Marine Aerosol Drop Size Effects on the Corrosion Behavior of Low Carbon Steel and High Purity Iron

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This research focused on the development and use of a novel methodology to study corrosion under aqueous electrolyte drops ranging in diameter from 20–1000 μm, the most common deposited aerosol size range found in coastal marine environments. A drop-on-demand inkjet printer was custom built by coupling a commercial jetting device with a programmable two-axis stage. Singular droplets of sodium chloride solution were deposited onto steel and pure iron substrates with various surface finishes, followed by an isohumidity exposure for 24 hours. The volume loss increased with drop diameter according to a power law with an exponent of approximately 2 for highly polished steel and iron, increasing to 3 for iron with higher surface roughness. Attack was primarily filiform-like for the smallest drops, whereas deep, separate pits formed under the largest drops. Corrosion was not consistently observed under all drop sizes. The fraction of drops that showed no corrosion increased with decreasing drop size for all substrates. This behavior appears to have a strong dependency on the microstructure and surface finish. Corrosion initiation on 1010 steel was dominated by manganese sulphide inclusions when a mirror surface finish was maintained. For high purity iron, initiation was dominated by surface roughness.

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Manuscript submitted August 15, 2014; revised manuscript received September 12, 2014. Published September 24, 2014. This was Paper 1736 presented at the San Francisco, California, Meeting of the Society, October 27-November 1, 2013.

In marine environments, corrosion is generally driven by the deposition of hygroscopic sea salt aerosols. These aerosols range from a few angstroms in diameter to several hundred microns. In coastal marine locations (<2 km from the beach), the most common aerosols deposited are in the ‘coarse-mode’ size range: 1–100 μm in diameter.1 Laboratory atmospheric corrosion studies and a number of accelerated tests, however, have traditionally focused on corrosion under large drops (several millimeters in diameter) or thin films.

From studies on large droplets, a pitting mechanism has been proposed. An aqueous droplet in contact with a metal surface creates a localized electrochemical cell—often called an “Evans drop”. In the classic Evans drop model, the cathode forms at the drop edge, where oxygen is readily available due to the short diffusion path length.2 The anode is then established in the center of the drop where oxygen is deficient and iron dissolution is sustained. This results in the formation of a pit at the center of the drop. This type of behavior has been commonly observed for a variety of alloy systems that are susceptible to corrosion (e.g., low carbon steel) for drop sizes in the microliter size range.3–6

Although corrosion behavior under ‘coarse’ droplets has received less attention, there is a growing body of evidence that suggests that it can deviate from Evans’ drop behavior, and that corrosion may not appreciably occur under drops on the lower end of the size range for plain carbon steel (<50 μm).

It has been recently reported that the corrosion rate appears to be a function of deposited aerosol drop size under field and laboratory-simulated marine conditions.7–9 Furthermore, several studies have reported drop sizes below which no corrosion occurs. Li and Hihara found that corrosion did not initiate under NaCl droplets with diameters smaller than 45 μm after 6 hours (at 80% RH) when manually deposited on 1018 steel.10 They attributed this observation to the reduced chance of contacting a slag-based inclusion or to the higher oxygen content in a small drop, which may lead to passivation of the substrate. Li and Hihara also recently found that naturally deposited salt particles smaller than 30 μm in diameter did not initiate corrosion on 1018 steel.11 In this latter study, however, the samples were exposed to outdoor marine environments for 30 minutes and the particle deposition was not rigorously controlled with regards to either arrangement or salt loading.

The inconsistent pitting behavior observed for small droplets may be linked to geometric effects on oxygen diffusion or the underlying metal microstructure. Grain boundaries, inclusions and other metallographic defects can provide initiation sites for corrosion.1 It is postulated that small drops will have a lower probability of covering an initiation site than large drops.7–9

Exposure experiments have shown alternative corrosion attack morphologies to that of the classic Evans drop for small drop sizes. Li & Hihara and Weissenrieder & Leygraf found that drops with diameters less than 200 μm exhibited filiform-type corrosion.10,11 Filiform corrosion is characterized by shallow pits, or filaments, which initiate under the initial drop area and extend past the droplet edge. Filiform-type attack has been observed on many substrates exposed to marine coastal exposures and can cause significant damage to structures.12–15 It is unclear, however, why filiform-type corrosion occurs under these small drop sizes on bare steel and how it affects the volume loss. One hypothesis is that as the drop size decreases, the oxygen delivery rate surpasses the consumption rate and the concentration gradient diminishes because the diffusion distance is no longer appreciable from any side of the drop; without the oxygen concentration gradient there is no driving force for Evans-type corrosion.11,7,9

Despite growing research in this area, information to date is insufficient to establish a rigorous correlation between drop size and corrosion rate under drops in the size range of coarse mode aerosols. The cause of the inconsistent corrosion behavior is still uncertain, and it has yet to be determined if factors other than drop size affect this behavior. Furthermore, the Evans drop model does not explain the presence of filiform-type corrosion or the fractional corrosion behavior under small drop sizes. Current knowledge gaps serve as motivation for this work: to what extent can the Evans drop model be applied? What causes inconsistent pitting and various pitting morphologies at small drop sizes? And finally, is there a universal drop size below which no corrosion occurs on ferrous materials, specifically, low carbon steel?

This study aims to elucidate the effect of electrolyte geometry on the corrosion initiation and rate, which can provide insights needed for a fundamental understanding for atmospheric corrosion modeling. To this end a novel inkjet method was developed and utilized to deposit sodium chloride solution droplets (20–1000 μm in diameter) onto steel and iron substrates. Substrates were exposed to 75% RH for 24 hours and the mode and extent of any corrosion was evaluated.
Experimental

**Samples.**— Both low carbon steel and high purity iron substrates were used in this experiment. Coupons of AISI 1010 plain carbon steel (Alabama Specialty Products, Munford, Alabama) measuring 25 × 25 mm were polished to a 0.01 μm colloidal silica mirror finish. A 13 mm diameter 6N (99.9999%) purity iron rod (ESPI Metals, Ashland, Oregon) was vacuum annealed at 680 °C for seven weeks and then cut into 3 mm thick samples. Three surface finishes were prepared on the iron to test the effect of substrate roughness on the corrosion behavior. One set of samples was polished to a mirror finish using colloidal silica, another was ground to 600 grit with silicon carbide (SiC) grinding paper, and the last was ground with 1200 grit paper. All grinding was done in the presence of water. After preparation, surfaces were rinsed with ultrapure (UP) water (18.2 MΩ·cm, <5 p.p.b. total organic carbon), cleaned with acetone (>99.5%) and ethanol (>99.5%), and then dried in a stream of zero grade compressed air. Samples were stored in a desiccator (<5% RH) for 10 days before exposure, Ra (ISO 4287), as measured with a sensor of this system had a calibrated accuracy of ± 1.5% RH under the study’s operating conditions. Both 20 μm and 50 μm diameter borosilicate glass capillaries were used in the jetting device to achieve a wide range of deposited drop diameters by either dispensing singular or multiple droplets on a site.

Solutions of NaCl (99% purity) in UP water and in absolute ethanol (>99.5%) were prepared and passed through a 0.2 μm particulate filter. Drops of each solution were deposited randomly on steel and iron substrates at ambient laboratory temperature (21 ± 2 °C) using an inkjet printer. Saturated aqueous sodium chloride solution (6.2 M) was used to generate droplets 100–1000 μm in diameter and was deposited at 75% RH. The ethanol solution (8.7 M) was used to create smaller drops. This was done by first depositing the ethanol salt drops onto the substrate, and then evaporating the ethanol away at 40% RH. The resulting NaCl particles were then rehydrated to 75% RH, the deliquescence relative humidity (DRH) of NaCl. The DRH is the relative humidity at which a soluble salt spontaneously absorbs water from the air to form a saturated salt solution. All drops deposited at 75% RH therefore had a concentration of 6.2 M NaCl. Due to the reduced NaCl solubility, the ethanol solution deposited less salt and thus produced smaller droplets when hydrated (30–100 μm in diameter). Drop diameters on steel and iron varied up to 14% and 7% from the calculated average, respectively. Each drop size was repeated at least 8 times; some sizes had as many as 18 drops printed. The number of drops printed depended on the required droplet spacing and the droplet spacing was chosen as to avoid contact of neighboring secondary salt spreading regions.

**Isohumidity exposure.**— After loading with droplets, the samples were left in the inkjet humidity chamber at 75 ± 1–2% RH and 21±1–2 °C for 24 hours. In-situ drop geometry was characterized by measuring the contact angle and the drop diameter on the surface of the coupon with optical microscopes in the inkjet chamber. Figure 2. The contact angle and drop geometry were measured based on the line of symmetry with the drop reflection on the substrate in Image software.

**Post-exposure analysis.**— Following the 24-hour exposure, the samples were immediately moved to a desiccator (<1% RH) until further analysis. Micrographs of the corroded area were taken with a reflected light optical microscope. A Quanta 650 emission field SEM-EDS (FEI, Oregon) was used to examine the corrosion morphology and to determine the composition of the corrosion product and salt spreading region. The SEM was operated in high vacuum, backscattered electron mode using a 15 kV accelerating voltage and a 10 mm working distance.

The corrosion product was removed by immersion in a 0.9 M ammonium citrate solution heated to 65 °C for 1–2 minutes (modified ASTM G-1). Subsequent damage evaluations and profilometry of the surface were conducted using a white light interferometer (Zygo Corp., U.S.).

Results

**Substrate characterization.**— The microstructure and surface characteristics of the as-prepared steel and iron coupons were characterized by SEM and surface profilometry. The average grain diameters for 1010 steel and 6N iron were 22.5 μm and 112 μm, respectively. The surface roughness and inclusion densities of the substrates are shown in Table I. Inclusions in the 1010 steel were primarily manganese sulphide (MnS), as determined from SEM micrographs per
Table I. Characterization of steel and iron substrates.

| Sample      | Finish         | Ra (nm) | Inclusions/ mm² | Inclusion Diameter (μm) |
|-------------|----------------|---------|-----------------|-------------------------|
| 1010 Steel  | Colloidal Silica | 1.69 ± 0.43 | 147 ± 12        | 3 ± 2                   |
| 6N Iron     | Colloidal Silica | 0.54 ± 0.10 | –               | –                       |
| 6N Iron     | 1200 grit       | 5.6 ± 0.3  | –               | –                       |
| 6N Iron     | 600 grit        | 119.4 ± 23.3| –               | –                       |

ASTM E45-11. The seemingly randomly dispersed MnS inclusions ranged from 1–5 μm in diameter and were spherical. No such inclusions were found on the pure iron, as expected. Smaller inclusions may also be present but were not detected during our analysis. Samples ground with SiC grinding paper were inspected with SEM after cleaning and did not have any visible SiC residuals embedded within the microstructure. However, in both sample types, there was a low density of small holes (<2 μm diameter). When examined with EDS, the holes appeared to be enriched with O and C.

In-situ observations.— During the exposure period, the drop diameters increased slightly (<5%) and contact angles decreased as much as 5 degrees, but remained between 55 and 70 degrees for all substrates. There were no observable trends between drop size and contact angle. At 75% RH, corrosion was observed under most deposited droplets. For each substrate, there was a drop size below which corrosion initiation was not consistent – referred to as “fractional corrosion”. Furthermore, for drops that initiated corrosion, a distinct region formed around the corroded region that was comprised of salt – herein referred to as the “secondary spreading region”. Finally, both attack morphology and volume loss varied with deposited drop diameter, indicating a strong dependency on drop geometry.

The attack morphology and surface location of attack was a function of deposited drop size, with attack primarily outside the original drop perimeter (filiform-type) prevalent in smaller drop sizes (<150 μm) and, in larger drop sizes, attack was confined to within the perimeter of the original drop. Examples of these two types of attack are shown in Figures 3 and 4. The progression of the filiform-type corrosion and resulting damage is exemplified in Figure 3. This type of attack initiated at the edge of the drops as indicated by the formation of small pools (Figure 3a, 3(i)). The filament head then traveled away from the original droplet as shown in (Figure 3b-3c, 3(ii)). Profilometry of the areas after removal of the corrosion product showed that attack occurred outside of the original droplet area (Figure 3d).

As the drop diameter increased, a smaller fraction of corrosion attack was filiform-type and pitting became more Evans-like (attack confined under original drop) for both iron and steel substrates (Figure 5). This type of corrosion attack initiates and grows within the original droplet area (Figure 4). In some cases, these large drops also formed small solution pools outside the perimeter (Figure 4a, 4i), yet corrosion still initiated within the drop (Figure 4c, 4(ii)).

Secondary salt spreading was observed for all drops that corroded. A field of small droplets (<5 μm in diameter, visible as dark spots in Figures 3, 4) was observed to spread radially from the original droplet throughout the exposure. The diameter of secondary salt spreading was obtained directly from the micrographs using ImageJ software and was defined as the maximum distance across the perimeter of the salt crystals visible in the micrographs. For steel, the salt spreading diameter increased linearly with the drop diameter in the 20–200 μm range. For both substrates, the spreading diameter did not increase significantly for large drops (>300 μm in diameter), reaching an...
upper limit of approximately seven millimeters for steel and two millimeters for iron (Figure 6). EDS analysis of the dried secondary droplets after exposure indicated they were rich in Na, C, and O with no detectable Cl. It is also notable that there is a small ‘halo’ (Figure 3c, 3(iii)) between the corrosion product and the beginning of the secondary salt spreading region, where EDS indicated that Na, Cl, C and O levels were no different from clean areas of the sample that were not affected by corrosion. Finally, a reduction in drop perimeter occurred during exposure for nearly all drop sizes and can be observed in Figures 3 and 4.

**Inconsistent corrosion.**—Both steel and iron samples showed fractional corrosion behavior after the 24-hour exposure (Figure 7). Each data point in Figure 7 represents a sampling of 8 to 18 drops of a particular size. From this figure it is clear that both the microstructure and surface finish influenced the probability of initiation. Comparison of the different surface finishes of the 6N iron showed that probability for initiation decreased with decreasing drop size and surface roughness.

To further explore the influence of surface defects on probability of initiation, a series of experiments was carried out whereby drops were targeted on defects and defect-free areas of each substrate. On 1010 steel, all drops deposited on visible inclusions corroded – regardless of initial drop size. However, 54% of the 28 drops deposited on apparent inclusion and hole free areas also corroded (Figure 8). For pure iron with a colloidal silica finish, no drops less than 100 μm corroded, as exemplified by Figure 7. Furthermore, no corrosion initiated even when drops were targeted onto the small holes from polishing (Figure 9).

**Volume loss.**—For drops that had detectable corrosion, the volume loss \(v_{\text{loss}}\) after the 24-hour exposure increased with drop diameter \(d_{\text{drop}}\) according to a power law (Figure 10). The equations below show the dependency of drop size on volume loss for the four substrates. Subscripts that do not indicate grit size refer to samples polished with colloidal silica.

\[
\begin{align*}
  v_{\text{loss, steel}} &= 1.134(d_{\text{drop}})^{1.9476} \\
  v_{\text{loss, Fe}} &= 1.407(d_{\text{drop}})^{1.8763} \\
  v_{\text{loss, Fe}(1200)} &= 0.129(d_{\text{drop}})^{2.9652} \\
  v_{\text{loss, Fe}(600)} &= 0.186(d_{\text{drop}})^{2.7743}
\end{align*}
\]

There was no significant difference in volume loss between the steel and iron samples of any surface finish (two sample t-test, 0.5 < \(p\) < 1.0). Furthermore, there was no significant difference in volume loss between samples exposed at two and ten days (two sample t-test, 0.5 < \(p\) < 1.0).

**Discussion**

**Inconsistent corrosion.**—The inconsistent corrosion initiation behavior observed on the steel and iron samples is attributed to the surface roughness and presence of inclusions. Grain boundaries did not appear to play a role in the fractional corrosion of small drop

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**Figure 6.** Average secondary spreading diameter after 24 hours versus initial drop diameter for drops under which detectable corrosion occurred.

**Figure 7.** Probability of initiation \(N_{\text{pit}}/N_{\text{total}}\) versus initial drop diameter after 24-hour exposure. \(N_{\text{pit}}\) is the number of samples that corroded with either morphology (Evans type + filiform type).

**Figure 8.** (a) 1010 steel (colloidal silica finish) prior to printing. (b) 130 μm NaCl drop deposited onto apparent inclusion-free area. (c) Corrosion response after 24-hour exposure to 75%RH. Evans type corrosion and secondary salt spreading were observed.
sizes. The average grain diameter of the 1010 steel was 22.5 μm. If grain boundaries had acted as the initiation sites for pitting, it would be expected that nearly all drops larger than 20–30 μm would corrode, because they would have intersected at least one grain boundary. However, data in Figure 7 demonstrate that this was not the case, with, for example, drops as large as 50 μm corroded only 63% of the time. Similar to the 1010 steel, fractional corrosion was observed at drop sizes larger than the average grain diameter of the iron samples, which was 112 μm.

For 1010 steel, a strong correlation between the MnS inclusion distribution and drop size suggests that these inclusions had a governing role in the inconsistent corrosion behavior observed. In an attempt to understand the inconsistent pitting, a probability simulation was created. The simulation predicted the probability of a randomly placed drop of a particular size landing on an inclusion if it was placed on a plane containing a random distribution of inclusions. The MnS inclusions are considered spherical and the diameters were assumed to follow a random distribution between 1 and 5 μm (range of sizes seen in SEM micrographs). The theoretical fraction of drops corroded can be determined as a function of drop diameter. The simulation assigned each drop a random location on a 1 mm × 1 mm substrate and if the drop is in contact with one or more inclusions, it is assumed to corrode. From the targeted drop experiments completed on the 1010 steel, this is a safe assumption.

The results of this simulation on steel are shown in Figure 11 and are compared to the original experimental data from Figure 7. Each simulation data point is the result of 30,000 placed droplets. The error bars in Figure 11 show the standard deviation in corrosion behavior over 10 simulation trials. The simulation was run with the average inclusion density (147 inclusions/mm²) and with the upper and lower standard deviation limits determined from the SEM (137 and 159 inclusions/mm², respectively) to see the sensitivity of inclusion density on the simulated corrosion behavior. This correlation between the two data sets indicates that surface heterogeneities play a large role in the atmospheric corrosion behavior for 1010 steel seen in our results and provides additional support to similar findings in the literature. It has been generally found that pitting almost always initiates at chemical or physical surface heterogeneities such as inclusions, second phase particles and dislocations on bare metal substrates when immersed in electrolyte solution. Furthermore, Li & Hihara conducted polarization experiments with saturated NaCl droplets 45–338 μm in diameter on 1018 steel and found that the tendency for corrosion increased with increase droplet diameter. They also found that the presence of inclusions underneath droplets resulted in a more negative open circuit potential, indicating active corrosion. They attributed this observation to inclusions preventing the formation of a continuous passive film. The results of our study confirm that inclusions are the primary initiator for corrosion on low carbon steel and show that the inclusion density highly affects the corrosion behavior of microdroplets.

The results for the 6N iron also show inconsistent behavior, but the lack of inclusions and a strong dependency on surface finish suggest that the variance in response to drop size is due to the geometry of the grooves from grinding. Although discrete particles of SiC from grinding were not observed under SEM and embedding of SiC in iron is not expected, the considerable enrichment of carbon within the small holes on the iron suggests that it cannot be ruled out as a possible
initiation site. However, the correlation between surface roughness and corrosion initiation was strong. When the iron was ground to 600 and 1200 grit, the drop size threshold above which significant corrosion initiation decreased. This is most likely due to the increased surface roughness. Table I. Tang et al. and Wang et al. maintain that pit initiation on pure iron immersed in chloride solutions is dominated by surface passivity and roughness.20,21 Increased surface roughness can provide active sites for pitting on substrates with reduced inclusion densities. Wang et al. ground pure iron samples with 280, 400, 600, and 800 silicon carbide grit paper, submerging them in 0.2 M NaNO₃ + 0.1 M NaCl solution, and carried out electrochemical measurements to observe the nucleation of pits. They hypothesize that pits nucleate at weak sites where abrasion grooves create gaps in the passive film. It has been suggested that the aspect ratio of the surface groove, the ratio of the width of the groove to the depth of the groove (w/d), dictates the corrosion initiation on ground stainless steel.21,22 A large aspect ratio represents a wide and shallow geometry, whereas a small aspect ratio represents a narrow and deep groove. Local electrochemical cells can form in deep and narrow grooves due to diffusion limitations, and pitting is more likely to initiate in these geometries. Zuo et al. also show that as surface roughness increases from grinding, the surface grooves become deeper but the width stays statistically the same; therefore, the aspect ratio and surface roughness (Ra) can be viewed as inversely proportional.23 This theory is supported by the results of this study. As the grit size decreased from 1200 to 600, the surface roughness increased and the aspect ratio became smaller, creating more active sites for pitting in the narrow and deep grooves. In turn, the fraction of small drops that corroded on samples ground with 600 grit paper was higher than the fraction that corroded on samples ground with 1200.

For those drops under which detectable corrosion occurred, there was no statistical difference in volume loss between the four prepared substrates (Figure 10). This may be due to the similarities in composition between the 6N iron and 1010 steel or the large variance in volume loss for each drop size. For some drop sizes, the standard deviation of volume loss was as large as the average, which is most likely because of the mixed (from drop to drop) pitting morphologies (filiform vs. Evans) observed in this size range, Figure 5. Finally, there was no statistical difference in volume loss between samples stored in the desiccator for two days and those stored for ten days. Work by Li and Hihara suggested that an increase in storage time affects the thickness and stability of the oxide layer, however, this effect was not observed in this work.10

Pitting morphologies.— The results of this study show that Evans’ drop corrosion behavior is not applicable to all drop geometries on bare metal substrates. The smallest drops for both the 1010 steel and iron experiments exhibited filamentary corrosion (Figure 3) instead of radial, Evans-type pitting (Figure 4). Filiform-type corrosion has been previously observed on 1018 steel and pure iron.10,12 Weissenrieder and Leygraf found that filiform corrosion occurs at the perimeter of NaCl-containing droplets on bare iron,12 which agrees with Li and Hihara’s observation that filiform corrosion starts at solution pools leaked at the perimeter of the original droplet.10 Weissenrieder and Leygraf, additionally, contend that the initiation is due to local weaknesses in the iron oxide film and do not mention these solution pools, or micro-droplets, can form outside the perimeter of the original drop. It is unclear the mechanism of the micro-droplet formation, but their presence has continuously been associated with the initiation of pitting at locations close to the initial droplet edge.23,24 Once the micro-droplets are formed, filiform corrosion is the primary mode of attack. Li et al. hypothesize that due to reduced ion transport at the meniscus of the micro-droplet, metastable pits can be sustained at a lower critical current density.25 In these cases, filiform-like attack will ensue because there is not enough cathodic current to sustain the growth of a deep pit.

It is unclear why the droplet diameter reduces drastically over the exposure period when corrosion occurs (as seen in Figures 3 and 4). It is possible that once secondary spreading occurs, the hygroscopic behavior changes drastically due to changes in chemistry as studied in our previous work.25

Secondary salt spreading.— The secondary salt spreading region appears to be the site of a net cathodic reaction. Nearly all of the drops in this work exhibited secondary salt spreading after the 24-hour exposure and drops that did not have salt spreading did not appear to corrode. When examined with SEM-EDS, it was found that the spreading regions were sodium-rich, but contained little to no chloride – an observation we made in previous work25,26 and by others.27,28 This behavior can be explained electrochemically. When the electrochemical cell is established in the droplet, Na⁺ ions migrate toward the perimeter of the droplet to balance the charge of hydroxyl ions produced in aqueous reduction of dissolved oxygen. Furthermore, water adsorption on planar metals increases with relative humidity. At 75% RH, there are several monolayers of adsorbed water, which allow ions to migrate away from the original droplet.29–31 Once corrosion has initiated, the Na⁺ and OH⁻ spread radially, increasing the cathodic area to sustain the electrochemical reaction. Therefore, it is expected that no secondary spreading would be observed in drops that did not corrode.

The diameter of secondary salt spreading was drop size and substrate dependent. The spreading diameter reached seven millimeters for steel, but only two millimeters for iron. This may be due to differences in composition of the corrosion product or the surface chemistry of the substrates. The secondary salt spreading region has been shown to contribute to the cathodic reaction, which could explain the differences in spreading diameter except that the volume loss, and thus anodic reaction, were statistically the same for the iron and steel substrates. Moreover, the secondary salt spreading occurred for all attack morphologies. Even for filamentary corrosion, there was a small halo followed by a radial salt spreading that surrounded the filaments, no matter how far they strayed from the original deposited droplet. It is unclear what drives the distance of the secondary salt spreading or how it affects the volume loss. Some contend that secondary spreading is caused by surface tension changes at the drop edge32,33 and that it is promoted by the separation of anode and cathode.34 Future work should explore this phenomenon more closely, as it may play a role in the corrosion behavior of a field of drops as opposed to singularly deposited drops.

Conclusions

In this study, a custom inkjet printer was used to deposit drops of sodium chloride ranging from 20–1000 μm in diameter onto 1010 steel and high purity iron coupons of various surface finishes. After a 24-hour exposure to 75% RH, the corrosion behavior was analyzed using SEM, EDS, profilometry and optical microscopy. The volume loss was dependent on both the surface finish and initial drop diameter. The measured volume loss under each drop size was statistically the same for all substrates. This can be attributed to the similar composition of iron and 1010 steel or the large variance in volume loss due to different pitting morphologies observed (Evans and filiform). However, not all droplets corroded. Grain boundaries did not appear to play a role in this fractional corrosion behavior, but the inclusion density governed the inconsistent pitting on 1010 steel when a mirror
finish was maintained, which is rationalized quantitatively by a sim-
ulation in which pitting is driven by the probability of a droplet of
a given size intersecting an inclusion. For the high purity iron sam-
ple where inclusions were not present, it is likely that the geometry of
the grooves from grinding (i.e., surface finish) acted as physical heterogeneities that caused inconsistent pitting at small drop sizes.

This study shows that Evans’ model for pitting cannot be applied
to all drop geometries on bare metal substrates. As the drop diameter
decreased, the fraction of filiform corrosion (Nfiliform/Ntotal) increased
and Evans’ single pits became less evident. The change in pitting
morphology is due to the location of the active sites below the initial
droplet. Spreading of an alkaline film (secondary spreading) from the
corroding region occurred for all drops that corroded and the diameter
of the salt spreading was drop size and substrate dependent.

The methodology developed here enables the study of aerosol-
driven atmospheric corrosion through controlled electrolyte
deposition and damage evaluation at resolutions oftentimes consid-
ered challenging to achieve. Confirmation of drop size effects on
corrosion behavior has serious implications for service life prediction
approaches. The results of this study strongly suggest that the manner
and geometry in which salt droplets are deposited onto a surface and
the surface finish will significantly affect volume loss along with the
mode of corrosion attack.

Acknowledgments

This work has been supported in part by the US Air Force Academy
under agreement FA8501-UVA-002 and the Double Hoo research
grant awarded by the Center for Undergraduate Excellence at the
University of Virginia. Daniel J. Dunmire, Director, DoD Corrosion
Policy and Oversight, OUSD(AT&L), Office of the Secretary of De-
fense and the SERDP/ESTCP program via contract W912HQ-09-C-
0042 are also gratefully acknowledged. This work was carried out in
part in cooperation with Ivan Cole and the CSIRO team.

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