

### Marine Aerosol Drop Size Effects on the Corrosion Behavior of Plain Carbon Steel

B. Risteen, E. Schindelholz, R. G. Kelly

University of Virginia, Materials Science and Engineering  
116 Engineer's Way  
PO Box 400745  
Charlottesville, VA 22904, USA

It has been recently reported in the literature that corrosion rate appears to be a function of deposited aerosol drop size under field and lab simulated marine conditions for steel.<sup>1-3</sup> It is postulated that this may be due to geometric limitations on oxygen diffusion<sup>2,3</sup> or the underlying metal microstructure and the probability of covering a metallurgical defect, which can initiate active corrosion.<sup>1-3</sup> However, empirical data are insufficient to establish a strong, quantitative correlation between drop size and corrosion rate. The ability to further examine this phenomenon requires rigorously controlled drop deposition on the micron level to quantitatively understand drop size and geometry effects.

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 $\mu\text{m}$ , the most common aerosol size range found in coastal marine environments. The objective of this work was to examine the relationship between drop size and corrosion attack of bare low carbon steel under simulated atmospheric marine conditions.

For this work, a drop-on-demand inkjet printer was custom built by coupling a commercial jetting device with a programmable two-axis stage. The printer is capable of producing drops of a variety of sizes in the picoliter volume range and allows for the creation of arrays of electrolyte drops on metal substrates. Singular droplets of aqueous sodium chloride were deposited on a polished 1010 steel coupon followed by exposure to 75% relative humidity for 24 hours. Following the isohumidity exposure, optical microscopy and SEM/EDS were used to analyze the corrosion product and secondary salt spreading. The corrosion product was then removed and subsequent damage evaluation of the surface was conducted using surface profilometry.

It was found that, in general, the volume loss increased with drop diameter according to a power law. Various corrosion attack morphologies were observed; attack was primarily filiform for drops 20-100 $\mu\text{m}$  in diameter whereas deep, separate pits formed under drops 300-1000 $\mu\text{m}$  in diameter. Filiform attack is characterized by shallow pits that initiate under and then extend to outside the initial drop area. Corrosion always occurred for drops greater than 150 $\mu\text{m}$  in diameter, but was not consistently observed under drops in the 20-100 $\mu\text{m}$  range. The fraction of drops that showed no corrosion increased with decreasing drop size below 100 $\mu\text{m}$  in diameter. However, when drops smaller than 100 $\mu\text{m}$  did corrode, they were found to have the greatest volume loss compared to their salt loading density. This result suggests that a given volume of electrolyte would cause more damage if it were deposited in the form of numerous small droplets instead of one large drop of equivalent salt loading. These findings will be discussed with respect to microstructure and oxygen diffusion behavior.

All drops exhibited secondary salt spreading except for those in the 20-80 $\mu\text{m}$  range where it occurred sparingly. Drops that did not have spreading did not appear to corrode. The salt spreading radius increased linearly with the drop diameter in the 20-200 $\mu\text{m}$  range. At

drop diameters greater than 200 $\mu\text{m}$ , the spreading radius did not increase significantly, reaching an upper limit of approximately 3.5 millimeters. Sodium-containing needle-like crystal deposits were found at the perimeter of salt spreading regions, indicating that this location was the site of a net cathodic reaction.

The results from this study indicate that the manner and geometry in which salt is deposited onto a surface will significantly affect the volume loss along with the mode of attack during the initial stages of corrosion. From a scientific standpoint, the methodology developed here enables the study of aerosol-driven atmospheric corrosion through controlled electrolyte deposition and damage evaluation at resolutions oftentimes considered challenging to achieve. From a technical standpoint, service life prediction approaches including accelerated testing have the potential to more accurately simulate natural atmospheres if electrolyte geometry is taken into account.

#### ACKNOWLEDGEMENTS

This work has been supported in part by the US Air Force Academy under agreement FA8501-UVA-002, the CSIRO Advanced Materials Transformation Capability Platform 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 Defense and the SERDP/ESTCP program via contract W912HQ-09-C-0042 are also gratefully acknowledged.

1. Azmat, N. S., *et al.*, *Corrosion Science* (2011) **53** (11), 3534
2. Li, S. X., and Hihara, L. H., *Corrosion Engineering, Science and Technology* (2010) **45**, 49
3. Li, S., Marine atmospheric corrosion initiation and corrosion products characterization. doctoral dissertation, University of Hawaii Manoa, 2010