Effect of NO$_2$ and/or SO$_2$ atmospheric contaminants and relative humidity on copper corrosion$^{(\bullet)}$

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Abstract
A study has been made of the individual and combined roles of NO$_2$ and SO$_2$ atmospheric contaminants on corrosion and patina formation on copper in humid atmospheres. In most cases the combined effect of the two contaminants has been greater than the sum of their individual effects, although exception have been found with the mixture of 800 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$. XPS analysis has revealed important composition changes in the outermost layer of films formed on copper, depending on the nature of the atmospheric contaminant and humidity level. The presence of sulphates and sulphites has been clearly observed in exposure to atmospheres contaminated with SO$_2$ at 50, 70 and 90 % RH. Nitrates and nitrites have been detected in exposure to NO$_2$ at 50 and 70 %RH, but not at 90 % RH. A hydrogenated nitrogen compound has been detected with the mixture of NO$_2$ and SO$_2$ at 90 % RH .In this atmosphere, a certain inhibiting effect has been seen.

Keywords
Copper. XPS. Humidity. NO$_2$. SO$_2$. Atmospheric corrosion.

Efecto de la humedad relativa y los contaminantes atmosféricos NO$_2$ y/o SO$_2$ en la corrosión del cobre

Resumen
Se ha estudiado el papel de los contaminantes atmosféricos NO$_2$ y SO$_2$ y de una mezcla de ambos, en la corrosión y formación de pátina sobre el cobre expuesto en atmósferas húmedas. Por lo general, el efecto combinado de los dos contaminantes es mayor que la suma de los efectos individuales, aunque se han encontrado excepciones con la mezcla de 800 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$. El análisis por XPS ha revelado cambios importantes en la composición de las películas superficiales más externas formadas sobre el cobre, según la naturaleza del contaminante y nivel de humedad. En la exposición al SO$_2$ se ha revelado la formación de sulfatos y sulfitos a todas las humedades ensayadas (50, 70 y 90 % HR). En la exposición al NO$_2$ se han detectado nitratos y nitritos, pero sólo cuando la humedad atmosférica era del 50 y 70 % RH, y no al 90 % RH. Curiosamente, en la exposición a la mezcla de NO$_2$ y SO$_2$ al 90 % HR se ha detectado la presencia de un compuesto hidrogenado de nitrógeno. En esta atmósfera se ha observado un ligero efecto inhibidor.

Palabras clave
Cobre. XPS. Humedad. NO$_2$. SO$_2$. Corrosión atmosférica.

1. INTRODUCTION

SO$_2$ is one of the corrosion contaminants with the greatest influence on the atmospheric corrosion of metals[1]. Less well known is the role played by NO$_2$ in the atmosphere, this being a precursor of nitric acid and other nitrogenated compounds that participate in materials degradation processes[2-6]. The concentration of nitrogen oxides in the atmosphere can exceed even that of SO$_2$ [7]. In urban atmospheres it is easy to find NO$_2$ levels of up to 120 µg/m^3, with maximum values several times higher[7-10]. Their effects on metallic corrosion seem, in general, to be of little importance, at least up to concentrations of some 500 µg/m^3 [7, 11 and 12]. Several papers have recently been published on the effect of NO$_2$, acting individually or in combination with SO$_2$, on the atmospheric corrosion of copper[7, 9-11 and 13-16]. The humidity content of the air seems to condition the corrosivity of NO$_2$ [17-19]. It even

seems possible that NO$_2$ can have an inhibiting effect, for instance in the case of steel and tin at high RH conditions[7, 20 and 21]. Some results on copper suggest that NO$_2$, in certain mixtures, does not appreciably raise the corrosion rate. However, in other circumstances NO$_2$ considerably increases the corrosion rate of this metal[7].

The scarcity of conclusive results on the effect of NO$_2$ on the atmospheric corrosion of copper justifies the need for further work[22]. To this end, this contribution reports laboratory research into the individual and combined effects of NO$_2$ and SO$_2$ contaminants, and of the air humidity level, on corrosion data and on the constitution of patina layers on copper.

The work will consider contaminated atmospheres at 50, 70 and 90 %RH. The practical case of the formation of visible moisture layers on the metallic surface (e.g. when the dew point is reached or due to the precipitation of moisture in open air exposure), is excluded from the study. The present study is representative of behaviour in indoor atmospheres with humidity values below 100 % RH. In such atmospheres it is only possible for very thin moisture layers to form due to the adsorption of water molecules and capillary and chemical condensation phenomena[23 and 24].

2. EXPERIMENTAL PROCEDURE

2.1. Test conditions

It was decided to work with contaminant concentrations as higher as to give measurable degrees of attack in relatively short testing times, and yet not too much greater than those really found in the atmosphere in order to not modify substantially the mechanisms of attack. Thus a maximum contamination level of 800 µg/m^3 was defined for both NO$_2$ and SO$_2$, which corresponds to peak concentrations in urban atmospheres at times of very high contamination.

A working temperature of 35 ºC ± 1 ºC was selected, this being a value that is easily controllable in the laboratory and similar to many surface temperatures in outdoor exposure conditions. In this way the obtainment of significant data in reasonable time periods was facilitated.

With regard to RH a value of 90 % ± 5 % was defined, typical of very humid atmospheres. Values of 50 and 70 % ± 5 % were also considered, being representative of the air humidity in many outdoor and indoor environments.

Copper was exposed in atmospheres with NO$_2$ and SO$_2$ contaminants, both individually and in combination. Similar tests were carried out in non-contaminated atmospheres for reference purposes.

2.2. Preparation of specimens

Copper specimens of 99.95 % purity and dimensions 10 × 5 × 0.1 cm were used. Their surfaces were prepared by dry polishing on successively finer SiC abrasive papers down to grade 600, degreasing with acetone and washing with detergent, followed by ultrasonic stirring in ethanol for 15 min and drying in a hot air jet. The quality of degreasing was verified by observation of the continuity of a water film on the surface.

Once prepared, the specimens were stored for 24 h in a desiccator over a silica gel. Immediately before testing they were weighed in an analytical balance with sensitivity up to 10 µg. Given that the specimens had a surface area of 100 cm^2, the sensitivity per unit of surface area was 0.1 µg/cm^2.

Five copper specimens were exposed for each exposure condition. Three were used to calculate the mass gain due to corrosion. The other two were used to characterize the corrosion product film formed (patina)[22].

2.3. Exposure to contaminants and mass gain determinations

The specimens were placed in a testing cabinet equipped with a sensorized system of contaminant gas dosing and continuous RH and temperature control. The air flow rate was 1 m^3/h, and thus the total mass inside the cabinet was renewed 8 times every hour, in completely laminar regime conditions. It was decided to use mass gain rather than mass loss determinations, in order to keep to a minimum the operations involving data obtained by weighing in conditions close to the precision limit of the balance.

2.4. Characterization of patinas

Photoelectron spectra were recorded using a Fisons MT500 spectrometer equipped with a hemispherical electron analyzer (CLAM2) and a Mg/Al Ka x-ray dual source operated at 120 W. The samples were mechanically fixed on an XYZ manipulator placed in the analysis cabinet. The residual pressure in this ion-pumped analysis cabinet was maintained below 5 × 10^{-7} Pa during

data acquisition. The spectra were collected for 20-90 min, depending on the peak intensities, at a pass energy of 20 eV which is typical of high-resolution conditions. The intensities were estimated after smoothing and substraction of the S-shaped background and fitting the experimental curve to a mix of Lorentzian and Gaussian lines of variable proportion. Although some sample charging was observed, accurate binding energies could be determined by referencing to the adventitious C1s peak at 285.0 eV. Atomic ratio percentages were computed from peak intensity ratios and reported atomic sensitivity factors[25]. Carbon was not included in the computation of elemental composition because it was only attributable to surface contamination typical of all metallic systems not freshly annealed under vacuum. The high resolution O1s spectra acquired on the copper surfaces were broad and featureless and no attempt was made to computer fit these spectra. A computer curve synthesis procedure was used to separate the individual components of the Cu $2p_{3/2}$, S 2p and N 1s high resolution spectra.

An attempt was made to calculate the thickness of the corrosion products layer on the copper surface using argon ion bombardment (AIB). A high oxygen content was detected on the copper surfaces even after bombardment times of 40 min (removed specimen thickness close to 80 Å). The fact that oxygen does not cease to be present on the copper surface after long bombardment times, probably due to the non-uniform distribution of the corrosion products (in the form of islands, mainly at 70 and 50 %RH), made it impossible to obtain an approximate estimation of the patina thickness.

3. RESULTS AND DISCUSSION

3.1. Humidity without contamination

In a non-contaminated reference atmosphere the copper specimens showed very slight mass gains after 7 d, less than 1 µg/cm². This value rose after 21 and 28 d of exposure to between 2-3 µg/cm².

According to the literature, at ambient temperature copper spontaneously becomes coated with a thin oxide film formed mainly of Cu_2O [17, 26 and 27]. In a humid atmosphere countless local corrosion cells can act on the metallic surface coated by a moisture film which acts as electrolyte[23 and 24]. The reduction of oxygen from the air dissolved in this film to produce hydroxyl

ions is the preferential cathodic process. Hydroxides, hydrated oxides and basic salts are therefore predictable products of atmospheric corrosion.

As was expected, XPS analysis of the non-exposed surface of the copper specimens used in this research showed the preferential presence of cuprous oxide Cu_2O [28-31] as was also found in exposure in non-contaminated atmospheres with 50 and 70 % RH (Fig. 1). Curiously, exposure in the atmosphere with 90 % RH considerably modified this result. Thus, figure 1 shows that after 7 d of exposure the majority oxide had become cupric oxide CuO [28-31] at 90 % RH. Significant amounts of this oxide have also been detected on the surface of patinas obtained after exposing copper in the different contaminated atmospheres studied (Fig. 2). In general, the relationship between the detected amounts of cuprous and
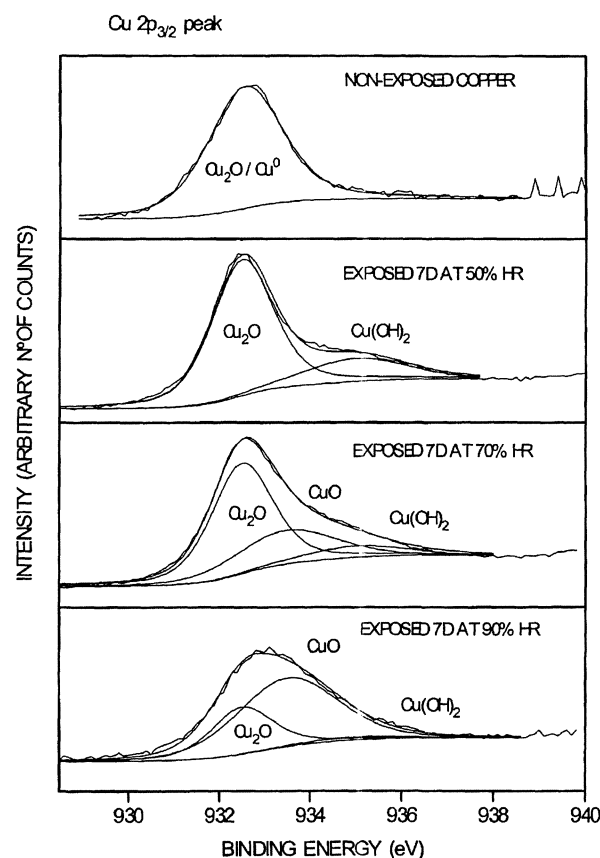

Figure 1. Cu $2p_{3/2}$ high resolution XPS spectra obtained on the outer surface of copper specimens in unexposed state and after 7 d of exposure to unpolluted atmospheres at 50, 70 and 90 % RH.

Figura 1. Espectros XPS de alta resolución Cu 2p₃/₂ obtenidos en la superficie externa de la muestra de cobre no expuesta y después de 7 d de exposición en una atmósfera no-contaminada y el 50,70 y 90 % RH.
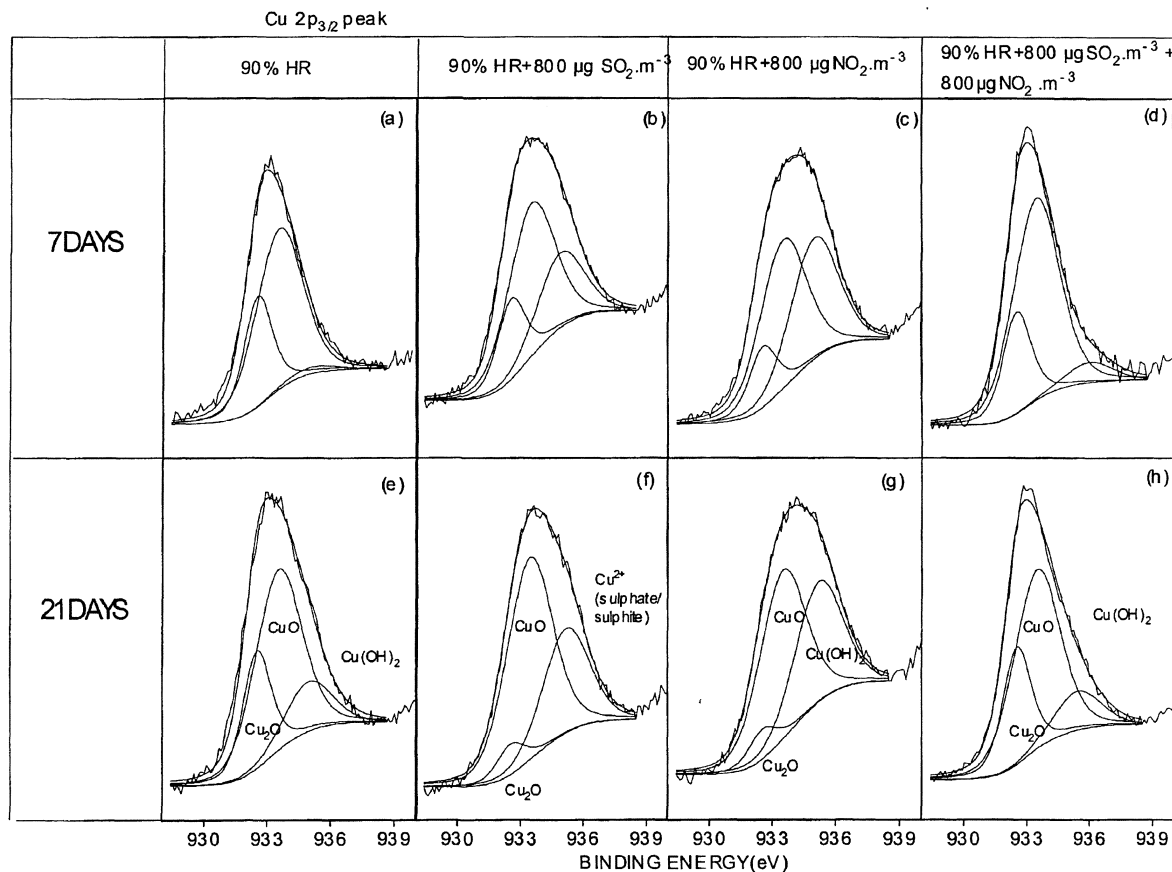
Figure 2. Cu $2p_{3/2}$ high resolution XPS spectra obtained on the outer surface of copper specimens after 7 and 21 d of exposure in atmospheres polluted with 800 $\mu g.m^{-3}$ SO_2, with 800 $\mu g.m^{-3}$ NO_2 and with 800 $\mu g.m^{-3}$ SO_2 +800 $\mu g.m^{-3}$ NO_2 at 90 % RH.

Figura 2. Espectros XPS de alta resolución Cu $2p_{3/2}$ obtenidos en la superficie externa de la muestra de cobre al cabo de 7 y 21 d de exposición en una atmósfera contaminada, con 800 $\mu g.m^{-3}$ SO_2, con 800 $\mu g.m^{-3}$ NO_2 y con 800 $\mu g.m^{-3}$ SO_2 +800 $\mu g.m^{-3}$ NO_2 y el 90 % HR.

cupric oxides seems to depend notably on the air humidity. In figure 1 it can be seen that as the RH of the non-contaminated atmosphere diminishes, so the Cu_2O content tends to rise, while at the same time the CuO content decreases. An increase in exposure time seems to lead to a partial transformation of CuO into $Cu(OH)_2$ [28-31] (Figs. 2a and 2e).

It is important to highlight the clear tendency towards the formation of CuO at the highest of the humidity levels tested (90 % RH). At low RH values the thin film of condensed moisture (electrolyte) on the copper surface must be insufficient for efficient communication between the local anodes and cathodes and for the functioning of the corrosion microcells[23], though this situation could change at humidities close to air saturation.

3.2. Effect of SO_2

In general, the presence of SO_2 gas in the air tends to increase the attack of metals and of copper in particular[23 and 32-34]. There are discrepancies regarding the specific role of SO_2 in this attack and in the composition of the patinas that are formed[2, 35 and 36]. The SO_2 that reaches the copper surface is transformed into sulphurous and sulphuric acids, and there is a notable drop in the pH of the moisture film[11]. Basic sulphites and sulphates, particularly the latter, are often found in patinas after long exposure times[11, 35 and 37-39]. The literature also notes a considerable presence of Cu_2O [11 and 12]. The basic copper sulphate $Cu_4(SO_4)(OH)_6$ is stable at pH > 4.0 [4], and for this reason the patinas can resist a certain acidity of the electrolyte.

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With an air humidity of 90 % RH, the colouring of the patinas formed on the copper specimens exposed in the atmosphere contaminated with 800 µg SO_2/m^3 presented no significant changes compared with those exposed in the non-contaminated atmospheres. After 7 d the mass gain was 5.32 µg/cm², which rose to 7.15 µg/cm² after 28 d. Somewhat lower mass gains were found for this contaminant at 50 % RH (Fig. 3)

XPS analysis of the patina surfaces reveals a transformation of the initial Cu_2O film into other species (Figs.2b and 2f), and that sulphur atoms come to form part of the patina composition (Fig. 4). It is a singular fact that after 21 d of exposure the presence of Cu_2O is barely observed (Fig. 2f). After oxygen (mainly in the form of hydroxide, hydrated oxides and basic salts), the main component of the patina surface was copper in the form of CuO and, to a lesser extent, copper sulphates and sulphites (Fig. 2f). After 21 d no increase was seen in the sulphur content on the patina surface, though there was a certain transformation of sulphite ions into sulphate ions.

3.3. Effect of NO_2

NO_2 gas is only slightly soluble in water[4 and 39] and its capture by the moisture film is a slow process[40]. In the interaction of NO_2 with water several
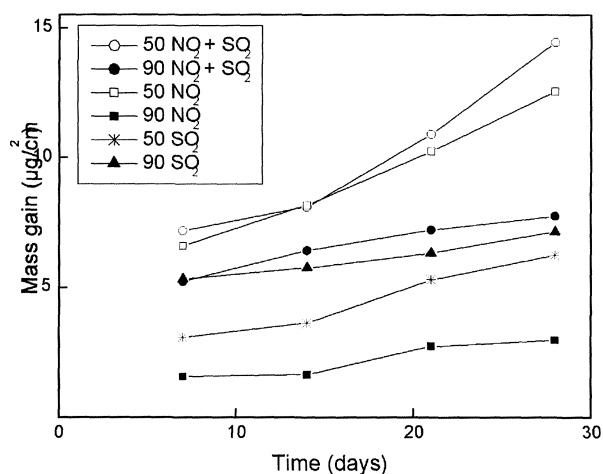

Figure 3. Copper mass gain with exposure time in atmospheres polluted with 800 µg.m⁻³ SO_2 and 800 µg.m⁻³ NO_2, individually or combined, at 90 and 50 % RH. Humidity levels and pollutants are indicated in the figure.

Figura 3. Variación de la ganancia de masa del cobre con el tiempo de exposición en atmósferas contaminadas con 800 µg.m⁻³ SO_2 y 800 µg.m⁻³ NO_2, individualmente o combinados, y el 90 y 50 % HR .Los niveles de humedad y los contaminantes se indican en la figura.
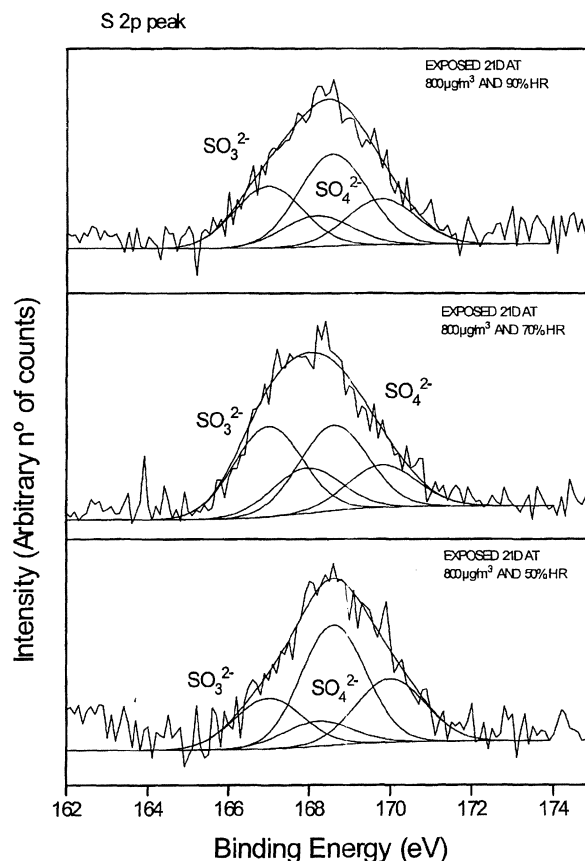
S 2p peak

Figure 4. S2p high resolution XPS spectra obtained on the outer surface of copper specimens after 21 d of exposure in atmospheres with 800 µg.m⁻³ SO_2 at 50, 70 and 90 % RH.

Figura 4. Espectros XPS de alta resolución S2p obtenidos en la superficie externa de la muestra de cobre después de 21 d de exposición en una atmósfera contaminada, con 800 µg.m⁻³ SO_2 y el 50,70 y 90 % RH.

reactions are possible, including the formation of nitrous and nitric acids[9 and 15]. The reduction of NO_2 by Cu_2O also gives rise to nitrous acid and the formation of nitrites[11]. Thus it is logical to find nitrates and nitrites among the corrosion products[11].

In the tests carried out with an air humidity of 90 % RH and 800 µg/m³ of NO_2, the colour of the patinas also showed no great changes compared with the patinas obtained in the non-contaminated atmosphere. XPS analysis of the patinas corresponding to atmospheres with and without contamination suggests a partial replacement of CuO by $Cu(OH)_2$ (Figs. 2c and 2g). Unlike the behaviour in the atmosphere contaminated with SO_2, in which sulphur compounds were identified in the patina composition, in the atmosphere contaminated with NO_2 nitrogen did not apparently come to form part of the patina composition, at least this

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was not detected in the XPS analysis of the outermost surface of the patina (Fig. 5). The absence of nitrates and nitrites in the patina contrasts with the behaviour observed at lower RH levels (Fig. 5), and some results reported in the literature[11 and 38].

According to figure 3, at 90 % RH the NO$_2$ contaminant seems to be less corrosive than SO$_2$ at 50 and 90 %RH; instead, the NO$_2$ appears to be particularly corrosive at 50 % RH in terms of the individual action of these contaminants.

3.4. Effect of the mixture of NO$_2$ and SO$_2$

The literature is not clear about the effect of air humidity on copper corrosion when this metal is exposed to mixtures of NO$_2$ and SO$_2$ contaminants. Several researchers have mentioned a synergetic effect of NO$_2$ and SO$_2$ gases when there is a high

Figure 5. N1s high resolution XPS spectra obtained on the outer surface of copper specimens after 21 d of exposure in atmospheres contaminated with 800 µg.m^{-3} NO$_2$ at 50, 70 and 90 % RH.

Figura 5. Espectros XPS de alta resolución N1s obtenidos en la superficie externa de la muestra de cobre después de 21 d de exposición en una atmósfera contaminada, con 800 µg.m^{-3} NO$_2$ y el 50,70 y 90 % RH.

presence of both ($\approx$ 2000 µg/m^3) and a high RH of the air ($\approx$ 90 %) [7, 9-12, 16, 36 and 38]. In these circumstances, the initial Cu$_2$O film dissolves in time and sulphur compounds appear on the copper surface, though oxygenated nitrogen compounds do not. In particular, mention has been made of the presence of Cu$_4$(OH)$_6$SO$_4$.2 H$_2$O [9 and 11]. In addition to the typical reactions of NO$_2$ and SO$_2$ acting individually, it is possible to find the reaction SO$_2$ + 2 NO$_2$ + 2 H$_2$O = 2 H$^+$ + SO$_4^{2-}$ + 2 HNO$_2$ which tends to create an electrolyte that is especially rich in sulphuric acid[41].

Figure 6 compares the mass gains of copper in an atmosphere with the 90 %RH and contaminated with different mixtures of NO$_2$ and SO$_2$ with the sum of the mass gains with the same gases acting individually. In most cases the combined effect of the two contaminants has been greater than the sum of the individual effects (Figs. 6b, c and d) in consonance with the aforementioned synergetic effect. Exceptionally, at the highest total concentration tested (800 µg/m^3 NO$_2$ + 800 µ/m^3 SO$_2$), the mass gains have been approximately 20 % lower than the sum of the gains produced with NO$_2$ and SO$_2$ acting separately, which seems to indicate, in this particular case, a certain inhibiting effect of the mixture of NO$_2$ + SO$_2$. Similar behaviour is suggested by figure 3, for atmospheres contaminated with 800 µg/m^3 NO$_2$ and/or SO$_2$ at 50 and 90 % RH, where gains due to the mixture of these gases are 15-22 % lower than the sum of individual gains.

The literature mentions the existence of an inhibiting effect of NO$_2$ mixed with SO$_2$ in the case of steel[7 and 20] and tin[21] in atmosphere with 95 and 90 % RH respectively. Other results in the literature also suggest a slight inhibition of the corrosion of copper exposed to mixtures of NO$_2$ and SO$_2$ gases for concentrations of 300-700 µg/m^3 and 95 % RH [7]. However, for higher concentrations of these gases, of the order of 900-1100 µg/m^3 [11], 1300-1500 µg/m^3 [7], and 3000-5000 µg/m^3 [9], the synergetic effects are evident even at high humidities. All of this disparity of behaviours suggests a high sensitivity of the phenomena responsible for the formation of patinas on copper to the interaction of a series of factors whose action is insufficiently clarified. These factors may include the contaminant concentration, RH level, specimen type and exposed area, preparation and characteristics of the metallic surface, etc. It would probably be useful to carry out further research in this respect.
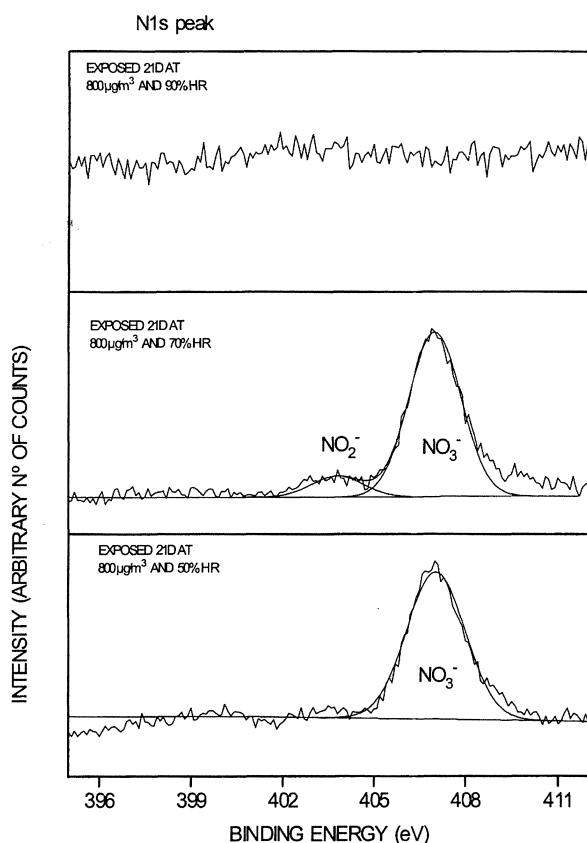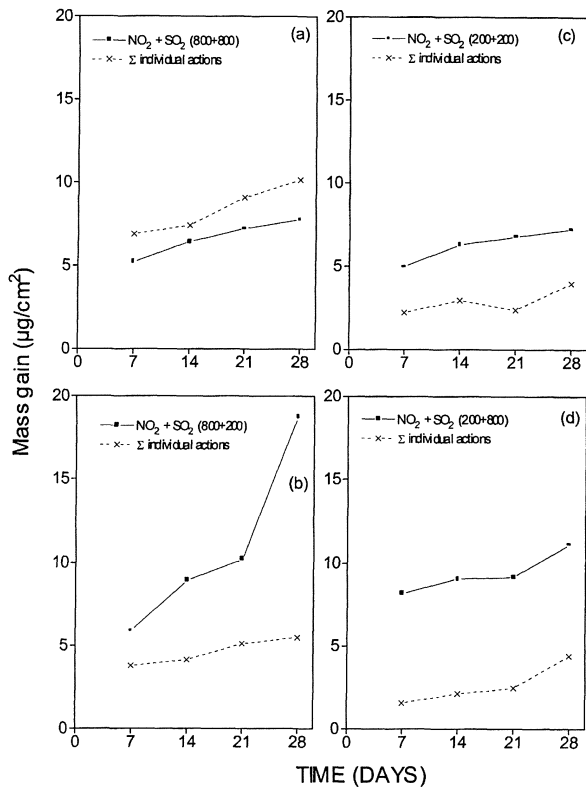
Figure 6. Mass gain of copper exposed to the mixture of 800 µg.m^{-3} SO$_2$ + 800 µg.m^{-3} NO$_2$ at 90 % RH compared with the sum of the individual effects of these gases.
a: 800 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$
b: 800 µg/m^3 NO$_2$ + 200 µg/m^3 SO$_2$
c: 200 µg/m^3 NO$_2$ + 200 µg/m^3 SO$_2$
d: 200 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$

Figura 6. Ganancia de masa del cobre expuesto a la mezcla de 800 µg.m^{-3} SO$_2$ + 800 µg.m^{-3} NO$_2$ y el 90 % HR en comparación con la suma del efecto individual de estos gases.
a: 800 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$
b: 800 µg/m^3 NO$_2$ + 200 µg/m^3 SO$_2$
c: 200 µg/m^3 NO$_2$ + 200 µg/m^3 SO$_2$
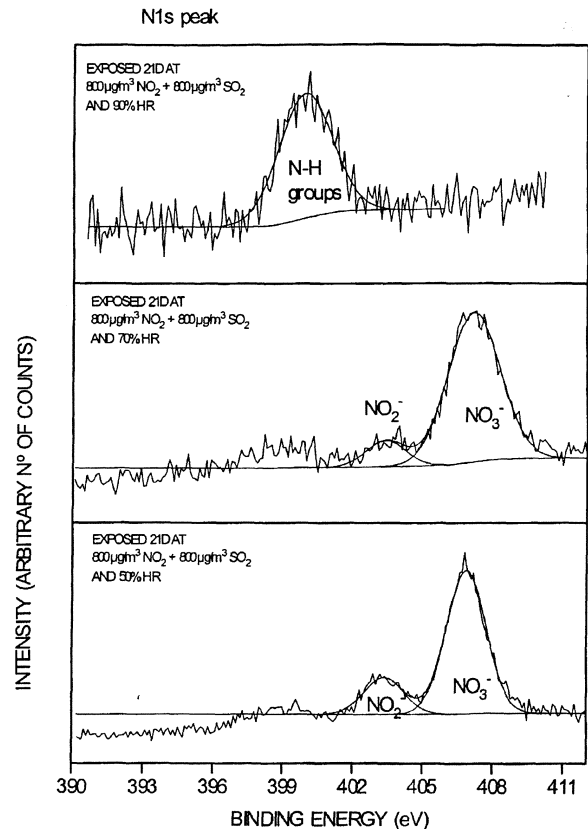*d: 200 µg/m^3 NO$_2$ + 800 µg/m^3 SO$_2$*

Figure 7. N1s high resolution XPS spectra obtained on the outer surface of copper specimens after 21 d of exposure in atmospheres polluted with the mixture of 800 µg.m^{-3} NO$_2$ + 800 µg.m^{-3} NO$_2$ at 50, 70 and 90 % RH.

Figura 7. Espectros XPS de alta resolución N1s obtenidos en la superficie externa de la muestra de cobre después de 21 d de exposición en una atmósfera contaminada, con la mezcla 800 µg.m^{-3} NO$_2$ + 800 µg.m^{-3} NO$_2$ y el 50,70 y 90 % RH.

XPS analysis of the surface of the patinas formed in the mixture of SO$_2$ and NO$_2$ did not reveal the presence of oxygenated nitrogen compounds (Fig. 7), which were also not seen with NO$_2$ acting individually (Fig. 5). This behaviour seems to be peculiar to atmospheres with 90 % RH, and was not found with 70 and 50 % RH (Fig. 7), where the presence of nitrate and nitrite was detected. On the other hand, this analysis detected the presence of the ammonium ion (or another hydrogenated derivative of the nitrogen atom not differentiable by XPS analysis[42]), which did not appear with the individual action of NO$_2$ (Fig.5), nor in the patina formed at 50 %RH (Fig. 7).

In theory, the formation of the ammonium ion is possible as a result of the reduction of an oxygenated nitrogen compound (e.g. nitric and nitrous acids, NO$_2$, NO, etc.), provided that the acidity of the medium and the potential of the electrode are appropriate[43]. For instance, the literature mentions the possibility of the reduction of nitrite to ammonia complexes through a cathodic reaction formation of ammonium from a mixture of nitric and sulphuric acids in contact with copper wool[41]. However, it is surprising that the ammonium ion should only appear with the mixture of NO$_2$ and SO$_2$ at 90 % RH, and not in the other tested exposure conditions in which the NO$_2$ contaminant is also present. Together with the greater thickness of the electrolyte film at 90 % RH another influencing factor may have been its higher acidity, since both of these factors tend to increase the effective potential difference that

allows the functioning of microcells which reduce the nitrogenated species and promote copper dissolution.

XPS analysis has also revealed a comparatively important presence of the cuprous ion among the corrosion products that accompany the oxides in the patina (Figs. 2d and 2h) on copper exposed to NO_2+SO_2 at 90 % RH, which is a singular fact considering the instability of Cu(I) salts; it would have been more normal to find the cupric ion, as occurs in all the other tested atmospheres. Both the ammonium ion (ammonium or another hydrogenated nitrogen compound) and the cuprous salts thus seem to be extraordinary products of exposure to the mixture of NO_2 and SO_2. This result suggests the idea that the cuprous ion is linked to the hydrogenated nitrogen compound which stabilizes it through the formation of a complex ion.

3.5. Inhibitive effect

The aforementioned inhibitive effect of the tested mixture of NO_2 and SO_2 is a peculiar behaviour that suggests a possible relationship with chemical passivation[44-46]. As is known, this phenomenon is possible when a sufficiently positive potential is established on the cathodic areas to draw the potential (in positive direction) from the anodic areas on the same metallic surface until passivation conditions are reached. For this it is necessary, in turn, to reach a critical anodic current density. In the case in hand, the anodic process would be the formation of copper oxides and the principal cathodic process would be the reduction of oxygen mainly from the air.

It is well known that the presence of some dissolved species in the electrolyte reduce the magnitude of the critical current and/or the Flade potential, facilitating the passivation phenomena[44-46]. In the case considered here, it is suggested that this could be a species derived from NO_2, perhaps the nitrite ion, bearing in mind the known predisposition of this ion to act as inhibitor[45 and 46]. Its effect would probably be exerted through an adsorption process rather than incorporation in the passivating film, since XPS analysis has not revealed the presence of oxygenated nitrogen compounds. The aforementioned sulphate, sulphite and ammonium salts, detected with the mixture of NO_2 and SO_2, could have formed in the phase prior to passivation.

At low RH the electrolyte films are very thin and the small amounts of water tend not to be evently distributed but to coalesce to clusters, particularly if hygroscopic particles are present on the metallic surface[15, 20 and 39]. The lack of continuity of the electrolyte layer should not prevent the functioning of local microcells. However, their activity area will now be confined to immediate vicinity of the anode-cathode junctions, giving rise to an intense localized attack at some points, as shown in figure 8, for a contaminated atmosphere at 50 % humidity.

4. CONCLUSIONS

– A laboratory study has been made of the individual and combined effect of NO_2 and SO_2 contaminants on the atmospheric corrosion of copper at 50, 70 and 90 % RH.

– XPS analysis has revealed the presence of copper sulphate and sulphite in the patinas formed in atmospheres contaminated with SO_2 at the three levels of humidity studied.

– Copper nitrate and to a lesser extent copper nitrite have been detected in exposure in atmospheres contaminated with NO_2 at 50 and 70 % HR. These compounds did not appear at 90 % RH, but only changes in the proportion of cuprous and cupric oxides were revealed.

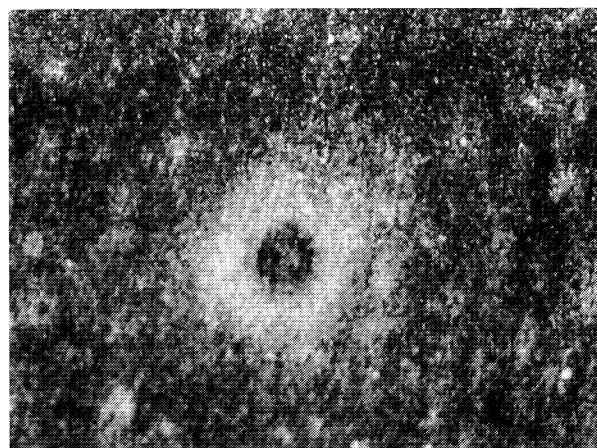– In the patinas formed in the mixture of SO_2 and NO_2 at 90 %RH sulphur compounds were

Figure 8. Point of localised attack formed on a copper specimen after 21 d of exposure in an atmosphere polluted with the mixture of 800 µg.m⁻³ NO_2 + 800 µg.m⁻³ NO_2 at 50 % RH. 65X.

Figura 8. Punto de ataque localizado formado sobre la muestra de cobre después de 21 d de exposición en una atmósfera contaminada, con la mezcla 800 µg.m⁻³ NO_2 + 800 µg.m⁻³ NO_2 y el 50 % HR. 65X.

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detected but oxygenated nitrogen compounds were not. This behaviour was not found at 50 and 70 % RH where the presence of nitrate and nitrite was detected. At 90 % RH, the XPS analysis seems to indicate the presence of ammonium ion, which did not appear at 50 and 70 % RH.

- The combined effect of NO_2 and SO_2 on the formation of the patina on copper (mass gain) has been greater than the sum of the effects of the two contaminants acting separately. Exceptionally, in the highest tested concentration (800 $\mu g/m^3$ NO_2 + 800 $\mu g/m^3$ SO_2) a certain inhibiting effect has been seen.

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