RESPONSE OF POROUS BUILDING STONES TO ACID DEPOSITION

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Abstract. This work investigates the response of porous carbonate building stones to acid deposition during a short-term exposure period and the characteristics that influence their reactivity and/or durability. Several carbonate porous stones used in Spanish and English monuments were exposed to English urban and suburban environments. In each location they were both exposed to and sheltered from rainfall. Monthly analyses were carried out in order to investigate any possible sign of reaction. In addition, some physical properties of the stones relating to transfer of moisture were determined. Results indicate that the reactivity of these stones is relatively high, significant signs of reaction were detected within only a few months of exposure. Under the same environmental conditions, the response and reactivity of porous carbonate stones are determined by their petrophysical characteristics.

1. Introduction

Limestones and dolomitic limestones are very often used as building stones. However these carbonate stones are very sensitive to environmental impact. As a result, in recent times exhaustive research into the response of carbonate building stones to the environment has been carried out (Butlin *et al*, 1985). The weathering of these stones is an interaction of physical, chemical and biological processes. Chemical degradation of carbonate building stones is due to dry deposition of acid gases and aerosols, dissolution by acid species in rainwater and dissolution by unpolluted water (Butlin *et a.l*, 1993; Livingstone, 1992; Cooke and Gibbs, 1993).

This paper continues this line of research and presents some results of the collaborative work between the University of Oviedo (Spain) and the Building Research Establishment (UK) on the interaction between atmospheric pollution and carbonate building materials. The aim of this paper is to assess the response of several carbonate porous stones to English urban and suburban environments during a short-term exposure period and to determine the physical characteristics of these stones that influence this response.

2. Experimental

2.1. MATERIALS

The selected materials were four carbonate stones frequently used as building materials in Spanish and English monuments: Laspra dolomite (Spain), Hontoria limestone

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(Spain), Portland limestone (UK) and one of the varieties of Bath stone: Combe Down limestone (UK).

Laspra is a Eocene micrite mainly composed of dolomite. The main component of the other stones is calcite. Portland and Combe Down are Jurassic oolite limestones and Hontoria is a bioclastic limestone from the Cretaceous.

2.2. EXPOSURE

The selected materials have been exposed for one year in two different environments: a) Central London (exterior of Westminster Abbey), urban environment; b) Garston-Hertfordshire (exposure site at the Building Research Establishment), suburban environment.

At each of these sites, pairs of freely rotating carousels of stone tablets (5 cm x 5cm x 1cm) were installed following the methodology used for many years by researchers at the Building Research Establishment (BRE) and others (Butlin *et al.*, 1985; Jaynes and Cooke, 1987). One of the carousels was sheltered from rainfall and exposed only to dry deposition. The other was exposed to wet and dry deposition. Table I shows the pollution conditions at both sites (average exposure period).

TABLE I

Environmental Conditions at exposure sites

Site	SO_2 (µg/m³)	Smoke (µg/m³)	NO_x (µg/m³)
London	11.7	18.7	61.33
Garston(1)	21	6.5	42.1

(1) Estimated from St. Albans data

2.3. ANALYSIS

In order to investigate any possible sign of reaction, monthly analyses were undertaken including analysis of soluble salts by ion chromatography, surface composition by means of Fourier Transform Infra-Red (FT-IR) spectroscopy, and measurements of reflectance and weight variation. Simultaneously, porosity and moisture transfer properties of stones were determined.

3. Results

Significant signs of reaction were detected only a few months after exposure both in samples exposed to and sheltered from rainfall in London and Garston. Notable amounts of sulphate were detected in sheltered positions, and an increase in sulphate was also found in exposed tablets. Some nitrates and chlorides were also present in sheltered stones. Oxalates were also detected in most of the samples. Ammonium salts were found in exposed samples of Laspra dolomitic limestone.

The surface recession measured by weight loss in exposed samples, was higher in the first months of exposure and then tended to stabilise.

3.1. SHELTERED SAMPLES

The concentration of anions and cations was determined by ion-chromatography in successive drillings of 0.5 mm from the surface to 2 mm depth. Table II shows the correlation between anions and cations in terms of the correlation coefficient r.

TABLE II

Correlation Table Cations/anions in sheltered samples

	Ca^{++}	Mg^{++}	Na^{+}
$SO_4^{=}$	0.97		
NO_3^{-}		0.77	0.93
Cl^{-}	0.70		

This table shows that sulphates correlate strongly with calcium, and nitrates with sodium. An ion balance showed that sulphates were present as calcium sulphate. Fourier Transform infra-red spectroscopy (FT-IR) showed that the calcium sulphate was in the form of gypsum ($CaSO_4.2H_2O$), which could be detected on the surfaces of sheltered stones by after three months of exposure. This agrees with results of other authors (Girardet and Connor, 1992).

3.2. UNSHELTERED SAMPLES

The surface recession of the stones was estimated from the weight loss in samples exposed to rainfall, assuming the material is lost evenly across the whole sample (Butlin *et al*, 1993) (Table III).

TABLE III

Surface recession of unsheltered samples

	≈ Surface recession (µm/year)	
	Garston	Westminster
Laspra	41.1	47.6
Hontoria	11.8	11.4
Portland	12.0	13.9
Combe Down	40.8	42.7

3.3. PHYSICAL PROPERTIES

Some physical properties that relate to transfer of moisture were determined in order to assess their relationship with the response of carbonate stones to the environment (Table IV).

TABLE IV

Physical properties relating to moisture transfer of the different carbonate stones

	Open porosity (%)(1)	% pore radius<1μm (1)	Specific surface area(1) (m^2/g)	Ψ_w (%)	K_V ($g.m^{-1}.h^{-1}.mmHg^{-1}$)	Ψ_H (mg/g) a	b
Laspra	≈ 31	94.4	4.03	12	$1.3x10^{-3}$	12.5	113.3
Hontoria	≈ 20	29.5	0.26	6	$8.5x10^{-4}$	0.05	0.24
Portland	≈ 20	51.6	1.21	7.5	$9.1x10^{-4}$	0.38	2.8
Combe Down	≈ 28	70.7	1.38	9	$9.0x10^{-4}$	0.81	3.6

(1) Determined by means Hg-porosimetry; Ψ_w = free water absorption by total immersion; Kv = Vapour permeability; Ψ_H = Hygroscopicity (water vapour adsorption) (T = 23°C) (a = 60%; b = saturated)

3. 4. DISCUSSION

Although there is not enough climatic data for a reliable relationship to be determined, a correlation table has been made relating the weathering data from the exposure sites to the physical properties of the stones. Results are summarised on Table V.

TABLE V

Correlation Table weathering data / physical properties of the stones

	Surface recession	[$SO_4^=$]	[NO_3^-]	R(s)	Kv	Ψ_H	Ψ_w
Specific surface area	*		**(2)		**(2)	**(2)	**
Open porosity	**(1)				*	*	**(1)
Pollutants	-	*		**			
[Ca^{++}]	*	**		*			

R(s) = % Reflectance variation (sheltered samples)
(1) related to porosity
(2) related to specific surface area

Pollutants: [SO_2], [NO_x] and [smoke]
(**) correlated (r>0.8)
(*) weakly correlated (r=0.6-0.8)

3.4.1. Surface recession

The three mechanisms responsible for the stone loss are dry deposition, natural dissolution and acid dissolution. The contribution of each of these will depend on the environmental conditions. Butlin *et al.*, (1993) indicates that acid rain can contribute 2.6% of weight loss in calcareous stones, unpolluted rain 61.6%, and dry SO_2 deposition 35.8%. Results of NAPAP (1990) show that 'rainwater' can account for up to 70% of erosion. Livingstone (1992) pointed out that natural dissolution may be important even in rural areas with significant acid rain. For the stone samples in this project, the importance of natural dissolution is reflected by the strong correlation of surface recession to open porosity (Table V). This is because the open pore structure allows more water into the sample and so allows more carbonate to dissolve. The surface recession was found to be higher in the first months, this is due to loss of carbonate cement or stone matrix (Cooke and Gibbs,1993).

The theoretical maximum weight loss due to acid rain was estimated following the model of Webb *et al.*, 1992, and assuming 1 m precipitation per year and a pH=4.2 (Lipfert, 1989) (Table VI). The dry deposition was calculated from the amount of gypsum in sheltered samples, this was converted into an equivalent calcite or dolomite weight. The resultant balance corresponded to natural solution being the most important factor in carbonate stone decay.

TABLE VI

Percentage of predicted carbonate losses after 1 year exposure

	≈ g of carbonate loss by dry deposition		≈ Dry deposition (%)		≈ Acid rain (%)		≈ Natural solution (%)	
	West	Garston	West	Garston	West	Garston	West	Garston
Lasora	0.13	0.04	19.0	8.4	3.3	3.8	77.7	87.8
Hontoria	0.04	0.02	26.0	12.8	6.5	6.3	67.5	80.9
Portland	0.04	0.02	20.7	11.8	5.3	6.2	74.0	82.0
Combe Down	0.05	0.03	8.3	5.0	1.9	2.0	89.8	93.0

TABLE VII

Sulphate concentration in sheltered samples (μg/g)

	Garston 4 months	Garston 12 months	Westminster 4 months	Westminster 12 months
Lasora	1078	3680	2731	11262
Hontoria	675	2910	1656	5553
Portland	934	3103	1657	5042
Combe Down(1)	3340	4306	1163	8170

(1)The background concentration in clean Combe Down samples is very variable.

3.4.2. Sulphate concentration

The presence of sulphate is caused by dry deposition of gaseous SO_2 and aerosols to the stone, thus the concentration of sulphates in sheltered samples (Table VII) should be related to the pollutant concentrations in the atmosphere (Table V). However, there is not enough data to determine this. The deposition of SO_2 on material surfaces will be affected by physical characteristics of the stone, such as surface area. Laboratory experiments have shown some relationship between sulphate deposition on dry stones and their specific surface area (Grossi *et al*, 1994). Other factors will also influence the deposition of SO_2. According to several authors (Spedding, 1969; Johansson et al, 1988; Spiker et al, 1992; Goturk et al, 1993) the uptake of SO_2 depends on the humidity. The specific surface area controls the uptake of moisture by the stone (Tables IV and V), and Spiker et al (1992) pointed out that SO_2 deposition may be controlled by the wetted surface area of the stone. The presence of some salts will alter this. $NaNO_3$ and $CaCl_2$, both found in the stone will absorb moisture at humidities over 75% and 35% respectively.

3.4.3. Other reaction products

Nitrates were found in sheltered samples, present as sodium nitrate and magnesium nitrate. Their concentration was related to specific surface area, water vapour adsorption and water vapour permeability. NO_x can transform to NO_3^- in the water adsorbed on the surface of the stone. However, the process is slow, the larger surface area could allow more nitrate to be absorbed into surface moisture layers. Finally, biological deterioration can be seen in the stones, mainly as oxalates. This was more evident in Garston than in London.

4. Conclusions

Degradation of carbonate stones is a result of the combination of environmental factors and stone characteristics. Carbonate stones are very reactive to rainwater, SO_2 deposition and biological agents. Gypsum and oxalates can be found in the surfaces of some stones after only a few months of exposure.

The physical characteristics of carbonate stones relating to moisture transfer will affect their response to the environment. Porosity and specific surface area are relevant properties conditioning this response. A study which includes a greater number of well characterised carbonate stones exposed to the same environment needs to be done in order to determine quantitative relationships between porosity, specific surface area and stone durability.

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