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Effectiveness of chemical, mechanical and laser cleaning methods of sulphated black crusts developed on granite

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HIGHLIGHTS

- Mechanical, chemical and laser ablation procedures were applied to clean sulphated black crust on granite.
- None of the evaluated methods completely removed the studied crust.
- All methods produced unwanted effects on the rock.
- *Papetta AB57* with *Carbopol Ultrez 21* and *Ethomeen C25* showed the highest cleaning effectiveness.

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ABSTRACT

A study of the cleaning effectiveness of sulphated black crust developed on granite is presented. The sulphated black crust, previously characterized, was subjected to a cleaning by 1) a mechanical procedure –*Hydrogommage*– based on micro-sandblasting, 2) chemical procedures based on the application of poultices made on different mixes of thickening agents and cleaners and 3) laser cleaning using a 355 nm Nd:YVO_4 nanosecond laser. Chemical, mineralogical and physical characterization of the cleaned surfaces were performed; the global effectiveness as well as the harmfulness were evaluated according to the level of black crust removal and the substrate damages. As result, none of the methods has been completely effective in removing the sulphated black crust and, also, all the methods produced undesirable effects on the stone. The crust nature, its degree of interaction with the stone and other factors related to the principle of the cleaning procedures were found as the main variables influencing the effectiveness of the cleaning procedures.

1. Introduction

Black crusts are blackening originated from the interaction between the stone substrate and the atmospheric contamination, mainly SO_2, NO_X and CO_2 [1]. Its impact on the historical building and monuments is considered so important that the Stone Weathering and Atmospheric Pollution Network (SWAPNET) was founded in 1993 to study the decay of the stones affected by the atmospheric pollution and to search for techniques to remedy it [2]. The final product of the reaction between sulphur oxide and Ca, from carbonate stones rich in calcium, is gypsum, which has different physical and chemical properties than the underlying stone [3,4].

The processes that generate this kind of black crusts continue to raise much interest today, but almost exclusively those developed on carbonated sedimentary stones and marbles [5,6]. In [7], the authors pointed that stones, besides to their surface transformation, acquire a black discolouration because the incorporation of carbonaceous material from the contaminated atmosphere, that is originated from the combustion of diesel and gasoline by automobiles and industrial activity. There are few studies about the black crust formation in granite. During a study performed under artificial exposure atmospheres showed that granite sulphation is even possible at relatively poor SO_2 atmospheres (10 ppm), as SO_2 can react with Ca from the joint mortar [8]. A more recent study confirmed the contribution of two sulphur sources, i.e. anthropogenic SO_2 and marine sulphate, in the development of black crust on coastal granitic constructions [4].

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In general terms, crusts cleaning process must be understood as a soft and delicate extraction procedure intended to release the surface dirt without affecting the stone [9]. The particular characteristics of this crust make not advisable to extrapolate its cleaning results to other crust types [10]. There are many cleaning methods and the selection of the most adequate must be done taking into account a lot of theoretical and practical considerations that include (a) diagnosis of the stone surface (stone kind, extent and severity of decay) and (b) work accessibility and the need of scaffolding. Once the most adequate methods are chosen, they must be essayed on specific areas of the degraded surface, in order to estimate the effectiveness and side effects on the stone (risk evaluation) [11].

Since the 90s, the search for more effective cleaning methods that cause less damage to the stone substrate was increased. There are different cleaning methods, being the mechanical and chemical ones the most traditionally used. Mechanical methods, derived from the old sandblasting method, are based on the projection of different kind of particles. Due to their aggressiveness because the high pressure range used (above 50 bar), they are only used in certain circumstances [11,12]. Among chemical methods, the *Papetta AB57* formulation (developed by the *Istituto Superiore per la Conservazione ed il Restauro* in Rome) has been hailed as an excellent cleaning agent for black crust developed on marble [13]. Laser ablation constitutes another cleaning procedure in heritage conservation which goes back to the 70s with the pioneering work by John Asmus about crust extraction in Venetian marble [14]. There are numerous bibliographic works based on the parameters of the laser systems, the mechanisms involved in the surface cleaning and the different uses of laser in restoration of Cultural heritage [15–17]. Concretely, works about its laboratory and *in situ* applications are very extensive, especially those related to carbonated stones [17–21].

Almost all the references regarding cleaning procedures to remove black crust are focused on carbonated stones (sedimentary or metamorphic) [18–21], therefore the studies related to granitic stones are scarce. This limited scientific production is centred particularly on laser cleaning [22–25]. Also, up to date, there are no works intending to compare effectiveness information between different cleaning procedures of black crust developed on granite.

Therefore, the aim of this work is to enhance the knowledge about the effectiveness of different mechanical, chemical and laser ablation-cleaning procedures, in the removing of sulphated black crust developed on a granite widely used in the construction of architectural heritage in NW of Iberian Peninsula. Taking into account the deep influence of the textural and mineralogical peculiarities of the granites in their durability and in their response to conservation treatments [26,27], the access to specific results on the cleaning effectiveness of different methods of black crust in granites would be of great significance in the direct intervention in granitic cultural heritage.

2. Materials and methods

2.1. Granite and sulphated black crust samples

In order to carry out this study, an ashlar affected by an intense development of sulphated black crust was extracted from an ancient building in the city of Vigo (NW Iberian Peninsula). This building is constructed with a fine grained (2–0.3 mm) equigranular granite, composed of quartz (29%), potassium feldspar (25%), sodium plagioclase (24%), muscovite (13%) and biotite (4%) as main minerals [28]. A 100 cm × 100 cm × 2 cm plate where cut parallel to the crusted surface of the ashlar, in order to obtain more manageable smaller stone 29 slabs of 14 cm × 7 cm. Previously to the cleaning process, the black crust was characterized following different techniques. Results of this characterization can be consulted in [4]: briefly, the sulphated black crust comprised a coating of 80–100 μm of thickness composed of acicular-shape crystals of calcium sulphate with occasionally biological structures. Chemically, besides calcium sulphate, alkane and carboxylic-type organic compounds were identified; being probably these compounds the reason of the black colour of the crust [4].

2.2. Cleaning methods

The cleaning methods used were the following:

1) Chemical procedures:
Following previously reported studies [13,29], it was decided to apply nine different chemical cleaning treatments (see Table 1). All these treatments, except one, consisted on the application of a poultice made on a mixture of a cleaning agent and a thickening compound (Table 1).

The selected cleaning agents were:

- Standard *Papetta AB57* composed of 25 g of EDTA, 50 g of sodium bicarbonate, 30 g of ammonium bicarbonate and 10 cm^3 of *Neodesogen* (a biocide based on benzalkonium chloride with fungicide effect which was provided by *BIC Materiales y Conservación S.L.*), all dissolved in 1000 mL of distilled water.
- Papetta AB57 without ammonium bicarbonate, prepared with 25 g EDTA, 50 g sodium bicarbonate and 10 cm^3 of *Neodesogen*, dissolved in 1000 mL of distilled water.
- Acidic mixture: 5% (vol.) HCl and 2.5% (vol.) $(NH_3)HF_2$ in aqueous solution.

The selected thickeners supplied by *CTS Slr* (details in www.ctseurope.com) were:

- *Carbopol Ultrez21* prepared at 3% (wt.) in 10% (wt.) ammonium bicarbonate solution. As Table 1 shows, this thickener was prepared with *Papetta AB57* without ammonium bicarbonate.
- *Carbopol Ultrez21* prepared at 3% (wt.) in 10% (wt.) *Ethomeen C25* solution.
- *Laponite RD*, a synthetic clay composed of sodium, lithium and magnesium silicates.
- *Carboxymethylcellulose* as water soluble sodium salt of the cellulose glycolic acid.
- *Carbogel*, a neutralized polyacrylic acid.

Eight different poultice based treatments were prepared mixing the above mentioned cleaning compounds and thickeners at different proportions until achieving a gel with good workability. In Table 1, the proportions and acronyms for all these treatments are shown.

The ninth chemical treatment consisted on the direct application of *Amberlite 4400 OH* which was also provided by *CTS Slr*. (www.ctseurope.com). It is a strong exchange resin. A poultice with a proper consistence was prepared mixing 50 g of *Amberlite* within 30.7 mL of distilled water (Table 1).

Table 1
Chemical cleaning treatments applied in this study. In the third column, the acronym and the cleaning compound-thickener proportion is indicated.

Cleaning agent	Thickener	Treatment Cleaning-thickener proportion
PAPETTA AB57	*Laponite RD*	*Papetta AB57* + *Laponite* (PL) 50 mL: 14.5 g
	Carboxymethylcellulose	*Papetta AB57* + *CMC* (PCMC) 50 mL: 2 g
	Carbogel	*Papetta AB57* + *Carbogel* (PC) 50 mL: 4.5 g
	Carbopol Ultrez 21 and *Ethomeen C25*	*Papetta AB57* + *Carb* + *Eth* (PCUE) 50 mL: 100 mL
PAPETTA AB57 without NH_4HCO_3	*Carbopol Ultrez 21* with NH_4HCO_3	*Papetta AB57* + *Carb* + *Bic* (PCUB) 50 mL: 100 mL
ACIDIC MIXTURE	*Laponite RD*	*Acidic* + *Laponite* (AL) 50 mL: 19 g
	Carboxymethylcellulose	*Acidic* + *CMC* (ACMC) 50 mL: 3 g
	Carbogel	*Acidic* + *Carbogel* (AC) 50 mL: 4 g
AMBERLITE 4400 OH		(AM)