

Comparison Of Atmospheric Corrosion Of Silver Across Multiple Locations

Ronald Zeszut
University of Dayton Research Institute
300 College Park
Dayton, OH, 45469
USA

David Rubino
University of Dayton, Department of Chemical
and Materials Engineering
300 College Park
Dayton, OH, 45469
USA

Douglas C Hansen
University of Dayton Research Institute
300 College Park
Dayton, OH, 45469
USA

ABSTRACT

Atmospheric corrosion of silver from multiple beachfront sites in Florida was examined by coulometric reduction. Exposure was performed at the US Naval Research Laboratory in Key West, Kennedy Space Center, and Daytona Beach. Coupons were exposed for 3-18 months. Silver chloride and sulfide were identified and quantified by a galvanic reduction technique, which separately characterized the corrosion products on the front and back of each coupon. Differences were observed between sites for both chloride and sulfide growth rate. Silver chloride grew fastest at Daytona Beach, but no silver sulfide was observed on any samples at this site. Additionally, corrosion was observed to occur differently on the front and back of the samples. Increasing exposure times showed increasing corrosion film thickness, and exposure at different sites showed different corrosion film thicknesses and compositions. Additionally, the coulometric reduction technique has been examined in-depth to identify and mitigate possible difficulties in results interpretation which arise from thick and/or multi-component films.

Key words: corrosion, silver, silver chloride, atmospheric corrosion, coulometric reduction

INTRODUCTION

Atmospheric corrosion of bare metals is a constantly occurring process that can cause significant damage to metal components and structures. For this reason, it has been extensively studied, especially for steel and aluminum alloys.¹⁻⁸ Environmental exposure testing is a common method for studying and characterizing the corrosion severity of a location, which allows for comparison with other regions. Much of this data collection is directed toward development of predictive models for corrosion processes, with the goal of estimating corrosion damage based on environmental conditions.⁸ In addition to modeling,

another area of interest in corrosion mitigation research is accelerated corrosion testing, in which corrosion damage due to long-term atmospheric exposure is replicated by a shorter controlled exposure.³ Mass loss is a commonly used metric to characterize the severity of corrosion in these studies^{2-6,8}, however, mass loss alone does not fully characterize the method of attack as it does not address chemistry or surface morphology. For this reason, silver has often been included in atmospheric corrosion testing to serve as an additional indicator of environmental conditions.⁹⁻¹⁶ Characterization of the corrosion products on silver can give further insight into the environment and which atmospheric species may be participating in the corrosion process on silver and any other exposed metals. Two of the main environmental factors that affect silver corrosion are ozone concentration and UV exposure from sunlight. Chen et al. demonstrated in a salt fog chamber, that without these factors, there is very little corrosion product formed.¹⁷ Because many environmental factors, including UV irradiation, affect the sample front differently than the back, utilizing a technique to separately characterize the front and back of the samples is desired.

One such technique is galvanic reduction, which is used for the determination and quantification of silver corrosion products.^{11-12, 14-15, 17-18} This method involves passing a constant cathodic current and monitoring changes in the applied voltage. For each species, a voltage plateau is observed, with different species distinguishable by their voltage plateau value. This technique can be performed on an entire exposure coupon at once, or on specific spots on the coupon using a flat cell or similar device. Specifically, utilization of a flat cell allows for differentiation between the sample front and back. However, silver samples with very thick corrosion films can become rough, porous and difficult to seal for testing with a flat cell. Leaking can easily occur even in a properly assembled test cell, which can cause difficulty in data interpretation.

This study builds upon earlier work in two main ways. First is a deeper investigation into the galvanic reduction technique, specifically characterizing and addressing use of this method in thick films. Several cases of species reducing outside of their normal range are observed and explained, along with recommendations for proper utilization of the technique to avoid errors in data interpretation. Secondly, three sets of silver coupon exposure data are analyzed from three sites in Florida: the Battelle Florida Materials Research Center in Daytona Beach, the NASA Kennedy Space Center Beachside Atmospheric Corrosion Test Site (KSC), and the Naval Research Laboratory in Key West (NRL-KW). Silver chloride and sulfide film thicknesses were measured and compared across sites and times. Additionally, samples were compared according to exposure orientation (front or back). Finally, these results are briefly compared to atmospheric conditions at each site.

EXPERIMENTAL PROCEDURE

Sheets of 99.999% silver purity were fabricated into exposure coupons with dimensions 3 inches x 0.5 inches x 0.032 inches (7.62 cm x 1.27 cm x 0.081 cm). Before exposure, samples were polished to American National Standards Institute (ANSI) 600 grit finish, then cleaned with acetone, methanol, and isopropanol. After polishing, the silver coupons were assembled onto exposure cards containing aluminum, copper, and steel coupons in addition to silver. The exposure cards were vacuum-sealed in Mylar bags with a desiccant and oxygen scavenger to prevent corrosion during storage and transportation. Samples were similarly sealed for storage and transportation after environmental exposure. Exposure started at NRL-KW in February 2019, with the exposure rack located 226 feet (69 m) from the high water mark, facing south. Exposure started at KSC in May 2019, with the exposure rack located 121 feet (37 m) from the high water mark, facing northeast. And exposure started at Daytona Beach in August 2019, with the exposure rack located 492 feet (150 m) from the high water mark, facing east/northeast. At each location, the coupons were exposed for 3, 6, 9, 12, 15, and 18 months from the initial deployment date. For NRL-KW, 5 cards were retrieved for each 3-month period, and 3 cards each were retrieved for each 3-month period for both KSC and Daytona Beach. Each site reported airborne chloride deposition from a wet candle, while NRL-KW also reported other wet candle species and airborne sulfur dioxide concentration.

Sample images were taken on an HP Scanjet 5590 document scanner after exposure both before and after reduction. Samples were analyzed by galvanic reduction according to the following parameters.¹⁷⁻¹⁸ Sample reduction was performed in a Princeton Applied Research glass flat cell with an exposed silver electrode area of 1 cm², using a Bio-Logic VMP potentiostat. The system was set up as a three-electrode cell, with the silver as the working electrode and a platinum mesh counter electrode. The silver sample area was sealed with a Teflon™ knife-edge washer, which was replaced every 3 tests. Alternately, for experiments conducted on a full coupon rather than a single spot, a Greene cell was used, with the whole silver coupon (masked at the top) immersed in solution serving as the working electrode and graphite rod counter electrodes. The flat cell system was used for most experiments, the Greene cell was used only for full coupon deposition or reduction. The electrolyte for reduction was 0.1 M Na₂SO₄ adjusted to pH 10 with NaOH.¹⁷ The solution was deaerated with nitrogen for at least 1 hour before use. A constant current of -0.1 mA/cm² was applied, and the voltage was measured against a mercurous sulfate reference electrode (MSE). The potential of the archive MSE used in this study was ~394 mV positive to the saturated calomel electrode (SCE) archive. Before and after each electrochemical test, the reference electrode, whether MSE or SCE, was measured against its respective archive reference electrode. Voltage plateaus occurred over time and represented different silver corrosion product species. The amount of charge passed for each species at its voltage plateau indicated the amount of that species in the corrosion film. After all reducible surface species had been removed, current passed through the cell resulted in hydrogen evolution, with a potential between -1.6 and -1.8 V vs. MSE. For each coupon, 3 reduction tests were done on different locations on both the front (facing upwards during exposure) and back, for a total of 6 reduction tests on different spots per sample.

For comparison with field data, single component corrosion films were generated on silver samples. Silver chloride, silver bromide, and silver iodide films were generated in a 3-electrode cell by immersion of clean silver coupons in 0.1 M KCl, KBr, and NaI electrolyte solutions, respectively.^{14, 17} An anodic current of 1 (Br and I) or 2 (Cl) mA/cm² was passed through the cell, with the silver as the working electrode, a platinum mesh counter electrode, and an SCE reference electrode. Films were deposited using a flat cell for spot deposition or a Greene cell for full coupon coverage. In all cases, the amount of material deposited could be calculated coulometrically. Comparison of the amount of material deposited and then subsequently reduced by the method discussed above yielded current efficiencies greater than 98%. The high current efficiencies indicated high levels of accuracy for both the deposition and reduction techniques. Silver oxide films were generated in a similar manner by immersion in a 0.1 M NaOH solution at 0.405 V vs. SCE.¹⁷ This method was only qualitative, as current efficiencies comparing the deposition and reduction steps varied (50-90%). Silver coupons, which had been exposed to lab air for several years, showed the presence of a sulfide film and were used as the sulfide, single component sample for this analysis. Films of different species were also grown sequentially on the same location before reduction to generate layered, multi-component (MC) films. For these films, after the deposition of the first layer, the electrolyte was removed and rinsed from the flat cell before the next solution was added. This was done while keeping the sample clamped in the same location whenever possible. After all desired layers had been deposited, the cumulative film was reduced.

Energy-dispersive X-ray spectroscopy (EDS) was used for surface composition analysis of several samples, for comparison with the galvanic reduction data. A Zeiss EVO-50XVP SEM-EDS at 100X magnification and 10kV accelerating voltage was used. Due to the nature of EDS analysis, particularly the uncertainty surrounding penetration depth, elemental surface analysis results are only semi-quantitative. For this study, elemental composition data are not directly correlated to galvanostatic reduction data, but instead large changes and trends in the EDS data are used for comparison. Several samples were also imaged on a Keyence VK-X1100 confocal microscope, which also calculated root mean square (RMS) sample roughness.

RESULTS

Reduced Species Identification

When utilizing the galvanic reduction technique for complex, atmospherically formed silver corrosion films, distinguishing and identifying the different species comprising the corrosion film is required. It is well established that silver chloride reduces at ~ -300 mV vs. MSE and the hydrogen evolution reaction (HER) occurs between -1.6 and -1.8 V.¹⁷ The expected reduction potential of many additional silver corrosion products are also reported. A reduction potential library was desired for simple comparison of known single component films with field data for the specific equipment and procedure used in this study. Figure 1 and Table 1 show the reduction curve and potentials for silver oxide, chloride, bromide, iodide, and sulfide at the standard reduction conditions used in this study.

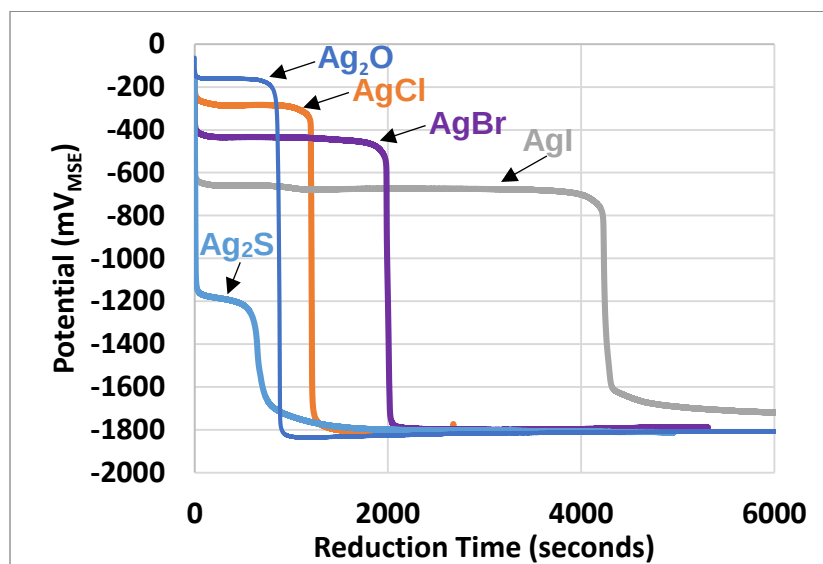


Figure 1: Reduction curves showing different reduction potentials of lab grown standards. Ag₂O, AgCl, AgBr, and AgI films generated from immersion and oxidation in salt solutions. Ag₂S generated by exposure to lab air

Table 1
Experimental and reported reduction potentials for each lab grown standard

Compound	Experimental Reduction Potential (mV _{MSE})	Reported Reduction Potential (mV _{MSE}) ¹⁴
Ag ₂ O	-180	-180
AgCl	-300	-300
AgBr	-420	-412
AgI	-650	-673
Ag ₂ S	-1200	-1190

All of these species showed good agreement with their respective reduction potentials reported in literature. Additionally, the curves show a well-defined plateau shape indicating the full reduction of the species followed by a rapid transition to hydrogen reduction.

Deposit Thickness Calculation

Deposit thickness is calculated from charge passed during reduction. Reduction time is determined, and when multiplied by the current, this gives the charge of the reduced species, which can then be converted into mass or thickness. For single component films, reduction starts immediately with the experiment. The reduction end time is determined for both single and multi-component films by drawing a straight line through the section of the curve after the plateau, most often through the inflection point.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP. Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).