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Atmospheric Corrosion Driven by Naturally Generated Reactive Halogens

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Objectives

The primary objective of the proposed program is to assess the concept that a major driver for atmospheric corrosion is the action of reactive halogen species that are naturally generated by the interaction of sea salt aerosols with ozone and UV light. Successful proof of this concept will be followed by preliminary designs for improved salt spray testing that will allow more accurate prediction of the effect of geographic location on atmospheric corrosivity.

The Challenge of Atmospheric Corrosion

Atmospheric corrosion rates of metals vary greatly over space and time due to variations in environmental conditions.¹ The corrosivity of moisture layers towards a given metal is determined by both the chemical composition of the air and the associated amount and composition of reactive material deposited on the surface. The majority of atmospheric corrosion research has involved simple characterization of relationships between ambient environmental conditions and corresponding corrosion rates of different metals,¹⁻³ but this phenomenology has been insufficient to produce a successful predictive model of atmospheric corrosion. Current predictive models of atmospheric corrosion consist of simple correlations among easily measured atmospheric variables (*e.g.*, relative humidity, temperature, salt deposition, pollutant gas concentration) and the observed corrosion rates. Phenomenological models of atmospheric corrosion usually include a major dependence on “deposited chloride” and “distance from the sea.” Unfortunately, regression analyses for corrosion rate that consider these “obvious” variables have been uniformly failures, with correlation coefficients consistently near or below 0.5.⁴⁻⁶ In addition, the standard laboratory cabinet tests (*e.g.*, ASTM B 117 Salt Fog) do a poor job of reproducing the corrosion behavior observed in the field.

We propose that a primary reason for these deficiencies in predicting corrosion rates is the inability to explicitly account for the speciation, spatial variability, and associated deposition fluxes of chemical species such as chlorine-(Cl) and bromine-(Br) containing compounds that are introduced into the lower atmosphere from both natural and anthropogenic sources and subsequently transformed by reactions involving oxidants such as ozone and hydroxyl radical in the presence of light and water.

The suite of reactive halogen species (RxHal, including halogen ions, acids, and atoms; hypohalous acids; and halogen oxides) include strong oxidants that are known to attack protective films naturally formed on metals. The formation and cycling of these aggressive species has been demonstrated by atmospheric chemists based on both field and laboratory experiments since the early 1990's.⁷⁻¹⁰ The production of sea-salt aerosols by turbulence at the ocean surface is the major global source for tropospheric Cl and Br. Sea salt, together with associated halogenated reaction products, can be transported far inland by prevailing winds. Other important global sources of tropospheric halogens, which may dominate on regional scales particularly at inland continental locations, include deflation of surface soils, biomass burning, fossil-fuel combustion, and incineration.^{8,11} To date, however, this understanding of atmospheric chemistry has not been incorporated explicitly into corrosion-related research efforts. We believe that a more comprehensive evaluation of the associated atmospheric processes will explain much of the observed dependencies of corrosion rates on environmental variables. For example, there are strong gradients in both the deposition of atmospheric halogens and corrosion rates of metals with distance inland from coasts.¹⁻³ In addition, the solution concentrations of deposited halogens on surfaces are typically quite high. Based on the hygroscopic properties of sea-salt aerosol and its associated rate of chemical modification, the chloride concentrations in aqueous brine solutions on metal surfaces exposed to coastal air at a typical relative humidity of 80% can be in the range of 5 to 10 M.¹² Finally, the concept of “deposited chloride” as primary a driver for atmospheric corrosion may be misleading because the simple methods currently used

by the corrosion community to estimate “deposited chloride” are not appropriate for analysis or interpretation of the full range of gaseous and particulate RxHal species.

Our proposal regarding RxHal plausibly addresses each of the “Field Results” described in the RFP:

1. *It is known that it is the synergistic effects of “chlorides” together with water that is rate controlling.*

RxHal are formed via aqueous chemical reactions, and their dissolution in water would accelerate the electrochemical reactions that are inherent in atmospheric corrosion.

2. *The presence of “chlorides” can be detected in virtually any environment throughout the world; i.e. this is not restricted to just coastal locations.*

The range of size of sea salt aerosols allows transport far inland via prevailing winds. In addition, the involvement of ozone (O₃) would exacerbate the creation of RxHal in areas of high ozone concentration due to anthropogenic sources – explaining the corrosivity of “urban” areas despite the large decrease in sulfur dioxide (SO₂) concentrations in recent decades.

3. *The reaction of solid silver in natural environments to form silver chloride (AgCl). An equally important finding is that when silver is exposed in a laboratory environment such as B117 there is no detectable AgCl formed.*

For metals, RxHal have two aspects to their potency. Their presence creates much stronger oxidizing conditions than does dissolved molecular oxygen due to both more positive reversible potentials, but also their solubility is very much higher than O₂, which leads to a higher diffusion limited current density at the same diffusion boundary layer thickness. In addition, their reduction product is the chloride ion, well known for its ability to attack protective oxide films. Although laboratory studies of the effects of chlorine have generally been carried out at concentrations well above that expected in the natural environment, it is well known that ppb concentrations of Cl₂ can dramatically increase the corrosion rates of many metals.

4. *No more than trace amounts of Na appear to be present on the surfaces of samples such as aluminum exposed in natural environments*

Sea salt aerosols are not than simply NaCl. In fact, they are complicated particles with many different cations (e.g., NH₄⁺, Mg²⁺, K⁺, Ca²⁺) and a range of pH. Once transported from source regions, both sea salt aerosols and particles generated through heterogeneous reactions (in polluted regions) can dissolve in solution and provide the necessary substrates for electrochemical reactions. That said, the reasons for the almost total lack of Na require further study.

5. *Recent work has shown that at the mated interfaces of structure such as in (a galvanic couple) overlap joint, corrosion reactions in the field are highly accelerated in comparison to the reactions on bare aluminum alone.*

The galvanic lap joint configuration provides two key accelerators in the context of RxHal atmospheric corrosion. The tight crevice associated with the mating surfaces will increase the time-of-wetness¹³, leading to corrosion during the hottest parts of the day when boldly exposed surfaces would be fully dry. In addition, the noble metal in the galvanic couple serves as an ideal surface for the cathodic reaction of the oxidizing RxHal, thereby accelerating the corrosion of the aluminum far beyond what it would be alone due to the fact that aluminum oxide is generally a very poor surface for electron transfer reactions.

Proposed Testing

1. Literature Search and Review

A thorough review of the literature on the atmospheric corrosion of silver, aluminum, and steel will be performed. In addition, the literature on the chemistry and transport of sea salt aerosols will be reviewed and incorporated as relevant to atmospheric corrosion. This review will form the basis for the interpretation of the exposure and electrochemical studies that will form the bulk of the work. In addition, the review will assist in the design of the improved accelerated test.

2. Exposure Studies

Exposure of several types of metallic coupons to a range of synthetic atmospheres will provide an initial assessment of the feasibility of the RxHal hypothesis. Exposures on the order of a month to six weeks will be made on triplicate specimens of steel, silver, AA6061, and a AA6061/Ag lap joint. Assessment of corrosivity will be via mass loss measurements as well as corrosion morphology. In addition, galvanostatic reduction of the silver surface will be performed to assess the amount of AgCl formed.

The metals to be tested will be carbon steel, silver, AA 6061, and a lap joint consisting of AA6061 and silver surfaces in contact. Four environments will be studied in a small-scale salt spray chamber. The scaled-down chamber is needed in order to prevent the many surfaces within commercial scale chambers from acting as getters of the RxHal introduced. Finlayson-Pitts¹⁴ has shown that minimizing the surfaces that are not of interest to be of importance in ensuring that the RxHal created from sea salts are measurable in a laboratory setting.

All of the environments are based on the ASTM B 117 Method. In addition to the standard salt spray test environment, three other environments will be studied: (a) salt spray + ozone, (b) salt spray + ppb levels of Cl₂, and (c) salt spray + RxHal created from sea salt via exposure of the sea salt to ozone and UV illumination per Finlayson-Pitts¹⁴.

We would expect that for all of the materials tested, the corrosivity of the modified salt spray tests that include either Cl₂ or the creation of RxHal species will be higher than that of containing just O₃, which will be higher than the standard salt spray environment.

3. Electrochemical Studies

Electrochemical studies will complement the exposure studies by providing mechanistic insights. Solution compositions will be selected based on surface solution chemistries expected in the exposure chamber studies. Anodic and cathodic kinetics will be determined by voltammetry on platinum, steel, silver, and AA6061. Stirring will be used in order to mimic the high mass transport conditions of the thin electrolyte films inherent in atmospheric corrosion.

4. Advanced Accelerated Test Development

Assuming that the hypothesis concerning the importance of RxHal are correct, the development of an advanced accelerated test will begin in Year 1. Initial design of several possible methods

to make a chamber-compatible accelerated test will be performed. Processes to create low to medium levels of RxHal will be considered. For example, the addition of an in-line reaction chamber that can be retrofit to commercial salt spray cabinets that could introduce RxHal in controlled amounts. The in-line reaction chamber may involve the formation of Cl₂ via the electrolysis of salt water through which air to the chamber is passed in order to humidify it, or the illumination of ASTM ocean water salts in a controlled RH with UV light.

In addition, future work can include numerical studies can be conducted that couple available global and regional scale models for aerosol creation and transport with an understanding of RxHal effects on corrosion. Such a coupling should allow an understanding of the impact of location on the corrosion rates of the metals of interest.

Personnel

Due to the limited funding available in Year 1, a post-doctoral research associate would handle the experimental work. If the Year 1 work was successful and led to additional funding at a higher level, a PhD student would be recruited and added to the project which would constitute the basis of his/her dissertation research.

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