Influence of SO_2 and NO_x on atmospheric corrosion of steel

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Recibido: 20 de diciembre de 2000. Aceptado: 13 de septiembre de 2001.

Palabras clave: corrosión atmosférica, contaminación atmosférica, corrosión, acero al carbono, lluvia ácida.
Key words: atmospheric corrosion, air pollution, corrosion, carbon steel, acid rain.

RESUMEN. Los contaminantes antropogénicos derivados del azufre y el nitrógeno han causado grandes daños a las construcciones tecnológicas y al patrimonio cultural en los países industrializados durante el siglo pasado. El costo asociado a estos daños es sustancial y se estima que en Europa actualmente la cifra está en el orden de los nueve mil millones de dólares al año. En trabajos sistemáticos realizados por otros autores, se ha demostrado que la contaminación por los compuestos de azufre, especialmente, el dióxido de azufre (SO_2), tiene un efecto de aceleración en los procesos que degradan a muchos materiales. Estudios más recientes han demostrado la importancia de otros contaminantes tales como el O_3, el dióxido de nitrógeno (NO_2) y los ácidos orgánicos. En el presente trabajo se estudió en dos estaciones de ensayos naturales, la influencia que sobre la corrosión atmosférica del acero de bajo carbono, tienen tanto los contaminantes convencionales, la salinidad y los compuestos de azufre determinados de forma acumulativa como los compuestos gaseosos que se determinan por métodos volumétricos. La corrosión del acero al carbono se determinó por el método de pérdida de peso. Los resultados demuestran que entre los factores aeroquímicos, los más influyentes en la explicación de las variaciones de la actividad corrosiva de la atmósfera en las estaciones estudiadas fueron el monóxido de nitrógeno y el amoníaco y que los iones cloruro y el NO son factores que refuerzan la actividad corrosiva sobre el acero AISI 1020, lo que explica su mayor incidencia en la estación ''Casablanca''; mientras que en las condiciones estudiadas, el SO_2 gaseoso no manifestó influencia sobre la corrosión del acero.

ABSTRACT. Significant damages have been caused by sulfur and nitrogen pollutants produced by man activity to buildings and constructions including those linked to the cultural heritage in industrialized countries during the last century. These damages caused a substantial cost. It is considered that at present the figure I about nine thousand million US dollars each year. It has been very well established, that sulfur compounds, particularly sulfur dioxide, accelerate the degradation processes of many materials. More recent studies have also shown that the importance of other pollutants, such as O_3, nitrogen oxides and organic acids on the degradation of materials. Salinity and sulfur compounds were determined every month by using accumulative methods at two test stations. Gaseous pollutants were also determined at two test stations by the use of volumetric methods. The corrosion of carbon steel was evaluated by weight loss. Data for pollutants and steel weight loss were processed. The results show that among the aerochemical factors, the most influential ones on the explanation for the variations of the corrosive activity of the atmosphere in the tested stations were nitrogen monoxide and ammonia, and that the interaction between chloride ions and NO causes an increase in AISI 1020 steel corrosion. It explains its great incidence detected at the Casablanca station, while SO_2 influence is not significant on the steel corrosion changes.

INTRODUCTION

The action of the atmosphere on metals is one of the greatest problems of corrosion. The direct and indirect losses caused by atmospheric corrosion are huge, what is logic if it is considered that the most part of the equipment and metallic constructions are outdoors. According to Tomashov,[1] more than 50 % of the losses caused by corrosion are produced by that situation.

The atmospheric corrosion of metals is a complex process depending on the climate and the geographic situation, and their mechanism considerably changes according to the metal.[2] Likewise, when considering the effects of the acid deposition on the materials, it is important to admit the differences between the urban and the rural areas. The effect of the mesoclimate on the urban areas must be added to the local and long scope effects. A more detailed study of the mesoclimatic parameters show that the temperature in the urban center can be 2 or 3º degrees higher then in the peripheral areas, while the humidity gradient will be higher in the coldest and greenest rural areas.[3]

The factor that first determines the intensity of the corrosive phenomenon is the chemical composition of the atmosphere (air polluted by gases, acid vapors and sea aerosols). The sulfur dioxide and the sodium chloride are the atmosphere's most common aggressive agents from the point of view of corrosion. In the coastal areas, the influence of the marine aerosol is prevailing, far from the sea, pollution depends on the presence of industries and population groups. In this case, because of its frequency and incidence on the corrosive process, the SO_2 from the combustion of sulfur-containing solids and liquids is the main pollutant.

The fast increase of pollution because of the production of energy and the self-motor traffic in the urban areas in many developing countries also is a menace to materials. Severe corrosion effects have been observed in these areas, several times higher than in the rural areas.

Even though the interest has concentrated on the effects of the above-mentioned pollutants in the last years, some attention has been given to the effects of the interaction with other pollutants such as ozone and nitrogen oxides, since more recent studies have shown the importance of those pollutant, as well as the organic acids.[4]

Pollutants affect the historical and cultural monuments and the constructive infrastructure that are an important part of the cultural patrimony of a country. Some monuments that have resisted the attacks of the environment for hundreds and even thousands years, have suffered a fast deterioration, for example, the Acropolis in the highly polluted atmosphere of Athens. This type of damages has a greater extent that cannot be only stated in economic terms, because in those cases, it occurs the loss of an original art object. The key question in this context is: How much do the acidifying pollutants in the atmosphere increase the corrosion process?

It is a very confirmed fact, through the practical experience on the behavior of real structures and the results of many assays, that the corrosion velocity of the metals in the atmosphere can be in some places ten or even hundred times higher than in other places, what justifies the interest for determining the fundamental variables influencing the atmospheric corrosion and originating this great dispersion of results and on the other part, for reaching a classification of the atmospheres' aggressivity.

This work had the purpose of valuating the effect of some pollutant compounds of the atmosphere on a low-carbon steel corrosion in two points of measurements with different environmental characteristics. The Test Station ''Casablanca'', with a direct antropic influence and responds to the level of impact pollution and the Test Station ''La Palma'' (rural), responds to the regional level of pollution.

The environmental factors to determine corrosivity were the following:

- Meteorological variables.
- Gas Pollutants (SO_2, NO_x and NH_3).
- Saline aerosol.

EXPERIMENTAL PART

The pollution processes distinctive of each geographic context substantially differ in their exhibition. The character of the predominant emission processes, the influence of determined meteorological variables and the relief characteristics fundamentally conditions this.

The present study was performed through the systematic sampling of the principal nitrogen and sulfur gaseous compounds at the stations of the Surveillance Network of Atmospheric Pollution of the Institute of Meteorology (Table 1), as well as the assays of metal corrosions, whose information is the basis of this work.

The station for the control of atmospheric pollution in ''La Palma'' is located in a rural area with predominance of extensive pinewoods, especially in the southern and western sectors, as well as the areas dedicated to the culture of sugarcane and other minor cultures. Approximately 6 km away from the northern coast, the soil changes from plain and low in the coastal area, to slightly undulated in the proximity of the station, located 3 km away eastern from ''La Palma''. The area has only one stable source of potent emission, a sugar factory, whose effluviums do not directly affect the station area because of its location.

The test station of Casablanca is located at the eastern side of the Havana bay basin. The relief in its eastern and western watersheds shows remarkable differences. About this place, it can say it is a coastal place and has a moderate industrial and urban influence.

Methods of sampling and analysis of the pollutant gases of nitrogen and sulfur

The Central Laboratory of the Center for Pollution and Atmospheric Chemistry of the Institute of Meteorology performed the sampling and analysis of the pollutant gases.

The uptake of the nitrogen oxides (NO_2 + NO)[5] and SO_2[6] from air was performed by using the absorption tubes procedure, by a column of glass granules impregnated in a solution.[7] For the NO_x, the solution was potassium iodide, while for SO_2 it was sodium tetrachloromercuriate. For both species, the absorption tubes CT 112 and CT 212 were used as bearers, respectively.

Other nitrogen compound evaluated in this study was ammonia (NH_3). This was sampled by using the method of the bubbling flask, across which air flow is passed through a sulfuric acid solution contained in the flask.

To determine the concentration of every pollutant gas spectrophotometric methods were employed.

Methods for sampling and analysis in the corrosion assays

The corrosion assays were performed by the Department of Cor-

Table 1. Principal characteristics of the test stations taking part in the sampling of the main atmospheric gaseous compounds of nitrogen and sulfur.

Test station	Latitude	Longitude	Height (msnm)	Type of station	Distance from the coast (km)	Predominant wind
La Palma	22° 46′	83° 33′	47,4	Rural	6,0	NE
Casablanca	23° 10′	82° 21′	50,1	Coastal with industrial and urban influence	1,5	NE

rosion of the National Center for Scientific Research.

The metallic material used for evaluating corrosion was a low-carbon steel AISI 1020. 10 cm X 15 cm X 1 mm test specimens were used and placed on metallic carriers at a scope of 45° and facing South. Inert-material isolators regarding corrosion were used to bear the sample. The test specimens were exposed for 1, 3, 6 and 12 month periods. Before exposure to atmosphere, they were washed with detergent, pickled in HCl solution (market) and weighed with a precision of ± 0.1 mg . The assay lasted 21 months at the test station in ''Casablanca'' and 18 months at the test station in ''La Palma''. All the test were performed according to the standard regarding this subject.[8]

The evaluation of corrosion was performed by mass variation, by using an analytical scale with 0.1 mg precision.

The evaluation of the atmosphere's salinity was performed by an accumulative method (dry candle) according to the Cuban Standard.[9]

The evaluation of the SO_2 from air was performed by the method known as Filtrasita, consisting in the use of a filter paper saturated with Sodium carbonate.[10] This method is also sensitive to other sulfur compounds (SO_3, SO_4^{2-}, SH_2).

The powder deposited on the surface of a Petri plate exposed to the atmosphere in order to represent more properly what happens with the metallic specimens in those conditions.[11] The content of chloride and sulfate ions was also determined in the powder deposited.

RESULTS AND DISCUSSION

At first, it could observe that the corrosion of steel increases at the two stations as the exposition time increases (Fig. 1).

This is, the corrosive aggressivity at the ''Casablanca'' station is much higher than that in ''La Palma'' station, therefore, and it can expect similar differences in the pollution levels between both stations.

The mean values of the deposition velocity of chloride ions and the sulfur compounds were determined for all the experiment (Tables 2 and 3). The difference was not so remarkable between the stations as the pronounced difference obtained in the corrosion values, for steel; however, higher values were found in the test station in ''Casablanca'', as expected. All this is related to the environment in each station, as mentioned above, the test station in ''La Palma'' is located in a rural area, while the ''Casablanca'' station is located in an industrial area, near from important sources of emission of pollutant gases. The scarce difference between the values of the velocity of deposition could be caused because of the proximity of the 'La Palma' station to the western northern coast.

The figures 2 and 3 show the behavior of the velocity of deposition for each pollutant for both stations in the period of test.

It could observe that the mean velocity of deposition of the sulfate ions in both stations was higher than that of chloride, that is why that outdoors, that factor (the sulfate ion) plays an important role in the corrosion process in this case. It must be considered that sulfate represents the contribution of the ions, both properly sulfate other sulfur compounds, such as SO_2, SO_3 and others, since the uptake method and the analytical technique used are sensitive to all those sulfur compounds.

Until this moment the behavior of steel under the influence of the traditional factors, this is, salinity and sulfur compounds obtained by cumulative methods have been studied. From now on, the influence that other atmosphere pollutants in

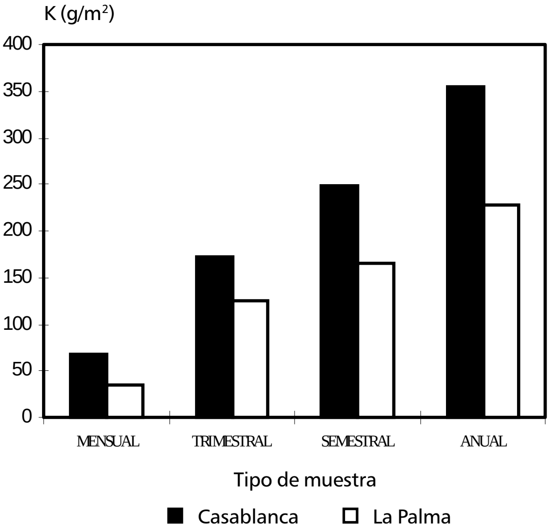

Fig. 1. *Mean values of the corrosion of steel for both stations.*

Table 2. Mean values of the velocity of deposition of pollutants in the test station ''Casablanca''.

Parameter	Cl^- (dry candle)	SO_4^{2-} [mg/(m^2 · d)]	(powder)	SO_4^{2-} (powder)
Mean	9.7	22.4	7.3	
Standard deviation	6.5	8.8		
Minimal			1.6	
	26.5	41.6	15.7	26.2

Table 3. Mean values of velocity of deposition of pollutants at the test station ''La Palma''.

Parameter	Cl^- (dry candle)	SO_4^{2-} (filtrasita) [mg/(m^2 · d)]	Cl- (powder)	SO_4^{2-}- (powder)
Mean	7.9	15.1	4.4	13.5
Standard deviation	3.5	5.3	2.7	5.2
Minimal	2.3	7.2	1.7	5.4
Maximal	13.5	23.4	10.0	20.1

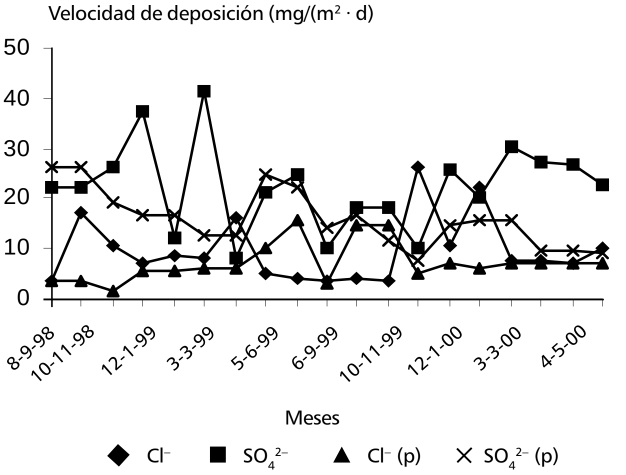

Fig. 2. *Mean velocity of deposition for the chloride and sulfate ions at the ''Casablanca''station .*

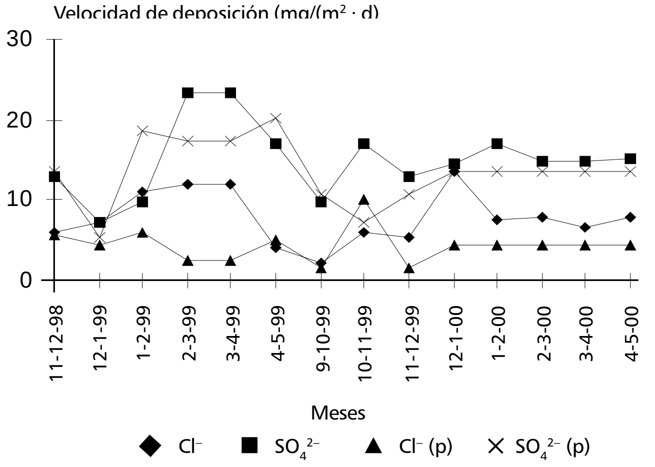

Fig. 3. *Mean velocity of deposition for the chloride and sulfate ions in the ''La Palma'' station.*

Table 4. Mean values of the concentrations of gases in the two stations for the studied period.

Parameter	"Casablanca" station				"La Palma" station			
	SO_2	NO_2	NO	NH_3	SO_2	NO_2	NO	NH_3
	(µg/m^3)							
Mean	1.3	2.8	1.6	3.9	0.2	1.6	0.4	1.2
Standard	1.1	2.3	1.0	2.2	0.1	1.1	0.2	0.7
Minimal	0.2	0.1	0.3	1.4	0.1	0.4	0.2	0.4
Maximal	4.5	7.4	3.4	8.2	0.4	3.9	0.9	2.8

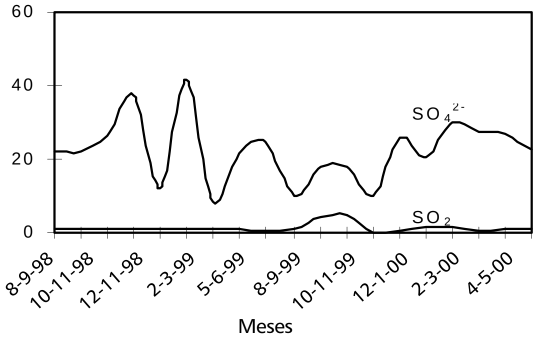

Fig. 4. *Relationship between the velocity of deposition of the sulfur compounds and the monthly mean concentration of gaseous SO_2 at the test station in ''Casablanca''.*

gaseous state, as SO_2, the NO_x the NH_3, can show on the corrosion process will be studied. To do this, the monthly mean concentrations of those pollutant gases (monthly mean) measured for each station in all the period of study were used (Table 4).

Figure 4 shows the relationship between the velocity of deposition of the sulfur compounds determined by the accumulative methods and the monthly mean concentration of gaseous SO_2 determined by volumetric methods at the test station in ''Casablanca''; that could indicate that there are sulfur compounds present different from SO_2, possibly sulfates from the marine aerosol or the soil. The concentration of this gas stayed at a low and steady level in all the period, so the figure cannot determine if there is any relationship between them or not. This behavior was similar in ''La Palma'' station. However, when a linear regression analysis is performed between both factors, no good correlation coefficients for 1 and 3 months were obtained, but for 6 months a correlation coefficient of 0.69 was obtained, what shows that the analysis must be performed for exposition times longer (1 year) to obtain a good correlation.

For the nitrogen gaseous compounds a good correlation was obtained of NO and NH_3 with the corrosion of carbon steel in the case of quarterly specimens exposed at the ''Casablanca'' station (Table 5).

The relationship of the NO and NH_3 concentrations with the corrosion of the steel specimens exposed for 1 and 3 months at the test station in Casablanca has been shown. (Figures 5 and 6). It is observed that in the case of monthly samples, the relationship is not so remarkable as it happens to be for the quarterly samples, notwithstanding in the case of the quarterly samples, the number of data is lesser. It must remark that this correlation had not been obtained in works formerly performed, maybe because those works were performed in rural areas where the NO_x concentrations were low, just like those performed in ''La Palma'' . Nevertheless, at the ''Casablanca'' station, where the pollution by nitrogen compounds is high because of its location in an industrial area, this behavior can be expected.

The significant equation for the three months of exposition was obtained when performing the regres-

Table 5. Correlation matrix corresponding to quarterly samples exposed at the ''Casablanca'' station.

	K_{steel}
K_{steel}	1.00
$[SO_2]$	0.21
$[NO_2]$	0.28
[NO]	0.99
$[NH_3]$	0.86

sion analysis step by step for all the pollutants regarding the corrosion of steel.

$$K_{steel} = 67.16 \pm 16.44 + 0.28 \pm 0.10[Cl^-] + 1.01 \pm 0.10[NO]$$
$$r = 0.95 \quad n = 12 \quad p < 0.001$$

where:

$[Cl^-]$ and [NO] velocity of deposition of chloride ions and the concentration of NO, respectively.

As can be observed, there is a factor reinforcing steel corrosion, what can explain the higher steel corrosion in ''Casablanca'', even though there are no big differences in the values of Cl^- deposition obtained in the test.

When only the gaseous pollutants were considered, the following equation was obtained:

$$K_{steel} = 162.54 \pm 34.91 + 0.92 \pm 0.11[NO] - 0.35 \pm 0.13\,[NH_3] - 0.17 \pm 0.14[SO_2]$$
$$r = 0.95 \quad n = 12 \quad p < 0.001$$

where:

[NO], $[NH_3]$ and $[SO_2]$ concentrations corresponding to the pollutants.

In this case, NO appears again as a factor incurring on the corrosion of steel in a positive way and the other two in a negative way. The nature of inhibitor of corrosion is known in the case of NH_3, but not for SO_2, that may be because of the small values obtained, there is an effect of competitive interaction with NO that causes this behavior. This can be clearly stated for higher times of exposition of steel, since three months is a too short period for obtaining definitive conclusions.

In the equation for 6 months of exposition can be observed that even though there are very few data, this situation changes for this time, since NO does not appear anymore and the SO_2 effect is present.

$$K_{steel} = 131.61 \pm 5.82 + 1.50 \pm 0.59[SO_2] - 0.70 \pm 0.59[NH_3]$$
$$r = 0.99$$

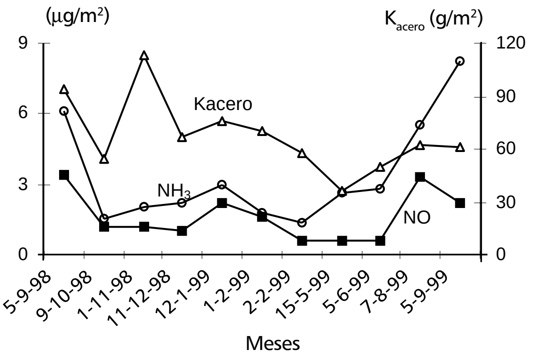

Fig. 6. *Relationship between the mean concentrations of NO and* NH_3 *and the corrosion of steel for quarterly test specimens at the ''Casablanca'' station.*

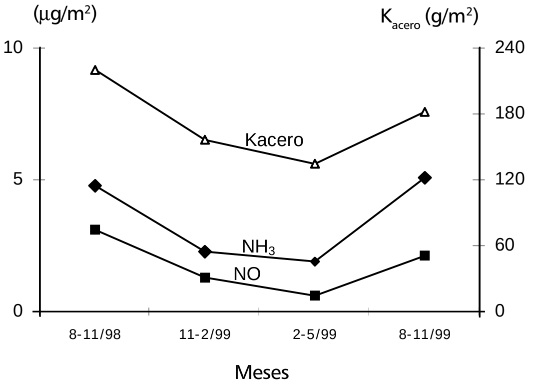

Fig. 5. *Relationship between the mean concentrations of NO and* NH_3 *and the corrosion of steel for test specimens monthly exposed at the ''Casablanca'' station.*

CONCLUSIONS

The results show that among the aerochemical factors, the most influential ones on the explanation for the variations of the corrosive activity of the atmosphere in the tested stations were nitrogen monoxide and ammonia, while in the studied conditions, the gaseous SO_2 did not show any influence on the corrosion.

The chloride ions and NO are factors reinforcing the corrosive activity on AISI 1020 steel, what explains their higher incidence at the ''Casablanca'' station. From the gaseous pollutants, NO influences the corrosion of steel in a positive way and NH_3 and SO_2, in a negative way.

The inhibiting nature of ammonia on steel corrosion is known, but that of SO_2 is not. It is recommend that the last aspect must be studied for longer periods of exposition of steel, even though there is a possibility of existence of a competitive adsorption effect between SO_2 and NO_x.

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