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Papel de los NOx en la corrosión y degradación de materiales
Role of NOx in materials corrosion and degradation

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Role of NO_x in materials corrosion and degradation

ABSTRACT

Nitrogen oxides are classified as Greenhouse gases. Given the complex nature of atmospheric processes, their influence on materials is still unclear. An increase in nitrogen oxides concentration is predicted by the Intergovernmental Panel on Climatic change (IPCC) for the present Century. The decreasing sulphur dioxide levels in most parts of the world and the increase in levels of nitrogen oxides has created a new multipollutant situation where interaction of pollutant is very important. Under laboratory conditions, the influence of NO_x on corrosion and degradation of materials is very low; however, in atmospheres containing SO₂ an increase of corrosion and degradation is reported when NO₂ is present. Nitrogen containing corrosion or degradation products are rarely reported. In general, the role of NO₂ (the nitrogen oxide more abundant in troposphere) is to catalyze corrosion and degradation reactions. In addition to common pollutants of anthropogenic origin, the presence of Chloride ions is another important factor to take into account. This situation, in general, has not been studied. It is very well known that Chloride ions significantly increase corrosion and degradation of materials. Very few reports about the influence of NO₂ in presence of airborne salinity on materials corrosion and degradation have been found. Based on literature information, considerations about corrosion and degradation behavior of metals and porous materials in the new multipollutant situation, taking into account the role of NO₂ in presence of other pollutants are made. The interaction of NO₂ and Chlorides is also considered.

Key words: NO_x, corrosion, degradation, climatic change, materials, Chlorides

RESUMEN

Los óxidos de nitrógeno son clasificados como gases de efecto invernadero. Dada la naturaleza compleja de los procesos atmosféricos, su influencia en los materiales no está totalmente clara. El Panel Intergubernamental sobre cambio climático (IPCC) pronostica un incremento en la concentración de los óxidos de nitrógeno durante el presente siglo. La disminución de los niveles de SO₂ en muchas partes del mundo y el incremento en los niveles de NO_x ha creado una situación multicontaminante donde la interacción entre éstos es muy importante. Bajo condiciones de laboratorio, la influencia del NO_x en la corrosión y degradación de materiales es muy baja; sin embargo, en atmósferas conteniendo SO₂ se reporta un incremento de la corrosión y la degradación cuando está presente el NO₂. Rara vez se reporta la presencia de productos de corrosión o degradación conteniendo nitrógeno. En general, el papel del NO₂ (el óxido de nitrógeno más abundante en la tropósfera) es actuar como catalizador de las reacciones de corrosión y degradación. En adición a los contaminantes comunes de origen antrópico, la presencia de iones cloruros es otro factor importante a tener en cuenta. Los iones cloruros incrementan significativamente la corrosión y la degradación de los materiales. Existen muy pocos reportes sobre la influencia del NO₂ en presencia de cloruros en la corrosión y degradación de materiales. En base a información bibliográfica se hacen consideraciones sobre el comportamiento de la corrosión y degradación de metales y materiales porosos en la nueva situación multicontaminante, tomando en cuenta el papel del NO₂ en presencia de otros contaminantes. Se considera la interacción del NO₂ y los cloruros.

Palabras clave: NO_x, corrosión, degradación, cambio climático, cloruros

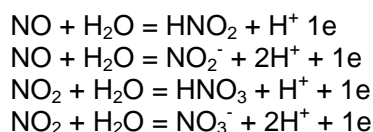
INTRODUCTION

World emissions of Greenhouse gases due to human activities have increased 70% between 1970 and 2004 [1]. Due to anthropogenic emissions, N₂O concentrations in the atmosphere are significantly higher respecting the preindustrial age.

Four fifths by volume of the atmosphere is free Nitrogen. Nitrogen compounds in the atmosphere are nitrous oxide (N₂O), nitric oxide (NO), nitrogen dioxide (NO₂), nitric acid (HNO₃), and ammonia (NH₃). Nitrous oxide photo dissociates in the stratosphere (about 90%) and reacts with excited oxygen atoms. Oxidation of N₂O by oxygen yields NO, providing the major input of NO to the stratosphere. Nitrogen dioxide (NO₂) is emitted in small quantities from combustion processes along with NO and is also formed in the atmosphere by oxidation of NO. Biomass burning is also a significant source. The sum of NO and NO₂ is usually designated as NO_x. It is produced mainly by man activities. Nitric oxide is the major oxide of nitrogen formed during high-temperature combustion. NO_x is considered the most important group of Nitrogen compounds influencing on materials degradation; however, Nitric acid and ammonia deposition on materials takes place very easily and their influence should be better investigated.

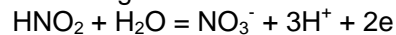
Air pollutants in combination with climatic parameters accelerate the corrosion and deterioration of many materials [2-3]. The influence of contaminants in materials degradation depends on the deposition characteristics of the different contaminants and the reactions occurring in the humid surface of the materials. The decreasing sulphur dioxide levels in most parts of Europe and the increasing car traffic causing elevated levels of nitrogen compounds, ozone and particulates has created a new multi-pollutant situation [4]. A synergistic corrosive effect of sulphur dioxide and nitrogen dioxide has been discovered. With decreasing levels, SO₂ is no longer regarded as the only important gaseous corrosion stimulator. Instead, its effect in combination with other gaseous pollutants such as NO₂ and their reaction products needs to be considered. A multi-pollutant situation has arisen where also two other pollutants deserve special attention, nitric acid and particles. Recently, a report about the influence of HNO₃ on limestone degradation in tropical countries has been made [5]. It is important to note that, up to the moment, no significant attention have been given to the influence of NO_x in atmospheric corrosion and degradation because traditionally, SO₂ influence is preponderant respecting other contaminants excepting chlorides in coastal zones. They are both potentially harmful to materials used in objects of cultural heritage and they are both less studied than other pollutants in the field of atmospheric corrosion. The interaction between air pollutants could significantly change their influence on materials degradation. An important air constituent not considered in research carried out in Europe is the influence of Chloride aerosols. Their influence could be significant for coastal zones and islands.

Atmospheric corrosion and degradation usually occurs in the presence of water layers or in water absorbed in porous systems. Hydrolysis of NO_x is of electrochemical nature. The following semi reactions are reported [6]:



As can be observed, NO_x reacts with water forming acids or nitrite/nitrate ions. Electrons produced could be consumed in anodic reactions. These reactions could occur in the surface water layer of metals or in the water contained in the porous systems of stone, concrete, ceramic and other porous materials. Acids and ions formed are undoubtedly agents of corrosion and degradation of materials; however, in

general, there are almost no reports about the presence of nitrogen compounds in corrosion and degradation products. It should mean that the above semi reactions are only intermediate in corrosion and degradation processes. Nitrous acid is essentially unstable. Consequently, HNO_2 tends, energetically, to decompose by oxidation according to the reaction:



Finally, the main transformation during NO_x hydrolisis will be in acids and nitrate ions. SO_2 shows a different behavior because this gas easily dissolves in water layers or water contained in porous systems. It does not react electrochemically with water.

Atmospheric corrosion is a complex phenomena because important processes occur in three phases and interfaces: atmosphere-gaseous phase, surface humidity-liquid and material-solid phase [7].

INFLUENCE OF NO_x ON POROUS MATERIALS DETERIORATION

Bonazza et al predicted for XXI century [8] that chemical dissolution of carbonate stones, via the karst effect, will increase with future CO_2 concentrations, and will come to dominate over sulfur deposition and acid rain effects on monuments and buildings in both urban and rural areas. Brimblecombe [9] estimates that Weathering, in a changing climate may have the greatest impact in the future. They do not take into account increases in NO_x concentrations and the existence of a multipollutant situation.

Some authors reported [10] (in laboratory tests) that NO_x gases cause a weight increase of calcium carbonate-based stones contributing to their decay, but also that NO_x enhances the adsorption of SO_2 in stones. Massey reported [11] the existence of catalytic effect of NO_2 in special laboratory test chambers at extreme concentrations of both sulphur dioxide and NO_x in stone degradation, but field exposure trials, where material is left out to weather naturally, have failed to demonstrate that NO_x has a significant catalytic effect.

Building materials suffer diverse mechanisms of deterioration due to chemical, physical and biological phenomena that are caused by atmospheric factors. One of the principal results of these kinds of deterioration is the formation of soluble salts. This damage takes place as a consequence of dissolution–crystallisation and hydration–dehydration cycles that contribute to the crystallisation of different salts within porous building materials, contributing to the porous material decay. The formation of gypsum is a classic example of salt induced degradation. In conditions of exposure to sea aerosol porous materials very often suffer degradation caused by accumulation of sea salts in the porous system. The role of nitrogen salts in porous materials degradation is still unclear.

Nitrate salts have been less studied than other salts (e.g.sulfates and carbonates). The reason could be that most of the reported works focused on the impact of sulfur pollutants (SO_x), which were very abundant in the environment up to a few decades ago. The presence of nitrates is reported in the surface of Greek buildings [12].

Sulphur dioxide and nitrogen oxides are gaseous components which react directly with the humid stone surface by forming acids or ions. Acids react with the stone to form salts which either crystallize out within the stonework resulting in physical damage or they are washed away resulting in a loss of material. Nitrate salts are more soluble and expand less than salts of sulphate, leading to little, if any, damage by this mechanism.

There is sufficient evidence that NO_x has a role to play in the oxidation of sulphite. However, the magnitude of influence NO_x and related compounds have in the environment is far from clear due to the prevalence of other stronger oxidants (ozone), the presence of metal oxide catalysts (Fe and Mn) in the stone and the possibility of organic oxidation inhibitors.

Deterioration of buildings is a problem which exists since man began constructions. Nowadays, corrosion of building materials causes a considerable loss in national property. Corrosion rate of the surface of historical and recent buildings seems to have accelerated during the last century, and it is believed that this is mainly due to air pollution

BIOLOGICAL ACTION ON BUILDINGS

Another important factor for corrosion and degradation [13] is seen in the activity of microorganisms which colonize the surface and subsurface of the facade of buildings, monuments and statues. These microorganisms can produce nitrogen compounds and cause materials deterioration.

Nitrifying bacteria make up a large fraction of the endolithic microflora of the building stones and concrete. These bacteria are able to grow chemolitho autotrophically with CO_2 as sole carbon source and gain their energy for growth either by oxidizing ammonium to nitrous acid (e.g. *Nitrosomonas*) or by oxidizing nitrous acid to nitric acid (e.g. *Nitrobacter*). Production of nitrous and nitric acid results in dissolution of calcareous stones, concrete, cement, etc. and may cause cracks by volume changes involved in crystallization of nitrate during dry periods. The microbial generation of HNO_3 at the surface of building stones has already been reported in the literature. In conclusion, the presence of microorganisms in the buildings can also produce chemical contaminants and increase their presence in the surface. In contrast to NO , NO_2 was generally taken up by all stone materials but was not released. In the case of microorganisms, degradation products reported contained nitrogen compounds. Observation that NO was released rather than taken up indicates that stone surfaces are not corroded by NO . Corrosion by NO_x in the polluted atmosphere thus can only be due to the effect of the NO_2 . The production of NO must be due to the chemolithotrophic nitrifiers which are present in large numbers at the surface of building stones.

It means that not only atmospheric nitrogen compounds could induce stone degradation, but also nitrogen compounds produced by microorganisms living in the stone.

INFLUENCE OF NO_x ON METALS

COPPER ATMOSPHERIC CORROSION

In the case of copper, some authors have found in laboratory studies a notable synergistic effect of NO_2 and SO_2 . This is attributed to an increase in the sulphite to sulphate oxidation rate in the presence of NO_2 . However, other authors have not encountered this effect in field studies [14].

Some laboratory tests have shown that NO_2 concentrations of a few parts per million have little effect on copper. Contradictory results have been reported by Mariaca [14]: Zaqipour and Leygraf found an increasing effect with the NO_2 concentration, and detected the existence of $\text{Cu}(\text{NO}_3)_2$ among the corrosion products: and, conversely, Schuber detected no nitrogen-based corrosion products at a similar NO_2 concentration. The last author highlighted the significant influence of the relative humidity: there was no reaction between NO_2 and copper at RH 65%, but above this value copper catalysed the reduction of NO_2 to NO

Copper corrosion in laboratory atmospheres polluted with NO_2 depends fundamentally on the RH. At 90% RH the attack is similar to that experienced in pure atmospheres, with the transformation of Cu_2O into CuO and $\text{Cu}(\text{OH})_2$. As the RH decreases, nitrite and nitrate ions are formed at isolated points on the surface and the resulting acidity causes local dissolution of the cuprite layer and the formation of basic copper nitrite

(soluble) and nitrate, gerhardtite ($\text{Cu}_2(\text{OH})_3\text{NO}_3$), and copper experiences localized attack.

In mixed atmospheres ($\text{NO}_2 + \text{SO}_2$), when $[\text{NO}_2] < [\text{SO}_2]$ copper corrosion experiences an inhibiting effect, whereas if $[\text{NO}_2] > [\text{SO}_2]$ the mixture of the two gases causes a synergic effect. At high RH, NO_2 contributes to the oxidation of SO_2 , reinforcing the formation of sulphuric acid, which is the species that reacts with copper, while low RH values favour the reaction of NO_2 with the adsorbed water, forming nitrous and nitric acids, which are the species that react with copper in this case, giving rise to an outer film of basic copper nitrite (soluble) and nitrate (insoluble) over an intermediate layer formed mainly of copper sulphite and sulphate resulting from the previous interaction of sulphuric acid with cuprite.

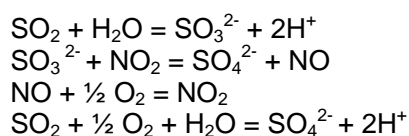
When electrolyte layer thickness diminishes in the atmospheric corrosion process, cathodic reactions are favoured because diffusion influence is lower. NO_x hydrolysis is of electrochemical nature (cathodic semi reactions). It is possible that the influence of NO_x increases at lower RH because a thinner electrolyte layer is formed, favouring the occurrence of NO_x cathodic semi reactions.

ZINC ATMOSPHERIC CORROSION

A small effect of NO_2 on zinc corrosion when it acts alone is reported, compared with the effect of other atmospheric agents. Similarly, it has been found that the kinetics of the corrosion process in the presence of SO_2 is significantly greater than in the presence of NO_2 at high relative humidity (90%), while at a relative humidity of 70% no appreciable differences are observed.

The effect of NO_2 is indirect given that nitrogen compounds have not been detected among the corrosion products and its influence is related with the increase in the rate of SO_2 oxidation to sulphate [15].

The global process of sulfur dioxide oxidation to sulfate and the catalytic action of nitrogen dioxide would correspond to the following general reactions:



where nitrogen dioxide would act as an oxygen carrying agent. The greater oxygen availability would produce an increase in the sulfur dioxide and sulfite oxidation [16].

In nitrogen dioxide laboratory atmospheres, corrosion was minimal, indicating that NO_2 does not promote the corrosion of zinc. $\text{Zn}(\text{OH})_2$ and ZnO were detected after exposure in this atmosphere at both 35°C and 25°C , with 90% RH. In sulfur atmospheres, zinc corrosion was enhanced, with the formation of a greater amount of corrosion products, mainly zinc hydroxysulfate and sulfite.

The presence of sodium Chloride in the surface of materials is a very probable situation for coastal atmospheres. Many cities are located beside the sea. The interaction of NaCl with other pollutants could promote synergic effects. This situation is almost not studied. Only one paper dealing on this subject has been found [17]. The main results reported are summarized below:

In laboratory atmospheres, sulphur dioxide inhibited corrosion slightly when large amounts of NaCl were present on the surface. The same was true for the combination of SO_2 and NO_2 . Nitrogen dioxide did not cause any measurable corrosion by itself at 70% RH.

In combination with small amounts of NaCl , NO_x stimulated corrosion. Unlike SO_2 , NO_2 did not inhibit corrosion at high NaCl levels. It could be related to the thickness of the electrolyte layer. Under a low surface concentration of NaCl , the hygroscopic nature of

this salt does not produce a thick electrolyte layer and cathodic NO_x semi reactions are favoured. At higher Chloride surface concentration, the electrolyte layer is thicker and NO_x cathodic semi reactions are unfavoured due to the influence of diffusion process through the metallic surface. Another aspect to consider is the possible interaction between Chloride and HNO₂ or other nitrogen compounds formed.

Table 1 presents the ion-chromatographic analysis of water rinses from the experiments with periodic NaCl additions combined with water leaching. About half the chloride added was removed by water rinsing in the exposures to pure air and to SO₂ and SO₂+ NO₂ containing atmospheres. In the NO₂ exposure, however, only about 10% of the chloride added was removed by water rinsing. The NO₂ exposure gave rise to large amounts of nitrite (NO₂⁻) and small amounts of nitrate (NO₃⁻) on the samples.

The results from the XRD analysis of the corrosion products formed at 70% RH are summarised in Table 2. In the NO₂ and pure air experiments zinc hydroxychloride (Zn₅(OH)₈Cl₂ • H₂O) and zincite (ZnO) were the only phases detected.

Sodium zinc hydroxychloride sulphate (ZnSO₄3Zn(OH)₂NaCl•xH₂O, x~6) was identified in all SO₂ + NaCl exposures in this work. It was not found in the earlier study with smaller NaCl additions. In the experiments where all the chloride was added before exposure zinc hydroxychloride together with traces of zinc hydroxysulphate (ZnSO₄3Zn(OH)₂•4H₂O) were found in addition to sodium zinc hydroxy-chloride sulphate. Periodic additions of NaCl combined with water leaching produced only sodium zinc hydroxychloride sulphate and zincite.

The corrosion products were evenly distributed after exposure to SO₂ and SO₂ + NO₂ environments, while the corrosion attack was localized in the NO₂ and pure air exposures.

Environments containing NO₂ produced the same crystalline corrosion products as did pure air, but in addition soluble nitrite and nitrate were found.

The NaCl-induced corrosion at 95% RH was about twice as great as at 70% RH. In the pure SO₂ runs, the influence of humidity was much greater, corrosion increasing by a factor of 15 on going from 70 to 95% RH.

Sodium chloride also stimulated corrosion in the SO₂ environment, although not as strongly as in pure air. In a manner similar to the 70% RH experiments, one may note that SO₂ may inhibit corrosion in the presence of NaCl. At 95% RH this effect occurred only at rather large NaCl additions (>70 ~g/cm²).

In the absence of NaCl, the deposition of NO_x on zinc was small and diminished below the limit of detection after about 5 h.

On the other hand, HNO₂ (g) was produced by the sample, initially corresponding to about 5% of the NO₂ added. The formation of HNO₂ decreased slowly with time and corresponded to about 3% of the nitrogen dioxide added after 20 h. In the presence of NaCl, the deposition of NO_x increased strongly, while no HNO₂ evolution was detected. In this case, larger amounts of nitrite were found on the surface by ion-chromatography compared with the cases when no chloride was present.

Conclusions: Nitrogen dioxide, which by itself is rather unreactive towards zinc, accelerated the atmospheric corrosion of zinc in the presence of small amounts of NaCl, whereas this effect was not observed at high surface concentrations of sodium chloride. This is an important information for prevention against the effect of Nitrogen Dioxide on materials.

CONCLUSIONS

The role of atmospheric nitrogen oxides in materials corrosion and degradation is increasing in the present multipollutant situation. It is still unclear.

Interaction between anions at different relative humidity ranges could play an important role in the mechanism of NO_x corrosion and degradation atmospheric process. In

particular, the effect of NO_x in presence of SO₂ and Chlorides in coastal sites should be studied.

Not only atmospheric NO_x could affect degradation of porous materials. The existence of bacteria producing nitrogen oxides in stone and other porous materials is another factor to be considered.

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Table 1. Ion chromatographic analysis of the leaching water from the experiments with periodic NaCl additions combined with water leaching. The percentage given denote the fraction of each ionic species found in the leaching water compared with the total amount added to or deposited on each sample. The number of moles found on each ionic species is also given. Sodium chloride was added to the samples periodically before and during exposure (periodic addition of 5×14 microgram/cm²) and it was combined with periodic water leaching. Data reported by [17].

Environment	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻
Pure air	50% (4.4×10^{-6})	--	--	--
SO ₂	50% (4.4×10^{-6})	10% (1.5×10^{-6})	--	--
SO ₂ + NO ₂	50% (4.4×10^{-6})	10% (1.5×10^{-6})	1.6×10^{-7}	--
NO ₂	10% (8.7×10^{-6})	--	6.5×10^{-7}	5.1×10^{-6}

Table 2.-XRD identification of corrosion products on Zinc samples exposed at 70%RH. NaCl was added to the samples either before exposure (single addition of 70 microgram/cm² or periodically before and during exposure (periodic additions of 5 x 15 microgram/cm²). The last column refers to an experiment where periodic additions of NaCl were combined with water leaching. Data reported by [17].

Environment	Single addition of NaCl	Periodic addition of NaCl	Periodic addition of NaCl + water leaching
Pure air	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO
SO ₂	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O Zn ₅ (OH)8Cl ₂ .H ₂ O ZnSO ₄ 3Zn(OH) ₂ .4H ₂ O	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O ZnSO ₄ 3Zn(OH) ₂ .4H ₂ O	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O ZnO
SO ₂ + NO ₂	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O Zn ₅ (OH)8Cl ₂ .H ₂ O ZnSO ₄ 3Zn(OH) ₂ .5H ₂ O	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O ZnSO ₄ 3Zn(OH) ₂ .5H ₂ O	ZnSO ₄ 3Zn(OH) ₂ NaCl.6H ₂ O ZnO
NO ₂	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO	Zn ₅ (OH)8Cl ₂ .H ₂ O ZnO