

Full Factorial Experiment of Laboratory Exposure of Ag with Ozone and Ultraviolet Radiation

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ABSTRACT

Previous results have shown that the atmospheric corrosion behavior of Ag could be simulated by exposure to a lab environment containing moist air, ozone, NaCl and UV light successfully. To better understand these effects, a full factorial experiment has been carried out with three factors: ozone concentration, UV intensity and relative humidity. AgCl was identified by XRD analysis as the only corrosion product in wet environments, while Ag₂O formed as well when relative humidity was lower than 75%. Corrosion products were quantified by galvanostatic reduction of exposed samples in 0.1 M Na₂SO₄ solution. At least two samples of Ag were exposed to each environment condition. The effect of UV is a net combination effect of acceleration by photolysis of ozone to create oxidizing species and photodecomposition of corrosion products. An equation to represent corrosion rate of Ag as a function of ozone concentration, relative humidity and UV intensity was determined, which is helpful for design of accelerated laboratory test of Ag.

Key words: atmospheric corrosion, silver, ozone, UV, photodecomposition, B117,

INTRODUCTION

Silver has been widely used for electronics and as an environmental corrosivity monitor [1]. During service in the field, formation of silver chloride and silver sulfide usually predominate [2]. Unfortunately, the most widely used accelerated laboratory test, ASTM B117, does not work for silver. Silver does not corrode in a salt spray chamber environment [3], probably because of a lack of a strong oxidant. To develop a new and effective laboratory exposure test for silver, ozone and UV light as well as NaCl have been studied and found to be a promising environment for acceleration corrosion testing of silver [3]. This paper presents results of a full factorial experiment of three factors, ozone, UV and RH. Based on these results, corrosion behavior of silver with ozone, UV and NaCl has been further understood, which also benefits the design of a new laboratory acceleration test for silver.

EXPERIMENTAL PROCEDURE

Silver coupons were first polished to 1 μm with diamond paste. Then 50 $\mu\text{g}/\text{cm}^2$ of NaCl was deposited on one side by evaporation of NaCl ethanol solution. The ethanol completely evaporated within 6 min after coupons were placed in a vacuum desiccator. Afterwards, coupons were exposed in a lab-built environment chamber for 22 h with ozone concentration and relative humidity accurately controllable. Three levels of ozone, 360 ppb, 600 ppb and 2000 ppb, and three levels of relative humidity, 28%, 58% and 87%, were tested. The total flow rate was 0.8 L/min. A short wavelength ultraviolet light (254 nm) was shined on the samples through a quartz window in the top of the chamber. UV intensity was adjusted by changing the distance between the light bulb and the window. Five levels of UV intensity were used: 0, 1.1, 2.0, 3.5, and 4.7 mW/cm^2 . After exposure, samples were analyzed by x-ray diffraction (XRD) and galvanostatic reduction in 0.1 M Na_2SO_4 , pH=10 at 0.1 mA/cm^2 .

RESULTS

Tables 1-3 summarize the results of the full factorial experiment. Reduction charge is proportional to the amount of corrosion products and the corrosion rate because the exposure time was constant. It is clear that ozone accelerates corrosion of Ag with UV radiation, since more atomic oxygen generated by photolysis of ozone. Without UV radiation, at low relative humidity (28%), corrosion rate of Ag was very slow, close to 0, with 360 ppb and 600 ppb, while it dramatically increased with 2000 ppb ozone. This might hint that, in the dark environment, the corrosion mechanism changes as ozone concentration increases.

The effect of relative humidity also varies with ozone concentration. With 360 and 600 ppb ozone and no UV radiation, the corrosion rate of Ag increases as RH increases. However, the corrosion rate decreases as RH increases when UV is incident on the sample during exposure. Liang proposed several possible reaction pathways for corrosion of Ag and they predominated at different RH [3]. In summary, oxidation of Ag by atomic oxygen results in the highest corrosion rate. However, atomic oxygen is so aggressive that it can oxidize water and chloride. The reaction products are still aggressive enough to oxidize Ag, but they are not as aggressive as atomic oxygen. That explains why the corrosion rate of Ag decreases as RH increases with UV radiation. In the dark environment, photolysis of ozone is negligible. The liquid layer on Ag samples behaves like a reservoir for oxidants, so the corrosion rate of Ag increases as RH increases.

The effects of UV are much more complicated than what was reported before, when only photolysis of ozone by UV was taken into account [3, 4]. The Ag corrosion rate was found to increase or decrease as UV increased depending on the conditions. Comprehensive analysis of all results reveals that UV has two opposite effects on silver. Photolysis of ozone by UV accelerates corrosion owing to the production of atomic oxygen. The effect is limited by the ozone concentration, and is also strongly affected by RH

because of the formation of wet layer on the silver surface that can block atomic oxygen. On the other hand, UV radiation can also cause photodecomposition of corrosion products [5]. AgCl is a well known photosensitive compound that is used in photographic film. This effect is independent of ozone concentration. In general, the resulting corrosion product on the surface after exposure is a net result of these two countervailing phenomena.

Table 1: Reduction charge of samples exposed at 28% RH, mC/cm².

UV Intensity, mW/cm ²	0	1.1	2	3.5	4.7
360 ppb ozone	2.6	27.5	17.8	13.7	8.4
600 ppb ozone	2.0	60.7	53.0	80.0	71.3
2000 ppb ozone	45.0	220.0	217.5	188.0	233.5

Table 2: Reduction charge of samples exposed at 58% RH, mC/cm².

UV Intensity, mW/cm ²	0	1.1	2	3.5	4.7
360 ppb ozone	7.5	13.3	11.7	11.1	6.3
600 ppb ozone	8.8	13.4	14.1	20.4	20.3
2000 ppb ozone	15.0	18.7	26.3	30.1	30.3

Table 3: Reduction charge of samples exposed at 87% RH, mC/cm².

UV Intensity, mW/cm ²	0	1.1	2	3.5	4.7
360 ppb ozone	9.8	7.5	2.6	3.2	3.2
600 ppb ozone	17.8	9.3	7.6	8.1	6.7
2000 ppb ozone	27.5	17.8	16.5	17.2	14.4

XRD analysis showed that silver oxide as well as silver chloride formed during exposure at 58% and 28% RH, while there was still residual NaCl left on samples after exposure. The critical deliquescence relative humidity of NaCl is 75% [4]. Below it, no aqueous NaCl layer forms on Ag so that mobile Cl⁻ is limited. Therefore silver oxide forms and is stable during exposure. This result predicts that formation of silver oxide or silver sulfate (which are not thermodynamically as favored as silver chloride) is possible in a location where there is low chloride deposition or that is very dry. Analysis of field samples proved this prediction.

CONCLUSIONS

The combined effects of ozone, UV and NaCl on atmospheric corrosion of Ag have been studied by laboratory exposures. The effect of UV is a combination effect of photolysis of ozone and photodecomposition of silver corrosion products. The corrosion rates of Ag and the corrosion products are different at different relative humidity. Formation of silver oxide and silver sulfate is possible in field.

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