Atmospheric corrosion effects of HNO_3—Influence of temperature and relative humidity on laboratory-exposed copper

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Abstract

The effect of HNO_3 on the atmospheric corrosion of copper has been investigated at varied temperature (15–35 °C) and relative humidity (0–85% RH). Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) confirmed the existence of cuprite and gerhardtite as the two main corrosion products on the exposed copper surface. For determination of the corrosion rate and for estimation of the deposition velocity (V_d) of HNO_3 on copper, gravimetry and ion chromatography has been employed. Temperature had a low effect on the corrosion of copper. A minor decrease in the mass gain was observed as the temperature was increased to 35 °C, possibly as an effect of lower amount of cuprite due to a thinner adlayer on the metal surface at 35 °C. The V_d of HNO_3 on copper, however, was unaffected by temperature. The corrosion rate and V_d of HNO_3 on copper was the lowest at 0% RH, i. e. dry condition, and increased considerably when changing to 40% RH. A maximum was reached at 65% RH and the mass gain remained constant when the RH was increased to 85% RH. The V_d of HNO_3 on copper at $\geqslant 65\%$ RH, 25 °C and 0.03 cm s^{-1} air velocity was as high as 0.15±0.03 cm s^{-1} to be compared with the value obtained for an ideal absorbent, 0.19±0.02 cm s^{-1}. At sub-ppm levels of HNO_3, the corrosion rate of copper decreased after 14 d and the growth of the oxide levelled off after 7 d of exposure.
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1. Introduction

Air pollutants together with moisture are key contributors to atmospheric corrosion, and their corrosivity depends largely on their surface reactivity and the deposition velocity on the material. As soon as a pure metal surface is exposed to humidity, it will be immediately covered with a thin layer of water, which provides a medium for dissolving the pollutant. The dissolved corrosive gases serve as an electrolyte for corrosion reactions on the metal surface and corrosion is initiated by an electrochemical mechanism. The thickness of the water layer depends on factors such as the surface roughness, relative humidity (RH) and temperature (Leygraf and Graedel, 2000).

In ambient environment, the effect of temperature on atmospheric corrosion is hard to predict. Although an increased temperature accelerates the chemical reaction activity, it does not necessarily

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increase the corrosion rate. For example, as a surface is exposed to sunlight the temperature increases and the surface dries, reducing the corrosion. However, a higher temperature can also increase the condensation of an aqueous film and enhance the corrosion (Jones, 1996).

In the field of atmospheric corrosion the effects of pollutants such as sulphur dioxide (SO_2), nitrogen dioxide (NO_2) or ozone (O_3) have been comprehensively investigated (Graedel et al., 1987; Graedel, 1987a, b, 1989; Tidblad et al., 1991; Eriksson, 1992; Svensson, 1995; Tidblad and Kucera, 1996; Strandberg, 1997; Weissenrieder, 2003; Chen 2005; Tidblad et al., 2005). The role of NO_2 on corrosion of copper was investigated extensively by Tidblad and Leygraf (1995) and Oesch and Faller (1997). However, so far very little effort has been dedicated to research on the effects of the secondary pollutant nitric acid (HNO_3). The high sticking coefficient of this gas, lack of commercial analytical instruments for continuous concentration measurements and its relatively low ambient concentrations (Ferm et al., 2005) may be reasons why this gas has been so little studied.

HNO_3 is formed mainly by reaction of NO_2 with the hydroxyl radical (OH•) (Grosjean and Bytnerowicz, 1993), and its high daytime and low night time concentration is consistent with the involved photochemical processes (Bytnerowicz et al., 2005).

There are a few reports on HNO_3-induced atmospheric corrosion effects on the deterioration of calcareous stones (Lipfert, 1989; Haneef et al., 1992; Kirkitsos and Sikiotis, 1995, 1996; Fenter et al., 1995). The only laboratory investigations so far reported on corrosion effects of HNO_3 on metals are, to our knowledge, our previous work presented in a series of articles. In the first paper, in this series, a new method was developed and successfully tested for the atmospheric corrosion effects of HNO_3 on laboratory-exposed copper (Samie et al., 2005). In the preceding paper, results were presented of the influence of HNO_3 concentration and air velocity on the corrosion of copper (Samie et al., 2006a, b). The aim of the present study was to investigate the role of temperature and humidity in the presence of sub-ppm levels of HNO_3 on the atmospheric corrosion of copper, using the same experimental set-up and techniques as in the previous papers.

This work is a part of an EU project entitled MULTI-ASSESS with the main aim to estimate dose–response functions suitable for the combined effects of pollutants and climate parameters on corrosion and soiling of significant materials in cultural heritage objects, e.g. copper, zinc, painted steel, glass and limestone. For further details on this project see Kucera et al. (2006). In a future article, results on the corrosion effects of HNO_3 on copper, zinc, carbon steel and Portland limestone will be compared with each other and also with reported results on their corrosion rate in presence of other pollutants, e.g. SO_2, NO_2 and O_3.

2. Experimental

The experimental technique was described in detail previously (Samie et al., 2005); however, for completeness a shorter description is given here below.

2.1. Sample preparation and exposure

Copper sheet (1 mm), with a minimum copper content of 99.99%, were cut to shape of 10 mm × 50 mm and a hole was drilled for suspending the sample vertically on a glass rod in the exposure chamber. The copper samples were polished with SiC-paper in ethanol to 2400 mesh, degreased twice in acetone using ultrasonic agitation and dried with a hairdryer. The samples were after the preparation stored in a desiccator at least 1 d and at most 4 d before being introduced in the exposure chamber. Immediately before and after exposure, the coupons were weighed with a microbalance with a precision of $\pm 2.0 \, \mu g$ ($\pm 0.2 \, \mu g \, cm^{-2}$).

The experimental conditions are summarized in Table 1. The relatively high concentrations were used to obtain measurable corrosion rates and also to enable comparison with studies of other corrosive gases performed.

The HNO_3 source was a temperature- and pressure-controlled permeation tube (Kin-Tek, La Marque, TX). Perfluoroalkoxy (PFA) Teflon fitting and tubing was used to connect the HNO_3 source to the mixing chamber and exposure chamber to minimize HNO_3 adsorption (Neuman

Table 1
Exposure conditions

Exposure time (h)	$(48–336) \pm 0.1$
Temperature (°C)	$(15–35) \pm 0.5$
[HNO_3] ($\mu g \, m^{-3}$)	$(80–400) \pm 20$
RH (%)	$(0–85) \pm 4$
Flow rate ($cm^3 \, min^{-1}$)	600 ± 5
Air velocity ($cm \, s^{-1}$)	0.03