DETERIORATION OF PENTELIC MARBLE, PORTLAND LIMESTONE AND BAUMBERGER SANDSTONE IN LABORATORY EXPOSURES TO GASEOUS NITRIC ACID

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Abstract—The effects of gaseous nitric acid on three calcareous stones (Pentelic marble, Portland limestone and Baumberger sandstone), used extensively in historic buildings, have been investigated under different conditions of relative humidity, mass of stone, nitric acid concentration, grain size of stone and flow rate of nitric acid mixture. It was found that all three stones are good sinks for gaseous nitric acid. Pentelic marble proved to be more vulnerable at relatively high humidities in spite of its low porosity. The other two stones behave similarly in spite of the difference in their chemical constitutions. Apparently this difference is counterbalanced by their great difference in porosity.

Key word index: Pentelic marble, Portland limestone, Baumberger sandstone, deterioration, nitric acid.

INTRODUCTION

Monuments and historic buildings made of calcareous stones are vulnerable to acidic air pollutants.

One of these, CO₂, has always been part of this planet’s atmosphere and although its concentration has increased appreciably from anthropogenic sources, its adverse effects on marble monuments have been relatively small (Winkler, 1970).

The effects of SO₂ and its oxidation products, on the other hand, have been much more serious. The product of the ensuing chemical reactions, gypsum, is much more brittle and soluble than marble. This phenomenon has been studied exhaustively, but it is still being investigated.

The study of the effects of NOₓ and their oxidation products, however, started much more recently. These substances are primary and secondary pollutants of “Los Angeles smog” (the term “smog” is a misnomer in this case), the mechanism of formation of which was elucidated by Haagen-Smith et al. (1952).

In 1979 it was proposed (Sikiotis, 1979) that the increasing air pollution in Athens was mainly photochemical in nature and that nitric acid and nitrates produced photochemically could have adverse effects on marble and other calcareous stones.

The presence of nitrates in the atmosphere of Athens and the adverse effects of their dry deposition on marble monuments was investigated in the field (Sikiotis et al., 1991, 1992; Sikiotis and Delopoulou, 1992; Delopoulou and Sikiotis, 1991, 1992; Kirkitsos and Sikiotis, 1991, 1992, 1993a, b).

The conclusions drawn from these investigations can be summarized as follows:

The concentrations of nitrates in the atmosphere of Athens were comparable with those in American cities with high levels of photochemical pollution.

The surface density of nitrates found on the columns of the Parthenon during the dry season was significant.

The nitration and sulphation of Pentelic marble on the Acropolis were found to be of the same order of magnitude.

The nitrates and sulphates in the Acropolis air are much more corrosive than the corresponding oxides, despite the fact that the concentrations of the oxides in the ambient air were much greater.

These field experiments have been complemented by the laboratory experiments described below. Laboratory conditions allow better control of the variables determining the degree of nitration of calcareous stones.

The first nitrogen containing pollutant to be tested in the laboratory was HNO₃ (Sikiotis and Kirkitsos, 1994). The field work mentioned above has shown that HNO₃ is relatively more aggressive than other nitrates and other nitrogen containing pollutants. It is also relatively more abundant than other NOₓ during the summer months since the dissociation of NH₄NO₃:

\[ \text{NH}_4\text{NO}_3 (s) \rightarrow \text{NH}_3 (g) + \text{HNO}_3 (g) \]
is almost complete and the formation of NaNO₃:

\[ \text{NaCl (s) + HNO₃ (g) → NaNO₃ (s) + HCl (g)} \]

is minimal at temperatures and relative humidities occurring frequently in Athens during the dry season (Stelson and Seinfeld, 1982a, b; Pilinis and Seinfeld, 1987).

**EXPERIMENTAL**

The HNO₃ generator used in the laboratory experiments is depicted in Fig. 1. This apparatus is a variant of a HNO₃ generator described in the literature (Nunnermacher et al., 1989). Gaseous HCl passed at a preset flow rate through the mass flow controller MFC1 and was converted quantitatively to gaseous HNO₃ in the two reactors containing AgNO₃ crystals. The HNO₃ was diluted with N₂, the relative humidity of which (RH%) was varied with the aid of bubblers 3 and 4 and measured with a "T and RH monitor". The diluted HNO₃ passed through the graded stone grains. Any unreacted HNO₃ was retained quantitatively in bubblers 1 and 2.

The stones were crushed, pulverized and graded. The grains to be used were of three sizes, 1-2, 0.5-1, and 0.2-0.5 mm. The graded grains were washed repeatedly with deionized water with the aid of an ultrasonic bath (U.B.), until the remaining nitrate per gramme of stone was less than 5% of the amount of HNO₃ to be retained by the stone in the exposure experiment to be performed. The washed grains were dried in an oven at 105°C for several hours. A combined sample from these grains was washed with 50 ml deionized water, using a U.B. for 30 min. The nitrate concentration of the supernatant liquid was determined by IC (Dionex 2010i) according to the Dionex protocol. The stone blanks are listed in Table 1. These blanks were negligibly small when compared with the NO₃⁻ quantities retained on the stone grains in the experiments described below.

Teflon filters, chamber rings and all components coming into contact with HNO₃ were washed as described above and the washings were analysed for nitrate by IC. These blanks were as follows: Teflon filters from first container: 0.57 μg NO₃⁻ per filter, Teflon filters from second container: 0.52 μg NO₃⁻ per filter and chamber rings: 2.266 μg NO₃⁻ per ring.

A known mass of stone grains was exposed under controlled conditions. After exposure the grains were flushed of any unreacted HNO₃ with N₂ and were transferred quantitatively into a beaker containing 100 ml of deionized water. The Teflon filters and chamber rings, which were in contact with the grains, were also placed in the same beaker. The beaker was placed in the U.B. for 30 min and the supernatant liquid was analysed for nitrate with IC. It was found that the conversion of HCl to HNO₃ was quantitative as reported in the literature (Nunnermacker et al., 1989).

250 ml of deionized water were placed in each of bubblers 1 and 2. Before the commencement of the experiment, 20 ml from each bubbler was taken out and analysed by IC for nitrate as a blank. At the end of the experiment the analysis was repeated on the contents of the two bubblers.

The percentage retention of HNO₃ on stone (R) was calculated by the following expression:

\[ R = \frac{S}{S + B} \times 100 \]

where S and B are the masses of NO₃⁻ retained on stone and bubblers (1 and 2), respectively.

The effect on R was tested by varying the following parameters: relative humidity, mass of stone, grain size, HNO₃ concentration and flow rate of HNO₃ mixture.

The relative humidity was adjusted with the aid of two bubblers No. 3 and 4 (Fig. 1), containing various quantities of water to adjust the humidity.
Effects of gaseous H\textsubscript{2}O\textsubscript{3} on calcareous stones

Table 1. Mean blank values in $\mu$g NO\textsubscript{3} per gramme and total pore area in m\textsuperscript{2} g\textsuperscript{-1} of stones

<table>
<thead>
<tr>
<th>Stone</th>
<th>Size (mm)</th>
<th>Mean</th>
<th>Std</th>
<th>N</th>
<th>Total pore area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentelic marble</td>
<td>1.0-2.0</td>
<td>0.230</td>
<td>0.070</td>
<td>3</td>
<td>0.066 ± 0.0008</td>
</tr>
<tr>
<td>Pentelic marble</td>
<td>0.5-1.0</td>
<td>0.423</td>
<td>0.009</td>
<td>3</td>
<td>0.053 ± 0.0011</td>
</tr>
<tr>
<td>Pentelic marble</td>
<td>0.2-0.5</td>
<td>0.404</td>
<td>0.154</td>
<td>3</td>
<td>0.096 ± 0.0009</td>
</tr>
<tr>
<td>Portland limestone</td>
<td>1.0-2.0</td>
<td>0.250</td>
<td>0.290</td>
<td>3</td>
<td>0.811 ± 0.0089</td>
</tr>
<tr>
<td>Portland limestone</td>
<td>0.5-1.0</td>
<td>0.390</td>
<td>0.490</td>
<td>3</td>
<td>0.896 ± 0.0140</td>
</tr>
<tr>
<td>Portland limestone</td>
<td>0.2-0.5</td>
<td>0.250</td>
<td>0.180</td>
<td>3</td>
<td>0.862 ± 0.0152</td>
</tr>
<tr>
<td>Baumberger sandstone</td>
<td>1.0-7.0</td>
<td>0.440</td>
<td>0.100</td>
<td>3</td>
<td>9.300 ± 0.1125</td>
</tr>
<tr>
<td>Baumberger sandstone</td>
<td>0.5-1.0</td>
<td>2.240</td>
<td>0.370</td>
<td>3</td>
<td>9.138 ± 0.1347</td>
</tr>
<tr>
<td>Baumberger sandstone</td>
<td>0.2-0.5</td>
<td>3.530</td>
<td>1.990</td>
<td>3</td>
<td>7.599 ± 0.0456</td>
</tr>
</tbody>
</table>

of water and measured with a digital temperature and relative humidity monitor. The flow rate was adjusted and measured with three mass flow controllers (Tylan MFC, No. 1, 2 and 3 Fig. 1). The total pore area of the grains was determined by the argon absorption dynamic B.E.T. method. The results are reported in Table 1.

Finally, the HNO\textsubscript{3} concentration was adjusted with MFC1 and measured by the following expression:

$$[\text{HNO}_3] = \frac{(S + B) \times 63}{(\text{MFC1} + \text{MFC2} + \text{MFC3}) \times 1000 \times 62} \quad (2)$$

where $[\text{HNO}_3]$ is the HNO\textsubscript{3} concentration in $\mu$g m\textsuperscript{-3}, S and B are the masses of NO\textsubscript{3} retained on stone and bubblers (1 and 2), respectively in $\mu$g, MFC1, MFC2 and MFC3 are the three flow rates in 1 min\textsuperscript{-1} and $t$ is the duration of the experiment, generally between 20 and 60 min.

**RESULTS AND DISCUSSION**

**Pentelic marble**

Figure 2a shows the variation of $R$ with relative humidity for Pentelic marble. All other parameters were held constant. It can be seen that $R$ rises sharply between relative humidities 5-25% and then approaches 100%, i.e., complete retention of HNO\textsubscript{3} on marble.

Figure 2b shows the variation of $R$ with mass from four experiments. These experiments were performed at high relative humidity, where $R$ is approximately 100%, in order to test the depth of the layer of grains removing HNO\textsubscript{3}. It is apparent that a relatively small depth of the layer is sufficient for complete retention of HNO\textsubscript{3}.

The effect of HNO\textsubscript{3} concentration of $R$ was also tested at high relative humidity. Figure 2c shows that it was negligible. The minimum HNO\textsubscript{3} concentration used was more than one order of magnitude higher than those occurring in the atmosphere during photochemical episodes. A concentration of 54.0 $\mu$g m\textsuperscript{-3} HNO\textsubscript{3}, approaching maximum ambient HNO\textsubscript{3} levels in polluted cities, was also used and the value of $R$ determined shows almost complete retention as in all the other cases (this experiment was not included in Fig. 2c because of the different flow rate employed).

Low relative humidities were used to test the effect of grain size on $R$. Figure 2d shows that $R$ increases sharply to approximately 100% for the smallest grain size. The explanation proposed for this increase is in terms of an increase in total pore area and the number of collisions of HNO\textsubscript{3} molecules with marble grains. The latter is due to the decrease in intergranular space resulting from a decrease in grain size.

To test the effect on $R$ of the speed of passage of the HNO\textsubscript{3} containing mixture, over the grains, the flow rate of the mixture was varied at high relative humidities. Figure 2e shows that a doubling of the flow rate has a negligible effect on $R$.

**Portland limestone**

Figure 3a shows the variation of $R$ with relative humidity for Portland limestone. All other parameters were held constant. In these experiments the mass of grains used was 19 g. For relative humidities (RH) under ~15% there is a decrease in $R$ of ~30%. Figure 3b shows again the variation of $R$ with RH. The mass of grains used in each case, however, was 10 g. A decrease in $R$ was observed for RH < 40% and this reached values in the range 40-55% for RH < 10%. These sets of experiments show an increase in the RH value corresponding to almost complete retention of HNO\textsubscript{3} ($R$ ~ 100%) with a decrease of the total pore area of stone.

Figure 3c shows the variation of $R$ with mass from three experiments. These experiments were performed at high relative humidity, where $R$ is approximately 100%, in order to test the depth of the layer of grains removing HNO\textsubscript{3}. It was found that unlike the case of marble (Fig. 2b) 5 g of Portland limestone retained only 60% of HNO\textsubscript{3}.

The effect of HNO\textsubscript{3} concentration on $R$ was also tested at high relative humidity. Figure 3d shows that, as in the case of marble (Fig. 2c), it was negligible. The minimum HNO\textsubscript{3} concentration used was more than one order of magnitude higher than those occurring in the atmosphere during photochemical episodes.

Low relative humidities were used to test the effect of grain size on $R$. Figure 3e shows that $R$ increases sharply to approximately 100% for the smallest grain size. Since the total pore area determined for the different grain sizes in the case of Portland limestone (Table 1) did not vary significantly, the high retention cannot be explained in terms of the variation in total pore area. A possible explanation can be based on the
Retention of HNO₃ on Marble (%)

(a) Relative Humidity (%)

(b) Mass of Marble Grains (gr)

(c) Concentration of HNO₃ (ppm)

(d) Diameter of Grains (mm)

Fig. 2(a)–(d).
Fig. 2. Retention of nitric acid on Pentelic marble grains vs (a) relative humidity, (b) mass of grains, (c) HNO₃ concentration, (d) diameter of grains and (e) flow rate.

Fig. 3(a)-(c).
Fig. 3. Retention of nitric acid on Portland limestone grains vs (a) relative humidity for 19 g of grains, (b) relative humidity for 10 g of grains, (c) mass of grains, (d) HNO₃ concentration, (e) diameter of grains and (f) flow rate.

fact that the intergranular space in the case of the small diameter grains is smaller, hence the number of collisions of the HNO₃ molecules with the stone surface is higher.

To test the effect on $R$ of the speed of passage of the HNO₃ containing mixture over the grains, the flow rate of the mixture was varied at RH 30–36% where $R$ reaches ~100% (Fig. 3b). Figure 3f shows that a doubling of the flow rate has a negligible effect on $R$.

Baumberger sandstone

Figure 4a shows the variation of $R$ with relative humidity for Baumberger sandstone. All other parameters were held constant. It can be observed that generally $R$ is high. In two cases, one at low RH and the second at an intermediate value, $R$ was significantly lower. This was probably due to the heterogeneity of Baumberger sandstone (Table 2).
Effects of gaseous HNO₃ on calcareous stones

Fig. 4(a)-(d).
Figure 4b shows the variation of $R$ with mass from two experiments. These experiments were performed at relative humidities $\sim 22\%$. In this case, there was a decrease in $R$ showing that the corresponding depth of grains was not sufficient to retain all HNO$_3$.

There was no significant variation in $R$ (Fig. 4c) when HNO$_3$ concentration was varied in the range of 1400–4600 $\mu$g m$^{-2}$ at humidities $> 22\%$.

Five experiments were performed at low humidities ($< 5\%$) by varying the grain diameter of the samples. Figure 4d shows a tendency for a decrease in $R$ with a decrease in grain diameter. Since this decrease in diameter does not represent a decrease in total pore area (Table 1), the variation in $R$ at these low relative humidities was probably due to the heterogeneity of the Baumberger sandstone (Table 2).

The variation of the flow rate of the gaseous HNO$_3$ mixture was tested in three experiments employing RH values $\sim 22\%$. A doubling of the flow rate had no effect on $R$ which remained $> 95\%$.

Comparison of stone vulnerability to gaseous HNO$_3$

In what follows it has been attempted to compare the vulnerability (deterioration index) of the three stones to gaseous HNO$_3$. This vulnerability must be due to two factors: the chemical reactivity of the stone with HNO$_3$ and its total pore area.

Table 1 shows that the total pore area of the three stones being studied varies greatly.

A parameter termed chemical reactivity (CR) was defined as follows:

$$CR = \frac{R}{M \times TPA}$$

where $M$ is the mass of grains and TPA is the total pore area of the grains per gramme in m$^2$ g$^{-1}$. CR can be used to compare different stones of the same grain size.

It can be claimed that for experiments in which $R$ was approaching 100% the mass of grains used hence the pore area available were more than sufficient to retain all the HNO$_3$. This means that the pore area that actually had retained the HNO$_3$ was smaller and hence the mass of grains used in computing CR was larger than it should be, resulting in an underestimation of CR values in those cases. This became obvious in the experiments employing low masses where $R \sim 100\%$ and CR values were much greater than the other cases.

Consequently, for each one of the three stones, all underestimated CR values but one were rejected. The remaining CR values were plotted against RH by using linear regression. Figure 5 shows that the rise of CR with RH for Pentelic marble is much larger than those for the other stones. The low CR of Baumberger sandstone is expected because of its high content in unreactive SiO$_2$.

The deterioration index per gramme of grains (DI$_g$) of the stones was obtained by multiplying the CR values by the corresponding total pore area. Thus DI$_g$ is given by the following expression:

$$DI_g = CR \times TPA$$

Figure 6 shows plots of the DI$_g$ of each stone vs RH for the same experiments as for Fig. 5.

A more useful comparison for monuments made from these stones would be in terms of a deterioration index per unit geometric surface area, DI$_s$. This deterioration index (DI$_s$) can be calculated by multiplying the previous DI$_g$ by the mass of grains ($M$) and dividing by the geometric surface area of the grains ($S$).
Effects of gaseous HNO₃ on calcareous stones

Fig. 5. Chemical reactivity vs relative humidity for Pentelic marble, Portland limestone and Baumberger sandstone.

Fig. 6. Deterioration index per gramme of grains (DIₜ) vs relative humidity for Pentelic marble, Portland limestone and Baumberger sandstone.

To compute \( M/S \), the grains were considered as smooth spheres. Thus \( M/S \) and DIₜ are given by the following expressions:

\[
\frac{M}{S} = \frac{d \times r}{3} \quad (5)
\]

\[
\text{DIₜ} = \text{DIₜ} \times \frac{d \times r}{3} \quad (6)
\]

where \( d \) is the bulk density of the stone (2.78 g ml⁻¹ for Pentelic marble, 2.23 g ml⁻¹ for Portland limestone and 2.03 g ml⁻¹ for Baumberger sandstone) (Hannef, 1993) and \( r \) is the radius of the sphere (average \( r = 1.50 \) mm).

Figure 7 is a plot of DIₜ vs RH for the same experiments as for Figs 5 and 6 and shows that Portland limestone and Baumberger sandstone behave similarly. On the other hand the DIₜ of Pentelic marble is lower than the DIₜ of the other stones for low relative humidities (< 26–28%) but higher for high relative humidities.

Linear regression equations between DIₜ, DIₜ and RH for the three stones are the following:

PM: \( \text{DIₜ} \) (± 0.653404) = 0.577898 + 0.199040 (± 0.010002) × RH (7)

PL: \( \text{DIₜ} \) (± 1.284927) = 4.229117 + 0.090587 (± 0.014352) × RH (8)

BS: \( \text{DIₜ} \) (± 2.289089) = 5.495510 + 0.095688 (± 0.063672) × RH (9)

PM: \( \text{DIₜ} \) (± 0.090823) = 0.080328 + 0.027667 (± 0.001390) × RH (10)

PL: \( \text{DIₜ} \) (± 0.143269) = 0.471547 + 0.010101 (± 0.000160) × RH (11)

BS: \( \text{DIₜ} \) (± 0.232343) = 0.557794 + 0.009712 (± 0.006463) × RH. (12)
Fig. 7. Deterioration index per geometric surface area of stone (DI,) vs relative humidity for Pentelic marble, Portland limestone and Baumberger sandstone.

CONCLUSION

The general conclusion is that all three calcareous stones (Pentelic marble, Portland limestone and Baumberger sandstone) are good sinks for gaseous HNO3. This means that gaseous HNO3, a secondary pollutant in cities suffering from photochemical pollution, is a significant cause of monument deterioration. More specifically Portland limestone and Baumberger sandstone deteriorate to similar extents at any given relative humidity. Apparently their difference in chemical constitution is counterbalanced by their difference in total pore area. Pentelic marble, on the other hand, seems to be extremely vulnerable to gaseous HNO3 at relatively high relative humidities in spite of its low porosity.

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