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STUDIES ON DEGRADATION OF LIME MORTARS IN ATMOSPHERIC SIMULATION CHAMBERS

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ABSTRACT

It is well known that the presence of pollution increases the degradation of some building materials. In order to understand the influence of individual pollutants as well as the role of oxidants and water in lime mortar degradation, those materials have been exposed in atmospheric simulation chambers.

According to the pollutants used in the chambers (NO, NO_2 and SO_2), NO_2^- and NO_3^- or SO_3^{2-} and SO_4^{2-} have been analysed and related with the reaction between the lime mortar and the pollutant.

The reactivity order of the different pollutant (NO, NO_2 and SO_2), in presence and absence of water and/or oxidant has been determined. © *1997 Elsevier Science Ltd*

Introduction

The presence of pollution increases the degradation of artificial (mortar, brick, etc.) and natural (stones) building materials. It is important to know the influence of pollutant gases on the building materials degradation. The study of the evolution of these materials in atmospheric simulation chambers allow us to predict their behaviour in polluted atmospheres.

Lime mortar was one of the most useful material used by Ancient Romans. Nowadays, lime mortar is one of the building materials used specially in reparation and restoration works. Therefore, it is important to study the behaviour of this material in different ways, basically in aggresive conditions to improve our knowledge of this ancient building material.

Simulation chambers have been designed (1) to allow the deterioration of different materials to be measured. The aggressive effects of gases such as SO_2 and NO_x, and the influence of water and ozone can be monitored. These chambers permit the addition of water over the specimens surface. The authors confirm a greater pollutant aggresivity in the presence of water, independent of the stone composition. Thus, for example, C.M. Grossi et al., (2), established that for a dolomite stone 98% pure, the salt formation reaction is greater in wet/dry cycles than in dry conditions. S.J. Haneef et al. (3) gave similar results for some stones with different porosities such as Pentelic marble, Massangis limestone, Portland limestone and Mansfield dolomitic sandstone. On the other hand, these authors point out the importance of porosity in the development of a moisture film and thus active reaction points. These data were confirmed by Lewry et al. (4), in the study of a Portland limestone and White Mansfield dolomitic sandstone.

S.J. Haneef et al. (3), point out that in the same conditions, the presence of ozone in the chambers, is less important than the presence of water. The same authors point out the importance of other catalysing agents such as transition metals, i.e., Fe, Mn, Ti. L. Cimitan et al. (5), use NO_2 and O_3 as SO_2 catalyses, finding similar results as those described by previous authors.

In atmospheric simulation chambers, factors such as wind action, relative humidity, etc., are usually kept constant. Furthermore, damage functions have been established to determine the influence of those factors on degradation processes. For example, F. De Santis et al. (6) have established a theoretical equation for the reactivity of Thassos marble that depends on SO_2 concentration, relative humidity, deposition rate, stone shape, etc. Similar factors are considered by M. Steigner and W. Dannecker (7) in the determination of sandstone degradation equation. M.H. Reddy and S.D. Leith (8) established a theoretical model of SO_2 transport based in diffusion processes, in two different stones, marble and limestone, comparing experimental and theoretical data.

As it has been described before, the role played by mortars on building degradation is very important. However, few studies have been done (9), comparatively with stones decay. For this reason, the objective of this paper is to determine the behaviour of one of the most traditional mortars, i.e., lime mortar, in atmospheric simulation chambers.

Experimental

A. Lime Mortar Preparation. Specimens of lime mortar 50 × 30 × 5 mm size with aggregate/binder 3/1 ratio and water/lime 0.9 ratio were prepared. These specimens were maintained in a carbonation chamber with constant CO_2 flow and 50% relative humidity until their complete carbonation. The carbonation process was studied and controlled according to quantitative analysis of free $Ca(OH)_2$, present in the mortar (10).

The aggregate used was quartz of 98% purity and size less than 400 microns. The binder was a slaked lime 97.8% $Ca(OH)_2$ pure.

B. Atmospheric Simulation Chambers Conditions. The design of the chambers allowed work to be carried out under four sets of conditions simultaneously:

1) In the first chamber, pollutant gas was introduced.
2) In the second chamber, pollutant gas was mixed with oxidant (O_3) making it possible to study the additional effect of the presence of oxidant in the chamber.
3) In the third chamber, daily for 1h., some water was run over the top of the samples. Samples were inclined to allow water to flow down from the top of the specimens. This water was collected and analysed every week. The total amount of water collected every week was about 35 ml.
4) In the last chamber, pollutant gas and oxidant were introduced simultaneously. In addition water was present under the same conditions as in the third chamber.

Chambers 1) and 2) are called of dry deposition and 3) and 4) wet deposition.

TABLE 1

Nitrite and Nitrate Ions (ppm) in the Run-off and Retained Salts in the Lime Mortar Exposed to NO

	Run-off		**Retained Salts**	
	NO_2^-	**NO_3^-**	**NO_2^-**	**NO_3^-**
NO	--	--	0.05	0.53
$NO+O_3$	--	--	0.15	0.43
$NO+H_2O$	0.06	0.80	0.20	0.36
$NO+O_3+H_2O$	0.80	3.20	0.01	0.29

In all cases the pollutant gases were mixed with air and/or ozone before going into the chamber. The chamber conditions were: temperature 20°C and relative humidity 84%. Test time was 21 days in all cases. The pollutant gases used were: NO; NO_2 and SO_2; O_3 was used as the oxidant.

The presentation rates, in terms of mg of pollutant $cm^{-2}\ s^{-1}$, feeding into the chamber were as follows:

$$v_{NO} = 9.3 \times 10^{-3}\ mg\ cm^{-2}\ s^{-1}$$
$$v_{NO2} = 10.06 \times 10^{-3}\ mg\ cm^{-2}\ s^{-1}$$
$$v_{SO2} = 16.5 \times 10^{-3}\ mg\ cm^{-2}\ s^{-1}$$

C. Mortar Analyses. After exposure the retained soluble salts were extracted from mortars by water dissolution and then they were analysed. The anion concentrations there were determined by Ionic Chromatography (IC). In the case of the samples exposed in chambers 3) and 4), the salts concentrations in the run-off were also analysed by IC.

After exposure, the mortars were examined by scanning electron microscopy (SEM).

Results and Discussion

Results obtained for each pollutant gas are shown separately.

NO (g) Pollutant. Table 1 presents the ppm of nitrite and nitrate ions analysed in run-off and retained salts.

The concentration of the nitrite ion was lower than the nitrate ones. The amount of ions in the run-off was higher than in the retained salts indicating that most of the salts formed were washed off and collected in run-off. Salts formed in these mortars are calcium nitrite and nitrate both of them with high solubility in water, so most of the formed salts are removed in the run-off.

Transforming the NO_2^- values presented in the run-off into NO_3^- equivalent and adding to the same value in the retained salts, it is possible to obtain the nitrate equivalent total value. Those values, presents in Figure 1, are related to the total amount of salts formed. Thus it is possible to relate with the reactivity of lime mortar in the chamber conditions.

In the most aggressive conditions ($NO + O_3 + H_2O$) the amount of nitrate equivalent was a maximum of 5 ppm, indicating that the reaction between lime mortar and NO pollutant is not very important. In the case of the mortar exposed in chambers with additional water (wet exposure), nitrate equivalent total is greater than in dry exposures. This indicates that the

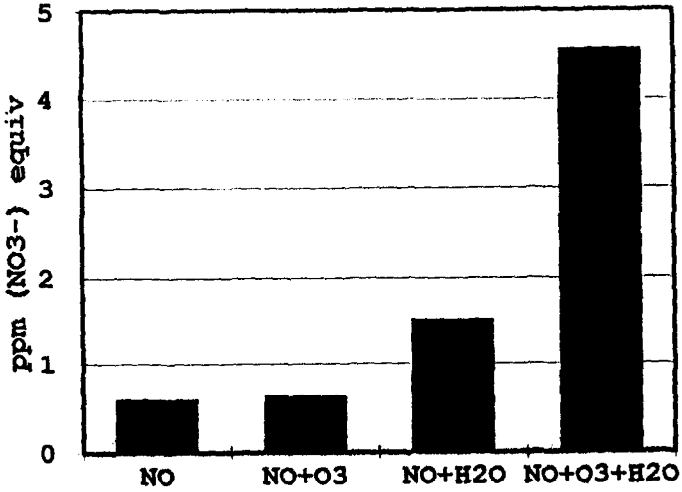

FIG. 1.
Nitrate equivalent total for lime mortar exposed in NO chambers.

dissolution of NO (g) in water is an important step in the reaction. The low solubility of NO (g) in water (7.34 ml per 100 ml of water) justifies the low reaction between lime mortar and NO pollutant even in wet exposures.

After exposure the SEM did not reveal any change in the appearance of the lime mortar.

NO_2 (g) Pollutant. Table 2 presents the NO_2^- and NO_3^- analysed in the run-off and in the retained salts. It is important to note that nitrites were only found in samples exposed in chamber 4, wet deposition with ozone ($NO_2 + O_3 + H_2O$).

As in the cases of the lime mortar exposed in chamber with NO pollutant, the amount of ions in the run-off were greater than in the retained salts, indicating that most of the salts are removed in the run-off. This was in agreement with the high solubility of the calcium nitrites and nitrates formed.

The values of the nitrate equivalent total are given in Figure 2. The larger value of nitrate equivalent total is for lime mortar exposed in $NO_2 + O_3 + H_2O$. It was no more than 3 ppm indicating a very low reaction between the lime mortar and the pollutant (NO_2) even in the presence of ozone and water.

TABLE 2

Nitrite and Nitrate Ions (ppm) in the Run-off and Retained Salts in the Lime Mortar Exposed to NO_2

	Run-off		Retained Salts	
	NO_2^-	NO_3^-	NO_2^-	NO_3^-
NO_2	--	--	0.0	0.06
NO_2+O_3	--	--	0.0	0.07
NO_2+H_2O	0.0	0.45	0.0	0.10
$NO_2+O_3+H_2O$	1.10	1.40	0.0	0.08

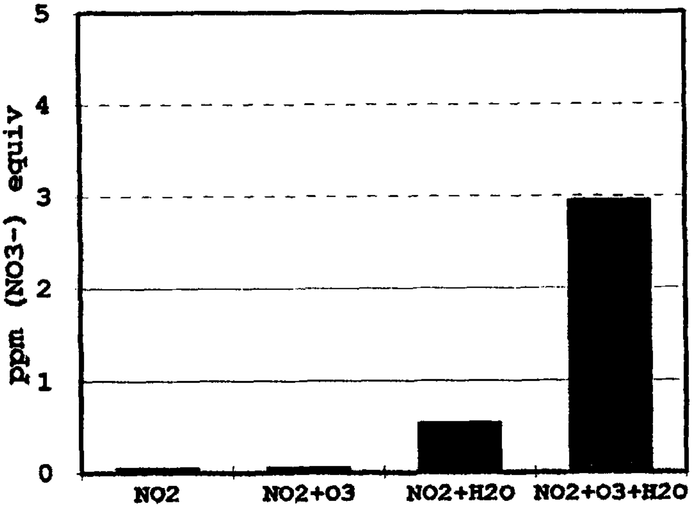

FIG. 2.

Nitrate equivalent total for lime mortar exposed in NO_2 chambers.

When lime mortar was exposed in wet conditions (additional presence of water, chambers 3 and 4), the reaction increased, indicating, again, that the dissolution of pollutant gas (NO_2) in water is one of the most important steps in the reaction between lime mortar and the NO_2 pollutant.

As for NO exposure, SEM examination did not reveal any change of lime mortar after 3 weeks exposure.

SO_2 (g) Pollutant. Table 3 shows the results of the analysis of the run-off and retained salts in lime mortar exposed in chambers with SO_2 pollutant gas. In this case only sulphate ions have been found. No sulphite was detected in any of the solutions, i.e., run-off and retained salts. According to P. Elfving et al. (11), the presence of sulphite ions in samples exposed in chambers with high relative humidity is very difficult to detect.

It was important to note the high concentration of SO_4^{2-} formed in the lime mortar exposed in the chamber with $SO_2 + O_3 + H_2O$.

Figure 3 shows the total concentration of sulphate ions formed in the lime mortar exposed in the SO_2 chambers. Those values are from the ion sulphate presented in the run-off and like retained salts in mortars. In this case, the presence of water or oxidant have similar

TABLE 3

Sulphate Ions (ppm) in the Run-off and Retained Salts in the Lime Mortar Exposed to SO_2

	Run-off SO_4^{2-} **(ppm)**	**Retained Salts** SO_4^{2-} **(ppm)**
SO_2	--	3.4
SO_2+O_3	--	19.2
SO_2+H_2O	17.0	4.8
$SO_2+O_3+H_2O$	9.3	536.0

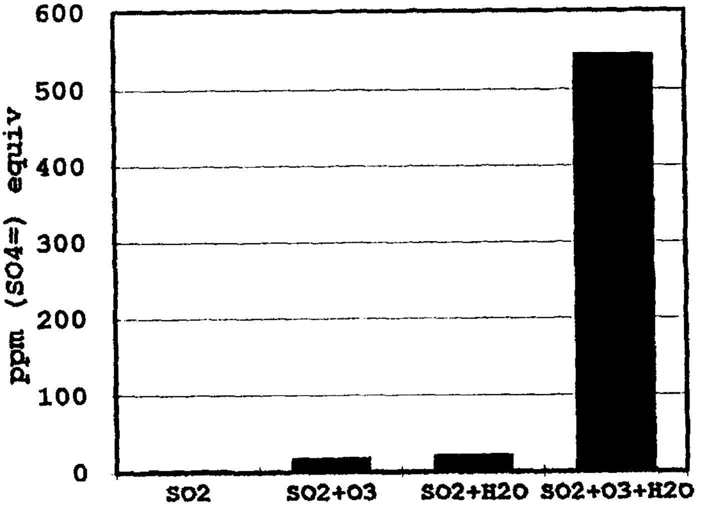

FIG. 3.
Sulphate total for lime mortar exposed in SO_2 chambers.

effect in the reaction. However, in the chamber with both together (oxidant and water) the reaction was increased to a very high level.

Further, when the exposed mortar was examined by SEM, different crystals were found. The presence of Ca, S and O (EDX analysis) suggested a calcium sulphate reaction product formed by reaction between lime mortar and pollutant gas.

C.M. Grossi et al. (2) in agreement with F. Girardet et al. (12) indicate the amount of gypsum formed in dolomitic stone by reaction with SO_2 depends on both the presence of a reactive phase in the stone and its exposure surface.

According to these authors (2,6,12) lime mortar reactivity depends on exposure surface, physical properties such as porosity, as well as, the presence of aerosol particles. From our point of view, the reaction also depends on the exposure conditions such as pollutant concentration, time exposure, number of samples in the chamber, etc. In order to reduce the influence of those parameters the concentration of anions (NO_2^-, NO_3^- and SO_4^{2-}) were transformed in presentation rates values. Furthermore to avoid the influence of pollutant gas concentration the "experimental presentation rate" (v_{exp}) to "pollutant presentation rate" (v_{gas}) ratio has been calculated (Table 4). The experimental presentation rates were calculated by transforming the NO_2^-, NO_3^- or SO_4^{2-} ppm values in terms of mg of pollutant per cm^2 per second.

TABLE 4

v_{exp}/v_{gas} Ratio

	NO	NO_2	SO_2
Gas	$2.6x10^{-5}$	$3.7x10^{-6}$	$9.3x10^{-5}$
Gas+Ozone	$2.7x10^{-5}$	$4.4x10^{-6}$	$5.3x10^{-4}$
Gas+Water	$6.6x10^{-5}$	$3.4x10^{-5}$	$6.0x10^{-4}$
Gas+Ozone+Water	$2.0x10^{-4}$	$1.8x10^{-4}$	$14.9x10^{-3}$

Wet deposition shows the importance of water as a reaction dissolution and transport medium for the reaction products as shown from the enhance of v_{exp}/v_{gas} ratio in gas + water or gas + water + ozone exposures.

In general ozone as oxidant increases the rate of the chemical reaction. According to S.J. Haneef et al. (3) the reaction between pollutant (NO; NO_2 or SO_2) and different stones depends on the porosity of the samples. For example, for Pentelic marble (0.3% porosity), the reactivity order is $SO_2 + O_3 > NO_2 + O_3 > NO + O_3$. However, for Portland limestone (up 15% porosity), more porous stone), the order changes as follow: $NO_2 + O_3 > SO_2 + O_3 \approx NO + O_3$. For lime mortar (30% porosity) exposures NO_2 has the lowest reactivity and SO_2 the highest, confirming the reactivity in ozone presence is changing for different porosity samples.

According to the values in Table 4 it was possible to determine the reactivity of lime mortar in different chambers with different pollutant gases, as well as, the influence of water and/or ozone. Following those values the next reaction order has been obtained:

$$NO_2 \leq NO_2 + O_3 < NO \leq NO + O_3 < NO_2 + H_2O < NO + H_2O < SO_2 < NO_2 + O_3 + H_2O \leq \\ NO + O_3 + H_2O < SO_2 + O_3 < SO_2 + H_2O << SO_2 + O_3 + H_2O$$

From to this scheme lime mortars exposed to NO and NO_2 pollutants under dry conditions (gas or gas plus ozone), have the lowest reaction. However, lime mortar exposed in the chamber with SO_2 pollutant has similar reaction to that in the cases of the same mortar exposed in $NO + O_3 + H_2O$ and $NO_2 + O_3 + H_2O$ conditions. Finally, the reaction between lime mortar and SO_2 in presence of ozone and water was very large.

Conclusions

The main conclusions that can be extracted from this work are the following:

1. The reaction between lime mortar and NO pollutant gas in atmospheric simulation chambers was low. Surface water enhance dry deposition effects mainly in the presence of ozone.

   From v_{exp}/v_{gas} ratio it is evident that NO pollutant gas is not oxidized to any significant extent in the presence of ozone.
2. NO_2 like pollutant has lower reactivity to lime mortar than NO pollutant gas. NO_2 in the gas phase oxidize in a few extent on O_3 presence.

   The reactivity of lime mortar slightly increase in the presence of water when NO_2 acts like pollutant.
3. Ozone increases SO_2 (g) oxidation in the absence of water. When water is running over the lime mortar surface, SO_2 increase reaction with lime mortar, in similar way than in ozone presence.

   Moreover, the presence of both water and ozone increase SO_2 pollutant gas reaction with lime mortar, to the extent of v_{exp}/v_{gas} ratio is two orders of magnitude bigger than in absence of ozone or water.
4. From v_{exp}/v_{gas} ratio, the aggresivity order of the pollutants to the lime mortar can be established in the following way:

$$NO_2 \leq NO_2 + O_3 < NO \leq NO + O_3 < NO_2 + H_2O < NO + H_2O < SO_2 < NO_2 + O_3 + H_2O \leq NO + O_3 + H_2O < SO_2 + O_3 < SO_2 + H_2O \ll SO_2 + O_3 + H_2O$$

indicating that dry deposition in chambers with NO and NO_2 like pollutants have the lowest reactivity.

5. The most aggressive environment for lime mortar is SO_2 in presence of water and ozone.

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