

# WEATHERING MECHANISM OF PENTELIC MARBLE UNDER AMBIENT ATMOSPHERIC CONDITIONS DERIVED FROM RUNOFF STUDIES

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**Abstract.** A field-exposure study has been carried out about the correlation between environmental conditions and marble weathering, using analyses of the run-off rain water. Several analysis techniques were invoked for the analysis of the bulk run-off water, and electron probe X-ray microanalysis for individual particles in the run-off. A damage function has been constructed to explain the  $\text{Ca}^{2+}$  loss as a function of the rain input and environmental conditions.

## 1. Introduction

It is very important to know the mechanisms of the decay of historical buildings on a quantitative basis, and to understand which factors are important for the degeneration and which have minor consequences. The weathering rate and mechanism of decay of building stone in a natural or polluted environment can be studied on a quantitative basis by analyses of run-off water, i.e. rain water that has run over a building wall or over a stone slab that is exposed to ambient atmospheric conditions (Cooper, 1986; Torfs and Van Grieken, 1996). Since  $\text{SO}_2$  is a major factor in the deterioration of these stones, gypsum is the main weathering product on historical monuments, composed of limestone, marble and sandstone, containing calcite.

Pentelic marble is a metamorphosed limestone, comprised almost entirely of an interlocking polygonal aggregate of calcite grains. The major Pentelic marble quarries lie on Mount Pentelicon, 18 km north-east of Athens. The variety under study is snow-white in colour. The marble has a moderate grainy structure, although locally it can be fine grained. Individual calcite grains, up to 1mm in diameter, can be seen with the naked eye. The marble exhibits a sugary texture. Some fine grained, creamy white dolomitic bands are occasionally present. The porosity is 0.05% by volume.

## 2. Sampling and analysis

The effects of atmospheric pollution on building materials are often studied in so-called reaction chambers, mostly under highly exaggerated conditions to speed up the deterioration process (Johnson et al., 1990). However, it is not certain that the results from such experiments can be extrapolated to real atmospheric conditions. Therefore, four specially constructed sampling devices, called "micro-catchment units" (Cooper, 1986; Jeffrey et al., 1985) were installed at the University of Antwerp to study the deterioration of Pentelic marble under ambient atmospheric conditions. In a micro catchment unit, a stone slab with dimensions 25cm x 25cm x 5cm is put on top of a polystyrene container which is filled with gravel (Figure 1). The entire setup is inclined so that the stone slabs make an angle of 15° to the horizontal, to minimise splash/blow-out losses and oriented towards the Southwest, the prevailing wind and rain direction in Belgium. The incident rainfall strikes the surface and runs over the inclined stone into a polyethylene tube, and is collected in a bottle for analysis.

For a two year period, 62 samples were taken for each of the four micro-catchment units. As a blank, the same setup is used, but the stone slab is replaced by a roughened and aged glass plate with the same area, presumed to be inert. In total three slabs of Pentelic marble and one glass blank are exposed. Together with the sample collection, environmental data were gathered from governmental organisations (IHE, 1988-1992; KMI, 1988-1992)

The bottles were collected for analysis on a weekly basis, i.e. samples were taken every Monday if there had been rainfall during the week preceding the sampling day. First the volume and pH were determined and then the run-off water was filtered. Weighing the filters before and after filtration provided the mass of the total suspended particulate matter (TSP). The filtrate was stored in a refrigerator prior to analysis by IC (ion chromatography), AAS/FES (atomic absorption/flame emission spectroscopy) and potentiometric methods. The filter was dried and analysed with EPXMA (electron probe X-ray micro analysis) and EDXRF (energy dispersive X-ray fluorescence).

### 3. Results

#### *Volume*

The mean run-off volume collected for the blank were not higher than the volume collected for the stones. This high run-off recovery implies that rainwater is not retained in the stone. Due to its nature (hard and with low porosity), marble has nearly the same run-off characteristics as the roughened glass in the blank setup. Rainwater will not transport weathering products deeper into the stone, but will only remove them from the surface.

#### *Ionic balances*

As a control for the quality of the collected data, ionic balances were calculated for each stone. The results were out of balance, with a large anion deficiency. A calculated bicarbonate term was introduced since no bicarbonate measurements were carried out. The assumption was made that calcium was initially removed either as sulphate or bicarbonate. This assumption allowed a simple calculation. With concentrations in equivalents, this implies:  $[\text{HCO}_3^-]_{\text{calc}} = [\text{Ca}^{2+}] - [\text{SO}_4^{2-}]$ . The computed bicarbonate concentration was included in the data matrix and ionic balances were calculated again. The balance now improved so that equilibrium was obtained. This proved that the assumption we made was valid. The average ionic balances, after bicarbonate correction, was:  $0.97 \pm 0.13$ .

#### *Ion exchange*

##### Cumulative ion exchange

Cumulative ion exchanges were computed for the three replicate stones. The average of the three stones was used to produce Figure 2. The data was corrected for the average blank value. From the cumulative ion exchange curve, the relative importance of the different ions in solution becomes clear. Bicarbonate turned out to be the most important anion in the runoff.  $\text{SO}_4^{2-}$  also has a significant contribution in the runoff. The other anions are of no importance.  $\text{Ca}^{2+}$  is the major cation whereas  $\text{H}^+$  and  $\text{NH}_4^+$  have significant negative ion exchanges. This means that  $\text{H}^+$  and  $\text{NH}_4^+$  are removed from the incident precipitation. Lower  $\text{H}^+$  concentrations, and thus higher pH, are due to the neutralisation reactions taking place at the stone surface. The average pH value is 4.3 for the stone runoff compared to 3.7 for the blank. The other cations have negligible contributions. The  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  molar ratio has been calculated. It steadily increases from 1.7 to 2.6, indicating that the longer the experiment goes

on, the less  $\text{Ca}^{2+}$  is lost in the form of  $\text{CaSO}_4$ . The amount of  $\text{Ca}^{2+}$  that comes from the stone samples is constant, since the cumulative  $\text{Ca}^{2+}$  exchange forms a straight line. The cumulative  $\text{SO}_4^{2-}$  curve is steeper during the begin period. All these observations indicate that the formation and subsequent removal of  $\text{CaSO}_4$  has a decreasing contribution to the total  $\text{Ca}^{2+}$  loss and that other processes, such as dissolution, become more and more important as a function of the exposure time.

#### Seasonal variability of ion exchange on marble

Most  $\text{Ca}^{2+}$  loss occurs during autumn and winter. These two seasons account for 67 % of the total  $\text{Ca}^{2+}$  loss. Most damage is thus done to the stone samples during autumn and winter: 78 % of the  $\text{SO}_4^{2-}$  loss takes place during this period. The time-of-wetness of the stone is larger in the cold season, and the ambient  $\text{SO}_2$  concentrations are somewhat higher then.  $\text{HCO}_3^-$  loss is more evenly distributed over the four seasons. It is not clearly understood why  $\text{Na}^+$  and  $\text{K}^+$  are retained during some seasons and lost during others.

#### Correlation between atmospheric $\text{SO}_2$ concentration and $\text{SO}_4^{2-}$ in the stone run-off

The  $\text{SO}_4^{2-}$  exchange is plotted against the average atmospheric  $\text{SO}_2$  concentration per sampling period. No straightforward correlation can be seen from Figure 3. This means that, although  $\text{SO}_4^{2-}$  can only originate from atmospheric input, there is no short-term relationship between  $\text{SO}_2$  concentration and  $\text{SO}_4^{2-}$  in the runoff. Comparable results were found by Furlan and Girardet (1992). Two explanations are possible. The first explanation is that the removal of  $\text{SO}_4^{2-}$  can be delayed so that variation in sulphate concentration is buffered. Second possibility is that the formation of  $\text{SO}_4^{2-}$  is influenced by other factors, such as atmospherical  $\text{NO}_x$  concentration, humidity, etc. Chamber studies provided evidence for a synergistic effect of  $\text{NO}_2$  on the  $\text{SO}_4^{2-}$  formation on calcareous stones (Johansson et al., 1988). The concentrations of pollutants that were used in these experiments were 100 times higher than real pollutant levels. Spiker et al. (1992) used testing chambers to establish the role of humidity on the deposition of  $\text{SO}_2$  onto a stone surface. They found that the relative humidity is a very important factor. High relative humidities would facilitate the  $\text{SO}_2$  deposition by lowering the surface resistance. Little or no  $\text{SO}_2$  deposition would occur on marble surfaces if the relative humidity is below 60 %. Thus even when  $\text{SO}_2$  concentrations would be high, no  $\text{SO}_4^{2-}$  will be formed as long as there is not enough moisture present.

#### *Material loss*

The material loss for marble was calculated based on the  $\text{Ca}^{2+}$  concentration in the runoff water. From the net  $\text{Ca}^{2+}$  exchange, the corresponding mass of  $\text{CaCO}_3$  can be calculated. Some 96.75 % of the stone is  $\text{CaCO}_3$ , so that the corresponding stone mass can easily be computed :

$$\text{Stone loss (mg)} = \text{CaCO}_3 \text{ (mg)} * \frac{100}{96.75} \quad (1)$$

$$\text{CaCO}_3 \text{ (mg)} = \text{Ca}^{2+} \text{ (mg)} * \frac{MM_{\text{CaCO}_3}}{MM_{\text{Ca}}} \quad (2)$$

Dividing this stone mass by the average density of the marble, gives the volume of removed stone material. The surface recession is then obtained by dividing this volume by the surface of the exposed stone sample :

$$\text{Surface recession (10}^{-3} \text{ cm)} = \frac{\text{Stone loss (mg)}}{\rho_{\text{stone}} \text{ (g/cm}^3\text{)} * \text{Stone surface (cm}^2\text{)}} \quad (3)$$

This value is related to the exposure time, so that finally a surface recession rate results, which is expressed in  $\mu\text{m/year}$ . The calculated yearly surface recession for the marble samples is ca.  $10 \mu\text{m/year}$ . This surface recession rate lies in the same range as values found in literature. Lipfert (1989) made a compilation of published estimates of carbonate stone recession. For marble the results range from 4 to  $34 \mu\text{m/year}$ . Baedecker et al. (1990) found recession rates from 15 to  $30 \mu\text{m/year}$  for marble studied in the NAPAP program. During the 106 weeks sampling period, a slight decrease of the surface recession rate could be seen, meaning that the weathering process slows down.

The surface recession is not a wholly satisfactory index for weathering, since it does not imply large scale weathering failures, like spalling, cracking, etc. (Jaynes and Cooke, 1987). Introduction of the surface recession is however essential to compare the results of weathering experiments with physical measurements of surface recession on real buildings and monuments. These measurements are often done when in situ reference points are available. Protected areas, lead plugs or durable inclusions are only a few examples of possible reference points.

#### *Damage function*

Damage functions are an essential tool for predicting the expected damage to a material in given environmental conditions, and for assessing the relative contribution of each damage factor. A damage function is a mathematical relationship between rates of material deterioration and damage causing factors (Benarie, 1991). An attempt was made to explain the  $\text{Ca}^{2+}$  loss, which is an indication of stone weathering, by the data of the blank and environmental and meteorological parameters. This multivariate analysis was done with partial least-squares regression, PLS (Geladi and Kowalski, 1986). The net  $\text{Ca}^{2+}$  loss (expressed in  $\mu\text{mol/cm}^2$ ) is predicted using the rain water characteristics (as obtained from the blank micro-catchment setup): Vol (in ml),  $[\text{H}^+]$ ,  $[\text{Cl}^-]$ ,  $[\text{NO}_3^-]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{Mg}^{2+}]$ ,  $[\text{Na}^+]$ ,  $[\text{K}^+]$  and  $[\text{NH}_4^+]$  (expressed in  $\mu\text{mol/cm}^2$ ), the environmental parameter 'average  $\text{SO}_2$  concentration' ( $\text{SO}_2$  expressed in  $\mu\text{g/cm}^3$ ) and the meteorological parameters: 'average temperature' (Te in  $^\circ\text{C}$ ), total rainfall amount (R in  $\text{ml/m}^2$ ) and total time of rain (Tr in min). The equation obtained is:  $\text{Ca}^{2+}\text{-loss} = 0.061 \text{ Vol} - 0.298 [\text{H}^+] + 0.088 [\text{Cl}^-] + 0.270 [\text{NO}_3^-] + 0.948 [\text{SO}_4^{2-}] + 0.353 [\text{HCO}_3^-] + 1.398 [\text{Mg}^{2+}] - 0.416 [\text{Na}^+] - 0.194 [\text{K}^+] - 0.216 [\text{NH}_4^+] - 0.032 \text{ SO}_2 - 0.100 \text{ R} + 0.110 \text{ Te} + 0.120 \text{ Tr} + 15.785$ . The importance of the various X-parameters in explaining the variance of Y ( $\text{Ca}^{2+}\text{-loss}$ ) can be deduced by weighting the estimated regression coefficients (B-coefficients) that describe the relation between the X-matrix and the Y-matrix ( $Y = \text{XB}^T + \text{B}_0$ ). The higher the weighted coefficient (Bw-coefficient), the more variance of  $\text{Ca}^{2+}$  is explained by that parameter. The weighted coefficients are given by:  $\text{Ca}^{2+}\text{-loss} = 0.152 \text{ Vol} - 0.165 [\text{H}^+] + 0.032 [\text{Cl}^-] + 0.044 [\text{NO}_3^-] + 0.560 [\text{SO}_4^{2-}] + 0.561 [\text{HCO}_3^-] + 0.094 [\text{Mg}^{2+}] - 0.112 [\text{Na}^+] - 0.135 [\text{K}^+] - 0.135 [\text{NH}_4^+] - 0.001 \text{ SO}_2 - 0.400 \text{ R} + 0.003 \text{ Te} + 0.610 \text{ Tr} + 0.071$ . From this equation can be seen that  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  have the most influence on the variation of  $\text{Ca}^{2+}$ . Seasonal variability is included in this model by the use of weekly sampling for a period of two years.

#### *Particulate matter in the run-off*

Individual particles in the run-off water were analyzed by automated EPXMA. Energy dispersive X-ray spectra were accumulated and stored for off line processing. The particles were divided in 9 groups, according to their composition. The abundance of each group in

the stone run-off was compared with the abundance of the corresponding group in the blank. The group with Ca-rich particles was the only one with substantially higher abundance in the run-off. The particles in this group do not contain S. This means that small CaCO<sub>3</sub> particles come off the marble surface. However, taken the mass of TSP into account, this effect must be small compared to the material lost in solution.

#### Stone leaching

Leaching experiments were carried out on the slices. Weighed portions of approximately 1 g of stone material were crushed in an agate mortar. Deionised water was added up to a total volume of 100 ml. The suspension was put in ultrasonic bath for 30 min and filtered on a 0.22 µm Millipore filter. The residue was dried and weighed. The amount of water soluble material was calculated. The ions in solution were measured by IC and AAS/AES (Table 2). Elevated concentrations of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> were found on the sheltered surface. SO<sub>4</sub><sup>2-</sup> could only be detected in the leachate of DD. This is in full agreement with the results of the microprobe analyses on the samples.

#### 4. Conclusion

The weathering of Pentelic marble has been studied under ambient conditions in Belgium. Dissolution processes proved to be important. Weathering rates about 10 µm/year were obtained from the runoff experiments. Statistical data analysis confirmed that dissolution was the most important factor for washed surfaces.

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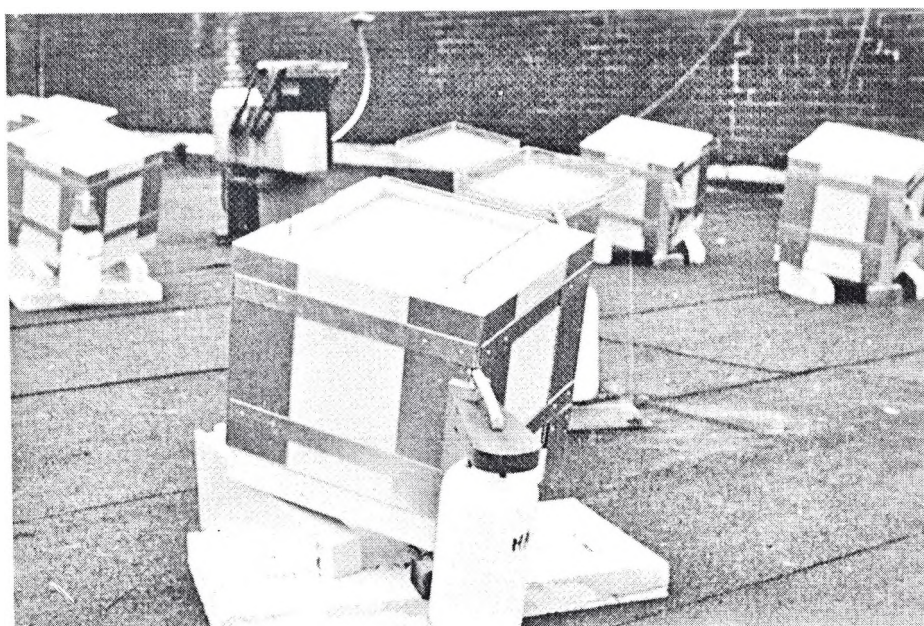
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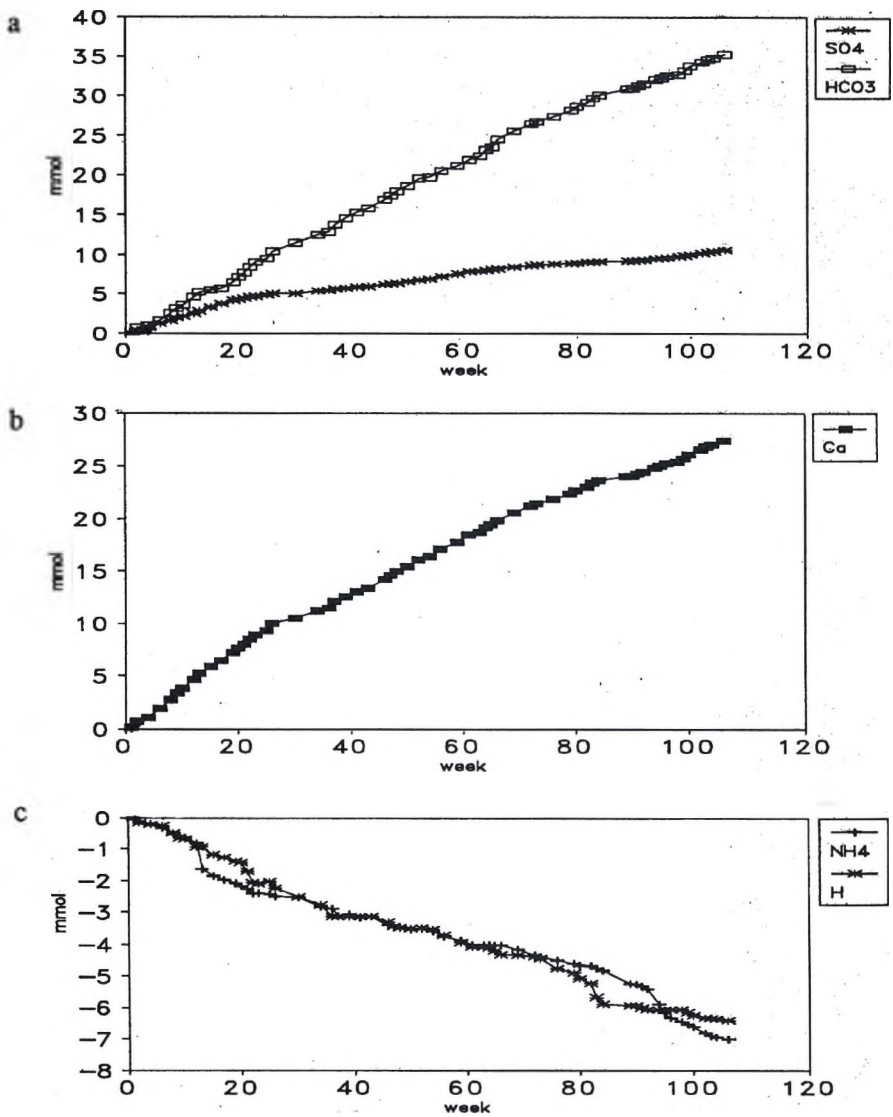


**Table 1** Leachable concentrations (mg/g) of water soluble material in marble slabs, n.d. is not detected.

	total deposition (TD)	reference (R)	dry deposition (DD)
Cl <sup>-</sup>	0.128 ± 0.003	0.126 ± 0.003	0.23 ± 0.01
NO <sub>3</sub> <sup>-</sup>	0.13 ± 0.02	0.13 ± 0.02	0.24 ± 0.03
SO <sub>4</sub> <sup>2-</sup>	n.d.	n.d.	1.56 ± 0.02
HCO <sub>3</sub> <sup>-</sup>	12.7 ± 0.7	10.5 ± 0.6	11.2 ± 0.7
Ca <sup>2+</sup>	3.5 ± 0.1	3.17 ± 0.08	3.75 ± 0.09
Mg <sup>2+</sup>	0.066 ± 0.005	0.035 ± 0.002	0.041 ± 0.003

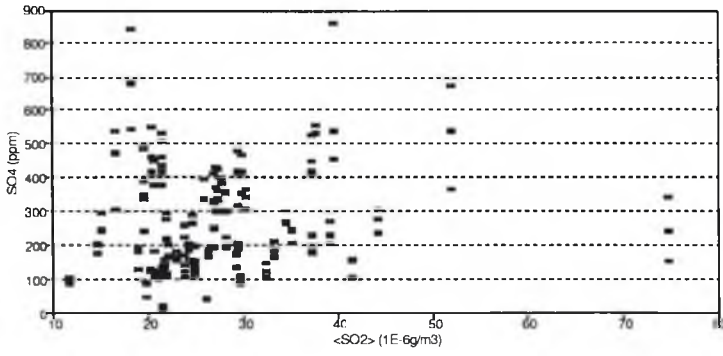


**Figure 1** Picture of a micro-catchment unit.



**Figure 2** Cumulative ion exchange from Pentelic marble.





**Figure 3** Correlation between atmospheric  $\text{SO}_2$  concentration and  $\text{SO}_4^{2-}$  in the run-off water of Pentelic marble.