A LABORATORY STUDY OF CORROSION REACTIONS ON STATUE BRONZE

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Abstract—The initial stages of the atmospheric corrosion of statue bronze in the presence of sub-ppm concentrations of SO₂ and NO₂ were studied in the laboratory. Trace amounts of NaCl were added, *ex situ*, to the samples prior to exposure to the corrosive atmosphere. Polished and artificially patinated samples were studied. It was concluded from the laboratory studies that NO₂ is more corrosive towards the bare bronze surface as compared with SO₂. A large increase in the rate of corrosion of polished samples was observed upon exposure to an SO₂ + NO₂-containing atmosphere, as compared with exposure to the single gas atmospheres. A similar synergistic effect was seen on polished samples, pretreated with NaCl, exposed to NO₂. Deposition rates of SO₂ and NO₂ were followed in real time by continuous monitoring of the inlet and outlet gas concentrations. HNO₂(g) was evolved from the surface of polished samples exposed to NO₂-containing atmospheres.

INTRODUCTION

THE CORROSION of copper and bronze monuments has been studied by several workers. In recent years there has been an increasing interest in these matters. This interest is mainly due to the increased awareness of modern air pollution damages to the physical cultural heritage. In 1987 a special issue of *Corrosion Science*¹ was devoted to this topic. In addition a conference, "Dialoge 89",² was arranged in Baltimore where this subject was discussed. In these two publications references can be found to almost all international publications on these matters up until 1989.

The aim of the present work is to contribute to a better understanding of the main reaction mechanisms of SO_2 and NO_2 , at sub-ppm concentrations, on statue bronze subjected to atmospheric corrosion. The work was performed as a set of laboratory exposures with exposure times ranging from 24 h to 12 weeks. During the exposures known amounts of SO_2 and NO_2 have continuously been added to flowing purified air. The experiments were performed at constant relative humidity of 90%. Various gases have been analysed for at the outlet of the reaction chamber. Corrosion rates have been measured and solid corrosion products identified.

The material studied was commercial statue bronze. The samples tested had been subjected to different surface treatments prior to exposure. Bare metallic surfaces and artificially patinated samples were used in the exposures. Sets of samples with known surface concentrations of NaCl were also included in the investigation.

The work is part of the research programme concerning degradation of the physical cultural heritage, which is coordinated and financed by the Central Board of

Manuscript received 10 February 1992; in revised form 23 December 1992.

National Antiquities in Sweden. It was coordinated with research work being performed within the EUROCARE project COPAL.

EXPERIMENTAL METHOD

Materials studied

The material studied was a commercial statue bronze with the following alloying elements apart from copper: 5.64Zn, 5.51Pb, 4.5Sn, 0.53Ni, 0.14Fe, 0.11Sb and P < 0.01. From this alloy samples with the dimensions $37 \times 17 \times 2.6$ mm were made (geometrical area = 15.4 cm²). Two different surface treatments were studied, polishing and artificial patination. The samples were prepared in the following way.

Polished samples. The specimens were polished on SiC-paper in ethanol to 1000 mesh. They were then repeatedly washed in ethanol using ultrasonic agitation and finally dried in air at room temperature. After drying the samples were kept in a desiccator until the start of the exposures. The samples exposed for 4 weeks were kept in a desiccator for 24 h while the samples used in the deposition studies were stored in a desiccator for 3 h.

Patinated samples. The polished specimens were treated by a professional patineur. Two different patination treatments were included:

- Green patination on bare bronze, using copper nitrate solution.
- Dark green patination using the same procedure as above on a bronze surface which had first been darkened with potassium sulphide solution.

The samples were equilibrated in clean air at 89% R.H. $(ZnSO_4 \cdot 7H_2O(s) + ZnSO_4(aq) at 22^{\circ}C)$ prior to exposure since it was expected that the patinated samples would absorb water from the test atmosphere (R.H. = 90%). According to this procedure we were able to differentiate the mass gain due to water absorption from that due to chemical reactions.

The influence of NaCl on the atmospheric corrosion of the material was studied by adding NaCl(s) to the surface. The chloride treatment consisted of spraying the samples with a 90% ethanol solution saturated with NaCl. The samples were then dried in air at room temperature. 6 ± 1 and $30 \pm 3 \mu g$ NaCl(s) per square centimetre were added to the surface of the samples. The larger amount of NaCl(s) was only added to samples used in the short-time exposures. It can be noted that the smaller ($6 \mu g \text{ cm}^{-2}$) amount of chloride added to the surface is of the same magnitude as that which is left from fingerprints on a handled metal surface.³

Types of exposures

The exposures performed can be divided into two categories:

- 4-week exposures of samples after which corrosion attack and corrosion products have been studied.
- 24-h exposures during which the nature of the NO₂, SO₂ and NaCl reactions on the bronze surface are elucidated by monitoring the deposition rates of the gaseous pollutants. The details of the two different experimental set-ups used have been described in detail previously.^{4,5} Therefore only the outlines are given below.

Four-week exposures. Four-week exposures were performed in an apparatus of the kind depicted in Fig. 1. It is made entirely of glass and Teflon. There are eight parallel corrosion chambers made of glass, each with a volume of 0.41 and an inner diameter of 55 mm. The chambers are submerged in a thermostatically controlled water tank with a volume of 2401. The experiments were performed at 295.15 \pm 0.03 K. Each sample is placed in a chamber of its own in order to prevent interactions between different samples. The test atmosphere is produced from dried and purified air to which corrosive gases can be added in a controlled way. The relative humidity is obtained by mixing dry and humidified air. The experiments reported here were performed at 90% R.H. Relative humidity was constant within \pm 0.3% during the experiments. The corrosive gases are added by allowing a part of the dry air to pass over permeation tubes containing the pollutant(s) studied. During a typical 4-week exposure the concentrations of the pollutants were constant to within \pm 1%. The concentrations of SO₂ and NO₂ used in the experiment were 0.48 and 0.54 ppm respectively. For analytical purposes SO₂(g) was absorbed, from the test atmosphere after passing the reaction chamber, in 1% H₂O₂ and determined as sulphate by Reversed-Phase Ion Pair Chromatography (RP-IPC) (3D HPLC system, Perkin-Elmer). The error in



FIG. 1. Experimental set-up used for 4 weeks exposure. (1) Molecular sieve preceded by air drier and activated carbon filter, (2) needle valves, (3) humidifier, (4) vessels for SO₂ and NO₂ permeation tubes, (5) mixer, (6) heat exchanger, (7) corrosion chambers, (8) absorption flasks, (9) solenoid valves, (10) thermostatted water tank.

these analyses was $\pm 1\%$ while sensitivity was about 5×10^{-9} moles. The amounts of SO₂ deposited on the samples were calculated as differences from one of the chambers which was kept empty.

The samples were weighed on a balance outside the chamber once a week. This procedure took about 10 min. The scatter in the weight measurements were $\pm 2 \times 10^{-6}$ g cm⁻².

After the exposure was completed the samples were examined by optical microscopy and FT-IR spectroscopy (KBr and *ex situ* FT-IRAS (Fourier Transform Infrared Reflection-Absorption Spectroscopy) techniques). The spectrometer used was a Perkin–Elmer 1800 Fourier Transform Infrared Spectrometer. Corrosion products were studied by X-ray powder diffraction, using a Guinier camera together with a computerized photoscanning system.⁶ It should be noted that in some cases weak reflections which were visible only to the naked eye were added to the data obtained by the photoscanner.

The corrosion attacks were evaluated as the mass difference between an unexposed sample and an exposed sample from which the corrosion products have been removed by pickling. For the pickling the following procedure was used:

- (I) Immersion in: 3M HCl (1 min);
- (II) Immersion in: Milli-Q water $(3 \times 15 \text{ s})$;
- (III) Immersion in: 3M HClO₄ (1 min);
- (IV) Immersion in: Milli-Q water $(3 \times 15 \text{ s})$;
- (V) Rinsing with 99.5% ethanol (30 s).

The pickling procedure was performed at room temperature. Ultrasonic agitation was used in all steps. All pickling solutions were de-aerated with N₂(g) prior to the pickling. The samples were dried in air at room temperature and put in a desiccator until weighing. This pickling procedure was tested and found to cause no measurable metal loss on unexposed samples ($<2 \times 10^{-6}$ g cm⁻²).

Deposition studies. Deposition studies were performed in an on-line gas analysis apparatus (Fig. 2). The studies comprised deposition of NO_2 and SO_2 and formation of gaseous reaction products, NO and HNO_2 , from NO_2 and SO_2 reactions on the sample surface. The concentrations of SO_2 and NO_2 were 0.47 and 0.63 or 0.50 ppm, respectively. The exposure time was 24 h. The bronze samples were suspended on a nylon string in the middle of the chamber with the gas flow direction parallel to the sample. The preparation of the synthetic gas mixture and the construction material are both the same as in the

apparatus briefly described above. The corrosion chamber had an inner diameter of 28 mm and was thermostatted at 295.15 \pm 0.03 K. The gas flow rate was 16.7×10^3 mm³ s⁻¹ resulting in a wind speed of 27 mm s⁻¹ in the exposure chamber. The flow conditions were laminar in the cell ($R_e \approx 50$). The gas flowed through the apparatus in such a way that it reached the analysers within 15 s after it had been mixed. It was then simultaneously analysed for SO_2 , NO_x and NO throughout the experiments. SO_2 was analysed for by the use of a fluorescence instrument (Environment AF21M). NO and NO_x were analysed for by using an instrument based on chemiluminescence (Environment AC 30M). The sensitivities of the instruments were 0.001 and 0.002 ppm, respectively. Both instruments had a time constant of 1 min and were connected in parallel in such a way that half the total flow was directed through each analyser. The SO_2 deposition on the samples was calculated from the decrease in the SO₂ concentration in the gas flowing through the exposure chamber. The evolution of $HNO_2(g)$ was measured using the NO-NO_x analyser, which is sensitive to NO_2 together with NO, HNO_2 and HNO_3 . All four species are analysed as NO_x by the instrument. In order to distinguish between HNO₂ and the other gases, a denuder tube coated with Na₂CO₃ was employed using the method developed by Ferm and Sjödin.⁷ Sampling for HNO₂(g) was performed after 3 and 24 h of exposure. Sampling time was 50 min. Decrease in the signal from the NO_x unit during the exposure was interpreted as resulting from formation of nitrite and nitrate on the sample surface.

EXPERIMENTAL RESULTS AND DISCUSSION

Four weeks exposure

Polished samples. The metal loss and mass gain of samples exposed to NO_2 and SO_2 -containing atmospheres are summarized in Table 1. The last column of Table 1 gives the ratio of the mass of the corrosion products (mass gain + metal loss) divided by the mass of corroded metal (metal loss). In Table 2 corresponding values are given



FIG. 2. Experimental set-up used for deposition studies of NO₂ and SO₂.

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Environment	Mass gain (cm ⁻²)	Metal loss (mg cm ⁻²)	Mass of corrosion products/ mass of bronze corroded
SO ₂	0.035	0.086	1.41
NO ₂	0.021	0.153	1.14
$SO_2 + NO_2$	0.392	0.621	1.63
$1.6 \text{ ppm NO}_2 + 1.3 \text{ ppm SO}_2^*$	2.673	2.831	2.06
NaCl	0.034	0.136	1.25
$SO_2 + NaCl$	0.069	0.174	1.40
$NO_2 + NaCl$	0.153	0.538	1.28
$NO_2 + SO_2 + NaCl$	0.416	0.688	1.60
$1.6 \text{ ppm NO}_2 + 1.3 \text{ ppm SO}_2 + \text{NaCl}^*$	2.638	2.775	2.04

TABLE 1. MASS GAIN AND METAL LOSS DATA FOR POLISHED BRONZE SAMPLES EXPOSED TO NaCl ($6 \mu g \text{ cm}^{-2}$), 0.48 ppm SO₂(g) and 0.54 ppm NO₂(g) at 90% R.H. for 4 weeks (The mass of NaCl is excluded in the total corrosion product mass)

*Exposure time = 88 days.

TABLE 2. MOLECULAR MASS OF CORROSION PRODUCTS / MOLECULAR MASS OF METAL FOR SELECTED CORROSION PRODUCTS OF Cu, Pb and Zn

Corrosion products of Cu, Pb and Zn	Molecular mass of corrosion products / Molecular mass of metal
Cu ₂ O	1.13
$Cu_{2.5}^{-}(OH)_3SO_4 \cdot 2H_2O$	2.15
Cu ₃ (OH) ₄ SO ₄	1.86
$Cu_4(OH)_6SO_4$	1.78
$Cu_2(OH)_3NO_3$	1.89
PbSO ₃	1.39
PbSO ₄	1.46
ZnO	1.25
ZnSO ₄ ·7H ₂ O	4.40
$Zn(OH)_6SO_4$	2.03

(total mass divided by mass of metal in the compound) for selected corrosion products of Zn, Pb and Cu. Figure 3 shows the mass gain during the exposure of samples exposed to atmospheres containing pure air, SO_2 and NO_2 at 90% R.H. Figures 4–6 show the corrosion attack on polished bronze in NO_2 and SO_2 -containing atmospheres. The horizontal bar in the Figs 4–6 corresponds to 0.2 mm. The influence of NaCl on the metal loss and mass gain of the samples is summarized in Table 1 and Fig. 7.

(1) Exposures without chloride. After exposure to an atmosphere with only SO_2 added, the samples appeared almost unaffected upon visual examination. The only signs of corrosive attack were some spots of oxide and small crusts located on top of these oxides (Fig. 4). By use of FT-IRAS, cuprite and trace amounts of zinc oxide and sulphates were identified.

The ratio in Table 1, 1.41, is in agreement with a mixture of oxide and sulphate. The samples, which were exposed to an atmosphere with only NO_2 added, were



FIG. 3. Atmospheric corrosion of polished bronze exposed to 0.48 ppm SO₂ and 0.54 ppm NO₂ at 90% R.H. for 4 weeks.

seemingly more corroded than those exposed to the SO_2 containing atmosphere. Spots of oxide sparsely spread on the surface were seen using optical microscopy (Fig. 5). Cuprite and trace amounts of water soluble nitrates were identified by the use of *ex situ* FT-IRAS and RP-IPC, respectively. The measured ratio, corrosion products mass/corroded mass of bronze, listed in Table 1 is close to the value of cuprite.

Exposure to an atmosphere containing both SO_2 and NO_2 increased the corrosion rate markedly. The distribution of corrosion products seen in Fig. 6 indicates that the surface has been covered with an electrolyte layer which has later been dried up. The corrosion rate was 4 and 7 times higher (Table 1) than in NO_2 and SO_2 containing atmospheres, respectively. Cuprite, $PbSO_3$ and trace amounts of nitrate and $Zn_4(OH)_6SO_4$ ·5H₂O were identified using XRD and FT-IR. A similar basic sulphate has been identified on zinc samples exposed to $SO_2 + NO_2$ -containing atmosphere at 95% R.H. using the same experimental arrangement.⁸ The high ratio in Table 1 is in accordance with a corrosion product consisting chiefly of a mixture of sulphates, sulphites and nitrates.

(2) *Exposures with chloride on the samples*. The corrosion rate of samples pretreated with NaCl in pure air is of the same order as in the single gas experiments, cf. Table 1. Cuprite and zincite were identified on the surface after the experiments using FT-IR spectrometry. The amount of chloride added to the surface was too small to be detected using XRD.

The corrosion rate with NaCl on the sample surfaces in an atmosphere containing SO_2 was slightly higher than in a pure NaCl environment (Table 1). Cuprite and trace amounts of sulphate and zincite were identified in the corrosion products.

A strong synergistic effect was seen when NO_2 and NaCl were simultaneously present in the test. The corrosion rate was about three times higher than that observed in the environment containing SO_2 and NaCl. Basic copper nitrate, gerhardite ($Cu_2(OH)_3NO_3$) and cuprite were identified in the corrosion products by using XRD. According to the low ratio in Table 1 the corrosion product seems to consist of a mixture of the identified compounds.

Adding NaCl to the samples prior to exposure to an atmosphere containing both SO_2 and NO_2 did not change the corrosion attack markedly compared with conditions without chloride, cf. Table 1. The corrosion products were practically the

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Fig. 4. Polished bronze exposed to 0.48 ppm SO₂ at 90% R.H. for 4 weeks. (Horizontal bar corresponds to 0.2 mm.)

- Fig. 5. Polished bronze exposed to 0.54 ppm NO₂ at 90% R.H. for 4 weeks. (Horizontal bar corresponds to 0.2 mm.)
- Fig. 6. Polished bronze exposed to 0.48 ppm $SO_2 + 0.54$ ppm NO_2 at 90% R.H. for 4 weeks. (Horizontal bar corresponds to 0.2 mm.)



FIG. 7. Atmospheric corrosion of polished bronze exposed to 0.48 ppm SO₂ and 0.54 ppm $^{-1}$ NO₂ at 90% R.H. for 4 weeks. 6 μ g NaCl cm⁻² was added to the samples prior to SO₂-exposure.

same as were found in the absence of chloride. An additional trace amount of lead sulphate was the main difference. The measured ratio of corrosion product mass/ corroded mass of bronze was about the same as in the absence of NaCl (Table 1) suggesting that the presence of chloride did not significantly change the composition of corrosion products.

(3) Exposure using higher concentration of SO_2 and NO_2 . An experiment using higher pollutant concentrations, 1.6 ppm NO_2 and 1.3 ppm SO_2 was performed in order to enhance the corrosion of the material. The exposure time in this study was expanded to 88 days.

Antlerite, $Cu_3(OH)_4SO_4$, PbSO₃ and $Zn_4(OH)_6SO_4 \cdot 4H_2O$ were identified in the corrosion products. The presence of more basic sulphates after prolonged exposure time is in accordance with the results of Ericsson and Sydberger.⁹ It was suggested that normal copper sulphate was a precursor in the SO₂-induced corrosion of copper while the ratio, nOH-/nCu, in the sulphates formed increased with exposure time, resulting in the formation of antlerite and brochantite.

The addition of NaCl to the surface prior to exposure did not change the corrosion rate significantly. In these conditions a recently characterized basic copper sulphate, $Cu_{2.5}(OH)_3SO_4 \cdot 2H_2O$,¹⁰ was formed in addition to the phases found in the absence of chloride. Its diffraction pattern was similar to that of the so called "phase I" reported by Ericsson and Sydberger.⁹

Patinated samples. The composition of the artificially produced patina was analysed using XRD. Basic copper nitrate, $Cu_2(OH)_3NO_3$, was found in the patina produced using copper nitrate solution. In addition to this basic copper nitrate, lead sulphite was identified in the artificial patina present on samples treated with potassium sulphide solution prior to the copper nitrate treatment.

Figures 8 and 9 show the mass gain curves of the patinated samples exposed to SO_2 -containing atmosphere in the presence or absence of NaCl.

The exposures started without SO_2 addition at 89% R.H. and continued for 60 days. As can be seen in the figures, constant mass of the samples was not achieved even after such a long equilibration time. Water loosely bound to the surface and maybe nitrogen containing species were evaporating from the sample surface during

this exposure. The start of SO₂-exposures is indicated by the arrows in Figs 8 and 9. No metal loss determinations were attempted due to the fact that the artificial patination treatments had a corrosive influence on the samples. The scatter in mass gain between samples pre-treated in the same way was significant. The spread in the mass gain data probably reflects differences in the manual handing of the samples during the patination procedure. No significant difference in mass gain between the two different patination procedures could be seen upon exposure to the SO₂-containing atmosphere.

The amounts of SO_2 deposited on the samples are summarized in Table 3. During the first 2 weeks of exposure twice as much SO_2 was deposited on nitrate patinated samples as compared with sulphide plus nitrate patinated samples. The rate of SO_2 deposition soon levelled off and was towards the end of the exposure approximately the same for the two kinds of patinated surfaces.

Lead sulphite and trace amounts of lead sulphate were detected on the surface of the samples patinated with nitrate after exposure to the SO_2 -containing atmosphere. After exposure to the same atmosphere antlerite was found on surfaces treated with sulphide and nitrate.

The addition of NaCl to samples treated with nitrate only caused a mass gain that seems to be somewhat larger than the scatter between the patinated samples without the addition of NaCl. No significant increase in weight due to the presence of NaCl could be detected on samples patinated with sulphide and nitrate. However, the NaCl addition accelerated the SO₂-deposition rate on all prepatinated samples (Table 3). This influence decreased with time of exposure.

The corrosion products formed on nitrate treated samples exposed to NaCl and $SO_2(g)$ did not significantly differ from the products formed in the absence of chloride. Using XRD brochantite was identified on samples where nitrate and sulphide were used in the prepatination step.

Deposition studies

Polished samples. The deposition rate of SO_2 on polished bronze in SO_2 and SO_2 + NO_2 -containing atmospheres in the absence and presence of NaCl is shown in Figs 10 and 11, respectively. The consumption of NO_2 in the NO_2 containing environ-



FIG. 8. Atmospheric corrosion of *copper nitrate* patinated bronze samples after preexposure for 60 days in clean air at 89% R.H. After this pre-exposure the samples were exposed in flowing air containing 0.48 ppm SO₂ at 90% R.H. Two of the samples (E, F) were added with NaCl(s).



FIG. 9. Atmospheric corrosion of *copper nitrate + potassium sulphide* patinated bronze samples after pre-exposure for 60 days in clean air at 89% R.H. After this pre-exposure the samples were exposed in flowing air containing 0.48 ppm SO₂ at 90% R.H. Two of the samples (E,F) were added with NaCl(s).

TABLE 3.	SO_2 -deposition on copper nitrate patinated and copper nitrate + potassium
SULPHIDE	PATINATED SAMPLES IN THE PRESENCE AND ABSENCE OF NaCl(s). EXPOSURE ATMOS-
	PHERE: $0.48 \text{ ppm SO}_2 \text{ and } 90\% \text{ R.H.}$

Accumulated amounts of SO_2 deposited on the sample surface during the first 2 weeks of exposure (the SO_2 deposited is expressed as % of the total amount of SO_2 supplied)			
Patina	μ g NaCl cm ⁻²	SO ₂ -deposition (%)	
Copper nitrate	6	48	
Copper nitrate		41	
Copper nitrate + potassium sulphide	6	30	
Copper nitrate + potassium sulphide		21	

Accumulated amounts of SO_2 deposited on the surface during the last 2 weeks of exposure (the SO_2 deposited is expressed as % of the total amount of SO_2 supplied)

Patina	μ g NaCl cm ⁻²	SO ₂ -deposition (%)
Copper nitrate	6	14
Copper nitrate	—	7
Copper nitrate + potassium sulphide	6	12
Copper nitrate + potassium sulphide		7

ments studied is summarized in Table 4. As can be seen in the table $HNO_2(g)$ was formed in all NO_2 -containing atmospheres.

(1) Exposures without chloride. The deposition rate of SO_2 , in the absence of NO_2 , was initially fast but decreased with exposure time and soon reached a constant rate.

Upon exposure to an NO₂-containing atmosphere $HNO_2(g)$ forms at a fairly constant rate (Table 4). In this way about 2% of the NO₂ is converted into HNO_2 .

Exposure to an atmosphere containing both NO_2 and SO_2 increased the depo-

sition rate of SO₂. Almost twice the amount was deposited compared with exposure to SO₂ only. The formation rate of HNO_2 in SO₂+NO₂-containing atmosphere was also twice that observed in the absence of SO₂. These estimations were based on the deposition and formation rates obtained towards the end of the experiments.

The reaction of SO_2 with NO_2 on a metal surface has been studied earlier. The formation of HNO_2 by reaction on gold surfaces has recently been reported by Eriksson and Johansson,⁵ e.g.

$$SO_2 + 2NO_2 + 2H_2O = 2H^+ + SO_4^{2-} + 2 HNO_2.$$
 (1)

It is proposed that a similar reaction is occurring on the bronze surface as indicated by the increased rate of NO_2 reduction and SO_2 oxidation registered when both trace gases are combined. The sulphuric acid formed in reaction (1) will tend to increase the corrosion rate of the bronze by dissolving the passive layer on the alloy and forming a solution of hygroscopic metal sulphate. The metal ions in this solution can be expected to be chiefly copper and zinc. Lead forms sparingly soluble sulphate and tin can be expected to form amorphous oxide ("stannic acid"). This later expectation is based on general knowledge of corrosion of tin bronze objects and the fact that no crystalline tin species have been identified in the present work with the analytical methods used.

(2) Exposures with chloride. In the experimental conditions (90% R.H., 22°C) NaCl forms an aqueous solution on the sample surface (the deliquescence point of NaCl at 22°C being 75.2% R.H.).¹¹ It was expected that SO₂ would dissolve in this surface film:

$$SO_2(g) = SO_2(aq)$$
 $K = 1.24 \text{ mole } l^{-1} \text{ atm}^{-1} \text{ }^{12}$
 $SO_2(aq) + H_2O = H^+(aq) + HSO_3^-(aq)$ $pK_a = 1.91 \pm 0.02.^{13}$

In order to study the absorption of SO_2 by such a surface film on an unreactive substrate a glass specimen with the same dimensions as the bronze samples and covered with 30×10^{-6} g cm⁻² of NaCl(s) was introduced into the test chamber. No measurable amounts of SO₂ were deposited on the sample since the SO₂ signal was unaffected by the introduction of the sample into the test atmosphere.



Time (h)

FIG. 10. Deposition rate of SO₂ on polished bronze as a function of time. R.H. = 90%. The SO₂ and NO₂ concentrations used were 0.47 ppm and 0.63 ppm, respectively.



FIG. 11. Deposition rate of SO₂, in the presence of NaCl (6 and $30 \,\mu g \, \text{cm}^{-2}$), on polished bronze as a function of time. R.H. = 90%. The SO₂ and NO₂ concentrations used were 0.47 ppm and 0.63 ppm, respectively.

Table 4. NO₂-consumption on the surface of polished bronze after 3 and 24 h exposure. Evolution of $HNO_2(g)$ and NO(g) and the formation of NO_2^- and NO_3^- is expressed within the parentheses. (The formation of the species is expressed as % of the total amount of NO_2 supplied)

	Exposure time		
Environment	3 h	24 h	
0.63 ppm NO ₂ 0.63 ppm NO ₂ + 0.47 ppm SO ₂	2% (HNO ₂) 8% (HNO ₂)	2% (HNO ₂) 4% (HNO ₂)	
0.63 ppm NO ₂ + $6 \mu g \text{ NaCl cm}^{-2}$	14% (7% NO ₃ ⁻ + NO ₂ ⁻ 4% HNO ₂ 3% NO)	7% (3% NO ₃ ⁻ + NO ₂ ⁻ 3% HNO ₂ 1% NO)	
$0.63 \text{ ppm NO}_2 + 0.47 \text{ ppm SO}_2 + 6 \mu\text{g NaCl cm}^{-2}$	23% (3% NO ₃ ⁻ + NO ₂ ⁻ 18% HNO ₂ 2% NO)	5.5%(-NO ₃ ⁻ + NO ₂ ⁻ 5% HNO ₂ <0.5% NO)	
0.63 ppm NO ₂ + 0.47 ppm SO ₂ + $30 \mu g \text{ NaCl cm}^{-2}$	37% (28% NO ₃ ⁻ + NO ₂ ⁻ -% HNO ₂ 9% NO)	$19\%(4\% \text{ NO}_{3}^{-} + \text{NO}_{2}^{-})$ 9% HNO ₂ 6% NO)	

In contrast, the addition of NaCl ($6 \mu g \text{ cm}^{-2}$) to a bronze sample caused a large increase in the SO₂ deposition rate compared to samples with no NaCl (Figs 10 and 11). The rate of deposition decreased with time, however, after 24 h it was still about 3 times greater than in the absence of NaCl. Increasing the amount of NaCl ($30 \mu g \text{ cm}^{-2}$) on the surface resulted in a higher SO₂ deposition rate. This effect was still seen after 24 h of exposure, indicating that part of the chloride contributed to the electrolyte present on the surface. These results illustrate the fact that the rate of deposition of SO₂ primarily depends on the rate of the reactions (oxidation, neutralisation) that convert SO₂(aq) into other species.

It is suggested that the acceleration of SO_2 deposition seen in the presence of NaCl is connected to the electrochemical corrosion process on the bronze surface. The anodic dissolution of zinc and copper from the metal is balanced by oxygen

reduction (and in NO₂ environments the reduction of NO₂ to form HNO₂(g) or NO₂⁻(aq)). The cathodic reduction of oxygen will tend to increase pH over parts of the surface. In the absence of NaCl the surface film will be buffered because of the precipitation of hydroxy sulphate salts of copper and zinc. In the presence of NaCl, Na⁺(aq) and Cl⁻(aq) will carry a part of the current in the electrolyte. Because of the solubility of Na⁺ ions in alkaline solution high pH may develop in the cathodic areas on the surface. These areas will absorb SO₂(g) readily because of the rapid acid–base equilibria in the sulphurous acid system. As the sodium chloride gradually is incorporated in the solid corrosion product this effect fades away.

Table 4 shows the influence of NaCl on the reactions of NO_2 with bronze. It was found that much greater amounts of nitrite, nitrate and nitrogen monoxide were formed in the presence of NaCl.

It should be emphasized that the corrosive effects of $NO_2 + NaCl$ and $SO_2 + NaCl$ on copper and its alloys are not fully understood and that further work is needed on these systems.

Patinated samples. Figure 12 shows the deposition rate of SO₂ at 90% R.H. on nitrate patinated samples exposed to SO₂, SO₂ + NO₂ and SO₂ + NaCl environments during 24 h of exposure. The slight difference in SO₂-deposition on the patinated surface in the absence and presence of NaCl is in accordance with the findings from the 4-week exposures. Exposure to an atmosphere containing NO₂+SO₂ did not significantly change the SO₂-deposition rate compared with the experiment containing SO₂ only. The SO₂-deposition on the nitrate patina seems to depend on the patina rather than on the corrosive species added.

CONCLUSIONS

The main conclusions with regard to the effects on polished samples are as follows:

- NO₂ has, as a single pollutant gas, a stronger corrosive effect than SO₂.
- Exposure to an NO₂-containing atmosphere gave rise to formation of HNO₂(g).
- There is a strong synergistic effect of NO₂ and SO₂ at 90% R.H.



FIG. 12. Deposition rate of SO₂ on copper nitrate patinated bronze as a function of time. R.H. = 90%. The SO₂ and NO₂ concentrations used were 0.47 ppm and 0.63 ppm, respectively, and the addition of NaCl was $6 \mu g \text{ cm}^{-2}$.

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- Additions of small amounts of NaCl caused a marked increase in the corrosion rate.
- The most profound synergistic effect in the NaCl-experiments was obtained with the combination of NO₂ and NaCl.
- The presence of NaCl on the bronze surfaces increased the deposition rate of NO₂ and resulted in the formation of NO(g) and nitrite and nitrate in the surface electrolyte, apart from HNO₂(g).
- The addition of NaCl gave no significant increase in the corrosion rate in SO₂ + NO₂-containing atmospheres.
- Corrosion products containing copper, zinc and lead but not tin were identified.
- The absence of crystalline tin compounds is probably due to formation of amorphous stannic oxide at the metal surface.

In the concentration range used, the following can be concluded about the patinated samples:

• Lead sulphite formed during one of the patination treatments seemed to provide partial mechanical passivation to the bronze surface.

It is evident that the chemistry of atmospheric corrosion of a technical alloy such as bronze seems to involve several parallel reactions. The situation becomes even more complex for a traditionally surface treated statue bronze. It should be remembered that, although the present study gives insight into reactions which can be expected on outdoor sculptures, it is not advisable to draw direct conclusions regarding the major factors for corrosion on real outdoor sculptures from the present study. This is mainly due to the following factors. The influence of washing by rain is not included in the present study. The present study does not permit conclusions regarding long time effects such as enrichment of stannic oxide on sculpture surfaces.

Acknowledgement—The present work was financed by the Central Board of National Antiquities in Stockholm.

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