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Cleaning methods assessment for the limestone façades of the formerly Workers Hospital of Madrid, Spain

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Abstract
Four methods for cleaning the limestone facades on what was originally the Workers' Hospital are analyzed in this paper. Due to the pollution in the surrounding air, just twenty years after a prior cleaning operation, sulfate crusts had developed on the entire stone surface of the building. The gypsum mortar used in the original masonry constituted an additional source of sulfur.
Limestone is a traditional building material in Madrid and surroundings. The petrography, mineralogy and petrophysical properties of the biomicrite, pelmicrite and biopelmicrite varieties identified in the hospital walls were determined. An analysis of the black layer on the stone surface showed that it consisted primarily of sulfate crusts. The cleaning methods tested were alkaline gels (sodium hydroxide and potassium hydroxide), pressurized hot water, glass bead blasting and latex peeling. The criteria for assessing the effectiveness and potential dangerousness of the various cleaning systems included changes in the chromatic parameters of the clean stone, as well as formation of alteration products (i.e., salts) and modification of the stone surface. The stones cleaned with the three most effective methods as well as the rain-washed stone used as a reference were washed to generate an artificial runoff.
The drain water collected was analyzed to determine possible cleaning process by-products.
The method found to be most effective and alter the stone surface the least was glass bead blasting, particularly after adjustment of the bead size and pressure conditions used for the test.
Keywords: limestone, cleaning methods, assessment, chromatic parameters, SEM-EDS

1. Introduction

The former Workers' Hospital, designed by architect Antonio Palacios, was built between 1909 and 1916, primarily of limestone. Also used on the surrounding wall (Figure 1), the stone is from the *Caliza del Páramo* geological formation located in the east and southeast of the Community of Madrid. Several stone varieties are found in this formation, all of which have been widely used in the built heritage of the region since the 18th century [1,2]. The building was used as a hospital until the early nineteen seventies, when it closed chiefly for want of financial support [3], and remained vacant for 15 years. In 1979 it was listed as a national artistic and historic monument. The regional Government of Madrid purchased the property in 1984 as the headquarters for the regional Department of Housing and Transport. In the comprehensive restoration and rehabilitation works performed between 1984 and 1986, one of the main tasks was to clean and protect the stone facades.

Accumulated surface deposits are responsible for the recent re-blackening of the facades, with the concomitant loss of aesthetic value [4]. The main forms of decay observed in the hospital's stone facades are related to such black layers, which on much of the stone surface is associated with the development of sulfate crusts. Where air pollution is severe, sulfate crusts tend to develop on carbonate stones not washed by rainwater, which progressively blacken due to the deposition of particulate matter [5-9]. While the polluted urban environment where the building stands is the primary cause of facade soiling and blackening, there are others, including the many insets in the facade and wall design that hinder the rainwater washing of the elements involved [10]; the rusticated finish of the ashlars that favours particle deposition [11]; and the passing of time itself.

The facade cleaning underway since June 2006, with completion scheduled about the middle of 2008, aims primarily to remove stone soiling and blackening and enhance building aesthetics. Prior studies to assess the most suitable cleaning method were requested. Today's preventive policies for historic buildings advocate maintenance and urban remodelling to reduce the effects of atmospheric pollution [12]. As a rule, however, it is difficult to balance air pollution and building material decay on the one hand and the aesthetic value and maintenance of buildings on the other [13-15]. A complete description of testing procedures to assess cleaning treatments is in [16], with a list of properties to measure, test methods to use, evaluated parameters and criteria for positive evaluation, as well as the characteristics of evaluation tests.

The present study aimed to identify the most appropriate method for cleaning the hospital's stone facades, taking into consideration the properties of the stone and their surface deposits.

2. Materials and Methods

Several studies were conducted to assess the most effective and suitable method for cleaning the stone. Four techniques were pre-selected and subsequently tested in situ on the stone in the surrounding wall. This area was chosen for testing because it is one of the most severely soiled parts of the building due to its direct exposure to heavy vehicle traffic (Figure 1) and to its position, set back from the edge of the lot (Figure 2). The surrounding environment was analyzed; the stone and the joint mortar were characterized; the nature of the soiling was analyzed before proceeding to clean the stone; and the advantages-drawbacks of the cleaning methods selected were studied, because building clean-up operations are governed by both aesthetic and materials science criteria [17].

2.1. Surrounding air

Twenty years after they were last cleaned (1986), the stone facades were severely soiled, due primarily to the building's location in a polluted urban area (Figure 1), one of the busiest in the city where vehicle traffic is especially heavy. The flyover that stood on the street bordering the building for 35 years (1969-2005) supported traffic on the order of 80 000 vehicles over top and 70 000 underneath per day. The vehicle entry to the present underpass built in 2005 to replace the flyover is just opposite the main facade of the building (Figure 1). Figure 3 shows the concentration by month of SO_2 and particulate matter from 1986 to 2006. The data were obtained from Madrid's Municipal Air Quality Surveillance Network. Specifically, the values were recorded at the *Cuatro Caminos* environmental measurement station, which was located just 150 m from the building, although since December 1998 it was sited at a distance of 380 m from the hospital. Note that the concentration of both pollutants has declined, particulate matter more slightly and SO_2 much more sharply, particularly as regards the highest levels. Even where air quality improves, stone has a "stored memory" of past pollution, although not all authors agree that this is the case [18]. In any event, periodic monitoring of stone facade soiling from this time on would be highly recommendable.

2.2. Building materials

Stone and mortar samples were studied with an Olympus BX51 polarized microscope fitted with an Olympus DP12 (6V/2,5Å) digital camera and proprietary software. Thin sections were stained with alizarin red-S to differentiate carbonate minerals. X-ray diffraction techniques were used to study stone mineralogy on a Philips PW1752, 40 kV, 30 mA diffractor with a Cu source anode, º2Ɵ, and PC-ADP diffraction software.

The petrophysical characterization of the limestone consisted in determining: the chromatic parameters (*L** -Luminosity-, *a** and *b** - chromatic coordinates, *a** accounts for red-green, and *b** for yellow-blue-, *C** -Chroma-, *WI* -White Index- and *YI* –Yellow Index-) [19] using a Minolta CM-2002 spectrophotometer with CIE Standard Illuminant D65 and a 10º observer angle; porosity accessible to water or open porosity and water saturation, obtained through the vacuum saturation method; pore size distribution (differentiating between micro and macroporosity, being 5 µm pore diameter the threshold), and porosity accessible to mercury, with a Micromeritics AutoPore IV 9520 Hg-porosimeter having a pore diameter range from 0.001 to 1000 µm and measuring conditions from atmospheric pressure to 60 000 psia (228 MPa); and the water-stone contact angle with a CAHN, DCA-315 dynamic contact angle analyzer, by means of which, a value expressed in degrees: the higher the value (>90º), the more water-repellent or hydrophobic the analyzed stone surface.

The stones found most commonly throughout the building are classified as biomicrites, pelmicrites and biopelmicrites [20] (Figure 4), with calcite as the main and quartz as the accessory mineral. While known locally as *Colmenar* stone, its petrology does not exactly conform to that variety. Despite the heterogeneity, in some measure, of its physical properties (Table 1), this limestone is a high quality building material. It has a low open porosity (or porosity accessible to water), although most of the pores are in the range of micropores. Water stone contact angle measuring show that it is not a very water-repellent or hydrophobic stone by itself, although the maximum quantity of water that the stone is able to contain (saturation water, under vacuum in the laboratory) is not significant (1.63%±0.76).

Several layers of mortars were found in the masonry joints. The outer-most cement mortar covers what is probably the original, gypsum mortar. The cement mortar contains siliceous aggregates (quartz, feldspar, rock fragments, mica) in a dark, lumpy, microcrystalline matrix. The mineralogical composition of the cement mortar includes a siliceous aggregate and an aluminium-rich cement (gehlenite, alite, belite, tricalcium aluminate and celite). The degree of carbonation (calcite) and sulfation (gypsum) of this kind of mortar, which is indicative of decay, varied depending on the area chosen for sampling (Figure 5).

The gypsum mortar also contained siliceous aggregate (quartz, igneous rock fragments, feldspar, mica and ceramic fragments or chamotte) in its composition, as well as some calcitic particles, in a dense and fibrous gypsum matrix (Figure 6). Large gypsum crystals (up to 6 mm), the result of incomplete mixing, were also observed (Figure 7). These crystals exhibited corrosion around the edges, an outcome of successive dissolution and precipitation. Gypsum ($CaSO_4 \cdot 2H_2O$) and bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$) were found in their mineralogical composition.

2.3. Type of stone surface deposits

The samples were first studied under a polarized microscope to determine their nature. Where warranted by sample thinness and lack of cohesion, the specimens were vacuum-impregnated with resin. Scanning electron microscopy (SEM) was also utilized, using a JEOL JSM 6400 SEM with an acceleration voltage of 2 to 40 kV, a beam current of 6 x 10-10 A, 10-5 Torr vacuum conditions, and resolution of 35 Å; the working distance was 8 mm at 35 kV. The images were recorded at an acceleration voltage of 20 kV. An Oxford-INCA X-ray Energy Dispersive Spectrometer (EDS) with a nominal resolution of 133 eV at 5.39 kV was coupled to the SEM. Samples were graphite sputtered (15-mm thick cover) with a Balzers Med010 sputter coater (Balzers, Liechtenstein).

2.4. Selection of cleaning methods

The grounds for selecting cleaning methods were: traditional use for a long time in heritage buildings, at least in Spain, and still nowadays, unfortunately (gel-based systems); satisfactory results in other stone buildings (glass bead blasting); or least aggressive approach (latex) [21-26].

Four groups of cleaning methods were selected:

1: alkaline gel-based system (sodium and potassium hydroxides). The testing area to be cleaned is water sprayed, the gel applied by brushing for 30 to 45 minutes, and then the product is removed with a water jet (at 5.88 MPa and 60 ºC).

2: pressurized hot water (at 5.88 MPa and 60 ºC)

3: wet glass bead blasting with a bead size ranging from 50 to 100 micrometers in diameter and a water:bead ratio of 1:4, under a pressure of 5.88 MPa

4: latex peeling with a product containing 10 % EDTA (ethylenediaminetetraacetic acid) and ammonia. The testing area must be dry and the product is applied by brushing, leaving it for 24 hours and then removing it, directly pulling from the latex as if it were a peeling mask.

While the use of the first three groups of methods for cleaning stone is widespread and amply documented, no results on stone cleaning with latex could be found in the literature.

2.5. Cleaning method effectiveness

The effectiveness of these cleaning methods was assessed by determining the chromatic parameters of the limestone prior to and after cleaning, as well as the overall colour change ($\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{½}$) [8,22,27-29]. The reference value was taken to be the colour of the naturally rain-washed limestone, primarily the limestone at the socle of the building, as per Fort et al., 2000c. The closer the colour of the clean stone was to the rain-washed stone reference, i.e., the lower the ΔE* value, the more efficient was the cleaning method.

Ca. of two hundred and forty parameters were obtained, by means of three measurements on every field area: fresh limestone, naturally rain-washed socle and on five different areas before and after cleaning with the five different methods.

The other criteria for assessing the suitability of the cleaning methods were the presence or absence of alteration products (i.e. salt formation) and stone surface modifications. A Metrohm 761 Compact IC ion chromatographer was used for this purpose, in conjunction with a chemical suppressor module N/S 1761002017199 and IC Net 2.3 software. The separation columns used were:

- a Metrosep A Supp 5 – 150, N/S 7209533 anion column, with a standard and maximum flow of 0.7 and 0.8 mL/min, respectively, and a pressure of 6.5MPa. Regarding to eluents, sodium hydrogen carbonate (168mg/2 L-1.0 mmol/L) and sodium carbonate (678mg/2 L–3.2 mmol/L) were used as carbonate eluent; and sodium hydroxide (1600mg/2 L-20.0 mmol/L) and p-Cyanophenol (476mg/2 L - 4.0 mmol/L) were used as hydroxide eluent.The injection flux was 20 µl and ultrapure water was employed for rinsing.
- a Metrosep C2 150 N/S 1116.0029 cation column, with a standard and maximum flow of 1.0 and 5 mL/min, respectively, and a pressure of 7.0MPa. Regarding to eluents, tartaric acid (1200mg/2 L-4.0 mmol/L) and dipicolinic acid (250mg/2 L–0.75 mmol/L) were used as

standard eluent; and nitric acid (c=1mol/L, 4mL/2L-2.0 mmol/L).The injection flux was 20 µl and ultrapure water was employed for rinsing.

Both the stones cleaned with the three most effective methods and the rain-washed stone were rinsed to generate an artificial runoff. The height of wall affected by the runoff – less than one litre of water – was around 1 m. The water collected was analyzed to determine possible cleaning process by-products on the stone surface. Anions determined were chloride, nitrate and sulfate; cations were sodium, potassium and calcium.

The selection of these anions and cations was performed considering them as forming part of some of the most frequent salts as by-products, especially taking into account the nature and composition of materials and by-products, as well as considering the nature of the cleaning gels.

3. Results and Discussion

3.1. Type of surface deposits

The main component of the accumulated surface deposits was gypsum (Figures 4-8). There were two layers of crust: the outer-most, not always present, was irregular and around 10-20 µm thick. It contained gypsum, Si, Al and C, as well as the remains of micro-organisms. This layer was compact, irregular and lumpy in appearance. The inner layer, in contact with the stone, was thicker and composed of more intensely crystallized gypsum and halite (NaCl). In some places, this crust was up to 3 mm thick. Prismatic gypsum crystals were sometimes found in stone fissures. This is one of the reasons that made stone cleaning necessary, for surface deposits accumulation and blackening cause not only aesthetic damage (soiling) but may actually lead to physical and chemical decay of the stone. The origin of this black crust may be traced to the polluted environment where the building is located; the main component, gypsum, forms from atmospheric SO_2 (high concentrations of which are in the air due to motor vehicle emissions) as the source of sulfur, and the calcium from the calcite in the limestone [6,30-33]. Another source of sulfur is the original gypsum mortar. A third possible source that cannot be ruled out is the sulfur from cement mortar sulfation. The primary sources of the water needed to dissolve the gypsum are the periodic sprinkling of the landscaped areas between the outer wall and the main building and rainwater.

3.2. Assessment of the stone cleaning methods

3.2.1. Overall colour change (ΔE^*)

The sodium hydroxide-based cleaning system proved to be acceptably effective. The results of the potassium hydroxide-based method, on the contrary, were unsatisfactory, for this product left a whitish veil on the stone surface. Glass bead blasting was also effective, removing the crust without generating surface by-products. Neither the latex nor the pressurized water methods were acceptable, for they led to no change in the surface visible to the naked eye (Figure 9); moreover, not all the latex was readily removable.

Table 2 shows that the alkaline gel- and glass bead-based cleaning methods yielded the highest luminosity (L*) values, approaching the values recorded for the rain-washed limestone. The yellow index (YI) values measured on the stone after cleaning with these systems were also very similar to the reference values. The lowest ΔE* value measured after cleaning was obtained with the NaOH-based gel, followed by the KOH-based method and glass bead blasting. The ΔE* values measured on the limestone cleaned with the pressurized water and latex methods declined slightly from the values found prior to cleaning. The smaller the modification of the yellow and white indices obtained (with respect to the naturally washed stone), the better and more efficient is a cleaning system. The white index found for the limestone tested with the NaOH alkaline gel treatment was very similar to the rain-washed stone index. The latex and pressurized water systems were less effective from this standpoint, for the limestone exhibited similar chromatic parameters before and after cleaning. In terms of overall colour change, the lower the values after cleaning, the more effective is the method, because the whole point of cleaning is to turn the colour of the soiled stone to a tone as close as possible to the colour of the naturally washed stone.

A comparison of the white and yellow indices of the samples cleaned with the various systems to the rain-washed reference showed that the glass bead and alkaline gel methods were the most effective in this regard, as they yielded the smallest chromatic differences (Figure 10).

3.2.2. Cleaning by-products

The analysis of the artificial runoff collected from the stones cleaned with the three most effective methods and from the rain-washed stone by means of ion chromatography is shown in Table 3. The high anion content measured on the naturally washed stone may have been partly due to the accumulation of urine and droppings [34] and the natural runoff over the above black crusts.

While the three most effective methods reduced the chloride, nitrate and sulfate content on the stone surface, none achieved complete removal. The most efficient in this regard was glass bead blasting.

All three methods raised the content of the selected cations (Na, K, Ca). In the case of the KOH gel, this compound would account for the potassium content and the whitish veil on the stone surface.

3.2.4. Textural changes on the stone surface

The degree of soiling removed from the limestone surface with the different cleaning methods was determined with SEM (+EDS). Gypsum crystals were found in sheltered areas of the stone surface cleaned with a sodium hydroxide-based gel (Figure 11a). Moreover, some of the calcite crystals in the area where the black crust was eliminated were slightly dissolved (Figure 11b), an outcome of the fairly aggressive nature of this product.

The KOH gel thinned the black crust but did not remove it entirely. In addition, the high potassium content may have induced salt formation (as already suggested by [35] and with it the whitish postcleaning veil observed on the stone surface (Figure 11b). Glass bead blasting was the most effective method, for it removed the black crust completely, i.e., both soiling and the gypsum crystals. In addition, bead impact left only faint marks on only a few of the calcite crystals (Figure 11c).

4. Conclusions

Of the four cleaning methods selected, pressurized water and latex peeling proved to be ineffective. In terms of chromatic criteria (ΔE^*, ΔYI and ΔWI), the most effective methods were alkaline gel-based systems and glass bead blasting. All three systems yielded clean stone whose colour was close to the colour of the naturally washed stone used as a reference. The methods were found to have drawbacks, however. The KOH based gel may lead to the formation of salt by-products (whitish veil) and the glass bead system may affect the surface texture slightly. The NaOH based alkaline gel, in turn, may increase the Na content on the surface of the stone, with the concomitant risk of a future build-up of potentially destructive sodium sulfates. Be it said, however, that the SEM/EDS results showed no sodium remains on the clean stone surface, at least on the samples that were analysed. Regarding the three methods to evaluate de effectiveness of the cleaning systems (colour parameters variation, cleaning by products by ion chromatography and textural changes on stone surface by SEM), the least reliable was the ion chromatography method, with results difficult to interpret, probably due to the methodology followed.

Given the properties of the stone in question, namely a stone-water contact angle that is not particularly high and a predominance of microporosity, the NaOH based alkaline gel was ruled out, for it would entail the use of vast quantities of water and the attendant likelihood of salt remobilization; the greater the microporosity, the higher is the potential for salt crystallization-mediated decay.

Consequently, the conclusion drawn from the results of this study is that the most effective method for cleaning the limestone on this building is glass bead blasting.

Nonetheless, a smaller bead size and lower working pressure are recommended to prevent damage to the stone surface. And indeed, this is the method that was used to clean the facades, with quite satisfactory results and no damage to the stone.

In light of the building location – in an area with heavy traffic –, black crusts will definitely develop and soiling will accumulate in the not-so-distant future. The recommendation, therefore, is for facade cleaning to be included as a part of building maintenance. On the one hand, facade maintenance should take place more frequently and involve simpler cleaning operations, rather than huge and expensive repair works.

And on the other, preventive maintenance, including *in situ* measurements and regular monitoring of relevant parameters to estimate the rate of facade soiling and blackening.

Final note from the authors: This case study represents a real example of how scientific method can contribute to optimal restoration and conservation of the architectural heritage. While it may appear to be obvious that some of the cleaning methods discussed should not have even been tested, unfortunately in the real world, some of these systems continue to be used indiscriminately despite the lack of any scientific endorsement. Even today, only a small number of institutions responsible for heritage conservation are aware of the need to conduct scientific studies prior to any manner of intervention. In this specific case, however, the Community of Madrid did undertake preliminary testing to ascertain the effectiveness of the cleaning methods under consideration for the building studied here. The outcome was that the methods that proved to be ineffective or damaging to the stone to be cleaned were ruled out. While this may appear to be obvious, scientific evidence was required to select the optimal method in terms of both efficacy and harmlessness for the stone. This type of collaboration aims to encourage the institutions responsible to trust in science to solve what may appear to be merely technical problems. A second objective is to generate the need for studies that contribute to the conservation of the cultural heritage and at the same time and no less importantly to medium- and long-term savings on the costs of such interventions.

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Table 1. Petrophysical properties of the limestone

Porosity accessible to water (%)		4.1 ± 1.8
Water saturation (%)		1.6 ± 0.8
Porosity accessible to Hg (%)		2.5 ± 1.7
Macroporosity >5 µm (%)		23.5 ± 25.6
Microporosity <5 µm (%)		76.5 ± 25.6
Average pore size (µm)		0.05 ± 0.02
Water-stone contact angle (º)		61 ± 5
Chromatic parameters		
	*L**	75 ± 2
	*a**	2 ± 1
	*b**	6 ± 1
	*C**	7 ± 1
	WI	27 ± 6
	YI	11 ± 2

Table 2. Chromatic parameters measured on the limestone prior to and after cleaning with the different methods: first table corresponds to the absolute values; in the second table the variations (increase/decrease) of the chromatic parameters before and after stone cleaning compared to rain-washed stone (reference colour) are shown.

		L*	a*	b*	C	YI	WI
NaOH	BC	51.2±9.5	1.9±0.1	7.5±1.0	7.7±1.0	18.4±0.2	5.4±2.3
	AC	72.4±1.0	1.4±0.5	7.0±0.6	7.2±.0.7	13.4±1.3	20.8±2.9
KOH	BC	42.3±1.3	3.6±0.3	12.6±0.5	13.1±0.6	33.6±1.6	-4.4±0.6
	AC	69.1±3.6	2.3±1.6	7.9±1.0	8.3±1.1	15.7±2.4	15.1±5.8
Glass beads	BC	47.5±2.6	2.4±07	9.6±1.1	9.9±1.2	24.6±3.5	0.4±2.4
	AC	66.9±3.4	1.9±0.2	8.2±0.8	8.4±0.8	16.5±1.2	12.5±2.1
Water	BC	46.2±4.4	3.0±0.5	11.4±1.1	11.8±1.2	29.2±3.4	-2.5±1.8
	AC	49.9±2.1	2.5±0.9	9.1±1.5	9.4±1.7	22.6±3.9	1.9±2.9
Latex	BC	44.8±0.8	2.8±0.3	9.5±0.5	9.9±0.6	25.3±1.0	-0.2±0.6
	AC	52.9±2.3	2.2±0.5	11.5±1.3	11.7±1.2	26.6±1.9	-1.5±1.7
Rain-washed stone (reference colour)		80.6±1.9	1.2±0.1	9.1±0.8	9.2±0.8	21.8±1.5	15.6±1.0

		ΔL*	Δa*	Δb*	ΔE*	ΔYI	ΔWI
NaOH	Before cleaning	-29.4	0.7	-1.6	29.4	2.8	-16.4
	After cleaning	-8.2	0.2	-2.1	8.4	-2.2	-1.0
KOH	Before cleaning	-38.2	2.4	3.5	38.5	18.0	-26.3
	After cleaning	-11.5	1.1	-1.1	11.6	0.1	-6.7
Glass beads	Before cleaning	-33.0	1.2	0.6	33.1	9.0	-21.4
	After cleaning	-13.7	0.7	-0.9	13.7	0.9	-9.4
Water	Before cleaning	-34.4	1.8	2.3	34.5	13.6	-24.3
	After cleaning	-30.7	1.3	1.0	30.7	7.0	-19.9
Latex	Before cleaning	-35.7	1.6	0.4	35.8	9.7	-22.0
	After cleaning	-27.7	1.0	2.4	27.8	11.0	-23.3

Table 3. Ionic composition of artificial rain water runoff over naturally washed stone and limestone samples cleaned with the three most effective methods, compared to domestic cold water (mg/l).

	ANIONS			CATIONS		
	Chloride	Nitrate	Sulphate	Sodium	Potassium	Calcium
Drinking water [a]	10.0-20.0	<0.9-7.8	8.0-30.0	4.0-20.0	<2.0	5.8-34.8
Rain-washed stone	46.6	119.1	101.8	12.6	4.9	8.6
NaOH	22.5	70.7	50.4	26.6	5.4	21.4
KOH	29.4	59.4	65.9	25.9	26.3	16.6
Glass beads	17.1	1.9	35.6	23.5	3.9	13.7

[a] Source: Canal de Isabel II. Madrid waterworks utility. Minimum and maximum values for 2005

Figure captions

Figure 1. General view of the Formerly Hospital. Façades of the northwest body, church and surrounding wall.

Figure 2. Differential soiling of the surrounding wall.

Figure 3. Monthly values of SO_2 and particulate matter concentration from 1986 to 2006. Source: Air Quality Surveillance Network, Madrid City Council.

Figure 4. Thin section (cross section) of the soiling on the stone. A and B are the two layers of the soiling crust. C corresponds to the stone.

Figure 5. XRD spectrum from a sample of cement mortar.

Figure 6. Thin section micrograph of a gypsum mortar sample. Detail of the gypsum rich matrix, with arrow-head shaped gypsum crystals.

Figure 7. Detail of the dissolution-precipitation borders of a large gypsum crystal.

Figure 8. SEM images (cross section, SE mode) showing A: surface soiling layer, B: gypsum crust in contact with stone, and, C: limestone

Figure 9. Wall stones appearance after (above) and prior (below) to the testing with the different cleaning methods.

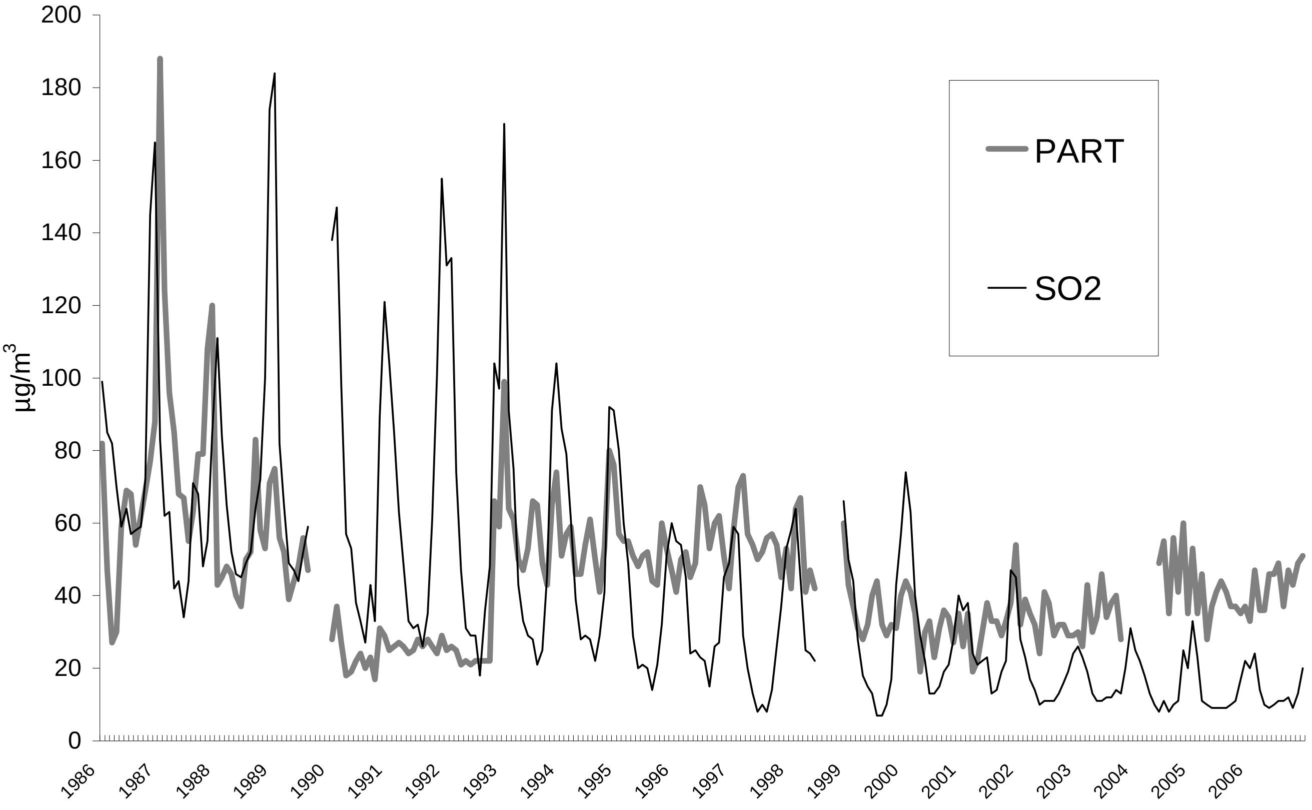
Figure 10. White and yellow indices increase of the cleaned stones with respect to the rainwashed limestone.

Figure 11. SEM photomicrographs, in secondary electrons mode), and the corresponding EDS area analysis on the cleaned stone for the three more effective cleaning methods tested. (a, b) NaOH; (c) KOH; (d) Microspheres. All of the images are cross sections of the cleaned stone (stone surface on the top of the image), except b), which corresponds to a view of the stone surface.

Figure 1.

Figure 2

Figure 3



200
180
160
140
120
100
80
60
40
20
0
µg/m3
PART
SO2
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006

Figure 4

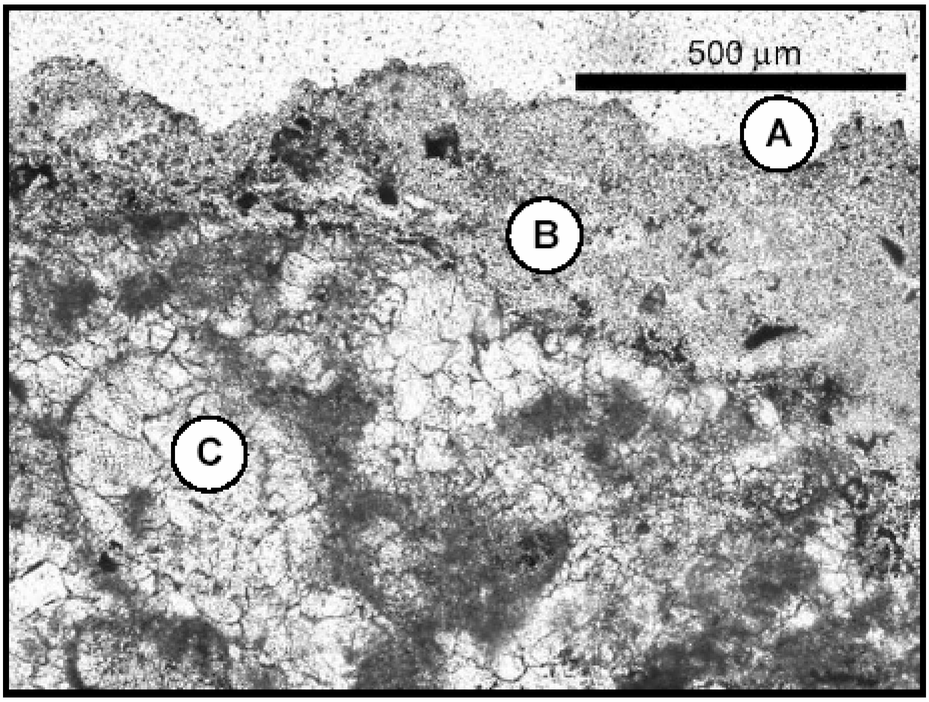
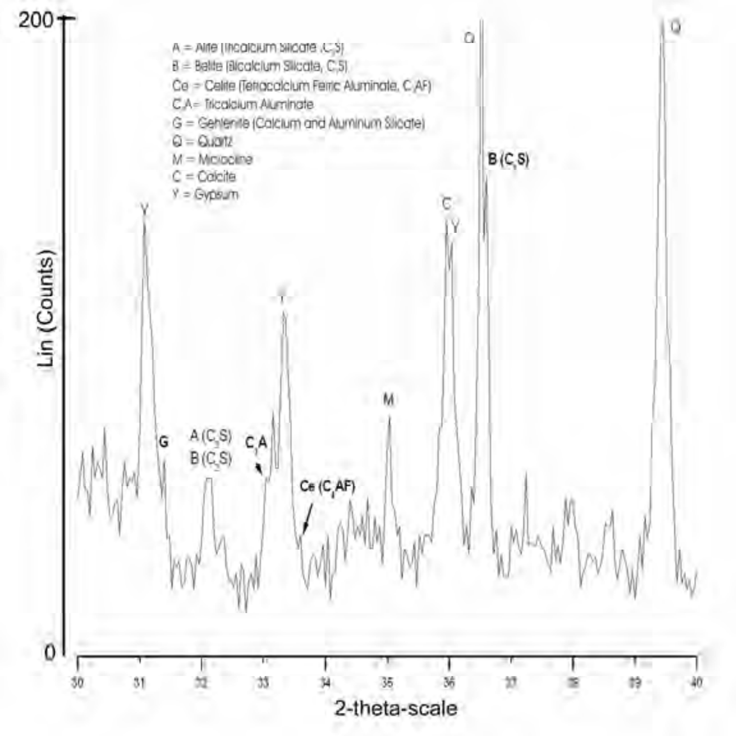


Figure 5



200
0
Lin (Counts)
2-theta-scale
30
31
32
33
34
35
36
37
38
39
40
A = Alite (Tricalcium Silicate, C3S)
B = Belite (Bicalcium Silicate, C2S)
Ce = Celite (Tetracalcium Ferric Aluminate, C4AF)
C3A = Tricalcium Aluminate
G = Gehlenite (Calcium and Aluminum Silicate)
Q = Quartz
M = Microcline
C = Calcite
Y = Gypsum
Y
G
A (C3S)
B (C2S)
C3A
Y
Ce (C4AF)
M
C
Y
Q
B (C2S)
Q

Figure 6

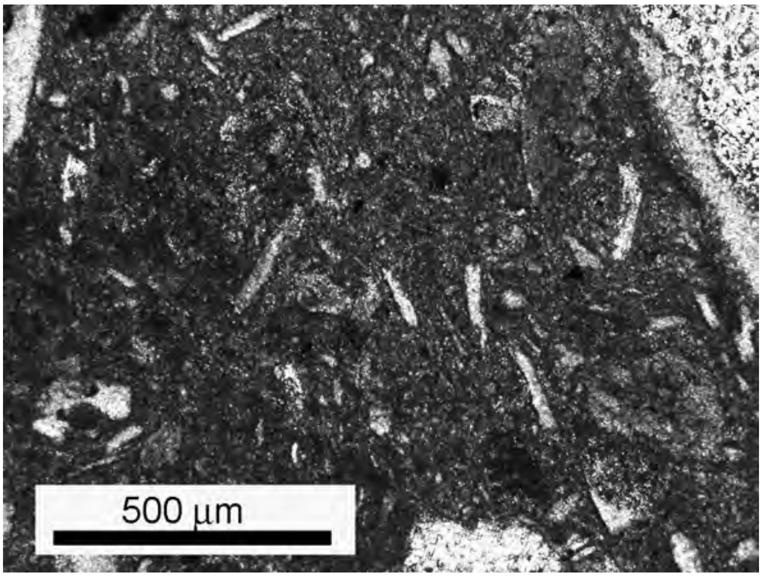


Figure 7

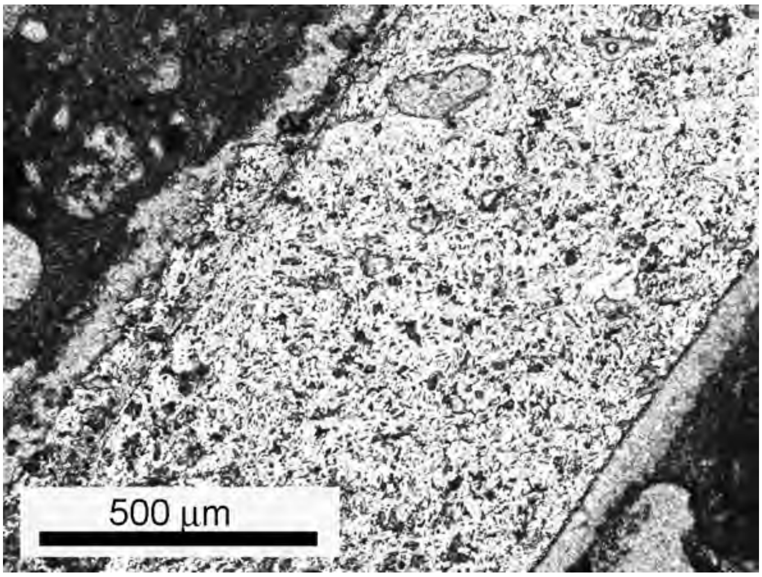


Figure 8

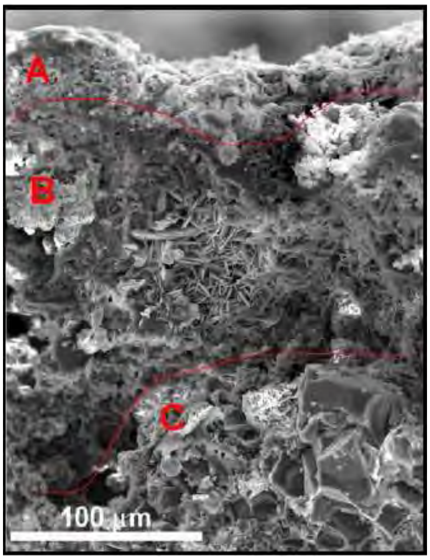


Figure 9.

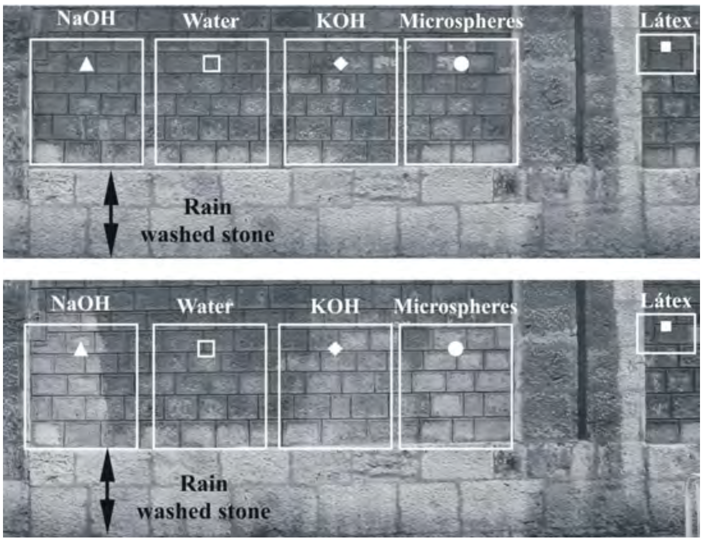

NaOH
Water
KOH
Microspheres
Látex
Rain
washed stone
NaOH
Water
KOH
Microspheres
Látex
Rain
washed stone

Figure 10.

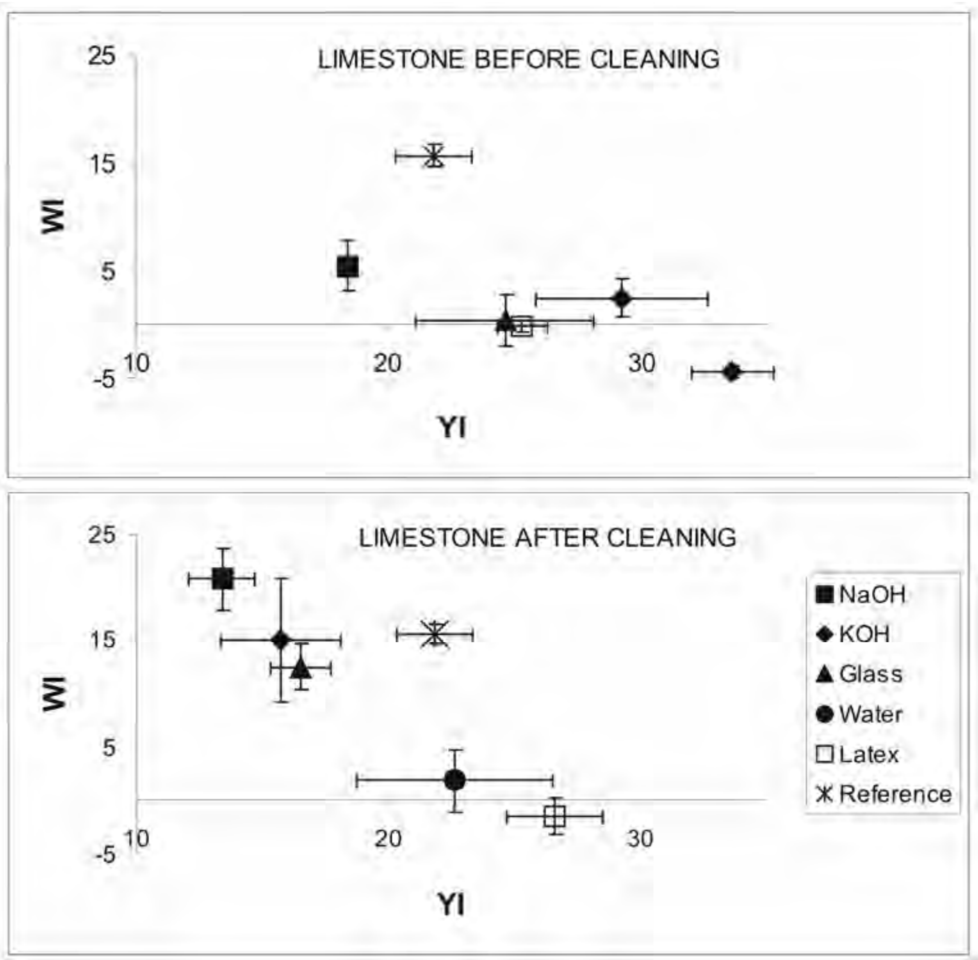
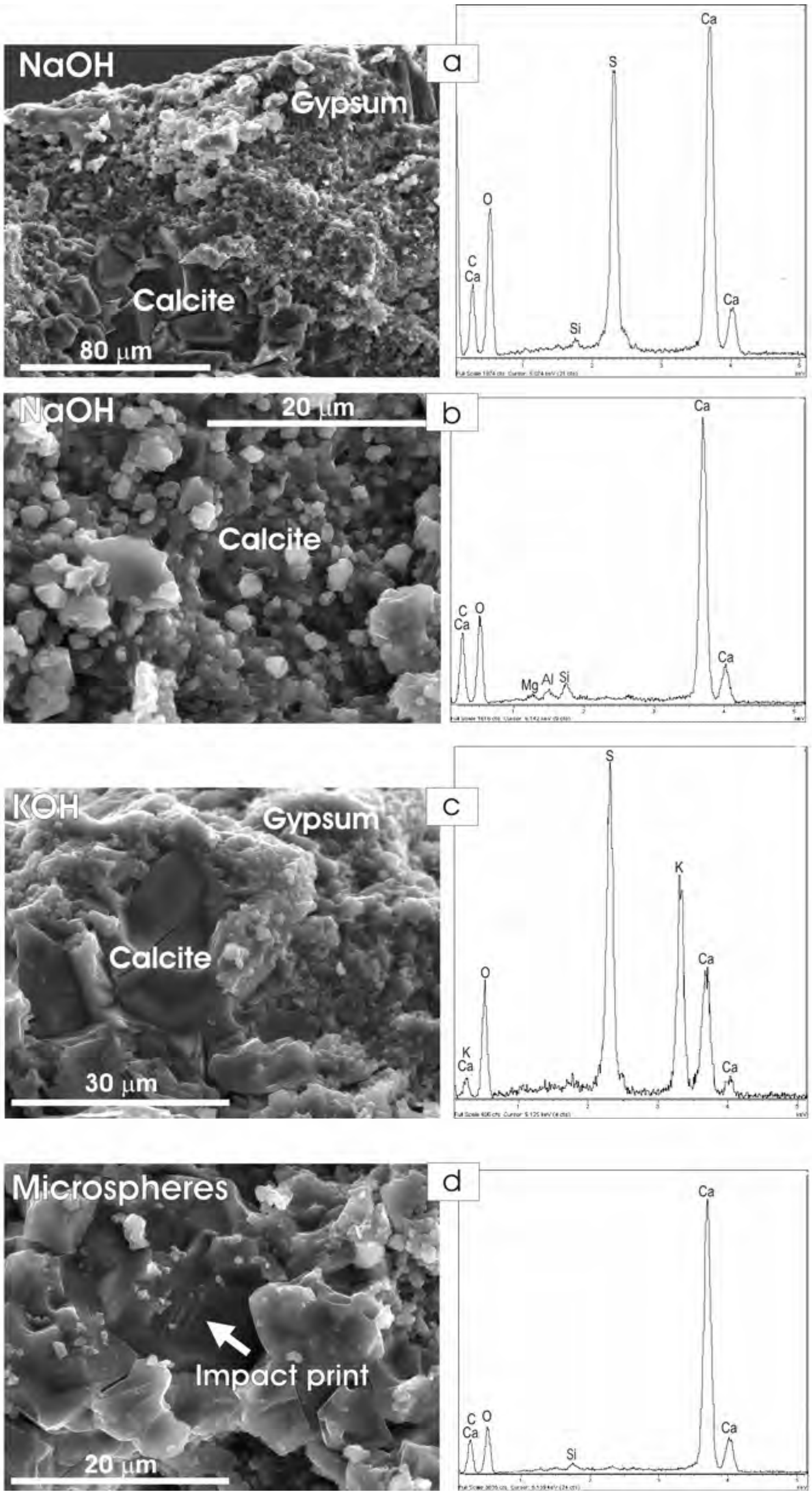

LIMESTONE BEFORE CLEANING
WI
YI
25
15
5
-5
10
20
30
LIMESTONE AFTER CLEANING
NaOH
KOH
Glass
Water
Latex
Reference

Figure 11.


NaOH
Gypsum
Calcite
80 μm
a
C
Ca
O
Si
S
Ca
Ca
NaOH
20 μm
Calcite
b
C
Ca
O
Mg
Al
Si
Ca
Ca
KOH
Gypsum
Calcite
30 μm
c
K
Ca
O
S
K
Ca
Ca
Microspheres
Impact print
20 μm
d
C
Ca
O
Si
Ca
Ca