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EFFECT OF DRY DEPOSITION OF POLLUTANTS ON THE DEGRADATION OF LIME MORTARS WITH SEPIOLITE

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ABSTRACT

The behaviour of lime mortars containing sepiolite or sepiolite plus pentaclorophenol in atmospheric simulation chambers has been studied. The pollutant gases used in this study have been NO, NO_2, and SO_2. The studies has been done in wet and dry conditions as well as with and without ozone.

In the case of NO and NO_2, the aggressive agent would be HNO_3, which reacts with lime mortar binder $CaCO_3$, producing $Ca(NO_3)_2$ formation. On this process, the influence of the presence of an oxidant as well as water has been studied. The catalyst effect of the oxidation is known to be accelerated by water presence, so mortars exposed to $NO + O_3 + H_2O$ and $NO_2 + O_3 + H_2O$ environments undergo a greater salts formation than those exposed to the rest of the aggressive media. The three mortars' behaviours are similar and independent of their composition, producing small amount of salts in every case.

When SO_2 is the gas used, the aggressive agent of mortar will be H_2SO_4 that reacts with mortar binder, $CaCO_3$ to produce calcium sulphate in the form of gypsum. Oxidant and/or water influence has been studied, and the ($SO_2 + O_3 + H_2O$) chamber was found to be the one with greater aggressivity to mortars. However, in these conditions, sepiolite presence within the mortars delayed gypsum formation. *© 1998 Elsevier Science Ltd*

Introduction

For several years, lime mortar has reappeared in use with cement mortars, whose materials have different physico-mechanical properties as well as composition. Unfortunately the damage caused by cement mortars in the Cultural Heritage is more serious than the advantages produced. In the last two decades, many reparation works have been done in order to increase the knowledge of lime mortar reparation.

Nowadays it is well known that materials used in the repair of Cultural Heritage must not

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accelerate the decay of adjacent materials. Therefore, the conclusions of the Symposium "Mortars, Cements and Grouts used in the Conservation of Historic Buildings" (1) recommended to use repair materials which are as similar as possible in properties and composition to the original ones. Rossi-Doria (2) suggests some preliminary studies to be done in the field of repair mortars.

Consequently, a fundamental task prior to any repair, is the determination of the properties of the new and original materials and their behaviour under relevant environments situations.

Currently, numerous repairs are undertaken with lime-based mortars; hence, studies of building materials based on that binder have been intensified (3–5). Further, a new repair mortar (6), with lime as the fundamental binder, has been designed.

The new repair mortar includes the addition of a clay mineral, sepiolite, of formula, determined by Brauner and Preisinger (7), given below:

$$Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4$$

The mineral has a fibrous structure with zeolitic channels along the fibre, giving it high absorption and adsorption properties. Such properties have been used to retain a pentaclorophenol on the sepiolite, giving biocide properties to the final mortar. Pentaclorophenol (Cl_5C_6OH) acts as a biocide on a great number of micro-organisms. As the biocide is supported on the sepiolite, a number of additional advantages are presented, including the delay of biocide decomposition processes by sunlight; additionally, the direct contact of toxic biocides with skin is avoid.

The behaviour of lime mortar with sepiolite under various conditions must be quantified. Thus previous works (8), has compared the physical, mechanical, and rheological properties of a lime mortar with different sepiolite additions to the mortar without this clay mineral. It has been shown that sepiolite additions above 5% by weight modify substantially the final properties (mechanical strength, rheology, porosity, etc.) of the lime mortar. In addition, characterisation studies on lime mortar with additions of sepiolite plus retained biocide (pentaclorophenol) (9) have established that adsorbed biocide on the mineral does not modify the lime mortar.

We have undertaken studies to determined the behaviour of lime mortars, with sepiolite and sepiolite plus biocide, in atmospheric flow chambers, which allow realistic presentation rates of gaseous pollutants (NO, NO_2, and SO_2) under dry deposition conditions, as well as the additional effects of surface water and oxidant.

From comparison with earlier studies of similar mortars without sepiolite and biocide, the influence of such addition of chemical degradation may be quantified.

Experimental

The composition of the three mortars used in this study are given in Table 1. Samples of dimensions $0.05 \times 0.03 \times 0.005$ m, were prepared and cured as described elsewhere (8). Mortar M5* with biocide properties contains sepiolite impregnated with biocide. Pentaclorophenol impregnation on the sepiolite was undertaken. Initially, the clay was actived by heating to 175°C for 1 h. A solution of pentaclorophenol in toluene was prepared by adding between 2–3 g of biocide to 0.200 L of toluene. Between 5–10 g of the previously actived sepiolite was added to the solution. The solution was stirred for 60 s, after which it was

TABLE 1
Composition of the mortars employed.

Mortar Code	Sepiolite (%)	Sand/Aggregate	Water/(Lime + Sepiolite)
M0	0	1/3	0.9
M5	5	1/3	0.9
M5*	5*	1/3	0.9

* represents 5% sepiolite with retained biocide

filtered and the solid residue was washed with toluene. The solid was dried at 100°C to evaporate excess toluene.

Physical and mechanical properties of the mortars are presented in Table 2. The mortar specimens were exposed to dry deposition pollutant gases in specifically designed atmosphere flow chambers. The chambers allowed entry of humid air (84% RH) at 294 K, containing 10 vppm of the individual pollutant gases (NO, NO_2, or SO_2) with or without O_3 as oxidant (10 vppm) (10). The chambers allow the addition of the individual gases pollutant (NO, NO_2, or SO_2) in the presence or absence of ozone as oxidant and surface water to provide run-off. The exposure time was 21 days.

According to sample size, air rate, gas, concentration, etc., the amount of pollutant going to each sample is:

$$v_{NO} = 9.30 \times 10^{-2}\ g/m^2s$$

$$v_{NO2} = 10.06 \times 10^{-2}\ g/m^2s$$

$$v_{SO2} = 16.50 \times 10^{-2}\ g/m^2s$$

In Chamber 1, only pollutant is added. In Chamber 2, the additional influence of oxidant (O_3) was determined. In Chamber 3, the influence of water was established. Finally, in Chamber 4, the influence of the joint action of ozone and water was examined. Water addition in Chambers 3 and 4 was sufficient to provide run-off, which was analysed for nitrite, nitrate, sulphite, and sulphate species, depending of the particular exposure regime employed.

At the end of the test, samples were removed from the chambers and percentages of water soluble salts retained in the specimens was determined. This was achieved by extraction from 1 g of the previously ground sample in 0.100 L of deionized water. The mix was stirred for 1 h; the pH determined after 1 h.

For the extracted liquids, the NO_2^-, NO_3^-, and SO_4^{2-} concentrations present in water-

TABLE 2
Physico-mechanical properties of the mortars.

Mortar Code	Compressive Strength (MPa)	Porosity (%)	Absorption coeff. ($kg/ms^{1/2}$)
M0	5.4 ± 1.0	30.62 ± 0.01	0.26 ± 0.01
M5	5.2 ± 0.5	30.53 ± 0.01	0.24 ± 0.01
M5*	4.1 ± 0.5	30.09 ± 0.01	0.24 ± 0.01

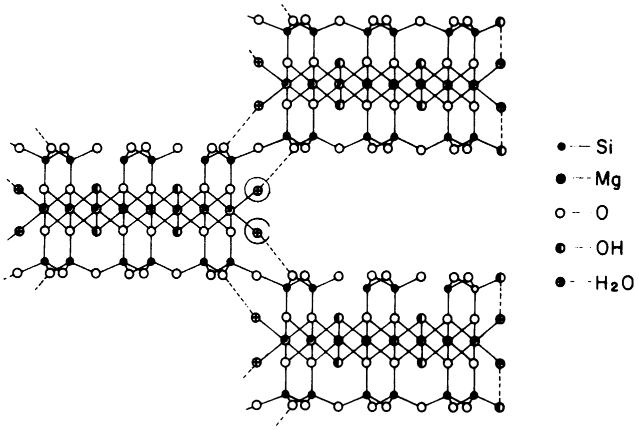

FIG. 1.
Sepiolite structure.

soluble salts were analysed by ion chromatography (IC). No SO_3^{2-} was detected in any cases.

For the specimens exposed in Chambers 3 and 4 environments, 0.035 L of water was passed over the specimens' exposed surfaces to produce run-off. The collected run-off was analysed on a weekly basis for NO_2^-, NO_3^-, SO_3^{2-}, and SO_4^{2-}.

Results and Discussion

Results are presented as concentrations of anions in run-off, retained salts, as well as percentages of pollutant conversion. In NO and NO_2 exposures, NO_2^- and NO_3^- were analysed. Total anion concentration are calculated transforming NO_2^- to $(NO_3^-)_{\text{equivalent}}$ and adding it to the NO_3^- ion concentrations. For SO_2 exposures, only SO_4^{2-} was detected. For Chambers 1 and 2, no run-off was available and the total anion concentrations presented in the figures correspond to soluble salts retained in the mortar. In the second case, mortars exposed in Chambers 3 and 4, involving mortars exposed to pollutant gas plus water and pollutant gas plus ozone plus water, the anion concentration in the run-off are given as well as anions retained in the mortars.

Total anion concentrations analysed are related directly to the amount of salts formed by reaction of the pollutant gas and the mortar constituent. The percentage of pollutant gas conversion gives information about the aggressivity of the pollutant to the mortar in the chamber conditions.

The pH value of the run-off and the solutions of extracted anions for the mortars were determined. In every case, the pH value was close to 7 for mortars without sepiolite and close to 11 for mortars with sepiolite in aqueous solution. The hydrolysis of the silanols present in the sepiolite structure (Fig. 1) produced those higher pH value (11).

In the case of the mortar with sepiolite plus biocide (M5*), the pH of the solution is lower ($pH = 8$) due to the reaction between the acid (HNO_3 or H_2SO_4) and the pentaclorophenol. This reaction decreases the pH of the solution.

TABLE 3
Total anions concentrations (ppm of total nitrate equivalent) analysed in mortars exposed in NO_2 chambers.

	$(NO_3^-)_{eq}$ (ppm) Mortar M0	$(NO_3^-)_{eq}$ (ppm) Mortar M5	$(NO_3^-)_{eq}$ (ppm) Mortar M5*
NO_2	0.06	0.10	0.08
$NO_2 + O_3$	0.07	0.10	0.09
$NO_2 + H_2O$	0.55	0.59	0.60
$NO_2 + O_3 + H_2O$	3.0	3.50	2.69

NO_2 (g) Medium

The anion concentrations from retained anions and anions in the run-off for specimens exposed in the four chambers are presented in Table 3. Only NO_2^- was detected in the run-off.

In the absence of run-off, concentrations are very low, <0.1 ppm, for NO_2 and NO_2+O_3 exposures. For exposure to $NO_2 + H_2O$, anion concentrations increase slightly to values close to 0.6 ppm. For $NO_2 + O_3 + H_2O$ exposure, nitrate and nitrite concentrations are almost three times greater than those of the previous exposure, reaching values close to 1.5 ppm.

The anion concentrations in the run-off (Table 3) of the samples exposed in $NO_2 + H_2O$ are greater than those retained in the mortars, indicating that most of the salts are presents in the run-off. In the mortar degradation process, highly soluble calcium nitrate is produced, favouring its loss to the run-off.

Table 4 shows the percentage of NO_2 conversion. According to those values, the presence of water and particularly water and oxidant increase the reaction between lime mortar and NO_2.

The values for the different mortars in the four chambers in increasing order are the following:

$$\text{For M0: } NO_2 < NO_2 + O_3 < NO_2 + H_2O < NO_2 + O_3 + H_2O$$

$$\text{For M5: } NO_2 = NO_2 + O_3 < NO_2 + H_2O < NO_2 + O_3 + H_2O$$

$$\text{For M5*: } NO_2 < NO_2 + O_3 < NO_2 + H_2O < NO_2 + O_3 + H_2O$$

Those values indicate that the presence of sepiolite does not modify the reaction order. The presence of ozone decrease the reactivity of the lime mortar with sepiolite in NO_2 chambers.

TABLE 4
Percentage of NO_2 conversion.

	Mortar M0	Mortar M5	Mortar M5*
NO_2	3.0×10^{-6}	5.0×10^{-6}	4.0×10^{-6}
$NO_2 + O_3$	3.5×10^{-6}	5.0×10^{-6}	4.5×10^{-6}
$NO_2 + H_2O$	27.5×10^{-6}	29.5×10^{-6}	30.0×10^{-6}
$NO_2 + O_3 + H_2O$	150.1×10^{-6}	174.9×10^{-6}	134.2×10^{-6}

TABLE 5
Total anions concentrations (ppm of total nitrate equivalent) analysed in mortars exposed in NO chambers.

	$(NO_3^-)_{eq}$ (ppm) Mortar M0	$(NO_3^-)_{eq}$ (ppm) Mortar M5	$(NO_3^-)_{eq}$ (ppm) Mortar M5*
NO	0.57	0.56	0.44
$NO + O_3$	0.63	0.49	0.61
$NO + H_2O$	1.51	2.11	2.47
$NO + O_3 + H_2O$	4.58	6.48	9.79

NO (g) Medium

Table 5 shows the concentration of nitrite and nitrate anions in run-off and retained salts, associated with the mortars exposed to the environments of the four chambers. It is observed that for mortars maintained in chambers with no additional water (NO and $NO + O_3$), the anion concentrations are similar and of relatively low concentrations, i.e., 0.6 ppm. The presence of sepiolite in the mortar, with or without biocide, does not influence this behaviour to any significant level.

In the presence of surface water to provide run-off, slightly increased anion concentrations are revealed, with values between 1.5 and 2.7 ppm. In this medium, it is evident that the anion concentrations increase in the presence of sepiolite and sepiolite with retained biocide.

Table 6 shows percentage of NO conversion. For the mortars with sepiolite, exposed in $NO + O_3 + H_2O$, the percentage of NO conversion is higher, indicating greater reaction between the mortar and NO pollutant.

The increasing order of those values for the three mortars are the following:

$$\text{For M0: } NO < NO + O_3 < NO + H_2O < NO + O_3 + H_2O$$

$$\text{For M5: } NO + O_3 < NO < NO + H_2O < NO + O_3 + H_2O$$

$$\text{For M5*: } NO < NO + O_3 < NO + H_2O < NO + O_3 + H_2O$$

The presence of sepiolite modifies the reaction order in the case of the lime mortar exposed in $NO + O_3$.

Comparing the values in Tables 4 and 6, the mortars M0 and M5 have low reaction in NO_2 in the absence of water, but this reaction is greater in the presence of water. Therefore, M5* always has a greater reaction in NO exposure.

TABLE 6
Percentage of NO conversion.

	Mortar M0	Mortar M5	Mortar M5*
NO	8.8×10^{-6}	9.3×10^{-6}	7.2×10^{-6}
$NO + O_3$	10.3×10^{-6}	8.3×10^{-6}	10.3×10^{-6}
$NO + H_2O$	25.3×10^{-6}	35.1×10^{-6}	41.3×10^{-6}
$NO + O_3 + H_2O$	76.4×10^{-6}	108.5×10^{-6}	163.7×10^{-6}

TABLE 7
Total sulphate (ppm) analyse in lime mortars exposed in SO_2 chambers.

	$(SO_4^{2-})_{total}$ (ppm) Mortar M0	$(SO_4^{2-})_{total}$ (ppm) Mortar M5	$(SO_4^{2-})_{total}$ (ppm) Mortar M5*
SO_2	3.4	11.2	13.5
$SO_2 + O_3$	19.2	8.0	4.7
$SO_2 + H_2O$	21.8	15.8	9.6
$SO_2 + O_3 + H_2O$	545.3	57.7	52.7

Comparing anion concentrations in the run-off to retained salts for mortars exposed to NO + O_3 + H_2O, the three mortars are less than 1 ppm. However, anion concentrations in the run-off are 4 ppm for M0, 5 ppm for M5, and 9 ppm for M5*. This reveals again that most of the salts formed are not retained in the mortar, but are lost to run-off. For this exposure, the salt formed is calcium nitrate, which is highly soluble (660 g per 100 cc H_2O at 30°C), and deliquescent, favouring its presence in the run-off.

Overall, it is evident that the presence of sepiolite and sepiolite with retained biocide favours soluble salts formation in mortar exposed in presence of water probably through their high water-absorption capacity.

SO_2 (g) Medium

The sulphate concentrations in mortars for the four exposure regimes studied are show in Table 7.

For exposure to SO_2 pollutant gas, SO_4^{2-} concentrations are greater than NO_2^- and NO_3^- concentrations for exposure to NO and NO_2 pollutant gases, i.e., about 100 times higher.

Sulphate concentrations in mortars exposed to $SO_2 + O_3 + H_2O$ are greater than the other three exposures with significant differences revealed for mortars with and without sepiolite. For the mortar without sepiolite (M0), the sulphate concentration is greater than 500 ppm, whereas for the two mortars with sepiolite, M5 and M5*, the sulphate concentrations range up to 50–60 ppm.

For the mortars exposed in the additional presence of water ($SO_2 + H_2O$), sulphate concentrations are similar, with values close to 20 ppm for M0 mortars, decreasing to 15 ppm for M5 mortars and 10 ppm for M5* mortars.

Table 8 shows percentages of SO_2 conversion. The increasing order of those values for the different mortar are the following:

$$\text{For M0: } SO_2 < SO_2 + O_3 < SO_2 + H_2O \ll SO_2 + O_3 + H_2O$$

$$\text{For M5: } SO_2 + O_3 < SO_2 < SO_2 + H_2O < SO_2 + O_3 + H_2O$$

$$\text{For M5*: } SO_2 + O_3 < SO_2 + H_2O < SO_2 < SO_2 + O_3 + H_2O$$

Again, the presence of sepiolite decrease the reaction in ozone presence.

Reactions produced between the mortar and the SO_2 pollutant gas occur by different mechanisms in water presence or absence; calcium sulphate dihydrate (gypsum) is the final product in every cases, formed by H_2SO_4 attack on mortar binder $CaCO_3$.

TABLE 8
Percentage of SO_2 conversion.

	Mortar M0	Mortar M5	Mortar M5*
SO_2	9.1×10^{-5}	30.1×10^{-5}	37.0×10^{-5}
$SO_2 + O_3$	52.7×10^{-5}	21.8×10^{-5}	12.7×10^{-5}
$SO_2 + H_2O$	59.4×10^{-5}	43.0×10^{-5}	26.1×10^{-5}
$SO_2 + O_3 + H_2O$	1490.9×10^{-5}	158.2×10^{-5}	144.2×10^{-5}

In the absence of water, chemical attack is initiated by a heterogeneous reaction between a solid ($CaCO_3$) and a gas (SO_2).

Cimitàn et al. (12) indicate that the reaction set giving place to gypsum formation in this type of materials requires an induction time necessary to overcome an energy barrier, probably in the SO_2 (g) oxidation phase. They indicate, also, the existence of a series of reaction catalyst substances as V_2O_5, Fe_2O_3, C; hence, that gas would adsorb on the catalyst surface, where the oxidation process would occur. The catalyst function is, therefore, to adsorb the gas and to favour the oxidation in its surface.

In the presence of water, SO_2 (g) dissolves and oxidation occurs in solution.

Sepiolite is a mineral with a high specific surface (close to 300 m^2/g) and high adsorption and absorption capacity (13), and it may act as catalyst on which SO_2 (g) would adsorb, favouring reactions and provoking mortar binder $CaCO_3$ attack.

In the chamber with SO_2-like pollutant, without water and oxidant, sepiolite could have the catalyst effect cited before, because the values of Table 8 for M0 are lower than for M5 and M5* mortars.

However, in the presence of the oxidant and/or water, the catalytic effect is not observed.

This can be interpreted as the occurrence of a process that invalids or compensates the sepiolite catalyst effect.

On the other hand, the induction time indicated by Cimitàn et al. (12) is close to 3 weeks. If this test duration is taken into account (21 days), we are in the limit to overcome the induction time barrier. It is not clear the effect on that time of sepiolite in the mortar, when oxidant and/or water is added in the chamber.

High sulphate concentrations are retained and present in the run-off (Table 7) from the M0 mortars exposed to $SO_2 + O_3 + H_2O$ as well as the highly reactive $(g\ SO_2)_{exp}/(g\ SO_2)_{th}$ (Table 8). This indicates the high reactivity of SO_2 in the presence of water and oxidant. In these conditions, a rate determinant step does not exist, favouring the high sulphate amount formed. As it has been indicated, it is possible that the induction time has not been passed, except for the M0 mortar exposed in $SO_2 + O_3 + H_2O$ medium, it is evident that water-soluble salt concentrations are higher than those in the run-off. This is due to the high salt amount formed, all of which cannot be washed in the run-off.

Conclusions

From a dry deposition study of mortars with 0% and 5% sepiolite in their composition, and mortars with 5% sepiolite retaining Cl_5C_6OH, the following conclusions are made:

1. NO_2 gas exposure has a reduced reactivity for NO exposure. Results obtained in both media are similar, indicating the higher aggressivity of the medium with oxidant and water contribution ($NO_2 + O_3 + H_2O$), likewise, it indicates how sepiolite or sepiolite with pentaclorophenol retained have no influence in salt formation on lime mortars. Most of the salts formed are in the run-off.
2. NO medium has relatively low interaction with the mortars. The chemical reactivity of the mortars is similar, and neither sepiolite nor sepiolite with retained biocide have a significant effect. The most reactive conditions is exposure to $NO + O_3 + H_2O$. The high solubility of the $Ca(NO_3)_2$ salt formed by reaction between the pollutant gas and mortar, favours its presence in the run-off.
3. SO_2 pollutant gas is the most reactive to this type of mortars, particularly in the presence of oxidant and water ($SO_2 + O_3 + H_2O$). In that situation, sepiolite in the mortar, reduces the reaction between pollutant gas and mortar. Sepiolite could have a catalyst effect in the sulphate formation process in the medium with only SO_2 contribution. That effect is delayed by O_3 and/or water action.

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