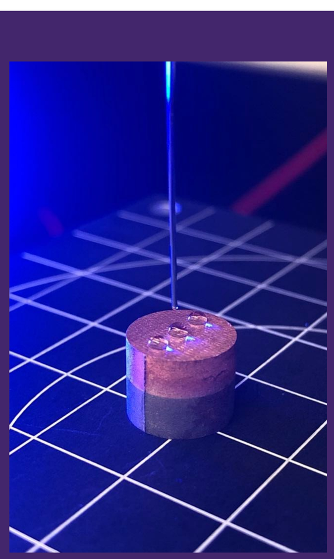

Contact Angle & Electrochemical Measurements of Metallic Atmospheric Corrosion on Copper and Carbon Steel

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Overview

- Performed contact angle measurements on two industrially relevant metals (copper and carbon steel) over a 1 min to 30-day time span to track the change in wettability due to the formation of an air-formed oxide layer (aged) as a function of surface roughness.
- Characterized the wetting of aged surfaces using the Wenzel wetting model.
- Compared the impact of using sonication, ultraviolet (UV) and UV/ ozone treatment experimentally as a cleaning method prior to contact angle measurements.

Background

- Understanding atmospheric corrosion has been incredibly challenging due to the complex interplay between surface microstructures, environmental variables, and electrochemical processes[2].
- This methodology is being developed to apply to atmospheric corrosion models of metals and other advanced materials by observing the change in contact angle in situ as a function of corrosion parameters.
- Different materials have various surface chemistries and topographies that can alter the observed contact angle measured at the triple phase point. The resulting contact angle is represented using Equation 1.
- The lower the contact angle, the more potentially hydrophilic the surface is. A larger contact angle suggests a hydrophobic surface[3]. The interaction between the liquid, solid surface, and the gas phase can be modeled by the Cassie-Baxter or Wenzel wetting models.
- The Wenzel model describes the homogenous wetting of the metal surface[3] (Figure 1).
- The Wenzel model was chosen to predict the hydrophobicity of the material concerning a relative range of surface roughnesses. Contact angles in the Wenzel state are more sensitive to physical changes in surface roughness as they form a more homogenous interaction with surface morphologies that affects wetting behavior. In the Cassie-Baxter state, contact between the surface and droplet is limited due to interfacial air bubbles.

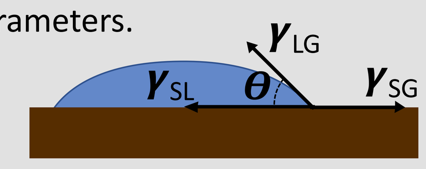

Figure 1: Contact angle (θ) of a sessile droplet wetted to a metal surface and the three interfacial tensions

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos(\theta)$$

Equation 1: The Young equation

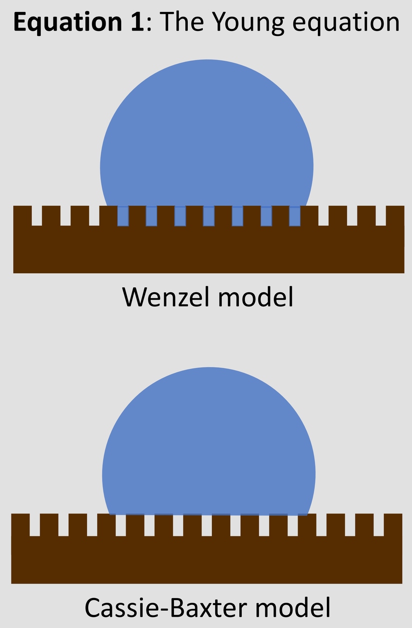

Figure 2: Metal-liquid interactions modeled by the Wenzel and Cassie-Baxter states

Methods

- Utilized an Automated Kruss Goniometer (Figure 3) and Advanced measuring software to elliptically model the contact angle of each sessile droplet.
- Contact angle values were taken once the droplet has equilibrated on the surface of the metal. Contact angle measurements were obtained on three different samples. For SKB Copper and Carbon Steel samples, contact angle measurements are polished over various time points between 1 min and 30 days. Each contact angle is averaged, and a standard error is applied.
- Surfaces were polished using a modular polishing wheel instrument (Struers LaboPol-20) with 320P, 1200P, 2500P, and 4000P silica carbide grit paper. Another set of samples was polished with a diamond finish. Type 1 distilled water was used as a solvent while polishing. After polishing, samples were dried using compressed air and stored under plastic cups.
- UV lamp (250 nm) and UV/Ozone (254 nm) oven were used to perform exposure tests on samples and measure their effects on wettability. These tests were done to track their impact on the surface chemistry of each material through contact angle measurements to validate their use as a surface cleaning method. This was performed between 1 minute and 2 hours, exposing the surface to each form of radiation in the specified time frame.

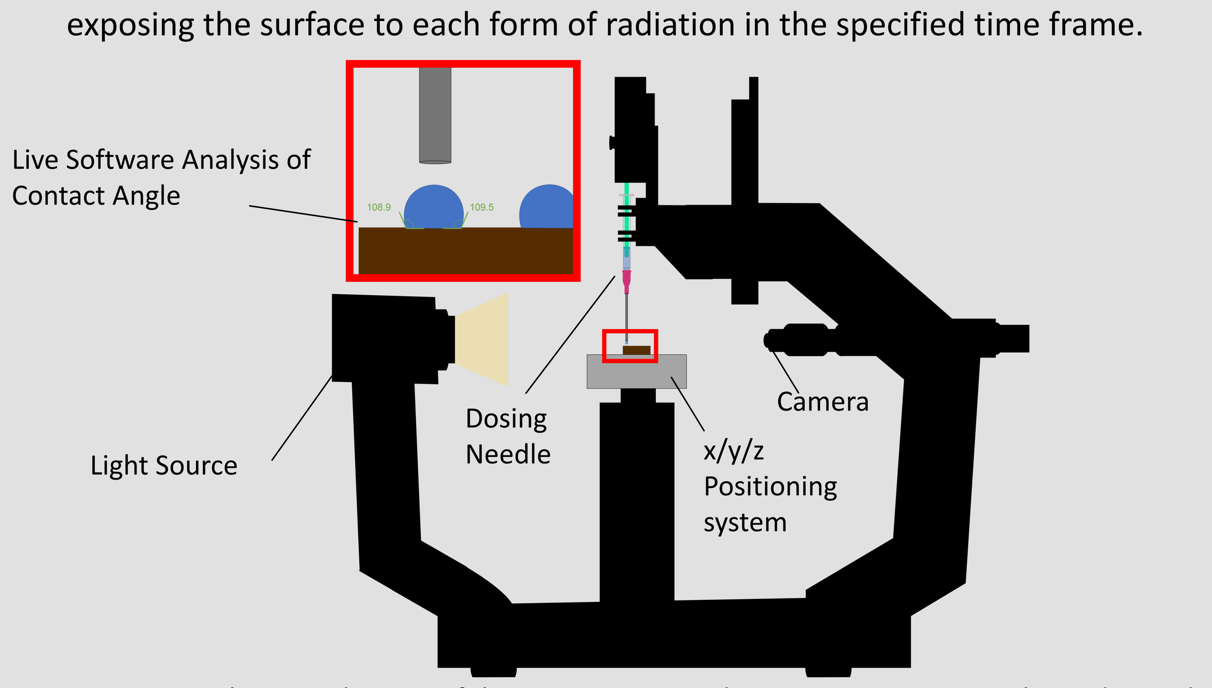

Figure 3: Schematic diagram of the Goniometer used to measure contact angles and record the initial interactions between sessile droplet and the metal surface

Results and Discussion

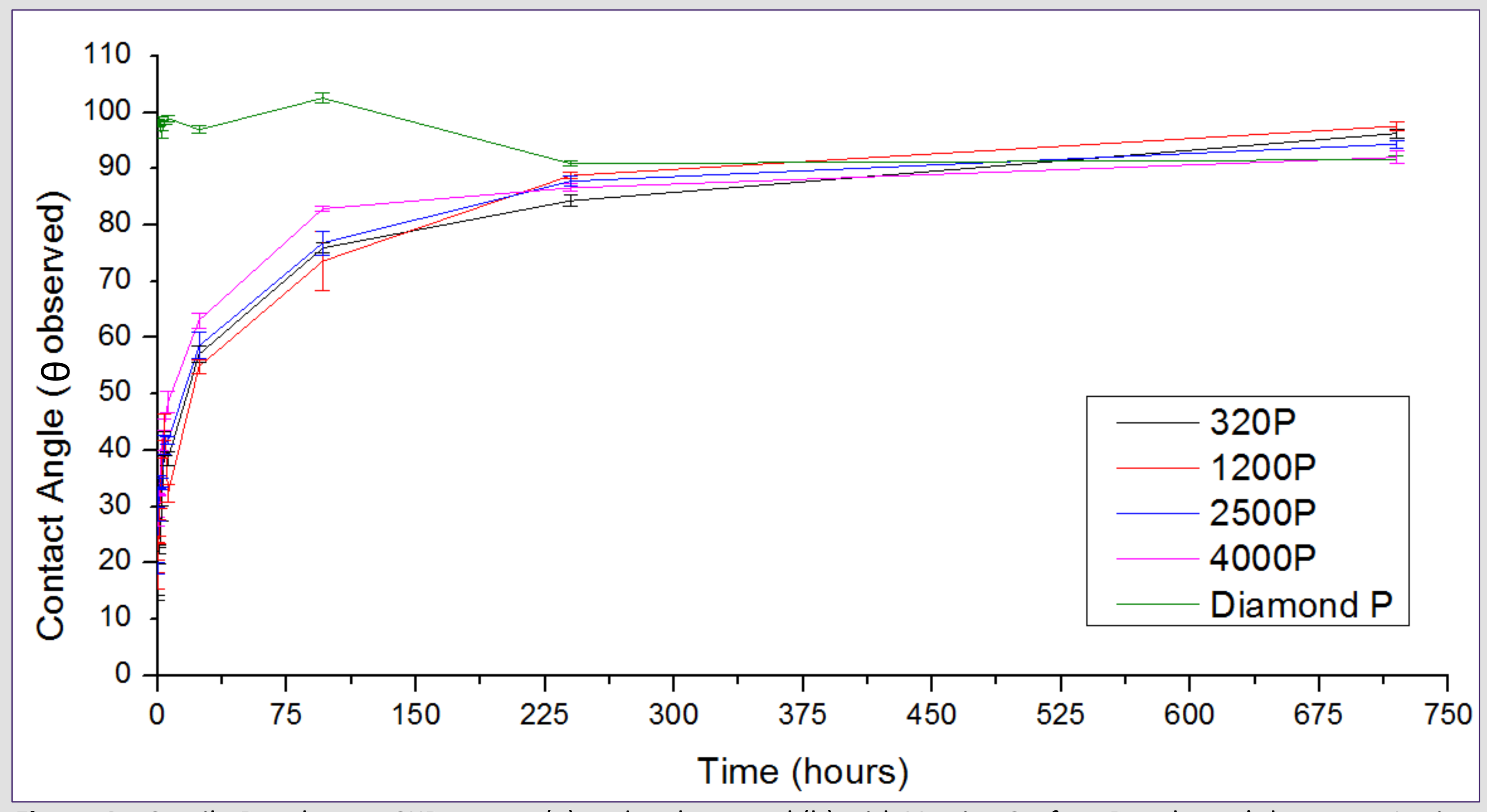

Figure 4a: Sessile Droplets on SKB copper (a) and carbon steel (b) with Varying Surface Roughness's between 1 min to 30 days

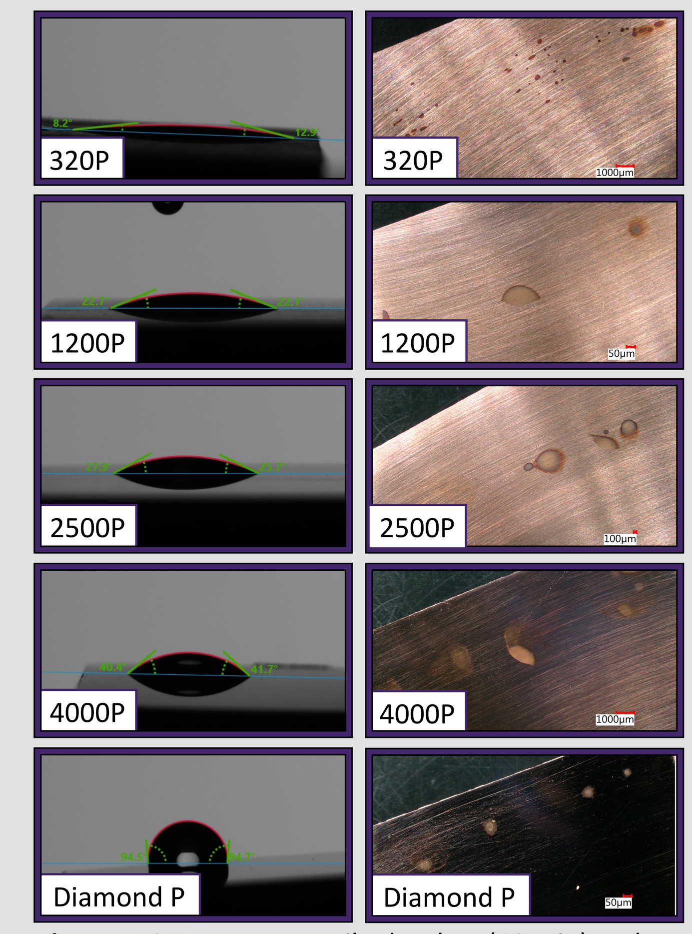

Figure 5: SKB copper sessile droplets (10 min) and corresponding corrosion products for each grit size

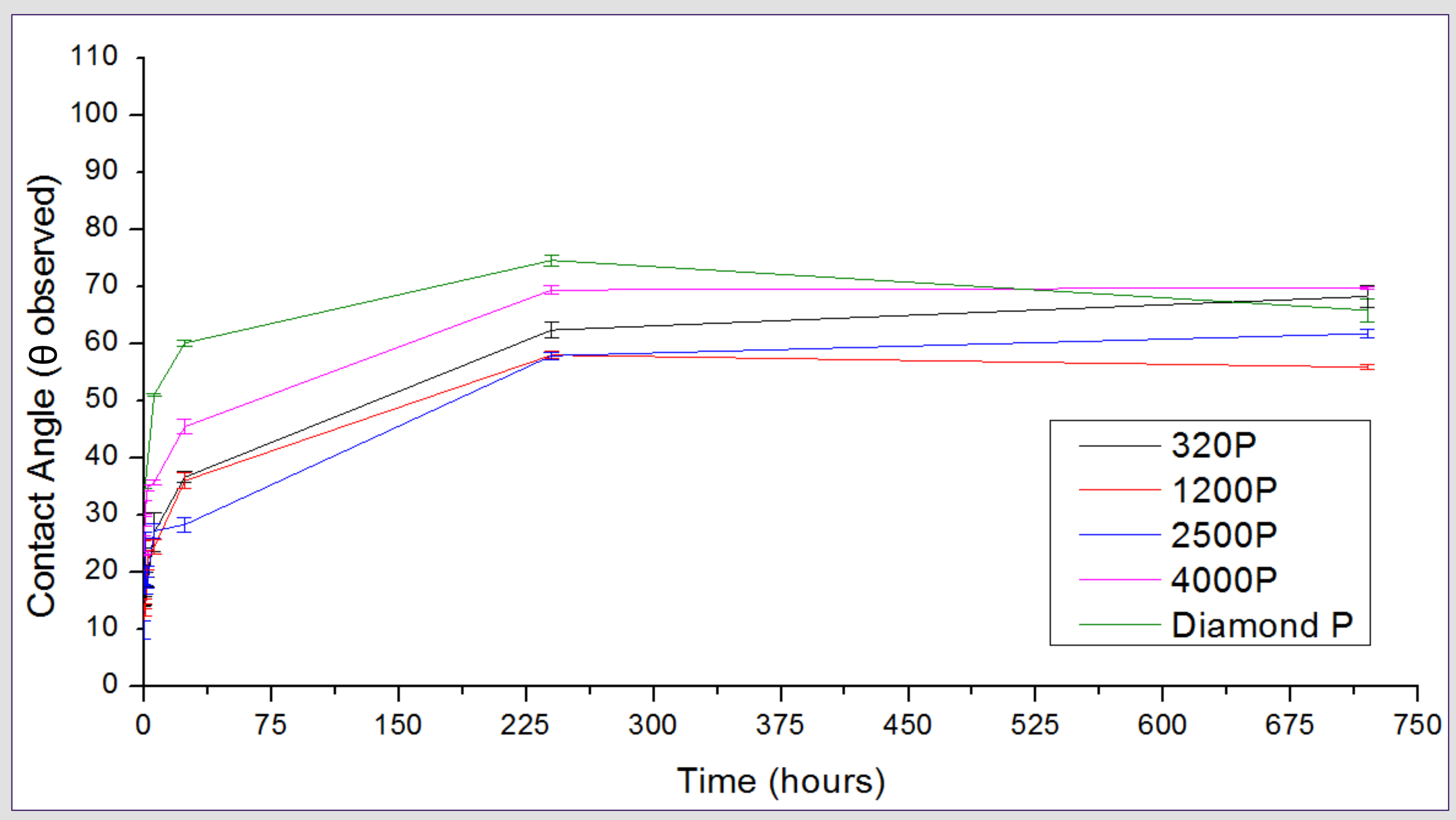

Figure 4b: Sessile droplets for Carbon Steel

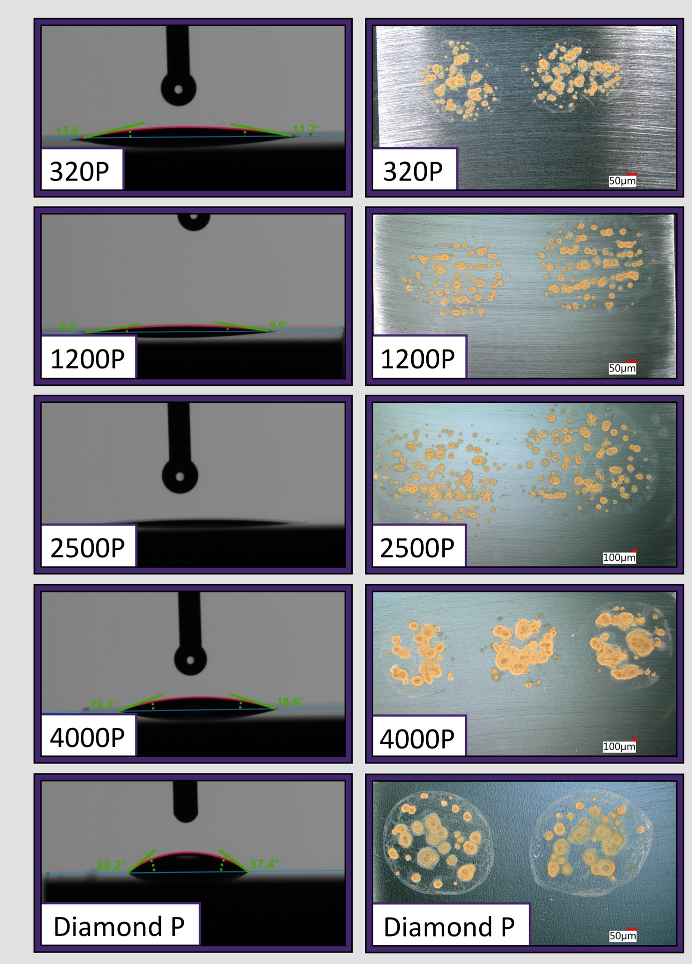

Figure 6: Carbon steel sessile droplets (10 min) and corresponding corrosion products for each grit size

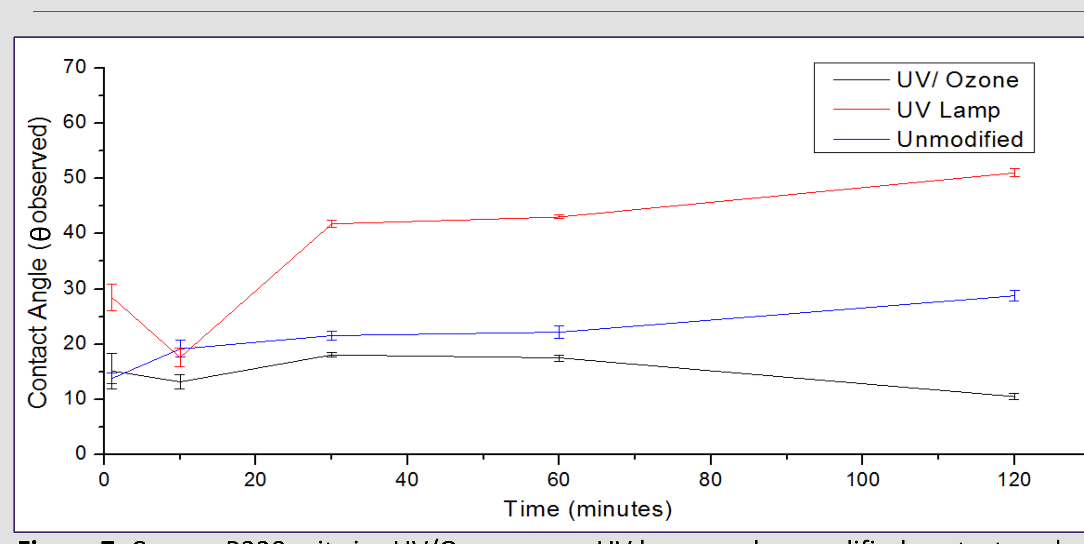

Figure 7: Copper P320 grit size UV/Ozone oven, UV lamp, and unmodified contact angle comparison

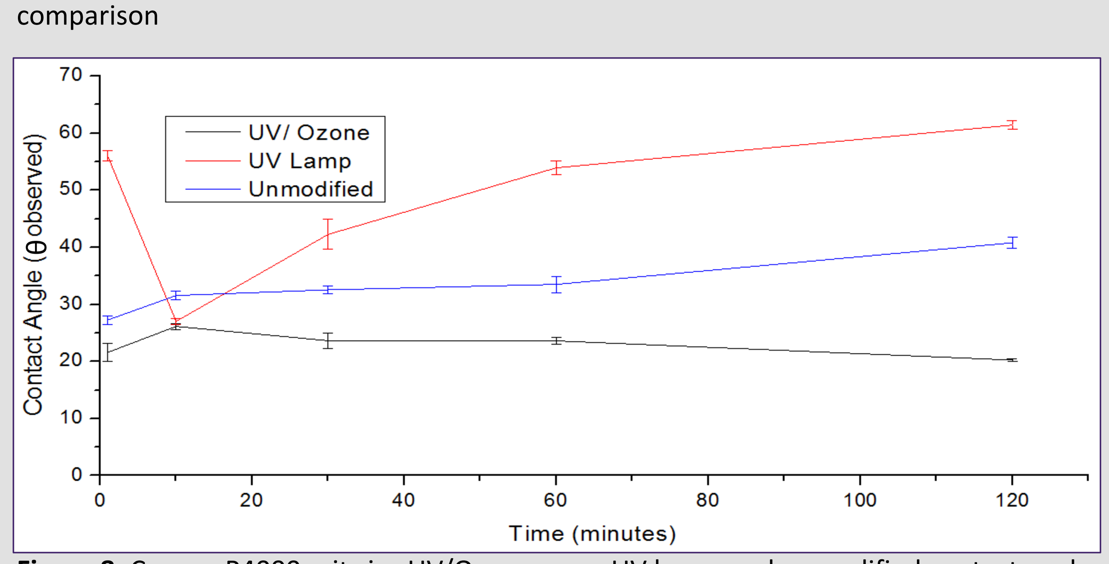

Figure 8: Copper P4000 grit size UV/Ozone oven, UV lamp, and unmodified contact angle comparison

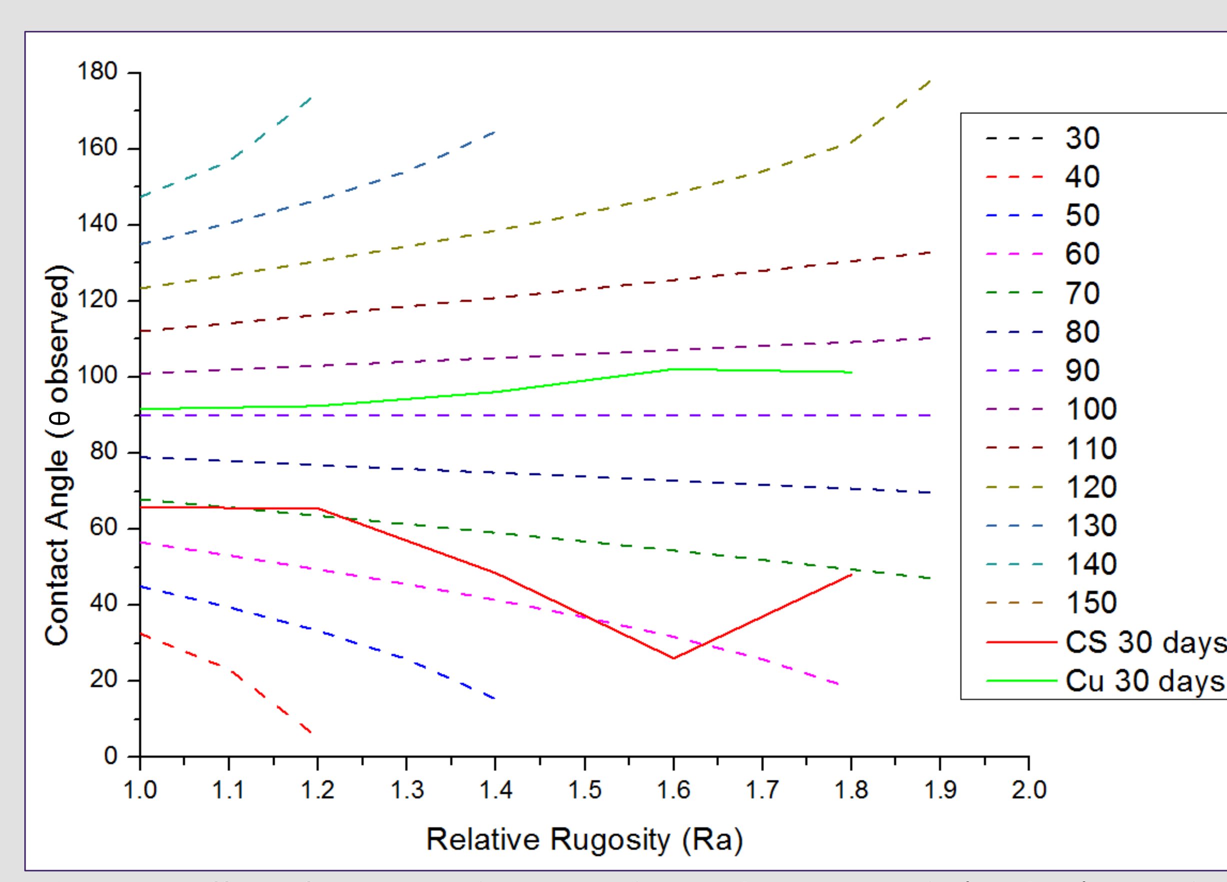

Figure 11: Effect of micro roughness on observed contact angle (30 days) on carbon steel and SKB copper, modeled using Equation 2 from the Wenzel wetting data[1].

$$\theta\ observed = r\cos(\theta\ true)$$

Equation 2: the Wenzel model, with r referring to rugosity

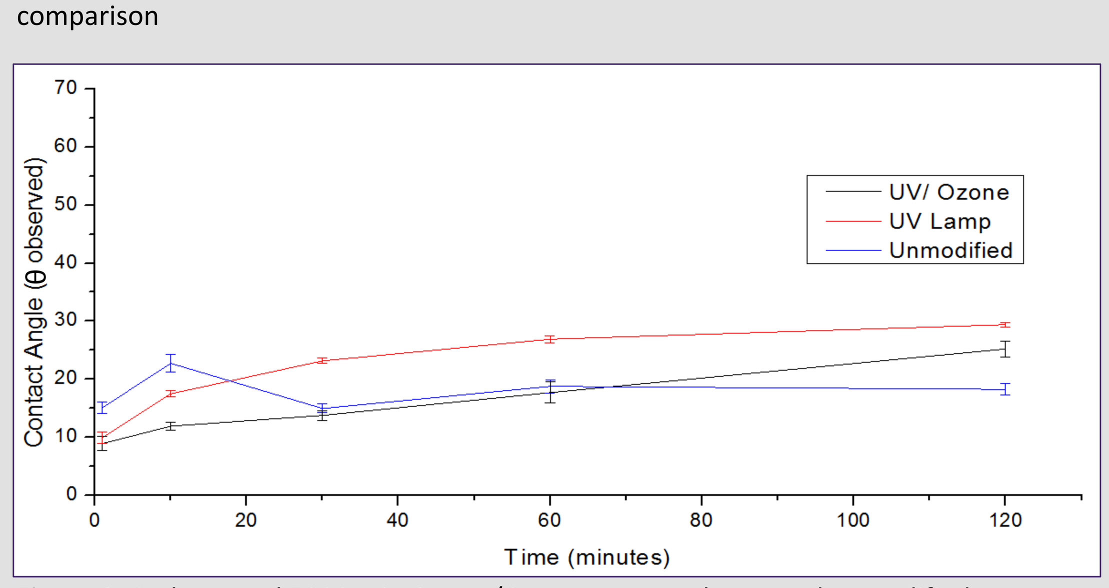

Figure 9: Carbon steel P320 grit size UV/Ozone oven, UV lamp, and unmodified contact angle comparison

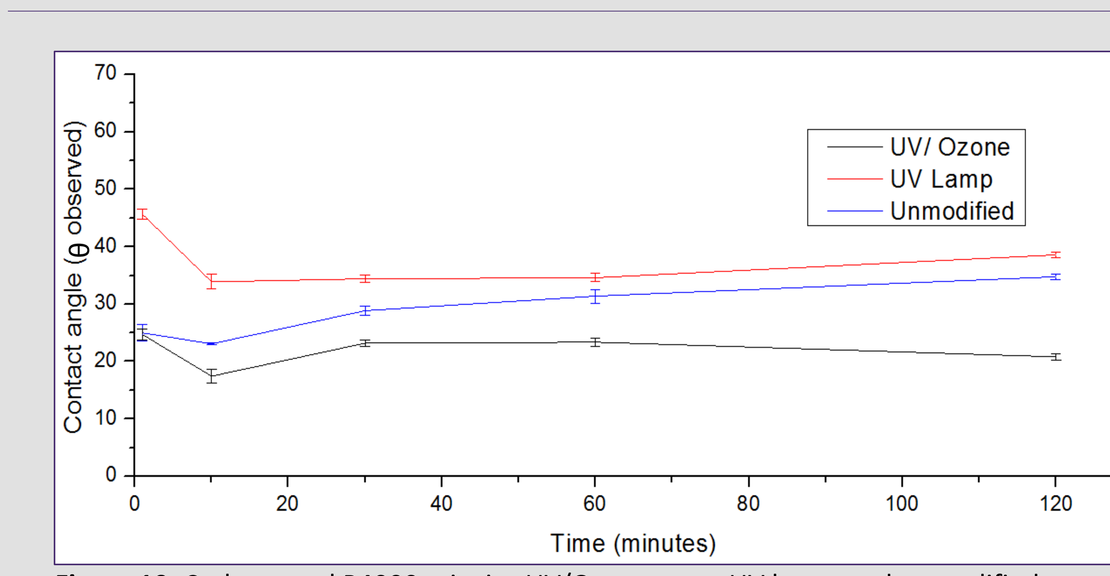

Figure 10: Carbon steel P4000 grit size UV/Ozone oven, UV lamp, and unmodified contact angle comparison

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Acknowledgements

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Conclusions & Future Work

- Measured contact angles show a change in surface chemistry due to the gradual growth of an oxide layer throughout exposure to air.
- For both carbon steel and SKB copper, the surface film formation did not reach a study state until 7 days of exposure. At 30 days, SKB copper material was found to be hydrophilic, while the carbon steel material reaches a hydrophobic state
- The change in surface roughness impacts the contact angle measurements as shown by the variance in contact angle between repeated samples shown through the variance between contact angles of each grit size in figures 4 and 5, the change in contact angle as a function of rugosity in figure 11, as well as the the qualitative imaging of droplets
- Contact angles measured under UV/ Ozone (254 nm) and short-wave UV light (250 nm) show a change in surface chemistry when compared to unmodified surfaces.
- Future work involves performing contact angle measurements while electrochemically polarizing the material surface to extract the corrosion parameters of each metal while monitoring the contact angle (Figure 12). Will also employ the sample preparation methodologies explored towards nano droplet corrosion measurements.

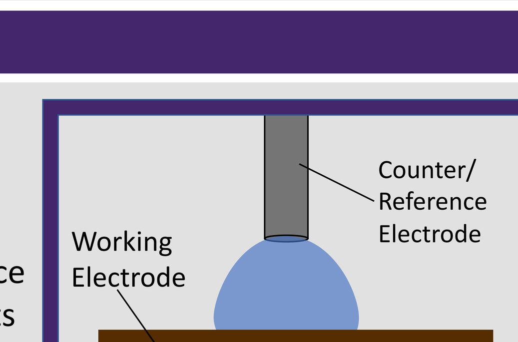

Figure 12: 2 electrode setup using the metal as the working electrode and needle as the counter/ reference electrode