures 39c and 42b), indicating that they both stabilized in the relatively acidic GR region. However, the local pH can not be too low (< 4) [43] for magnetite to form. Actually, the reduction of lepidocrocite to magnetite was believed to be one of the cathodic reactions that balance the anodic oxidation of iron during corrosion.[91] The study of lepidocrocite reducing to magnetite by applying a constant reducing current was also conducted by Keiser et al. [93] through in situ Raman spectroscopy.

6.2.5.4 Green Rust Transformation due to Oxidation

We found that GR transformed to lepidocrocite after being oxidized in ambient, a phenomenon that was also reported by others. Boucherit et al. found the spontaneous transformation of GR to lepidocrocite in their study of corrosion films grown on iron and Fe-6Mo alloy in pitting conditions[45] and to other iron oxides and oxy-hydroxides in other environments.[47]
Unlike the Raman spectra from lepidocrocite clusters (Figures 37d, 39d and 40d), those from the transformed GR (Figure 43a and b) do not show sharp bands at ~377 cm\(^{-1}\), possibly due to the existence of other phases especially amorphous phases, which broaden the band at ~377 cm\(^{-1}\). The broad band at 703 cm\(^{-1}\) could be ascribed to amorphous FeOOH and/or Fe(OH)\(_3\). Keiser et al.[94] found that the Raman spectrum of amorphous FeOOH consists of only one broad band at 700 cm\(^{-1}\).

Dünnwald et al.[95] found the formation of amorphous FeOOH and/or Fe(OH)\(_3\) with Raman band at 701 cm\(^{-1}\) from an iron electrode corroded in an SO\(_2\)-containing atmosphere for 1 h. Fe(OH)\(_3\) might have come from the oxidation of Fe(OH)\(_2\) and amorphous FeOOH was possibly another transformed phase from GR.

6.2.5.5 Rust Transformation due to Laser Heating

The transformation of GR into lepidocrocite under a droplet solution due to laser heating (especially the 532 nm laser with higher power) was also observed (Figure 48). After directing the laser (1 – 2 mW) to the GR region surrounding the corrosion pit, GR (marked by an oval in insert (a)) transformed to lepidocrocite (marked by an oval in insert (b)) within several seconds depending on the laser power. The laser induced lepidocrocite looks exactly like the lepidocrocite clusters formed surrounding and sometimes in the GR region and generates similar Raman spectrum with major bands at 254, 375, 522 and 645 cm\(^{-1}\) (Figure 48). So, under certain thermal effects, GR transforms to lepidocrocite even under the protection of droplet solution, an indication that lepidocrocite is more stable than GR.
Figure 48. Raman spectrum obtained from laser induced lepidocrocite. Inserts: optical microscope images of the GR region close to the corrosion pit (marked by an arrow) (a) before and (b) after acquiring the Raman spectrum.

The rust (GR and lepidocrocite) that is not under the protection of water and exposed to ambient can be easily burned by the laser (normally with power >1 mW) and transform to other phases. The Raman spectra from the burned GR or lepidocrocite show the formation of hematite. The lepidocrocite that transformed from GR could also be easily burned by laser heating and transform to hematite (Figure 49a) with typical Raman bands at 220, 288, 403, 498, 606 and 1300 cm$^{-1}$ (not fully shown).
Comparing the two Raman spectra in Figure 49, we noticed that the spectrum in Figure 49a has an extra broad band at 664 cm\(^{-1}\), which might be due to two broad bands, one at 648 cm\(^{-1}\) from pure hematite (Figure 49b) and another at 704 cm\(^{-1}\) from amorphous FeOOH and/or Fe(OH)\(_3\) as discussed above. Since lepidocrocite and other iron hydroxides transform to hematite under high laser power,[79] it is likely that amorphous FeOOH also does. In this case, the broad band at 700 cm\(^{-1}\) in Figure 49a is not from amorphous FeOOH but from compounds other than oxy-hydroxides. This result may explain the existence of Fe(OH)\(_3\) in the transformed GR region if assuming that Fe(OH)\(_3\) cannot be burned by laser with high power.

Though being a great tool for identifying steel corrosion products, Raman spectroscopy has to be used with extra cautions, such as always trying to keep the laser power low (less than 1 mW) to avoid laser induced sample degradation.

**Figure 49.** Raman spectra from (a) the transformed GR region (lepidocrocite) after laser burning (marked by an arrow in the insert) and (b) a commercial pure hematite powder (from Alfa Aesar®).
6.3 Conclusion

Raman spectroscopy has been used to study the very initial stage of NaCl particle-induced corrosion on carbon steel. We report for the first time the *in situ* and *ex situ* identification of corrosion products formed on carbon steel under NaCl droplets that formed by deliquescence of pre-deposited NaCl particles upon exposure to high humidity (RH>80%). Corrosion initiated quickly under the NaCl droplets in the form of pitting. *In situ* and *ex situ* Raman spectra show the formation of GR in regions close to the anodic sites and the precipitation of lepidocrocite clusters over cathodic sites surrounding the GR region. Magnetite was detected mostly in the rust clusters formed in the transitional region from GR to lepidocrocite. Upon exposure to ambient, GR transformed to the more stable lepidocrocite due to oxidation.

Other than revealing the corrosion mechanism of steel under NaCl droplets, this study discovers that the presence of local anode and cathode facilitates the formation of different types of rust.

In addition, this preliminary Raman spectroscopic investigation of NaCl particle-induced marine atmospheric corrosion provides insights for future studies involving wet-dry cycle exposures, representing real atmospheric corrosion.
Chapter 7

Raman Spectroscopic Characterization of Evans’ Droplet Experiments

7.1 Experimental

7.1.1 Sample and Solution Preparation

The procedure of 1018 steel sample preparation was the same as that shown in Section 3.1.1.

A 3.15% NaCl solution and a 0.5 M Na₂SO₄ solution which were made from analytical grade salts and ultrapure water (18.0 MΩ-cm) were used to form Evans’ droplets on the polished 1018 steel surface.

7.1.2 Experimental Setup

A humidity chamber (Figure 50) that was modified from the one shown in Figure 21 was used.

![Figure 50. Schematic representation of the experimental setup used for in situ Raman spectroscopic study of Evans’ droplet experiments.](image-url)
7.1.3 Experimental Procedure

Droplets (NaCl and Na₂SO₄) with volumes of 5 – 6 µl and diameters of 3 – 4 mm were placed on the steel surface using a syringe (D = 1.73 mm) and through the view port in Figure 50. Then, the view port was covered using a piece of thin glass and sealed with Scotch® tape. Images of the droplets were taken using either the Raman microscope or the contact angle meter (CAM) camera (Figure 50).

A 3.15% NaCl droplet on top of the 1018 steel surface is seen in Figure 51. The volume, diameter and contact angle of this droplet were calculated using the CAM 200 (KSV Instruments) software.

![Figure 51. A 3.15% NaCl droplet placed on steel surface (V=5.89 µl, D=3.73 mm and contact angle = 60°).](image)

The corrosion that initiated immediately after the deposition of salt droplets on steel was observed and recorded using an optical microscope.

7.1.4 Raman Measurements

Details of Raman measurements are same as those shown in Section 6.1.4.

7.2 Results and Discussion

7.2.1 3.15% NaCl Droplets

Corrosion initiated quickly on steel under the NaCl droplet within 2 – 5 min by forming corrosion pits, mostly in the center of the droplet area. After several
minutes, fluffy corrosion products could be observed using the optical microscope (especially the dark field mode) moving around in the steel substrate/droplet interfaces, similar as a Brownian motion. The corrosion pits grew bigger with time; and more corrosion product clusters precipitated on the steel substrate. Notice that the rust clusters (yellowish in color) actually formed in a circular pattern surrounding the central pitting area. This result is similar as that mentioned by Evans [51] who discovered that the central anodic zone under a salt droplet (i.e., NaCl, KCl or Na₂SO₄) placed on a horizontal steel sheet and the peripheral cathodic ring (immune from corrosion) was separated by a ring of rust. After extended corrosion, the corrosion products spread to a larger area under the droplet, towards both the central anodic area and the peripheral cathodic area.

In situ Raman spectrum (Figure 52a) from one of the corrosion pits (after 30 min corrosion) shows a strong broad band in the range of 215 – 350 cm⁻¹. Similar as described in Section 1.6.2.5.2, these Raman bands were assigned to FeCl₂ that precipitated onto pit’s wall and its chlorides ions, such as FeCl₄²⁻ and/or FeCl₅⁻. The Raman spectrum (Figure 52b) from regions close to the pit shows Raman signal of GR with two bands at 430 cm⁻¹ and 502 cm⁻¹. A shoulder band at 525 cm⁻¹ was actually a ghost band of the 780 nm laser system. The Raman spectrum (Figure 52c) from the yellowish rust clusters formed in between the central pitting area and the peripheral cathodic area shows Raman signal typical of lepidocrocite, with major bands at 248, 378 and 529 cm⁻¹.
Figure 52. *In situ* Raman spectra obtained from different locations on steel under a 3.15% NaCl droplet after 30 min corrosion: (a) corrosion pit, (b) regions surrounding the corrosion pit, (c) rust clusters that formed in between the central anodic pitting region and the peripheral cathodic region.

Notice that the GR actually formed as a hardly noticeable, thin, and porous rust film surrounding the pitting area. It was barely observable under the optical microscope, as a green-colored corrosion product.

7.2.2 0.5 M Na$_2$SO$_4$ Droplets

Evans’ droplet experiments were also conducted using 0.5 M Na$_2$SO$_4$ droplets. The results turned out to be similar as those of NaCl droplets. Pitting initiated quickly under the droplets within several minutes, and usually in the center of the droplet areas. A ring of rust precipitated in between the central pitting area and the peripheral area.

*In situ* Raman spectra (Figure 53a) obtained from one of the corrosion pits shows a broad band at 826 cm$^{-1}$ and a sharp band at 981 cm$^{-1}$. The band at 981 cm$^{-1}$
was due to SO$_4^{2-}$ from the solution, while the reason for the broad band at 827 cm$^{-1}$ is not clear. The Raman spectrum (Figure 53b) from the thin rust film formed surrounding the pitting area shows strong Raman bands of GR at 430 cm$^{-1}$ and 506 cm$^{-1}$, and a band at 982 cm$^{-1}$ due to SO$_4^{2-}$ from the solution. Again, the shoulder Raman band at 525 cm$^{-1}$ was a ghost band obtained using the 780 nm laser. The Raman spectrum (Figure 53c) from the yellowish rust clusters formed in between the pitting area and the peripheral cathodic area shows Raman bands of lepidocrocite at 249, 379 and 529 cm$^{-1}$ and a band at 981 cm$^{-1}$ due to SO$_4^{2-}$.

![Figure 53](image)

**Figure 53.** *In situ* Raman spectra obtained from different locations on steel under a 0.5 M Na$_2$SO$_4$ droplet after 30 min corrosion: (a) corrosion pit, (b) regions surrounding the corrosion pit, (c) rust clusters that formed in between the central anodic pitting region and the peripheral cathodic region.

According to the above results, reference [53] was not accurate in stating that the rust formed in between the central anodic site and the peripheral cathodic site under Evans’ droplets was Fe$_2$O$_3$.H$_2$O.
The explanation of the formation of different rust phases under the Evans’ 
droplets is similar as described in Section 6.2.5.3.

7.3 Conclusion

Central anodic regions (pitting) and peripheral cathodic regions developed 
under both 3.15% NaCl droplets and 0.5 M Na₂SO₄ droplets (D = 3 – 4 mm) placed 
on 1018 carbon steel surface.

*In situ* Raman spectra from the rust film formed on steel substrate near the 
pitting area showed the presence of GR, while those from the yellowish rust clusters 
formed in between the central anodic region and the peripheral cathodic region 
showed the existence of lepidocrocite.
Chapter 8

Summary

The marine atmospheric corrosion of carbon steel was studied by short-time (30 min) outdoor exposure experiments, SEM/EDXA characterization, small-scale electrochemical tests and in situ Raman spectroscopic characterization. The following results were obtained.

The very initial stage of marine atmospheric corrosion of 1018 steel was studied by short-time (30 min) field exposure experiments. On samples that were exposed to the KI test site, both sea salt particles (D < 5 µm) (mainly NaCl) and salt particle clusters (D < 10 µm) (mainly NaCl) that formed after dehydration of relatively small seawater droplets (D < 30 µm), and corroded regions caused by larger seawater droplets (D > 50 µm) were found. Salt particles or corroded regions that were from seawater droplets with diameter in the range of 30 – 50 µm were not deposited during the sampling events. Corrosion products were not detected on steel near small sea salt particles/clusters, but were detected under larger seawater droplets (D > 50 µm). Corrosion occurred on pure zinc samples under seawater droplets ranging from 10 – 50 µm, and a dependency of corrosion initiation on droplet size was not observed as in the case for steel. Few or no sea salt particles and the subsequent corroded regions were found on both 1018 steel and pure zinc samples that were exposed to the CI test site due to low wind velocity (< 3 m/s) during sample
exposure period. A wind velocity above the critical value (3 m/s) is needed to generate airborne chlorides.

Similarly, corrosion initiation studies conducted in the laboratory showed that corrosion did not initiate on 1018 steel under NaCl droplets (formed by deliquescence) having diameters less than approximately 45 µm, while corrosion always initiated under larger NaCl droplets with diameter greater than approximately 45 µm. Secondary droplets formed around the larger NaCl droplets, and spread out over a region covering an area at least several times that of the original droplet area. The areas under the secondary droplets served as cathodic sites and were free of corrosion. EDXA elemental mapping showed that Cl\(^-\) migrated to anodic regions and Na\(^+\) migrated to cathodic regions. Sometimes, filiform corrosion initiated from the larger NaCl droplets. The head of the filament was anodic, and hence found to be rich in Cl. The base of the filament and the original droplet region appeared to serve as cathodic sites, and were richer in Na as compared to Cl. Hence, the original droplet site which was initially anodic, transformed to a cathodic site with the emergence of the growing filament.

Electrochemical measurements showed that the OCP values for small NaCl droplets (formed by deliquescence) on steel were in the range of -0.10 V\(_{\text{SCE}}\) – 0 V\(_{\text{SCE}}\), indicating that the steel passivated as no corrosion was observed under the droplets. Larger droplets had much lower OCP values in the range of -0.50 V\(_{\text{SCE}}\) – -0.30 V\(_{\text{SCE}}\), with corrosion occurring underneath. Anodic polarization showed passivation under smaller NaCl droplets and active dissolution under larger droplets. Cathodic
polarization indicated the oxygen reduction was the primary cathodic reduction. The cathodic current density increased as the NaCl droplets size decreased, due to the shorter diffusion path for dissolved oxygen from the surface of the droplet to the corroding surface. The cathodic oxygen diffusion-limited current density was found to be inversely proportional to the droplet size in the range of 426 – 103 µm, which was the smallest droplet that was examined.

The rust products formed in the very initial stage of NaCl particle-induced corrosion on carbon steel were identified using both in situ and ex situ Raman spectroscopy. In situ and ex situ Raman spectra show the formation of GR in regions close to the anodic sites (pitting areas) and the precipitation of lepidocrocite clusters over cathodic sites surrounding the GR region. The formation of different rust phases was due to the difference in local pH environment. Upon exposure to the ambient atmosphere, GR transformed to the more stable lepidocrocite due to oxidation.

In-situ Raman spectroscopy also enabled the identification of rust formed on steel under classical Evans droplets (both NaCl and Na₂SO₄). The rust film that formed in the central anodic pitting area was identified as GR, while the rust ring on the boundary demarcating the central anodic region and the peripheral cathodic region was found to be lepidocrocite. The formation of different rust in different locations was due to the local pH environment. It was concluded that different types of rust formed in different areas wherever there was a variation of local pH caused by the separation of local anodes and cathodes.
Part II

Characterization of the Rust Formed on Carbon Steel that were Exposed to Hawai‘i’s Diverse Micro-climates using Advanced Techniques
Chapter 9

Introduction

9.1 Background

Marine atmosphere is one of the most corrosive environments to metallic structures due to its high content of airborne chlorides, mainly NaCl. Marine atmospheric corrosion is a serious problem especially for Hawai‘i due to its specific location and the large military presence.

The high corrosion rates in marine environments significantly reduce the lifetimes of steel structures. More knowledge about corrosion behavior of steel will help us understand the corrosion mechanism, evaluate the material’s performance and seek approaches to extend the lifetimes of steel structures.

9.2 Objectives of Research

The objectives of this research were

- to characterize the rust formed on 1008 steel samples that were exposed to Hawai‘i’s diverse micro-climates for a 1 year period.
- to study the effects of different environments on the corrosion behavior of 1008 steel.

9.3 Materials

The material used was 1008 carbon steel with the chemical composition shown in Table 4. The dimensions of the steel plates were 2×4×0.12 inch.
Table 4. Chemical composition of the carbon steel used in the present study.

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>0.04</td>
<td>0.30-0.60</td>
<td>balance</td>
</tr>
</tbody>
</table>

9.4 Sample Exposure

The 1008 carbon steel samples were attached to exposure racks designed with a 45° angle facing the northeast (trade wind direction). The exposure racks were exposed to seven test sites located in Campbell Industrial Park (CP), Lyon Arboretum (LA), Lualualei (LU), Ewa Nui (EN), Coconut Island (CI), Kaka’ako Park (KP) and Mokule’ia (MO) in Oahu, Hawai`i—representing industrial, rainforest, dry, agricultural, mild marine, moderate marine and severe marine environments, respectively (Figure 54 and Table 4). In each test site, three parallel samples were exposed. After a 1 year exposure, samples were taken to the laboratory for the corrosion products to be characterized. Only one sample from each test site was used for the present study. The seven samples were labeled as sample S1-S7 for referencing.

Figure 54. Locations of the seven test sites in Oahu, Hawai`i.
Table 5. Information on the seven test sites shown in Figure 54.

<table>
<thead>
<tr>
<th>Test Sites</th>
<th>Samples</th>
<th>Location</th>
<th>Environment</th>
<th>Chloride (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>Campbell Industrial Park</td>
<td>Industrial</td>
<td>49.8</td>
</tr>
<tr>
<td>2</td>
<td>S2</td>
<td>Lyon Arboretum</td>
<td>Rainforest</td>
<td>10.7</td>
</tr>
<tr>
<td>3</td>
<td>S3</td>
<td>Lualualei</td>
<td>Dry</td>
<td>13.6</td>
</tr>
<tr>
<td>4</td>
<td>S4</td>
<td>Ewa Nui</td>
<td>Agricultural</td>
<td>35.7</td>
</tr>
<tr>
<td>5</td>
<td>S5</td>
<td>Coconut Island</td>
<td>Mild Marine</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>S6</td>
<td>Kakā'ako Park</td>
<td>Moderate Marine</td>
<td>352.1</td>
</tr>
<tr>
<td>7</td>
<td>S7</td>
<td>Mokule'ia</td>
<td>Severe Marine</td>
<td>1036.2</td>
</tr>
</tbody>
</table>

9.5 Sample characterization

Various techniques including SEM/EDXA, Raman spectroscopy, FTIR and XRD were used to characterize the rust. Generally, these techniques offer complimentary information. A comparison of these techniques is shown in Table 6.

Details of each technique will be discussed in the following sections.

Table 6. Comparison of the techniques used for rust characterization.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Probing</th>
<th>Acquired information</th>
<th>Probing area</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Electron beam</td>
<td>Morphology</td>
<td>≥~1×1 µm</td>
</tr>
<tr>
<td>EDXA</td>
<td>Electron beam</td>
<td>Elemental composition</td>
<td>depending on magnification</td>
</tr>
<tr>
<td>Raman</td>
<td>Laser (532 nm)</td>
<td>Chemical bonding</td>
<td>0.9×0.9 µm</td>
</tr>
<tr>
<td>FTIR</td>
<td>Infrared</td>
<td>Chemical bonding</td>
<td>100×100 µm</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray</td>
<td>Crystal structure</td>
<td>2×0.5 cm</td>
</tr>
</tbody>
</table>
Chapter 10

Literature Review

10.1 Outdoor Exposure Experiments

To study the corrosion performance of the material in certain environments, normally samples are exposed to an environment for a certain time period. This method represents the real application of the studied materials and thus produces authentic information. One common analysis method is to measure the weight loss of the outdoor-exposed samples.

In addition to the weight loss study on the outdoor-exposed samples, a full analysis of the chemical and phase composition of the corrosion products on steel surfaces is necessary since these products are thought to determine the long-term corrosion rates of steel.

The main constituents of corrosion products that formed during atmospheric corrosion of steel are lepidocrocite ($\gamma$-FeOOH), goethite ($\alpha$-FeOOH), akaganeite ($\beta$-FeOOH) and feroxyhite ($\delta$-FeOOH). Lepidocrocite is believed to form in the initial stages of atmospheric corrosion and transforms to goethite in certain conditions, which is the most stable and protective rust phase. Akaganeite forms only in the presence of salinity [98, 100] and is widely found in marine environments [101, 102] as well as in chloride-rich solutions [103-105] and soils [106, 107]
10.2 Raman Characterization

Raman spectroscopy is an effective way to characterize corrosion products, especially different phases of iron oxides. Raman spectra of various common iron oxides, either commercial or synthesized, have been obtained in the literature for references.\[79, 106, 108-113\] The summary of these results is presented in Table 7.

A problem during Raman spectra collection is the thermal effects caused by laser heating on the iron oxides. For example, Faria et al. [79] proved that hematite formed under intense laser excitation when collecting Raman spectra of magnetite and the oxyhydroxides including $\alpha$-FeOOH, $\gamma$-FeOOH, and $\delta$-FeOOH. Given this, extra precautions are needed to avoid inaccurate interpretation of the Raman spectra.

Raman spectroscopy has been successfully used for identifying corrosion products that formed on steel or iron in immersed [103-105] or buried conditions [106, 107] and in various atmospheric environments.[94, 101, 102, 114-116]

Cook et al. [101] investigated the corrosion products on steels that were exposed to the Gulf of Mexico using micro-Raman analysis. They found that the inner rust layer consisted of $\alpha$-FeOOH and nano-sized $\gamma$-Fe$_2$O$_3$ phases while the outer layer was predominantly $\gamma$-FeOOH. On samples after extended exposure (up to 16 years), small clusters of pure magnetite were also detected in the inner rust layer. Randomly scattered akaganeite was also found in the corrosion products on samples exposed near the shoreline.[102] The high concentration of chloride near the shoreline explains the presence of large fraction of akaganeite.
Townsend et al. [114] characterized the rust (cross-section) formed on weathering steels exposed for up to 11 years in industrial and rural environments using Raman spectroscopy. They found that the porous rust immediately adjacent to the steel substrate was lepidocrocite, while the less porous region above the porous layer consisted of a mixture of lepidocrocite and goethite. A smooth and dense layer of hematite mixed with magnetite was also detected.

Oh et al. [115] studied atmospheric corrosion of steel exposed in marine, industrial and rural test sites for up to 16 years and found regions of pure goethite, goethite mixed with superparamagnetic maghemite and pure superparamagnetic maghemite (small island cluster) on the cross-section of the rust. Lepidocrocite was believed to have initially formed in the surface rust layer and later flaked off, resulting in not detecting it during the Raman analysis.

Antunes et al. [116] studied carbon steel and weathering steel exposed in Brazilian tropical sites for 1 to 3 months using Raman spectroscopy. The red oxide showed Raman spectra typical of lepidocrocite, with intense bands at 245 and 375 cm\(^{-1}\), while the yellow oxides corresponded to a mixture of lepidocrocite and goethite (245, 299, 385, 479, and 550 cm\(^{-1}\)). The black rust showed typical bands of magnetite at 535 and 662 cm\(^{-1}\), together with lepidocrocite and goethite bands.

Neff et al. [111] investigated the rust scales on archaeological iron artifacts using Raman spectroscopy to understand the long-term atmospheric corrosion mechanism. Goethite was found as the main phase in contact with the metal substrate, while lepidocrocite was detected in confined areas all over the sample,
usually associated with cracks. Akaganeite had a similar distribution pattern but also presented in the inner rust layer.

Table 7. Raman band positions of various pure iron oxides from the literature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Band positions (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>226, 245, 293, 298, 413, 500, 612</td>
<td>[113]</td>
</tr>
<tr>
<td>((\alpha)-Fe(_2)O(_3))</td>
<td>227, 245, 293, 298, 414, 501, 612</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td>225, 247, 293, 299, 412, 498, 613</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>226, 245, 292, 411, 497, 612</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>226.5, 245.5, 293.5, 300, 413, 498.5, 612.5, 659, 817.5, 1049, 1103, 1318</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>225, 290, 405, 495, 605, 1310</td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>298, 397, 414, 474, 550</td>
<td>[108]</td>
</tr>
<tr>
<td>((\alpha)-FeOOH)</td>
<td>243, 299, 385, 479, 550, 685, 993</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>205, 247, 300, 386, 418, 481, 549</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>247, 300, 386, 483, 549</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>206, 247, 301, 388, 416, 482, 552, 685, 1003</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>205, 245, 300, 390, 415, 480, 550, 685, 1005, 1300</td>
<td>[110]</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>252, 380</td>
<td>[108]</td>
</tr>
<tr>
<td>((\gamma)-FeOOH)</td>
<td>245, 373, 493, 522, 650, 719, 1303</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>219, 252, 311, 349, 379, 528, 648</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>250, 302, 343, 379, 525, 650, 1055, 1300</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>250, 300, 380, 525, 650, 1055, 1300</td>
<td>[110]</td>
</tr>
<tr>
<td>Magnetite</td>
<td>616, 663</td>
<td>[108]</td>
</tr>
<tr>
<td>(Fe(_3)O(_4))</td>
<td>300, 532, 661</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>532, 667</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>311, 541, 666</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>308, 542, 669</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>310, 540, 670</td>
<td>[110]</td>
</tr>
<tr>
<td>Maghemite</td>
<td>350, 500, 700</td>
<td>[79]</td>
</tr>
<tr>
<td>((\gamma)-Fe(_2)O(_3))</td>
<td>381, 486, 670, 718</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>380, 460, 510, 670, 720</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>380, 460, 510, 670, 720, 1160, 1400</td>
<td>[110]</td>
</tr>
<tr>
<td>Ferroxyhite</td>
<td>400, 680</td>
<td>[79]</td>
</tr>
<tr>
<td>((\delta)-FeOOH)</td>
<td>297, 392, 666</td>
<td>[109]</td>
</tr>
<tr>
<td>Wustite</td>
<td>616, 663</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td>652,</td>
<td>[79]</td>
</tr>
</tbody>
</table>
10.3 FTIR Characterization

As a complementary tool to Raman spectroscopy, FTIR is also very useful for the identification and even quantification of various iron oxide phases normally found in steel corrosion products. Misawa et al. [96, 117, 118] did the pioneer work on FTIR identification of corrosion products formed on low carbon steel in atmospheric condition and found the rusts as a mixture of $\alpha$, $\gamma$, $\delta$-FeOOH and $\text{Fe}_3\text{O}_4$, or $\alpha + \gamma +$ amorphous FeOOH. After Misawa, extensive work was conducted on the FTIR study of iron or steel corrosion system, mostly for qualitative identifications. [94, 99, 101, 114, 119-123]

Yamashita et al. [99] obtained infrared spectra from the rust formed on both weathering and mild steels exposed for 25 years in an industrial region and found the predominant presence of mainly lepidocrocite and goethite as well as a small amount of magnetite.

Cook et al. [101] studied the corrosion products on steel samples exposed to the Gulf of Mexico for up to 12 months using the diffused reflectance technique. They found that the rust formed after a short exposure time period (1-3 months) contained a predominance of amorphous and crystalline lepidocrocite as indicated by both broad and narrow infrared bands at 1020 cm$^{-1}$. Very weak bands possibly due to akaganeite and goethite were also detected. After a longer exposure (4-6 months), the amorphous lepidocrocite transformed to a crystalline phase, which showed sharp bands at 750 and 1020 cm$^{-1}$. On samples after 12 months exposure, both lepidocrocite (750 and 1020 cm$^{-1}$) and goethite (790 and 890 cm$^{-1}$) were present.
Townsend et al. [114] conducted FTIR analysis on the rust scraped from weathering steels exposed for up to 11 years in industrial and rural environments and detected only goethite and lepidocrocite.

Wan et al. [122] characterized the rust formed on carbon steels pre-corroded with various gaseous pollutants and after 12 months of exposure using FTIR. The infrared spectra of the rust layers on samples with different pre-treatments (NO2, damp air, SO2, and H2S) were similar and showed a mixture of goethite (780 and 885 cm\(^{-1}\)), lepidocrocite (750, 1020, and 1450 cm\(^{-1}\)) and amorphous ferroxyhite (794 and 1124 cm\(^{-1}\)).

Ramana et al. [123] characterized the rust formed on low carbon steel exposed to marine test sites in Chennai Harbor in South India using FTIR. They found highly crystalline lepidocrocite (1022 cm\(^{-1}\)) as the most dominant phase on samples exposed in the atmospheric zone for 2 months. The same phase appeared at 741 cm\(^{-1}\) for amorphous lepidocrocite, which became more prominent after longer exposure (12 months). The second most dominant iron oxide phase was ferroxyhite at 886 cm\(^{-1}\) followed by hexagonal goethite at 800 cm\(^{-1}\), which also became sharp and prominent after longer exposure. A broad band at 1625 cm\(^{-1}\) appeared because of amorphous rust and the band at 1112 cm\(^{-1}\) was due to ferroxyhite. A maghemite band was seen at 470 cm\(^{-1}\).

On samples exposed to the splash zone for 2 months lepidocrocite (1022 cm\(^{-1}\)) and akaganeite (858 cm\(^{-1}\)) were the dominant rust phases.[123] The chloride-rich environment in the splash zone was responsible for the formation of akaganeite. The
absence of lepidocrocite band at 1022 cm\(^{-1}\) after 12 months exposure indicated the transformation of lepidocrocite into akaganeite due to the deposition of more chloride. The second dominant phase was ferroxyhite with infrared bands at 1117 and 1479 cm\(^{-1}\). Hematite band at 469 cm\(^{-1}\) was detected only on samples exposed for 2 months. In addition, bands at 564 cm\(^{-1}\) corresponding to magnetite were seen in all spectra.

Quantitative analyses of iron oxides using FTIR were also conducted.[124, 125] For this purpose, transmittance infrared spectra of iron oxides in KBr pellets were obtained. However, extra bonds may be created if akaganeite is present in the investigated corrosion products due to the possibility of Cl being replaced by Br.

For references, the infrared band locations of various iron oxide phases from literature are tabulated in Table 8.

Table 8. FTIR band positions of iron oxides found in iron/steel corrosion products.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Band positions (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidocrocite</td>
<td>750, 1020</td>
<td>[101]</td>
</tr>
<tr>
<td>((\gamma)-FeOOH)</td>
<td>475, 595, 750, 1025, 1125</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td>750, 1020, 1450</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>741, 1022</td>
<td>[123]</td>
</tr>
<tr>
<td>Goethite</td>
<td>790, 890</td>
<td>[101]</td>
</tr>
<tr>
<td>((\alpha)-FeOOH)</td>
<td>800, 887, 3405, 3146</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td>780, 885</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>[123]</td>
</tr>
<tr>
<td>Ferroxyhite</td>
<td>794, 1124</td>
<td>[122]</td>
</tr>
<tr>
<td>((\delta)-FeOOH)</td>
<td>886, 1117, 1479</td>
<td>[123]</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>858</td>
<td>[123]</td>
</tr>
<tr>
<td>((\beta)-FeOOH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maghemite</td>
<td>470</td>
<td>[123]</td>
</tr>
<tr>
<td>((\gamma)-Fe(_2)O(_3))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
10.4 XRD Characterization

X-ray diffraction is another commonly used technique for identifying steel corrosion products because most rust phases have crystalline structures.

Extensive work has been conducted on atmospheric corrosion using XRD. [99, 101, 102, 115, 116, 122, 123] Lepidocrocite and goethite were the two major rust phases detected on steel samples that suffered atmospheric corrosion, while akaganeite was detected on samples only after exposure in marine environments. Magnetite was detected in certain conditions but was difficult to be separated from maghemite.[101]

In this dissertation, SEM/EDXA, Raman spectroscopy, FTIR and XRD were used to characterize and identify the rust layers grew on carbon steel that were exposed to Hawai‘i’s diverse micro-climates for 1 year period. The effects of different environments on the atmospheric corrosion behavior of carbon steel were discussed.
Chapter 11

Morphological Characterization

11.1 Experimental

A Hitachi S-3400N SEM equipped with an Oxford Instruments energy dispersive X-ray analyzer system was used to characterize the corrosion products on steel samples after 12 months exposure. Both the rust in the surface layer and that close to the substrate (at the bottom of peeled-off regions) was examined.

11.2 Results and Discussion

Extensive corrosion occurred on all the steel samples, especially the one from the severe marine test site (S7). The colors of the surface rust on each sample are summarized in Table 9.

SEM images (Figure 55a-d) of the typical yellow rust (sample S2 (rainforest)) show a porous structure, while those (Figure 55e and f) from the black rust bumps (high Cl content) on sample S6 indicate a relatively compact structure but with micro-cracks. The yellow rust is normally lepidocrocite, while the black rust is the Cl-containing akaganeite, as identified in the following sections. The lepidocrocite with either a porous cotton ball structure (Figure 55b) or a nest structure (Figure 55d) is believed to be a non-protective rust phase to the substrate. However, the compact akaganeite rust is also not protective due to the non-uniformity of the rust layer and the high Cl concentration in the environments.
Figure 55. SEM micrographs of the surface rust on sample S2 (a-d) (rainforest) and S6 (e-f) (moderate marine).

The morphology of the inner rust close to the substrate was also investigated (Figure 56) by scraping off the surface rust layer. Notice that these images actually represent the fracture morphology of the inner rust layer. Generally, the inner rust (goethite, as identified in the following sections) had a micro scale and compact nest structure, as shown in the SEM image in Figure 56a form sample S5. On samples with black rust (akaganeite, as identified in the following sections), crystal-like rust was detected, as shown in Figure 56b for sample S3 (face-down side) and in Figure 56c and d for sample S6. These crystals all had very high Cl concentration and were identified as akaganeite (see following sections).
Figure 56. SEM micrographs of the inner rust close to the substrate (or at the bottom of peeled-off regions): (a) sample S5 (mild marine), face-up side; (b) sample S3 (dry), face-down side; and (c) and (d) sample S6 (moderate marine), face-down side.

11.3 Conclusion

SEM characterization of the rust grew on steel samples exposed to Hawai‘i’s diverse environments show that the dominant yellow and/or red rust had a porous structure while the black rust especially that from marine test sites show a compact structure but with micro-cracks.

Rust crystals (akaganeite) with high concentration of Cl were detected in the inner rust layers on samples that suffered corrosion in high Cl environments.
Chapter 12

Layered Identification using Raman Spectroscopy and EDXA – Correlating the Techniques

12.1 Experimental

12.1.1 Raman Spectroscopy Principles

When a monochromatic radiation of frequency $v_0$ is incident on certain molecular systems, different scatterings of the radiation may occur. The scattering with a frequency the same as the incident radiation is called Rayleigh scattering, while the one with changed frequency is called Raman scattering, which was first discovered by the Indian scientist Sir Chandrasekhra Venkata Raman [126] in 1928. The frequencies of the Raman scatterings are $v_0 \pm v_m$ where $v_m$ is the vibrational frequency of the molecule. Raman bands at frequencies less than the incident frequency ($v_0 - v_m$) are referred as Stokes bands, and those at frequencies greater than the incident frequency ($v_0 + v_m$) as anti-Stoke bands. The Stokes bands are commonly obtained in Raman spectra.

Raman spectroscopy is capable of probing the structure of gases, liquids, and solids—both amorphous and crystalline—by revealing information about chemical bonding.

12.1.2 Raman Measurements

A Nicolet Almega XR dispersive Raman Spectrometer (Thermo Scientific Corp.) equipped with multiple Olympus objectives and a Peltier-cold charge-coupled
device (CCD) detector was used for the experiments. Objectives with magnification of ×50 and ×100, with estimated spatial resolutions of 1.6 µm and 0.9 µm respectively, were used. The instrument was operated with laser sources of a green Nd:YAG laser with 532 nm wavelength excitation and an infrared diode laser with 780 nm wavelength excitation. The laser power was always kept lower at 1 mW to avoid sample degradation due to the laser heating effects. The laser power was measured at the sample. An aperture of 100 µm pinhole was used, giving a relatively low estimated resolution in the range of 8.4 – 10.2 cm⁻¹. The low resolution spectra were frequently compared with high resolution spectra (require longer acquisition time) to prevent missing possible Raman bands. The accumulation time was 1200 seconds.

Raman spectra were obtained from both sides of the steel samples. Since the steels samples were stored in plastic zip lock bags after being removed from exposure racks, some rust on the sample surfaces flaked off during handling, leaving many crater-like peeled-off areas randomly scattered on the sample surfaces. Fortunately, these peeled-off areas facilitated the acquisition of Raman spectra from different rust layers (layered Raman spectroscopic identification).

Band decomposition analysis was achieved using PeakFit® scientific software (Systat Software Inc.) to reveal hidden bands and to distinguish between contributions from different components. Baseline correction was conducted using the same software before band-fitting using a Gaussian + Lorentzian area function. Squared correlation factors were maintained greater than 0.95 for all the fittings.
12.1.3 EDXA Elemental Quantification

To facilitate locating the Raman acquisition locations under SEM, they were marked using small pieces of copper tapes cut with fine tips. The same Hitachi S-3400N SEM equipped with an Oxford Instruments energy dispersive X-ray analyzer was used for surface morphology characterization and chemical composition analysis of the rust layers.

12.2 Results and Discussion

12.2.1 Industrial Test Site

The Raman spectrum (Figure 57a) of the inner rust on the face-up side of sample S1 shows the presence of goethite with major Raman bands at 251, 291, 388, 480 and 690 cm\(^{-1}\). Two weak goethite bands at 992 and 1128 cm\(^{-1}\) were also detected. Notice the weak broad band at \(\sim 1305\) cm\(^{-1}\), which is not shown in the frequency region but actually existed according low resolution spectra with wavenumber in the range of \(0 – 4000\) cm\(^{-1}\). The Raman spectrum from the intermediate rust layer (Figure 57b) shows a mixture of lepidocrocite, the strongest band of which is at 250 cm\(^{-1}\), and goethite, the strongest band of which is at 385 cm\(^{-1}\). The Raman spectrum (Figure 57c) from the surface yellow rust shows the presence of pure lepidocrocite (250, 301, 378, 525, 649, 1055, and 1297 cm\(^{-1}\)).
Figure 57. Raman spectra from the face-up side of sample S1 (industrial).

To distinguish between the Raman bands of goethite and lepidocrocite (Figure 57b), band decomposition analysis was conducted using PeakFit software (Figure 58). The fitting revealed bands at 218, 250, 345, 378, 526, and 644 cm\(^{-1}\) for lepidocrocite and bands at 243, 299, 393, 411, 477, 550, and 685 cm\(^{-1}\) for goethite.

Figure 58. Raman band decomposition analysis of the spectrum in Figure 57b.
Band decomposition was also conducted on the spectrum in Figure 57a in the range of 950 – 1050 cm\(^{-1}\) (Figure 59). The result show two shoulder (sh) bands near the goethite band at 994 cm\(^{-1}\). The two bands at 978 cm\(^{-1}\) and 1012 cm\(^{-1}\) are possibly due to traces of \(\text{SO}_4^{2-}\) and \(\text{CO}_3^{2-}\) in the rust.

**Figure 59.** Raman band decomposition analysis of the spectrum in Figure 57a in the range of 950 – 1050 cm\(^{-1}\).

Elemental quantification analyses (Figure 60) using EDXA were also conducted on the rust in and near the peeled-off region shown in Figure 57. The EDXA result of the inner rust layer (location (a) in Figure 57) shows the presence of approximately 1% S, a finding that corroborates the Raman analysis, which shows the existence of \(\text{SO}_4^{2-}\) (Figure 59). EDXA results of the rust in other locations ((b) and (c) in Figure 57) shows less S as compared to that shown in Figure 60a, which explains why Raman bands for \(\text{SO}_4^{2-}\) (~980 cm\(^{-1}\)) were not observed in Figure 57b and c.

Additional EDXA results of the rust on sample S1 show a high content of S (>1%) in scattered locations, both at the bottom of peeled-off regions (Figure 60b) or in the surface rust (Figure 60c). The S with relatively high concentration generally came from industrial pollution in this specific test site.
Figure 60. EDXA spectra and quantification results of the rust on sample S1 (industrial).

The EDXA result in Figure 60b also shows traces of Cl (0.14%). Actually, Cl with relatively high concentration was detected in scarce locations in the inner rust layer (Figure 61). The Raman spectrum (Figure 61a) from the Cl-containing rust shows the presence of akaganeite (301 and 714 cm$^{-1}$) and goethite (249, 300 (hidden), 398, 480, 547, and 680 cm$^{-1}$ (sh)).

Though the industrial test site (sample S1) was selected to represent an industrial environment it also has characteristics of a marine setting. Airborne sea salts, mainly NaCl, are present in this location because it is close to the ocean (Figure 54). A few NaCl particles that deposited on the steel sample caused the formation of akaganeite in scattered locations.
Figure 61. Raman spectrum (a) and EDXA results (b) of the inner rust layer in a peeled-off region on sample S1 (industrial).

12.2.2 Rainforest, dry and agricultural test sites

Raman analysis of sample S2 (rainforest) shows similar results as those of sample S1 (industrial). Lepidocrocite was the dominant rust in the surface rust layer on both sides of the sample, while goethite was detected in the inner rust layer. One difference is that akaganeite was not detected on sample S2 in both the inner and surface rust layers. Since the rainforest test site is far from the ocean and has a lot of rain that washes off sea salts so Cl is generally absent and thus the Cl-containing rust-akaganeite.

Similarly, lepidocrocite was detected as the major component in the surface rust layers on both sides of samples S3 (dry) (Figure 62a). Goethite was found in the inner rust layers, and akaganeite was detected in a relatively large region
(approximately 1/3 of the sample surface) on the face-down side, either mixed with lepidocrocite (Figure 62b and c) or in a relatively pure form (Figure 62d). Since the band at \( \approx 250 \text{ cm}^{-1} \) is the strongest band for lepidocrocite (Figure 62a), it is used for the identifying lepidocrocite. Therefore, the rust from which the Raman spectra in Figure 62a-c were obtained all had lepidocrocite, while the one from which spectrum d was obtained had a negligible amount of lepidocrocite, as indicated by the extremely weak band at 250 cm\(^{-1}\). In addition, the weakness of the band at 250 cm\(^{-1}\) in spectrum d indicates that the rust was approximately pure akaganeite, with the strongest band at 722 cm\(^{-1}\) and a second strongest band at 305 cm\(^{-1}\). So, the band at 722 cm\(^{-1}\) can be used for the identification of akaganeite.

![Raman spectra](image)

**Figure 62.** Raman spectra from the face-down side of sample S3 (dry): (a) yellow rust; (b) red rust; and (c) and (d) black rust.

For quantitative comparison of different rust phases, the intensity ratio of band at 722 cm\(^{-1}\) to 250 cm\(^{-1}\) \((I_{722}/I_{250})\) can be used. Higher band intensity at 722 cm\(^{-1}\)
than that at 250 cm\(^{-1}\) indicates that there is more akaganeite and less lepidocrocite in the rust. The values of \(I_{722/250}\) in spectra b-d (Figure 62) are approximately 0.45, 1.03 and 2.32, respectively, indicating an increase of akaganeite concentration in the rust from location b to d.

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**Figure 63.** EDXA results from the same locations as those for Raman analysis (Figure 62) on sample S3 (dry).

The EDXA results (Figure 63) from the same locations as those for Raman acquisition indicate the presence of Cl in all the akaganeite-containing rust, with an increased concentration of Cl from 0.52% to 1.87% and to 2.51% (Figure 63b-d). The increase of Cl concentrations from location b to c and to d supports the Raman analysis (Figure 62b-d), indicating that more Cl promoted the formation of more akaganeite.
Table 5 shows that the Cl deposition in the dry test site (sample S3) is much lower than that in the industrial test site (sample S1) and a little higher than that in the rainforest test site (sample S2). The reason why a lot of akaganeite was found on sample S3 but not on other two samples is due to the smaller amount of rain in this test site compared to the other two. There was not enough rain to wash off the attached sea salts on the sample, especially the face-down side. The accumulation of sea salts facilitated the formation of akaganeite.

Raman and EDXA results of sample S4 (agricultural) are similar as those of the sample S3. One difference is that akaganeite was found in a smaller region (approximately 1/5 of the sample surface) than with sample S3, possibly due to more rain in the agricultural test site.

12.2.3 Marine Test Sites

12.2.3.1 Mild Marine Test Site

Layered Raman analysis of the rust on sample S4 (mild marine) showed similar results as above discussed, but with the detection of more akaganeite, even on the face-up side (Figure 64). The Raman spectrum (Figure 64a) from the inner rust shows the predominant presence of goethite since the strongest peak appeared at 391 cm\(^{-1}\). However, the relatively high band intensity at 248 cm\(^{-1}\) indicates the presence of lepidocrocite. In addition, the shoulder at 720 cm\(^{-1}\) suggests the existence of akaganeite. Band decomposition analysis enabled the separation of contributions from goethite at 241, 297, 391, 415 (sh), 478, 546, and 682 cm\(^{-1}\) as well as those from lepidocrocite at 248, 335 (sh), 375, 515, and 641 cm\(^{-1}\) and those from akaganeite at
311 and 720 cm\(^{-1}\). The Raman spectrum (Figure 64b) from the intermediate rust layer shows a mixture of lepidocrocite (251, 311, 348 (sh), 378, 524, and 651 cm\(^{-1}\)) and goethite (241, 297, 394, 411 (sh), 481, 548, and 692 cm\(^{-1}\)). The Raman spectrum (Figure 64c) from the surface rust layer again shows the existence of lepidocrocite (248, 305, 339 (sh), 377, 521, and 646 cm\(^{-1}\)). A weak band at 694 cm\(^{-1}\) (Figure 64c) is probably due to amorphous phases in the rust layer.

![Figure 64. Raman spectra from the face-up side of sample S5 (mild marine): (a) bottom of a peeled-off area; (b) intermediate rust layer; and (c) surface rust layer.](image)

Additional Raman spectra from more peeled-off areas on the face-up side of sample S5 show similar results as listed in Figure 64. However, high concentrations of akaganeite were also detected at the bottom of very few peeled-off regions—the band at \(~723\) cm\(^{-1}\) being the strongest band) (Figure 65). Unlike the Raman spectrum in Figure 62d, the Raman spectrum in Figure 65a does not show a
noticeable band at ~248 cm$^{-1}$, excluding the presence of lepidocrocite and goethite. Therefore, this Raman spectrum represents the one of pure akaganeite. Similar to a previous study [107], band decomposition analysis reveals 10 bands of pure akaganeite at 268, 304, 331, 382, 419, 493, 539, 603, 688, and 723 cm$^{-1}$. The Raman spectrum from another peeled-off area (Figure 65b) shows similar akaganeite bands (302, 338, 388, 421, 466, 534, 684, and 724 cm$^{-1}$) as those in Figure 65a with a prominent band at 248 cm$^{-1}$, indicating the presence of either goethite or lepidocrocite or both. The existence of goethite is corroborated by a relatively strong contribution at 388 cm$^{-1}$. Note that both akaganeite and goethite have contributed to most of the bands, especially those at 302, 388, 421, and 684 cm$^{-1}$, since the two rust phases have common Raman band positions.

Figure 65. Raman spectra from the bottom of two peeled-off areas on the face-up side of sample S5 (mild marine).

Elemental quantification using EDXA (Figure 66) was conducted at the same locations for Raman spectra acquisition. The results show that the bottom of the peeled-off area had a higher concentration of Cl (1.15%), compared to 0.24% in the
intermediate rust layer and none in the surface rust layer. The relatively high Cl concentration explains the presence of akaganeite in the inner rust layer. Additional quantitative EDXA results from the locations (Figure 65) where akaganeite was detected all show higher concentration of Cl in the range of 2-4%.

**Figure 66.** EDXA results from the same locations as shown in Figure 64.

Raman analysis of the face-down side of sample S5 shows similar results as those of the face-up side: 1) lepidocrocite was found in the surface rust layer and 2) goethite and akaganeite (scarce) were detected in the inner rust.

### 12.2.3.2 Moderate Marine Test Site

More akaganeite (as compared to sample S5) was detected from sample S6 (moderate marine), especially on the brown-colored face-down side. The Raman spectra (Figure 67a and b) from the inner black rust layer on the face-up side all show the presence of relatively pure akaganeite. However, the two akaganeite spectra show differences in band intensities at ~381 cm\(^{-1}\). The relatively high band intensity at 383 cm\(^{-1}\) in Figure 67b is probably due to a small mount of goethite that coexisted
with akaganeite in the rust layer. Another goethite band at ~248 cm\(^{-1}\), which can be used to distinguish between goethite and akaganeite, is not present or noticeable because of its lower intensity compared to that of the band at 383 cm\(^{-1}\) (Figure 67b). Other goethite bands, e.g., those at 297 and 684 cm\(^{-1}\), are hidden under the more intensive akaganeite bands.

The Raman spectrum (Figure 67c) from the red rust that is dominant in the surface layer shows the predominant presence lepidocrocite with Raman bands at 247, 305, 345 (sh), 376, 523, and 647 cm\(^{-1}\). The yellow rust that dispersed in between the red rust regions was also identified as lepidocrocite. However, a few brown rust bumps on the surface showed Raman signal of akaganeite (306, 405, 442, 497, 532, 605, 668, and 723 cm\(^{-1}\)) in addition to that of lepidocrocite (245, 349 (sh), 378, and 641 cm\(^{-1}\)) (Figure 67d). Notice that the lepidocrocite bands at ~306 and ~525 cm\(^{-1}\) were not separated from the akaganeite bands because of their relatively low intensities.
Figure 67. Raman spectra from the face-up side of sample S6 (moderate marine): (a) and (b) bottom of a peeled-off area; (c) surface rust layer; (d) a rust bump on the surface.

The Raman spectra from the face-down side of sample S6 show the existence of akaganeite over the whole sample area. The inner rust layer, which was revealed by manually scraping off the surface layer, akaganeite was found most frequently in a relatively pure form (Figure 68a) and less frequently mixed with goethite (Figure 68b). The Raman spectrum in Figure 68b shows bands similar to those of pure akaganeite (Figure 68a), but with different intensities at certain bands, especially those at 302 and 389 cm$^{-1}$. Again, goethite contributed to the relatively strong bands at 302 and 389 cm$^{-1}$. 
cm\(^{-1}\). The surface brown rust layer (Figure 68c) also had a high content of akaganeite (304, 335, 388, 421, 494, 535, and 723 cm\(^{-1}\)). Since the strongest band of goethite at 388 cm\(^{-1}\) is much lower than that of lepidocrocite at 245 cm\(^{-1}\), goethite was absent in the brown surface rust layer and the band at 245 cm\(^{-1}\) came from lepidocrocite. Another prominent lepidocrocite band was at 374 cm\(^{-1}\), while other weaker lepidocrocite bands, i.e., those at \(~305\), \(~343\), \(~522\), and \(~646\) cm\(^{-1}\), were all hidden under akaganeite peaks and were not revealed by band decomposition.

![Raman spectra](image)

**Figure 68.** Raman spectra from the face-down side of sample S6: (a) and (b) the bottom of a peeled-off area; (c) a rust bump on the surface.

The EDXA quantification result of the inner rust in the peeled-off region, (Figure 56c and d) from where the Raman spectrum in Figure 68a was obtained shows a very high Cl concentration, namely 45.56% atomic (Figure 69a). Another location (Figure 56c) in this peeled-off region also shows a high Cl content (11.81%) and a
Raman signal of pure akaganeite. Since both of the Cl-concentrated regions show Raman bands of akaganeite and extremely high Cl concentration, the rust must consist of akaganeite without any goethite or lepidocrocite. Therefore, the Raman spectrum (Figure 68a) from this region represents a typical Raman spectrum of pure akaganeite.

The existence of akaganeite with an extremely high Cl concentration in the inner rust layer was probably due to the previous entrapment of Cl-containing sea salt, mainly NaCl. Actually, this akaganeite looks like salt crystals in the fracture surface (Figure 56c and d).

![Figure 69](image)

**Figure 69.** EDXA results of the akaganeite phase (as shown in Figure 56c and d) found in the inner rust layer on the face-down side of sample S6.

### 12.2.3.3 Severe Marine Test Site

Raman analysis of the extensively corroded sample S7 (severe marine) shows less akaganeite compared to that of the sample S6 (moderate marine). The Raman spectrum (Figure 70a) from the thick, compact brown rust layer on the edge of the face-up side of sample S7 shows the presence of mainly akaganeite. We know this
because the band at 720 cm\(^{-1}\) is the strongest band. The band at 386 cm\(^{-1}\) has a relatively high intensity and the existence of a band at 251 cm\(^{-1}\) indicate the existence of goethite. Note that akaganeite and goethite must have both contributed to the bands at 301, 386, 410, 486, 538, and 722 cm\(^{-1}\). The band at 251 cm\(^{-1}\) may also indicate that a small amount of lepidocrocite is present in this rust layer since it usually exists in the surface rust layer, as discussed before for other samples. The Raman spectrum (Figure 70b) from the central loose region on the face-up side shows the presence of mainly lepidocrocite since the band at 251 cm\(^{-1}\) for lepidocrocite is the strongest band. The second largest component is akaganeite with major bands at 301, 327, 388, 415, 486, 538, 677, and 722 cm\(^{-1}\). That the band at 388 cm\(^{-1}\) is the strongest band among all the akaganeite bands indicates that goethite coexist with lepidocrocite and akaganeite. In addition, the relatively higher bands ratio of 667/720 cm\(^{-1}\) as compared to that in Figure 70a may suggest the existence of magnetite, which has a strong feature at 665 cm\(^{-1}\). Another Raman spectrum (Figure 70c) from the central loose rust shows the presence of only lepidocrocite (246, 303, 339, 381, 528, and 654 cm\(^{-1}\)) and akaganeite (723 cm\(^{-1}\)). The much higher band intensity at 246 cm\(^{-1}\) than that at 723 cm\(^{-1}\) suggests the prevalence of lepidocrocite in certain parts of the surface brown-colored rust layer.

The Raman spectra from the face-down side of sample S7 show similar results to those from the face-up side of the sample with the detection of lepidocrocite and akaganeite in most locations, some of which were mixed with goethite and magnetite.
Figure 70. Raman spectra from the face-up side of sample S7 (severe marine): (a) brown-colored compact rust layer on the edge as well as (b) and (c) brown-colored loose rust in the center.

To reveal the inner rust, the thick surface rust layer (1 – 3 mm) was readily peeled off using a steel blade. The black rust that dominated this inner rust layer showed a Raman signal of akaganeite either in a pure form (Figure 71a) or mixed with goethite (Figure 71b). Again, the presence of goethite is indicated by the much stronger band at 389 cm\(^{-1}\) than that in pure akaganeite (~385 cm\(^{-1}\)). The Raman spectrum (Figure 71c) from the occasionally found brown rust in the inner layer shows mainly lepidocrocite bands at 247, 304, 345, 379, 526, and 654 cm\(^{-1}\). A relatively weak band at 723 cm\(^{-1}\) is due to the presence of trace amount of akaganeite.
Figure 71. Raman spectra from the inner rust layer on the face-up side of sample S7 (severe marine) after peeling off the thick rust layer: (a) and (b) black rust; and (c) brown rust.

Akaganeite is known as a common corrosion product that forms on steel samples exposed to Cl-containing marine environments. However, sample S5 (mild marine) showed very less akaganeite and only in the inner rust layer. The sea salts that deposited on steel samples first initiated corrosion and mixed together with corrosion products. Later on, the rain rinsed off most of the remaining sea salts on the sample surface and left only a small number of salt particles entrapped in scattered locations in the previously formed corrosion products. When the surface rust layer became wet again, corrosion spread in the inner layer toward the steel substrate. During the process, Cl ions migrated from the surface to the steel substrate due to the rust layer’s high Cl permeability. The concentrated Cl in the inner rust layer facilitated the formation of akaganeite.
More akaganeite was found on sample S6, especially on the face-down side, due to the increased airborne chlorinity. On the face-up side, akaganeite was detected mostly in the inner rust layer because a large number of Cl ions (from sea salts) migrated to the rust/substrate interface from the surface while it was wet. The sea salts in the surface rust layer were also washed away by rain, rendering the formation of mainly lepidocrocite instead of akaganeite. The finding of akaganeite in black bumps was due to the entrapment of sea salt in scarce locations. The face-down side of this sample showed widespread akaganeite since the deposited sea salts were not easily washed off by rain.

The extremely high airborne chlorinity (Table 5) in the severe marine test site caused extensive damage to sample S7, with a lot of corrosion products peeled off from the face-up side. The loose peeled-off region was dominated by lepidocrocite since the deposited sea salts had been washed off by rain. The inner rust layer was dominated by akaganeite due to the permeation of Cl. Only a small amount of rust flaked off from the face-down side of this sample because corrosion products were not effectively washed off by rain. However, this side also became loose and porous due to the severe corrosion damage.

To summarize the results of the 7 samples, the color and the composition of the rust based on Raman results are tabulated in Table 9. The “t”s (trace) marked in parenthesis suggest that the rust phase was detected in few locations or had very weak Raman signals.
Table 9. The color and composition of the rust found on the 7 samples. Lep – Lepidocrocite; Aka – Akaganeite; Goe – Goethite; t – trace.

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12.3 Conclusion

The following conclusions could be drawn from the combined Raman spectroscopic and EDXA study of the rust formed on steel samples that were exposed to Hawai‘i’s diverse environments for 12 months:

On steel samples from industrial and rainforest test sites lepidocrocite, either in red or yellow color, was the dominant rust found in the surface layers on both face-up and face-down sides, while goethite grew only in the inner layers close to the substrate.

Except lepidocrocite and goethite, akaganeite was also found on the face-down sides of samples from the dry and agricultural test sites, due to the small amount of precipitation that did not effectively wash off the sea salts.

In addition to lepidocrocite and goethite, akaganeite was also detected on both sides of the sample from mild marine test site, mostly in the inner rust layer.
More akaganeite was found on the face-up side of the sample from moderate marine test site, in both the surface and inner rust layers. The face-down side of this sample showed a ubiquitous presence of akaganeite (with little goethite) due to high airborne chlorinity and less effective “wash-away” of sea salts by rain.

The brown-colored rust in the surface layers on both the face-up and face-down sides of the sample from the severe marine test site was composed of mainly lepidocrocite and akaganeite with small amounts of goethite and magnetite. The inner rust layers on both sides of this sample showed the dominant role of black-colored akaganeite.
Chapter 13

FTIR Characterization

13.1 Experimental

13.1.1 FTIR principles

Fourier transform infrared spectroscopy (FTIR) is another vibrational spectroscopic technique that is similar to as well as complementary to Raman spectroscopy. During FTIR measurements, a broadband light source containing a full spectrum of wavelengths is directed to the sample, after which how much of that beam is absorbed at each wavelength by the sample is measured. The resulting spectrum shows molecular absorption or transmission bands, which correspond to the vibrational frequencies of the bonds of the atoms that make up the material. Such spectra represent molecular fingerprints of materials. FTIR is non-destructive and has relatively high sensitivity.

13.1.2 FTIR measurements

A Thermo Electron Nicolet Nexus 760 instrument integrated with a continuum microscope was used. A blank background spectrum was collected prior to collecting a spectrum of the sample. An area of 100 μm×100 μm was used for FTIR acquisition. A minimum of 3600 scans (1 s/scan) of the specimen was employed for each spectrum. The resolution was 2 cm⁻¹.
13.2 Results and Discussion

13.2.1 Infrared Spectra of Pure Iron Oxides

The transmission infrared spectra of lepidocrocite and goethite obtained from KBr pellets (0.1% wt. iron oxides) are shown in Figure 72. Lepidocrocite has major bands at 748, 890, 1021, and 1153 cm\(^{-1}\), while goethite bands are at 615, 670, 797, 905, 1660, and 1795 cm\(^{-1}\). The band at 1627 cm\(^{-1}\) in Figure 72a, a shoulder band at ~1630 cm\(^{-1}\) in Figure 72b and the shoulder bands at ~3430 cm\(^{-1}\) in both are due to moisture. The prominent band at 3126 cm\(^{-1}\) is assigned to the O-H bonding in goethite.

![Figure 72](image)

**Figure 72.** Transmission infrared spectra of pure iron oxides (Alfa Aesar®): (a) lepidocrocite and (b) goethite.

13.2.2 Infrared Spectra of Corrosion Samples

The infrared spectrum (Figure 73a) of the inner rust on the face-up side of sample S1 (industrial) shows mainly goethite bands at 826 and 925 cm\(^{-1}\). The band
at 714 cm\(^{-1}\) is probably from goethite as well as system ghosts close to the infrared cut-off. The band at 1163 cm\(^{-1}\) is due to a trace of lepidocrocite in the inner rust layer. Since the FTIR collection area was relatively large (100 µm×100 µm), it is unusual to find a region with only goethite and no lepidocrocite. Notice that both the lepidocrocite and goethite bands are shifted by approximately 20 cm\(^{-1}\), compared to those of pure iron oxides (Figure 72). The shifts were possibly caused by the thermal effects due to long-time layer heating.

The infrared spectrum (Figure 73b) from the surface rust layer on sample S1 shows mainly reflectance bands of lepidocrocite at 769, 814 (sh), 936, 1024, and 1174 cm\(^{-1}\). All the bands were shifted by approximately 20 cm\(^{-1}\) except for the one at 1024 cm\(^{-1}\), indicating that thermal effects affect only certain vibrational modes.

![Figure 73](image_url)

**Figure 73.** Reflectance infrared spectra of the rust on the face-up side of sample S1 (industrial): (a) inner rust and (b) surface rust.

Similar infrared spectra as presented in Figure 73 were obtained from samples S2 (rainforest), S3 (dry) and S4 (agricultural) and indicate the presence of lepidocrocite and goethite. However, the black rust bumps that grew on the face-down sides of samples S3 and S4 show bands of akaganeite (Figure 74a) at 749
and 889 cm$^{-1}$. A weak band at 1146 cm$^{-1}$ is due to a small amount of lepidocrocite. A infrared spectrum (Figure 74b) from another black rust bump on the face-down side of sample S3 shows a mixture of akaganeite (765 and 918 cm$^{-1}$) and lepidocrocite (1016 and 1153 cm$^{-1}$). The FTIR results are similar to the Raman analysis of sample S3, which shows that the black rust bumps on the face-down side of sample S3 were either relatively pure akaganeite (Figure 62d) or a mixture of akaganeite and lepidocrocite (Figure 62c).

![Infrared spectra](image)

**Figure 74.** Reflectance infrared spectra of black rust bumps on the face-down side of sample S3 (dry).

The infrared spectra from both sides of sample S5 (mild marine) also shows the presence of lepidocrocite in the surface rust layer and goethite in the inner rust layer. In addition, akaganeite was detected, mostly at the bottom of peeled-off regions, in agreement with previous Raman analysis.

The infrared spectra from the black rust on the face-up side of sample S6 (moderate marine) shows the presence of lepidocrocite, goethite and akaganeite, while those from the face-down side of this sample show a prevalence of akaganeite. Relatively pure akaganeite (Figure 75a) or akaganeite mixed with lepidocrocite...
(Figure 75b) was detected in the inner rust layer on the face-down side, while a mixture of akaganeite and lepidocrocite (Figure 75c) was found in the red surface rust.

![Reflectance infrared spectra of black rust on the face-down side of sample S6 (moderate marine): (a) and (b) black inner rust; and (c) red surface rust.](image)

**Figure 75.** Reflectance infrared spectra of black rust on the face-down side of sample S6 (moderate marine): (a) and (b) black inner rust; and (c) red surface rust.

The infrared spectra from sample S7 (severe marine) show similar results as those from sample S6. The surface rust on both sides of the sample was identified as mixtures of akaganeite and lepidocrocite, while the inner rust was found mostly as akaganeite.

Band decomposition analysis was conducted on hydrogen-bond regions from typical infrared spectra show above (Figure 76). The results indicate that the surface (lepidocrocite) and inner (goethite) rust layers (on sample S1) had similar hydrogen bonds (Figure 76a and b), while the akaganeite-containing bumps on the face-down side of sample S3 (Figure 76c and d) had an extra band at ~3526 cm\(^{-1}\). Therefore,
the band at \( \sim 3526 \, \text{cm}^{-1} \) is assigned to the hydrogen bond in akaganeite, which is different from the hydrogen bonds in goethite and lepidocrocite because of the Cl ion impurities being the hydrogen-bond acceptors (O–H –···Cl bonds). All other bands are probably due to O–H bonding in lepidocrocite (Figure 72a) or H\(_2\)O bonding. Notice that a strong hydrogen bond in goethite at 3126 cm\(^{-1}\) (Figure 72b) was not observed in the inner rust (goethite) on samples S1 (Figure 76a), the reason for which is unclear.

![Figure 76. Band decomposition analysis results of the hydrogen-bond regions in infrared spectra in Figure 73 and Figure 74. (a)-(d) hydrogen-bond regions from the infrared spectra are shown in Figure 73a, Figure 73b, Figure 74a and Figure 74b.](image)

**13.3 Conclusion**

FTIR identification of the rust on steel samples that were exposed to Hawaiʻi’s diverse environments concurred with Raman analysis.

On samples S1-S4, lepidocrocite was the dominant rust in the surface layers on both sides, while goethite grew only in the inner rust layers. Akaganeite in the forms of black bumps was also found on the face-down sides of samples S3 and S4.
In addition to lepidocrocite and goethite, sample S5 showed the presence of more akaganeite on both sides and in both the inner rust layer and the surface rust layer.

More akaganeite was detected on sample S6 compared to that found on sample S5, especially the face-down side, which was covered with akaganeite.

The surface rust layers on both sides of sample S7 showed the presence of akaganeite together with lepidocrocite, while the inner rust layers were dominated by akaganeite.
Chapter 14

XRD Characterization

14.1 Experimental

14.1.1 XRD principles

X-ray is a form of electromagnetic radiation, with wavelengths in the range of 10 to 0.01 nm. When X-rays hit an atom, they make the electronic cloud move as does any electromagnetic wave, radiating waves with the same frequency (or elastic scattering). The re-emitted wave fields interfere with each other either constructively or deconstructively, producing a diffraction pattern, which is used for analysis.

Bragg’s law states the condition for constructive interference:

\[ n\lambda = 2d \sin \theta \]  

\( n \) is an integer determined by the order given, \( \lambda \) is the wavelength of the X-rays, \( d \) is the spacing between the planes in the atomic lattice, and \( \theta \) is the angle between the incident ray and the scattering planes.

Figure 77. Illustration of Bragg’s law: \( n\lambda = 2d \sin \theta \).
14.1.2 XRD measurements

A Rigaku MiniFlex™ II benchtop XRD system equipped with a Cu (Kα) radiation was used for XRD measurements. X-ray diffraction spectra were obtained directly on the corroded steel sample surfaces. The scans were done in the range of 3 – 90° (2θ). A scan speed of 0.01° (2θ)/min was used. All major peaks were assigned to the oxides structures listed in the PDF cards. [127]

14.2 Results and Discussion

14.2.1 XRD spectra

Lepidocrocite and goethite were the major rust phases identified on both sides of sample S1 (industrial), according to the X-ray diffraction patterns (Figure 78). Since goethite was present only in smaller areas (peeled-off regions) compared to lepidocrocite, which dominated the surface rust layer, fewer goethite peaks showed up and were less intensive than those of lepidocrocite.

![Figure 78. X-ray diffraction pattern of the rust on the (a) face-up and (b) face-down sides of sample S1 (industrial).]
The rust on both sides of sample S2 and that on the face-up sides of samples S3 and S4 show similar X-ray diffraction patterns as those shown in Figure 78. However, the X-ray diffraction patterns from the face-down sides of sample S3 and S4 also show the presence of akaganeite (e.g., Figure 79b for sample S3), which concurs with previous Raman and FTIR results. Notice that the black akaganeite regions on the face-down side of samples S3 and S4 occupy only a portion of the sample surface (1/3 for sample S3 and 1/5 for sample S4). Other areas show X-ray diffraction patterns of lepidocrocite and goethite.

![X-ray diffraction patterns](image)

**Figure 79.** X-ray diffraction patterns of the rust on the (a) face-up and (b) face-down sides of sample S3 (dry).

The X-ray diffraction patterns (Figure 80) of the rust on sample S5 (mild marine) show more akaganeite peaks with relatively high peak intensities, indicating the prevalence of akaganeite on samples from marine test sites. To reveal hidden peaks and distinguish between contributions from different rust phases, peak decomposition analysis was also conducted using PeakFit, as an example shown in Figure 81.
Figure 80. X-ray diffraction patterns of the rust on the (a) face-up and (b) face-down sides of sample S5 (mild marine).

Figure 81. Peak decomposition analysis of detailed regions in the spectrum in Figure 80a.

The X-ray diffraction patterns (Figure 82) of the rust on sample S6 (moderate marine) shows the dominance of akaganeite on both sides of the sample. The face-up side of this sample also shows the presence of lepidocrocite (Figure 82a), while the face-down side had only akaganeite (Figure 82b), a finding in agreement with Raman and FTIR results.
**Figure 82.** X-ray diffraction patterns of the rust on the (a) face-up and (b) face-down sides of sample S6 (moderate marine).

Similar to the other two samples from marine test sites, sample S7 (severe marine) shows the presence of akaganeite in the surface rust layers on both sides of the sample according to X-ray diffraction patterns (Figure 83a). However, relatively strong lepidocrocite peaks are present compared to those for sample S6 (Figure 82), indicating the dominant role of lepidocrocite. The X-ray diffraction pattern (Figure 83b) of the inner rust, which was revealed by peeling off the thick surface rust layer (1-3 mm) on the face-up side, shows the predominant presence of akaganeite.
The rust that initially formed on sample S7 (especially on the face-down side) is believed to be mainly akaganeite, similar to that found on sample S6. After the rust formed, corrosion developed toward the substrate. The extremely high airborne chlorinity (Table 5) facilitated the migration of Cl to the substrate and the formation of akaganeite. However, the akaganeite that formed on the surface became loose and flaked off due to the extensive corrosion. In addition, some akaganeite in the surface rust layer might have transformed to lepidocrocite, rendering the coexistence of akaganeite and lepidocrocite. Cook et al. [101] also found that more akaganeite occurred on samples exposed for a short time period while less (or no) akaganeite was detected on samples after longer exposures.
The X-ray diffraction pattern (Figure 83c) of the powder made from the rust flake from the face-up side of sample S7 shows peaks of akaganeite, lepidocrocite and goethite, all with relatively high intensities. Lepidocrocite came from the surface rust layer, while akaganeite and goethite were from the inner rust layer.

14.2.2 Cell dimension calculations

To verify the peak assignments in X-ray diffraction patterns, crystal unit cell dimensions of different oxides were calculated using Equations 8 and 9. An example of the calculation according to the data shown in Figure 84 is tabulated in Table 10. The results are also compared with those from the literature.[128]

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (9)
\]

Table 10. Unit cell dimensions of iron oxides.

<table>
<thead>
<tr>
<th>Iron oxides</th>
<th>Literature</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>a = 0.9956</td>
<td>a = 0.9933</td>
</tr>
<tr>
<td></td>
<td>b = 0.3022</td>
<td>b = 0.3015</td>
</tr>
<tr>
<td></td>
<td>c = 0.4608</td>
<td>c = 0.4642</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>a = 0.307</td>
<td>a = 0.304</td>
</tr>
<tr>
<td></td>
<td>b = 1.253</td>
<td>b = 1.260</td>
</tr>
<tr>
<td></td>
<td>c = 0.388</td>
<td>c = 0.342</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>a = 1.0546</td>
<td>a = 1.0532</td>
</tr>
<tr>
<td></td>
<td>b = 0.3031</td>
<td>b = 0.3026</td>
</tr>
<tr>
<td></td>
<td>c = 1.0483</td>
<td>c = 1.0521</td>
</tr>
</tbody>
</table>

Generally, the calculated unit cell dimensions agreed well with those from the literature, indicating that the peak assignments were correct.
Figure 84. X-ray diffraction pattern used for the calculation of unit cell dimensions of three iron oxide phases: Goethite (G), Lepidocrocite (L) and Akaganeite (A). For each iron oxide, three peaks were used for the calculation.

14.3 Conclusion

The XRD study shows similar results as those obtained from Raman and FTIR analyses.

Lepidocrocite was the major rust identified in the surface rust layers on both sides of the samples from non-marine test sites. Goethite from the inner rust layers on these samples was also identified using XRD. Akaganeite was identified in confined regions on the face-down sides of samples from the dry and agricultural test sites.

Akaganeite mixed with lepidocrocite was the major rust identified on samples from marine test sites. Very small amounts of goethite were identified on the samples from mild and moderate marine test sites, while comparable (to lepidocrocite
and akaganeite) amount of goethite was identified in the rust powder ground out of
the rust flake from sample S7.
Chapter 15

Summary

The corrosion products that formed on 1008 carbon steel exposed in Hawai‘i’s diverse micro-climates for 1 year period were characterized by using SEM/EDXA, Raman spectroscopy, FTIR and XRD.

On steel samples from industrial and rainforest test sites, lepidocrocite (in red or yellow color) was the dominant rust found in the outer layers on both face-up and face-down surfaces, while goethite grew only in the inner layers close to the substrate.

Except lepidocrocite and goethite, akaganeite was also found on the face-down surfaces of steel samples from the dry and agricultural test sites, due to the small amount of precipitation that did not effectively wash off deposited sea salts.

In addition to lepidocrocite and goethite, akaganeite was also detected mostly in the inner rust layer on both sides of the sample from a mild marine test site.

More akaganeite was found on the face-up side of the sample from moderate marine test site, in both the surface and inner rust layers. The face-down side of this sample showed ubiquitous presence of akaganeite (with traces of goethite) due to the deposition of airborne chlorides that are not effectively washed off by rain (in comparison to the top side).

The brown-colored rust in the surface layers on both face-up and face-down sides of the sample from the severe marine test site was composed of mainly
lepidocrocite and akaganeite with small amounts of goethite and magnetite. The inner rust layers on both sides of this sample showed the dominant role of black-colored akaganeite.
Chapter 16

Conclusions

This dissertation focused on salt particle-induced marine atmospheric corrosion of carbon steel. Unique findings include 1) the discovery of a salt-droplet size effect on the initiation of marine atmospheric corrosion, 2) the identification of various corrosion mechanisms that are dependent on droplet size, and 3) the identification of environmental parameters that affect the formation of various forms of rust on carbon steel.

The following can be concluded:

- In short-time (30 min) outdoor exposure experiments, corrosion did not initiate on 1018 steel from seawater droplets (D < ~30 µm) but occurred under larger seawater droplets (D > ~50 µm). Droplets with diameter in the range of 30 – 50 µm were not detected during the outdoor sampling event.
- Similar as in the field study, laboratory studies showed that corrosion did not initiate on 1018 steel under NaCl droplets (formed after deliquescence) having diameters less than ~45 µm, while corrosion always initiated under larger deliquescent NaCl particles with diameter greater than ~45 µm.
- The droplet-size effect was also verified by electrochemical tests. Anodic polarization conducted in NaCl droplets on steel showed passivation under smaller NaCl droplets (D < ~100 µm) and active dissolution under larger droplets (D > ~100 µm).
The droplet corrosion mechanism was revealed by *in situ* and *ex situ* Raman spectroscopic characterization of the corrosion products. It was found that GR formed in regions close to the anodic sites (pits) while lepidocrocite clusters precipitated over cathodic sites surrounding the GR region. The formation of different rust phases was due to the difference in local pH. Similarly, GR in anodic regions and lepidocrocite in cathodic regions were identified in Evans’ droplet experiments.

The study of the corrosion products formed on carbon steel exposed outdoors for 1 year period showed that 1) lepidocrocite was the major rust product in the surface layers on both sides of the samples at non-marine test sites, 2) goethite was identified in the inner rust layers on these samples, 3) akaganeite was identified in confined regions on the face-down sides of samples (which can accumulate deposited airborne chlorides) from the dry and agricultural test sites, and 4) akaganeite mixed with lepidocrocite was the major rust products identified on samples at marine test sites.

16.1 Future Work

This work focused on the very initial stages of NaCl particle-induced marine atmospheric corrosion of carbon steel, and the characterization of the corrosion products formed on carbon steel after 1 year exposure in Hawai‘i’s diverse micro-climates. More work is needed to understand the transformation and aging process of iron oxide corrosion products during wet-dry cycles. Direct information
on the transformation of various rust species, especially from lepidocrocite to goethite, would be very helpful in understanding atmospheric corrosion.
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