Italian Journal of Engineering Geology and Environment
www.ijege.uniroma1.it

STATISTICAL ANALYSIS OF STONE DECAY BY SALT MIST - THE CASES OF ROSA ARRONCHES AND SPI PORTUGUESE GRANITES

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EXTENDED ABSTRACT

L'obiettivo principale del presente lavoro è analizzare e quantificare statisticamente il decadimento delle proprietà meccaniche e dell'aspetto ornamentale che potrebbe verificarsi in due graniti portoghesi se esposti ad un'atmosfera di cloruro di sodio oltre a prevederne il comportamento nell'utilizzo sul lungo periodo. Si è inoltre voluto verificare il mantenimento e la conformità ai requisiti delle norme europee per il loro utilizzo come materiali da costruzione. I graniti Rosa Arronches (RA) e SPI sono utilizzati come pietre ornamentali e come materiale da costruzione nei mercati nazionali ed internazionali. Sono ampiamente commercializzati essendo esportati in diversi paesi del mondo, in particolare in Spagna, Germania e Francia (principali importatori dai paesi dell'UE) e Cina (principale paese importatore di granito SPI). È ampiamente riconosciuto nella comunità scientifica che la nebbia salina è un importante agente di alterazione dei materiali da costruzione applicati nel litorale costiero, determinando notevoli danni anche nel patrimonio edilizio lapideo. Per prevedere lo sviluppo nel tempo del decadimento avvenuto, è stata eseguita un'analisi di regressione non lineare con i dati di laboratorio ottenuti da perdita di massa su cicli ricorrenti di esposizione a questa atmosfera. Questi due graniti sono macroscopicamente diversi per colore, granulometria e consistenza.

La resistenza all'invecchiamento da nebbia salina è stata determinata esponendo 14 campioni di ciascun granito ad un'atmosfera di cloruro di sodio (SCA). Le principali proprietà identificative, fisiche e meccaniche sono state determinate, prima e dopo il test di invecchiamento accelerato, secondo le procedure degli standard europei. Un totale di 150 cicli SCA sono stati eseguiti in una camera di nebbia salina ad atmosfera controllata Ascot S120T, programmata elettronicamente per produrre cicli comprendenti 4 ore di nebbia salina seguite da 8 ore di essiccazione a (35 ± 5) ºC. La soluzione salina è stata preparata con una concentrazione di (100 ± 10) $g.L^{-1}$, secondo EN 14147:2003. La porosità aperta, l'assorbimento d'acqua a pressione atmosferica e la resistenza alla compressione uniassiale sono state determinate per ciascuna litologia prima e dopo l'esposizione a 150 cicli di SCA e dopo ogni 15 cicli i campioni sono stati osservati visivamente e documentati con foto (utilizzando un Olympus SP - 500 UZ e una macchina di visione digitale Mitutoyo Quickscope QS – LZB).

Dopo il test SCA l'assorbimento d'acqua a pressione atmosferica è aumentato fino al 64% per il granito RA e la porosità aperta è aumentata del 43%. È stata inoltre registrata una forte diminuzione della resistenza a compressione uniassiale da 196 MPa a 160 MPa. Tuttavia il valore medio di 160 MPa ci consente comunque di classificarlo come granito ad alta resistenza e ad alte prestazioni (> 100 MPa). Per il granito SPI, l'aumento dell'assorbimento d'acqua alla pressione atmosferica è stato inferiore del 33%, la porosità aperta è diminuita di un valore del 7% e la diminuzione della resistenza a compressione uniassiale (4%) è stata molto inferiore a quella presentata dal granito RA. L'evoluzione del decadimento nel tempo si è presentata con una continua perdita di massa per entrambe le litologie. Per tutti i campioni testati il miglior fit di regressione ottenuto è una funzione esponenziale. Il miglior fit ottenuto per i graniti SPI e RA corrisponde alle equazioni di regressione con $\lambda = -2E^{-5}$ e $R^2 = 0.94$ e $\lambda = -1E^{-5}$ e $R^2 = 0.89$ (con $p < 0{,}001$), rispettivamente. Il valore della costante di decadimento dei due graniti indica che essi presentano diversa resistenza all'azione SCA. Infatti i graniti SPI e RA, non hanno tassi di disintegrazione uguali $\lambda(SPI) = -0.00002$ e $\lambda(RA) = -0.00001$.

I risultati ottenuti hanno messo in evidenza il decadimento dei graniti quando esposti ad un'atmosfera di nebbia salina, favorendo un cambiamento nel loro aspetto ornamentale e nelle proprietà meccaniche. I cambiamenti ornamentali osservati consistono in una leggera ossidazione dei minerali ferromagnesiaci, tradotta in aloni bruno-arancio che invadono i minerali di colore chiaro. Questa atmosfera ha inoltre interagito negativamente con le proprietà fisiche e meccaniche dei due graniti, con una continua perdita di massa, aumento della porosità aperta e dell'assorbimento d'acqua e diminuzione della resistenza a compressione uniassiale. Tuttavia, il decadimento presentato non compromette l'utilizzo di entrambi i graniti per le principali applicazioni delle pietre naturali, in accordo con i requisiti per l'utilizzo dei graniti come materiale da costruzione. Tuttavia, in paesi con test più impegnativi e/o standard più restrittivi rispetto ai paesi europei la diminuzione delle proprietà osservate può essere problematica.

IJEGE, 1 (2023): 37-43, DOI: 10.4408/IJEGE.2023-01.O-03
E-ISSN 2035-5688 | ISSN 1825-6635 / ©Author(s)

ABSTRACT

This study investigates the decay behaviour promoted by salt mist on "Rosa Arronches" and "SPI" Portuguese granites. These are two widely applied granites in the national and international markets, traded and exported to several countries. For the purpose of better understanding their behaviour and mechanical properties under a salt mist atmosphere two series of 150 cycles of a salt mist-controlled atmosphere was applied to sound samples. Petrographic and major mechanical properties were determined, according with European Standards, before and after the artificial weathering, and a statistical analysis of the mass loss between successive cycles was conducted using the exponential model suggested by Mutlutürk *et alii* (2004). The results revealed a decrease in all the mechanical properties evaluated for both granites, however without compromising their use as dimension stones, thus representing a new insight into the mechanical response to be considered, especially in regions affected by this decay mechanism.

Keywords: *statistical analysis, stone decay, salt mist, granite, mechanical properties*

INTRODUCTION

Natural stone has been used by man since the early Stone Age till nowadays, as a construction material with great plastic beauty. However, despite the commonly held belief that granite is not as prone to weathering as other natural stones, even granite is susceptible to it when exposed to aggressive environments, such as, for instance, soluble salts present in coastal areas.

It is also widely recognized that the salt mist is an important weathering agent of the building materials applied in the coastal shoreline, promoting the alteration and degradation of the natural stone in these areas (that could spread to zones up to about 20 km from the shoreline) leading to notable damage also in the stone-built heritage, being able to accelerate the weathering process by a factor of 1.59 (Kovacs, 2009).

According to I-STONE (2006), the durability of a stone element is the time period in which the properties of the element remain unchanged, in the best scenario, during its life service. Nevertheless, natural stone, when exploited and used as a construction material, is subjected to very different conditions from those present at its genesis, giving sometimes rise to significant changes in relation to the initial expectation when selected by the consumer. Predicting the useful life of construction materials is fundamental for the optimization of its choice, application criteria and maintenance in the short and long-term. This prediction contributes to avoid economic losses associated with repair interventions.

The main goal of the present work is to analyze and statistically quantify the amount and development in time of the damages in the mechanical properties and ornamental pattern that might occur in two Portuguese granites when exposed to a sodium chloride atmosphere, in order to predict its behavior in the long-time service life. At the same time, it is also intended to check maintenance and compliance with the requirements of the European standards for their use as construction materials.

These two granites [Rosa Arronches (RA) and SPI] are widely used as ornamental and as dimension stones in the national and international building construction and widely traded in the national and international markets being exported to several countries in the world, namely to Spain, Germany and France (major importers from EU countries) and China (major importer country of SPI granite) (Borges, 2019).

MATERIALS AND METHODS

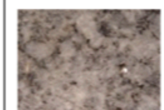
The Rosa Arronches (RA) and SPI granites, primarily quarried in Portalegre district (SE Portugal), differ macroscopically in their color (pinkish or grey), their grain size and also by the presence or absence of a porphyritic texture. The mineralogical composition of these granites is also different regarding the predominance of K-feldspar and plagioclase over quartz.

The RA granite has a slightly pink color that make it very much appreciated and in high demand by consumers in the national and international markets of natural stone. This natural stone is a coarse-grained porphyritic granite, with slightly K-feldspar phenocrystals in a white-grey matrix, with a predominance of K-feldspar and plagioclase over quartz.

The SPI granite is a fine-grained monzonitic biotite granite with a homogeneous bluish grey color and less predominance of K-feldspar and plagioclase over quartz. This granite is also in high demand due to its homogeneous color and granulometry (Table 1).

The resistance to ageing by salt mist was determined by exposing 14 sound samples of the selected granites to an atmosphere of sodium chloride (SCA). The main identification, physic and mechanical properties were determined before and after the accelerated aging test, according to the European standards procedures (Table 2). A total of 150 SCA cycles (75 days) were performed in a controlled atmosphere salt spray chamber/Ascot S120T, electronically scheduled to produce cycles comprising 4 h of saline spray followed by 8 h of drying at (35 ± 5) ºC. The salt solution was prepared in order to achieve a concentration of (100 ± 10) $g.L^{-1}$ according to EN 14147:2003.

Every 15 cycles the samples were removed from the chamber and immersed in deionized water for desalination (the water was replaced daily, for five days, and its conductivity measured until the value of water conductivity, measured after placing the samples to be desalinated, did not exceed twice the value measured before their immersion in water) and then dried, weighed (in order to determine the mass variation, according to Eq. [1]), their surfaces were visually inspected (using a binocular stereoscope Olympus

Granite	RA	SPI
Macroscopic Appearance		
Petrologic Description	Coarse-grained porphyritic granite (mean size crystals 8 mm, with K-feldspar phenocrystals mean sized 1.5 cm) slightly pink K-feldspar in a white-grey matrix.	Fine grained monzonitic biotite granite (mean size crystals 0.8 – 1 mm) with homogeneous bluish grey colour.
Mineralogy	Microcline (40%); Plagioclase (30%); Quartz (20%); Biotite (8%); Zircon, Apatite and Opaques (2%)	Quartz (33%); Plagioclase (33%); Microcline (25%); Biotite (6%); Muscovite, Zircon, Apatite, Sphene and Opaques (3%)
Open Porosity (%)	0.42	0.89

Tab. 1 - Rosa Arronches and SPI identification properties (sound samples) (Borges et alii, 2019)

Natural stone test	European standard
Petrographic examination	EN 12407:2000
Determination of resistance to ageing by salt mist	EN 14147:2003
Determination of water absorption at atmospheric pressure	NPEN 13755:2005
Determination of uniaxial compressive strength	NPEN 1926:2008
Determination of real and apparent density and of total and open porosity	NPEN 1936:2008

Tab. 2 - Performed tests and European standards applied

SZ) and documented with photos (using an Olympus SP - 500 UZ and a Mitutoyo Quickscope QS – LZB digital vision machine).

$$\Delta m = \frac{M_n - M_0}{M_0} \text{ x } 100\ (\%) \quad [1]$$

In [1], M_n is the sample dry mass after every 15 cycles of salt mist and M_0 is the initial sample dry mass before every cycle of salt mist.

The open porosity, water absorption at atmospheric pressure, and uniaxial compressive strength were determined for each lithology in 14 cubic fresh samples [50x50x50 (± 5) mm] before the exposure to 150 cycles of SCA and in another 14 cubic samples, after the exposure to the test. The variation for each determined property (ΔP) was calculated according to Eq. [2], where PB is the mean value of the property after the 150 cycles of SCA and PA is the initial value.

$$\Delta P = \frac{PB - PA}{PA} \text{ x } 100\ (\%) \quad [2]$$

In order to statistically analyze the mass loss between successive cycles, as a percentage of initial mass of RA and SPI granites promoted by the exposure to salt mist atmosphere, a non-linear regression analysis with the laboratory data obtained (mass loss - dependent variable, versus immersion time - independent variable) was performed. An exponential function [3], suggested by Mutlutürk *et alii* (2004), was the one that best fitted the laboratorial data obtained

$$I_N = I_0 e^{-\lambda N} \quad [3]$$

where I_N is the sample mass at the Nth cycle, I_0, is initial sample mass, N is the number of cycles, λ is the decay constant (positive rate) fit to each data set (which indicates the mean relative mass loss by the action of any single cycle) and $e^{-\lambda N}$ is the decay factor, which indicates the proportion of the mass loss after N cycles, that decays exponentially at a rate that depends on the decay constant.

This mathematical model describes the mass loss (or disintegration rate), that is proportional to the rock mass present at the beginning of each cycle. This proposition can be mathematically quantified by

$$\frac{dI}{dN} = -\lambda I \quad [4]$$

where λI is the disintegration rate (mass loss) that explains how these two granites behave under such cyclic action, and λ as we described before is a decay constant. To measure the rate of the decay constant we should consider that N is the decaying quantity corresponding to the different number of cycles that the granites are subjected to. It is possible to compute the average length of cycles necessary to predict the stone behavior in terms of the rock durability, after N cycles. That gives the mean lifetime, $\mu=1/\lambda$, also called the exponential time constant. We can write the exponential decay equation in terms of the mean lifetime μ, e.g., the equation [3] can be rewritten as it follows:

$$I_N = I_0 e^{-N/\mu} \quad [5]$$

When the base of the exponential is chosen to be two, rather than *e*, a more intuitive characteristic of the exponential decay can be obtained, which can be considered as the number of cycles required for the decaying quantity to fall to one-half of its initial value, that is called the half-life, and often denoted by $N_{1/2}$. So, we can say that the *half-life*, $N_{1/2}$, of the stone can be defined as the number of cycles necessary to reduce the durability to half its value, which is inversely related to the decay factor (Mutlutürk *et alii*, 2004). The relationship between the half-life, $N_{1/2}$, and the decay constant, λ, or the mean relative integrity loss, is given by:

$$N_{1/2} = \mu \ln(2) = \frac{1}{\lambda} \times 0.693 \quad [6]$$

with ln (2) ≈ 0.693

RESULTS AND DISCUSSION

Table 3 presents the results obtained for the properties tested, before (B) and after (A) the exposure to SCA, as well as the mass variation of the samples, namely mean values, number of samples tested [x] and the coefficient of variation (V) determined according to equation [7]

$$V(\%) = \frac{s}{\bar{x}} \times 100 \quad [7]$$

where *s* is the standard deviation and *x* is the arithmetic mean.

From Table 3 it can be seen that after the exposure of RA granite to the SCA test, the water absorption at atmospheric pressure has increased from 0.14% up to 0.23%, corresponding to 64%. The same behavior has been observed regarding the open porosity, with an increase of 43% after the SCA test. However, according to Pinto *et alii* (2006) and Assimagra (2015) it can still be classified as presenting low values.

Properties (mean values)		RA	SPI
Open porosity (%)	B SCA	0.42 [14] V (%) = 14	0.89 [14] V (%) = 4.5
	A SCA	0.60 [14] CV (%) = 17	0.83 [14] V (%) = 9.6
	Δ (%)	+ 43	-7
Water absorption at atmospheric pressure (%)	B SCA	0.14 [14] V (%) = 14	0.24 [14] V (%) = 12
	A SCA	0.23 [14] V (%) = 4	0.32 [14] V (%) = 15,6
	Δ (%)	+ 64	+ 33
Uniaxial compressive strength (MPa)	B SCA	196 [14] V (%) = 12	233 [14] V (%) = 16
	A SCA	160 [14] V (%) = 26	224 [14] V (%) = 11
	Δ (%)	-18.4	-3.9
Mass variation (%) after 150 cycles of SCA	n.a.	- 0.19 [14] V (%) = 0.5	- 0.15[14] V (%) = 2.3

Tab. 3 - RA and SPI granites mean properties values before (B) and after (A) the SCA test; Δ (%) - property percentage variation, V (%) - coefficient of variation, [x] - number of samples tested

It was also registered a sharp decrease in the uniaxial compressive strength, from 196 MPa to 160 MPa after the SCA test, corresponding to a 18% decrease. This decrease is another clear sign of the damage caused by the salt atmosphere in the RA granite. Nevertheless, the mean value of 160 MPa still enables us to classify it as a granite with high resistance and high performance (> 100 MPa) (Pinto *et alii*, 2006 and Assimagra, 2015).

For the SPI granite, the increase of water absorption at atmospheric pressure was 33% lower, almost half presented for RA granite. The open porosity has risen by a 7% value, and the decrease in the uniaxial compressive strength (4%) was much lower than the decrease presented by the RA granite.

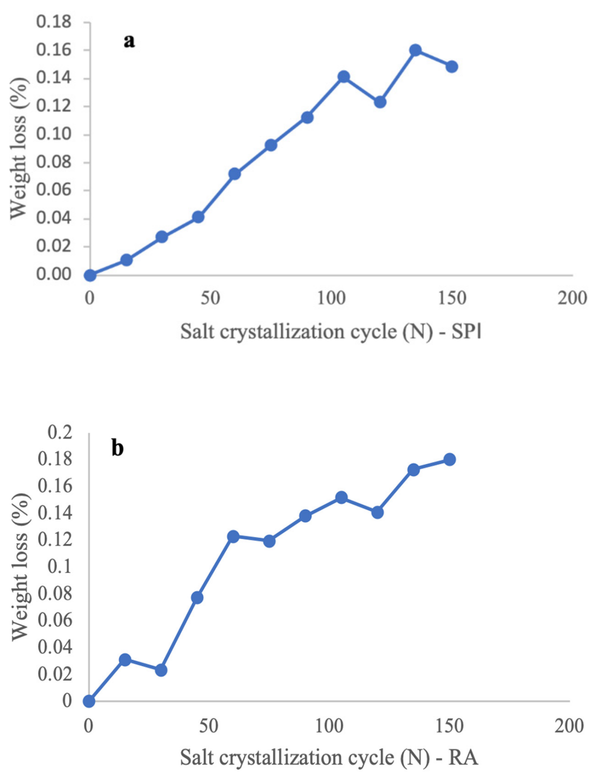


Fig. 1 - Weight changes vs. the number of salt crystallization cycles: (a) SPI granite weight loss (%) and (b) RA granite weight loss (%)

The evolution of the stone decay over time (regarding the average mass loss) caused by the SCA is presented in Fig. 1. From this figure it can be seen that there was a continuous mass loss over the 150 cycles performed for both lithologies, which evidences a decrease in the sample average mass as the test proceeded.

Nevertheless, for the RA granite (with a coarse-grained porphyritic grain) this loss was slightly more pronounced, but only until the 60th cycle of exposure. After this cycle, the results regarding the average mass loss were similar for both granites, although some differences in the first cycles were observed between the two lithologies.

The non-linear regression analysis with the laboratory data obtained (mass loss - dependent variable, versus immersion time - independent variable) using an exponential function is presented in figures 2 and 3. In Fig. 2 it is presented the regression analysis for the worst sample tested and in Fig. 3 it is presented the regression analysis for the best sample tested for the SPI and RA granites.

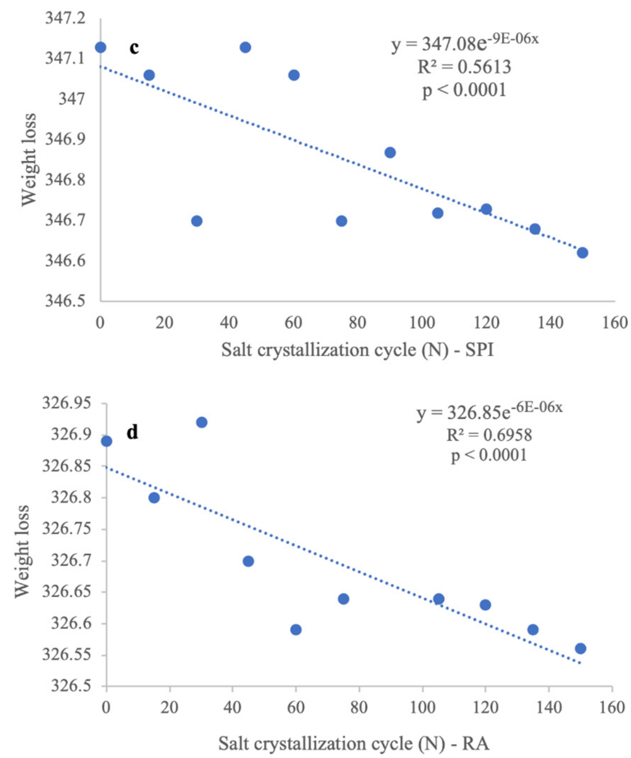


Fig. 2 - The worst fitted model for (c) SPI granite and (d) Rosa Arronches granite exposed to SCA atmosphere (150 cycles)

It is clear, in both cases that the exponential decay function provides a good fit for the mass loss data to all samples tested. The λ parameter in the exponential decay equations for the two granites was strongly correlated with the initial concentration of SCA. In Fig. 3, the line in (e) and (f) is the regression equation with $\lambda = -2E^{-5}$ and $\lambda = -1E^{-5}$ for the granites SPI and RA respectively, with $R^2 = 0.94$ in case of SPI, and $R^2 = 0.89$ in case of RA, with $p < 0.0001$ (Table 4).

The values for the coefficient of determination R^2 (Table 4) before and after the exposure to the SCA aging test confirm that the chosen model fits the data (Figs. 2 and 3), pointing also that the proportion of the variation in the dependent variable (mass loss) can be explained by the variation (or change) of the number of cycles applied (Binal *et alii*, 1997). In this case, we can say that the explanatory power for the two granites is 95% or more before the SCA cycles, and 90% or more after the SCA

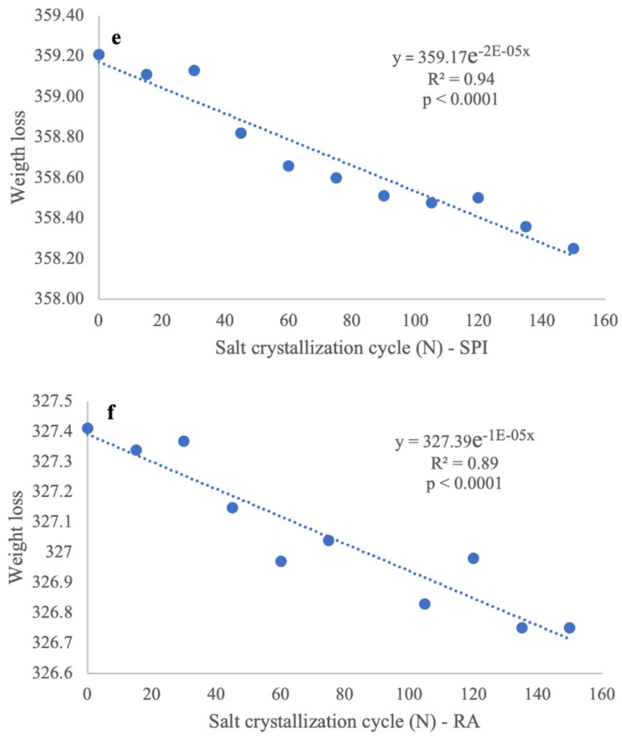


Fig. 3 - The best-fitted model for (e) SPI granite and (f) RA granite exposed to SCA atmosphere (150 cycles)

Granite type	R^2	
	Before SCA	After SCA
Rosa Arronches (RA)	0.951	0.891
Cinzento de Alpalhão (SPI)	0.994	0.941

Tab. 4 - The coefficient of determination (R^2) for the models fitted to the laboratory data

cycles and that the two coefficients of determination are found statistically significant beyond the 1% level.

Therefore, this implies that the observed relationship between integrity and mass loss of the two granites in the course of the 150-cycles of SCA action is not simply due to sampling variation in the measured values of granite integrity but to a manifestation of a real link between the number of cycles and the mass loss, meaning that the model we consider is valid for our purposes for both studied lithologies.

The values of the decay constant λ for the two granites, after the SCA test are given in Table 5 and can be interpreted as the rate of the RA and SPI granites durability under the cycle experimental conditions. These results indicate that the two types of granites present different resistance to the SCA action.

In fact, SPI and RA granites, don't have equal rates of disintegration, 0.002% and 0.001% respectively [$\lambda(SPI)$ = -0.00002 and $\lambda(RA)$ = -0.00001].

Granite type	λ
	After SCA
RA	- 0.00001
SPI	-0.00002

Tab. 5 - Decay constant values (λ) of the granites under study

With respect to the aesthetic criteria of the samples tested, the visual surveillance of the surfaces allows us to verify a loss of the pink color, due to the leaching of K in the K-feldspars minerals, in the RA granite. Flaking, micro-fissuring, loss of biotite and feldspars minerals, corroded minerals and a slightly yellow tarnishing of the white minerals have also occurred in both granites but with a greater expression in the RA granite.

CONCLUSIONS

Globally, the results obtained have put in evidence the decay of granites when exposed to a salt mist atmosphere. This aggressive atmosphere has promoted a change of their ornamental aspect and in their physical and mechanical properties. In addition to a negative chromatic change of the exposed surface, with brown spots around the dark minerals, an increase of microcracks has led to the loss of mineral grains. The minor alterations common to the two granites consist of a slight oxidation of the ferromagnesian minerals (such as biotite and some opaques), which is translated into orange-brown haloes that invade the light-coloured minerals.

The statistical analysis of the data shows that the exposure to this atmosphere also interact negatively with the physical and mechanical properties of both granites, with a generalized and continuous mass loss, increased open porosity and water absorption (more pronounced in the RA granite) and decreased uniaxial compressive strength (lower in SPI granite). Nevertheless, the decay presented does not compromise they use for the main applications of natural stones as building materials. However, in other countries with more demanding tests and/or more restrictive standards than the European standards, the decrease of the properties observed can be problematic.

When statistically analysing the evolution of mass loss data over time, it was found that it is not linear but rather, a relationship expressed by an exponential regression model. The values of the decay constant for the two granites reveal that they don't have equal rates of durability, which indicate that the resistance of the two granites is not the same with respect to the exposure to recurrent SCA cycles, with the SPI granite showing greater resistance.

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Received November 2022 - Accepted March 2023