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Stress corrosion cracking of untreated Pentelic marble of artificially weathered or treated with pigmented or unpigmented polymer

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ABSTRACT

The mechanical behaviour of pentelic marble under Stress Corrosion Cracking (S.C.C.) conditions was examined by accelerated laboratory tests.

The marble specimens were double notched; they were tested (strain stress) untreated or after artificial weathering (exposure in an acidic environment simulating acid rain conditions, or in air + SO_2 + humidity, simulating sulfation conditions) or treated with n-semiconductor pigmented or unpigmented polymer. The dispersion of the measured load to failure was high due to the natural unhomogeneity of the marble and consequently of the specimens. These measurements contribute to the evaluation of the static situation and to the prediction of the change of the mechanical behaviour of fractured marble of monuments in a polluted atmosphere; they also contribute to the possibility of retarding further decohesion of marble pieces by appropriate protective treatment.

To the same purpose more influencing factors are under investigation: constant loading - three levels - of specimens, constantly exposed in the corrosive environment, and measurement of the times to failure.

INTRODUCTION

The Acropolis monuments are constructed by pentelic marble, a very known special type of marble with the lowest porosity: 0.3% up to 0.7% after natural weathering (surface porosity).

Its physical properties are: specific density 2.73 gr/cm^3, apparent density 2.71 gr/cm^3, coefficient of thermal expansion 9.10^{-6}/°C between 15÷100°C.

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Its physicomechanical properties are: compressive strength 778 Kp/cm^2, bending strength 184 Kp/cm^2 shear strength 129 Kp/cm^2,impact strength 1.8 $Kp.cm/cm^2$, dynamic modulus of elasticity 428,800 Kp/cm^2.

The marble resistance to dissolution from acid rain attack and to sulfation is high. Nevertheless the high level of pollution (SO_x, NO_x, SO_4^{2-}, O_3, suspended particles) in the Athens region, mainly after 1955 that coincides with its intense industrialisation, have provoked serious deterioration of the marbles [1- 4] and of the steel clamps and metal skeletons [3,4] introduced during the two main restorations of Pittakis (1837-1842) and of Balanos (1902-1937). Thus beside the decay of the statues and ornaments, i.e. the high relief which becomes partially flat, static problems became evident. The first author, member of the "Committee for the Conservation of the Acropolis Monuments" responsible for the physicochemical problems, suggests the replacement of steel clamps and metal skeletons - the accelerated corrosion of which produced cracks in the marbles - with Titanium. This was done for Erechtheion, for the Propylae and the upper part of the Athens Parthenon according to the static calculations from the team of Civil Engineers. On the other hand, the Caryatids, the Cecrops statue and the eastern and western frizes were transported into the museum and, after suggestion of the first author, the Caryatids and Cecrops were placed in transparent cases with nitrogen circulation to avoid SO_2, SO_3 + humidity attack in the museum.

The remaining monuments (buildings, flat surfaces, column e.t.c.) suffer of physicochemical deterioration, a type of which is pitting corrosion. This type of corrosion under the mechanical stress even of the own weight of marble blocks is developed to Stress Corrosion Cracking (S.C.C.) of the marbles.

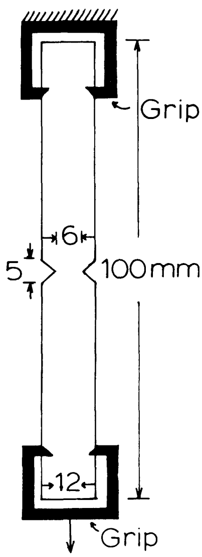

Figure 1. Shape and dimensions (mm) of the specimens, way to stress.

The complete similarity of the sulfation mechanism of marbles to the uniform corrosion of metals: galvanic cell model [5-8], as well as the other types of metal corrosion allow the use of the terminology, the methodology and the experimental methods applied to the study for S.C.C. of metals into the marbles.

In the present work the behaviour of pentelic marble under S.C.C. (strain stress) conditions before and after artificial weathering (simulating acid rain and sulfation), as well as after treatment with a polymer pigmented or not with n-semiconductors [9-12] was studied.

Materials, shape and dimensions of the specimens

The specimens were cut from a plate of pentelic marble of a thickness of 5mm. The longitudinal axis of some of these specimens were cut parallelly to the grain orientation and some normally. Thus the longitudinal axis of some specimens were parallel to the future stress direction and of some, normal. The shape and dimensions of the

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specimens are shown in Figure 1. The specimens were double notched and were polished to 150 grit. Two grips were attached to each specimen in order to apply stress.

There were also used 0.1 H_2SO_4 solution, SO_2 50% + 50% water vapour saturated air at 25°C, Paraloid B72 (P) 13% w/v solution in toluene, Al_2O_3 specially prepared to have pronounced n-semiconductor properties (measurement of resistivity) 30% w/w versus solid P. The types of the specimens and their treatments are shown in Table 1.

Table 1
Types of specimens and their treatments

Type of specimens		Artificial Weathering	
		Pre-exposed in 50% SO_2 + 50% water vapour saturated air for 4 days	Pre-exposed in 0.1N H_2SO_4 for 1 min
1	Uncoated	-	-
2	Uncoated	+	-
3	Uncoated	-	+
4	Coated with P (50μm)	-	-
5	Coated with P (50μm)	+	-
6	Coated with P (50μm)	-	+
7	Coated with Paraloid Pigmented with 30% Al_2O_3 (50μm)	-	-
8	Coated with Paraloid Pigmented with 30% Al_2O_3 (50μm)	+	-
9	Coated with Paraloid Pigmented with 30% Al_2O_3 (50μm)	-	+

Procedure

5 specimens from each of the 9 types were stressed (strain stress) till failure and the σ: N/mm^2 was calculated.

It must be emphasized that the results of S.C.C. of metals, i.e. σ (N/mm^2) to failure, are qualitatively the same and comparable when the specimens are placed in a corrosive environment and then are stressed to failure with the results when

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the specimens were placed in the same corrosive environment and simultaneously stressed. Naturally for marbles this must be further investigated.

RESULTS AND DISCUSSION

The results are shown in Table 2.

TABLE 2
Load to failure (N/mm^2)

	Uncoated			**Coated with Paraloid B72**			**Coated with Paraloid Pigmented with Al_2O_3**		
	1	2	3	4	5	6	7	8	9
	-	SO_2	H_2SO_4	-	SO_2	H_2SO_4	-	SO_2	H_2SO_4
a	1.65	1.59	1.14	1.64	1.79	1.13	1.69	1.60	1.0
b	2.38	2.31	1.46	2.76	2.65	1.72	2.26	2.85	1.3

where (a) grain orientation normal and (b) parallel to stress direction.

From Table 2 and the histograms of Figures 2 and 3 at first two general remarks can be deduced:

i. When the grain orientation of the specimens is parallel to stress direction (b) the mechanical properties (the σ' s) are higher - as expected - than when the grains are oriented normal (a) to the stress direction.

ii. The results for these two types of specimens do not qualitatively coincide with each other. Because the sensitivity to cracking of the specimens (a) eliminates and equalises the eventual differences of behaviour of the several types of specimens; the most sure method to draw conclusions is from the values of specimens (b).

Precisely from Figure 2 it follows:

- For uncoated specimens SO_2 pre-exposure does not influence the σ vs unexposed specimens, because the replacement of a marble layer by gypsum is compensated from the sealing of the tip of the notch. The H_2SO_4-solution pre-

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exposure decreases appreciably the σ because it forms in the tip of the notches an active path [13-15]. The following inequality is valid 1≥2>3.

- For P coated specimens the σ decreases from unexposed to SO_2 pre-exposed and to H_2SO_4-solution pre-exposed: 4≥5>6.

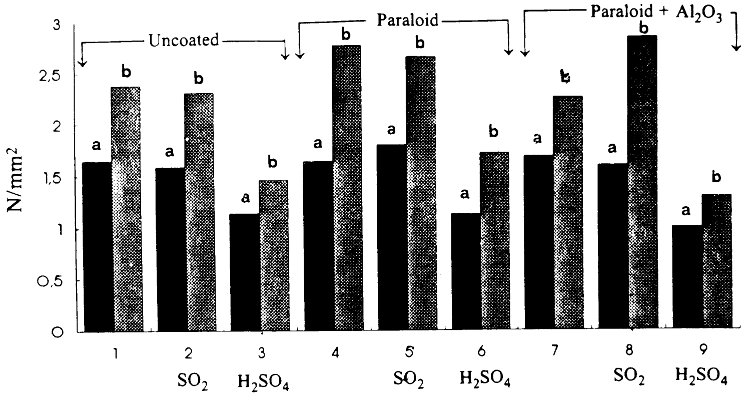

Figure 2. Histogram illustrating the S.C.C. behaviour of pentelic marble by emphasizing the pre-treatment.

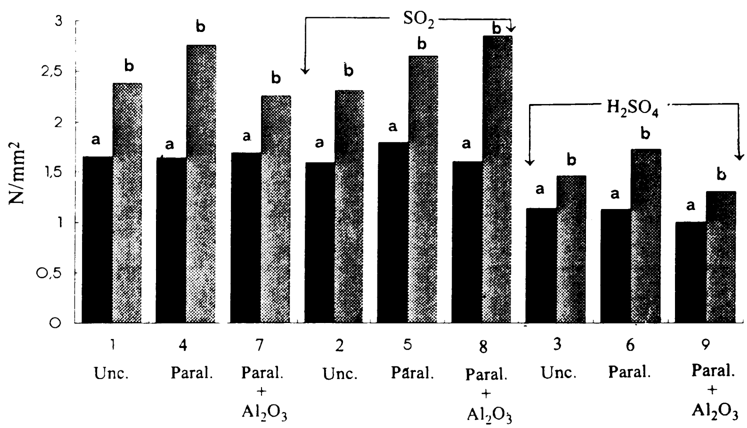

Figure 3. Histogram illustration the S.C.C. behaviour of pentelic marble by emphasizing the pre-exposure.

- For P+Al_2O_3 coated specimens, when the Al_2O_3 is specially prepared to have pronounced n-semiconductor properties [16-18] the σ increases from unexposed specimen to SO_2 pre-exposed and then decreases for H_2SO_4 pre-exposed specimens 8>7>9. This high value of σ for the P+Al_2O_3 coated specimens pre-exposed in SO_2 is due to the higher protective properties of this system (Figure 2:8) than the plain (Figure 2:5) Paraloid [9-12].

From Figure 3 it follows that:

- For unexposed specimens the Paraloid coated specimens have a higher mechanical resistance (sealing of the tip of notches) than the uncoated and the P+Al_2O_3 coated. The latter seems that does not influence the properties compared to the uncoated specimens and that decreases the properties in comparison to the unpigmented Paraloid. 4>1≥7.

- For SO_2 pre-exposed specimens the following unequality is valid 8>5>2 due to the already revealed protection of P+Al_2O_3 coated marble against sulfation [9-12].

- For H_2SO_4 pre-exposed specimens the following unequality is valid: 6>3>9.

CONCLUSIONS

From the above mentioned it follows:

- The mechanical resistance of pentelic marble against tensile cracking and against stress corrosion cracking is, as expected, much higher for mechanical loads parallel to its grain orientation than normal to it.

- The grain orientation of the specimens normal to the stress direction eliminates in some cases and equalises the differences according to their sensitivity for cracking. The same is true for specimens pre-exposed in H_2SO_4-solution. Thus it is more convenient to work with the first type of specimens (grain orientation parallel to stress direction) or adopt milder conditions.

- The σ to failure for uncoated specimens decreases slightly from unexposed specimens to exposed in SO_2 and appreciably to H_2SO_4 - solution. The same is true for SO_2 pre-exposed and Paraloid coated specimens.

- For P+Al_2O_3 coated specimens the mechanical resistance for SO_2 pre-exposed specimens increases in comparison with the unexposed and the Paraloid coated ones, probably because of the sealing of the tip of the notches and the better resistance of this system to SO_2 attack than of the plain Paraloid.

- For not polluted atmosphere the non pigmented Paraloid imposes a higher mechanical resistance vs uncoated and Al_2O_3 pigmented specimens.

- For SO_2 polluted atmosphere pigmented Paraloid has a higher mechanical resistance than the uncoated and the unpigmented Paraloid, due to its high protective properties against sulfation.

The general conclusion is that the Al_2O_3-pigmented Paraloid in addition to the protection against sulfation protects also marbles from S.C.C.

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