DECAY AND PRESERVATION OF BUILDING STONES IN NON POLLUTED ENVIROMENTS (SPAIN)

Vicente Rives,[1,2]* Jacinta García-Talegón,[1,3] Adolfo C. Iñigo,[1,3] Eloy Molina[1,4] and Santiago Vicente-Tavera[1,5]
[1]Unidad Asociada IRNA-CSIC Salamanca/Universidad de Salamanca, Salamanca, Spain - Red Temática del Patrimonio Histórico y Cultural;
[2]Dpto. Química Inorgánica, Universidad de Salamanca, 37008-Salamanca, Spain;
[3]Instituto de Recursos Naturales y Agrobiología, CSIC, 37008-Salamanca, Spain;
[4]Dpto. Geología, Universidad de Salamanca, 37008-Salamanca, Spain;
[5]Dpto. Estadística, Universidad de Salamanca, 37007-Salamanca, Spain.
Corresponding author: Vicente Rives, e-mail:vrives@usal.es.

Abstract

Preservation of our Historical Cultural Heritage built in stone requires studies on the material itself, on the environment where the monument is located, and even on the microclimate affecting a particular stone in the building. Conservation treatments should be also non-agressive and restoration works should respect the chemical and mineralogical properties and surface characteristics or aesthetic aspect (colour) of the stones already existing in the monument.

We have studied the intrinsic factors of several types of stones and their role in the type of degradation found in each case. Together with air pollution, salt crystallization seems to be one of the most important agents of decay, especially on porous stones and in environments where heating/cooling and wetting/drying cycles exist. Most of the results reported have been obtained on sandstones (arkosic) and granite materials used in building and restoration of monuments in Avila and Salamanca (World Cultural Heritage cities in Spain). The positive effect of several conservation and prevention treatments containing organic silicates and polysiloxane compounds, as well as methods for extracting salts by natural clays, have been studied. The results obtained represent an adequate way to evidence the problems and some of the solutions to solve them.

Introduction

The behaviour of a building stone will depend upon its intrinsic properties (composition, texture, structure, colour, etc.) as well as the environmental conditions to which it is subjected, either inside or outside of the building [1].

The studied areas, Avila and Salamanca, World Cultural Heritage cities, are under the influence of a Mediterranean climate, semiarid, with a continental trend and low atmospheric pollution. Consequently, the main processes involved in the decay of ornamental stones will be thermoclasty, gelifraction and crystallization of salts in the pore network, as well as the flowing through of polluted fluids, mainly water loaded with different ions, in the dry summer season characterized by a very low relative humidity and high temperatures. [1-3].

The three studied types of granites in Avila have been widely used in buildings of cultural interest. At present their original quarries belong to the National Reserve, and are exclusively destined for purposes of restoration and conservation of historical monuments. An emblematic monument where the three varieties of granites were used on is the Cathedral, which construction commenced in the XII century and ended in the

XVI century. The cloister includes a cresting where Gothic pinnacles and Renaissance spirals were combined [4, 5].

On the other side the four varieties of studied sandstones are currently being used as a building stone in the city and the province of Salamanca. Two of the historical monuments where those types of sandstones were utilised are the Old (Romanesque, XII-XV c.) and the New (late Gothic, XVI-XVIII c.) Cathedrals.

This study on such granites and sandstones will analyse the variations on their intrinsic properties when they are subject to consolidation (RC-70) and waterproofing (RC-80) treatments, and how these affect their efficacy and harmfulness. Additionally, a 'non aggressive' methodology based on the use of natural clays poultices to extract salts.

Materials and Methods

Materials

The three types of *granite* often used in construction and successive restorations of the Avila Cathedral were selected. They are:

- M-3: Ochre granite, a naturally weathered facies with 2:1 layered silicates (smectites).
- M-4: Red granite, with a high CT-opal content, 1:1 layered silicates (kaolinites) and iron oxyhydroxides
- M-5: White granite, with a high CT-opal content and 1:1 layered silicates (kaolinites).

Each variety comes from differents levels of a weathering profile appearing over the Hercynian Basement, which was originated by different processes leading to a deep paleoweathering mantle between Upper Cretaceous and very early Tertiary age in the southwestern border of the Duero Basin, Iberian Peninsula [6, 7].

The Villamayor *sandstone* is an arkosic stone of Middle Eocene age [8]. It comes from the Cabrerizos Sandstone Formation, which constitutes an independent unit within the Eocene deposits of the southwest of the Duero Basin, where this joins the Ciudad Rodrigo Depression [9]. The four most representative varieties of this stone were selected:

- DM: Ochre, fine grain, very clayey and with carbonate concretions.
- S-I: Ochre, fine grain, sandier than variety DM (80% fine sand).
- S-II: White, medium grain, the thickest facies.
- S-III: Red medium grain and sandy (30% fine sand, 48% coarse sand).

The mineralogical composition of these varieties are very similar: quartz is the main component, followed by feldspars, 2:1 layered silicates (smectites), palygorskite-type fibrous silicates, and small amounts of micaceous minerals (illite). The DM variety contains in addition carbonates [10, 11].

The products used in the treatments, Rhodorsil 70 consolidant (RC 70) and Rhodorsil 80 consolidant and waterproofer (RC 80), were supplied by Rhône-Poulenc (France). Application of the products was carried out following a modified NORMAL directive.

The clay poultices used for salt extraction from buildings stones were sepiolite (S) and bentonite (B); they are commercial natural clays and were kindly supplied by TOLSA (Madrid, Spain). Their specific surface areas are 240 m^2/g (S) and 120 m^2/g (B).

Methodology

The physical properties (open and total porosity, real and apparent density, and absorption coefficient in water) were determined following standard directives [12, 13], while the L*, a*, b* colour system [14] was selected to determine colour numerically with a MINOLTA (Chroma Meters) colorimeter. The L* value refers to lightness (or darkness), while a* and b* are the chromaticity coordinates. Changes in a* coordinate, ranges between positive values of a*, identified with red, and negative values, associated to green. The negative values of b* coordinate are associated to blue and the positive ones to yellow. Changes in each of the chromatic coordinates for each of the tests corresponds to the difference between the magnitude of such a coordinate for the treated (or aged) sample, with respect to the value for the original sample, thus obtaining parameters ΔL*, Δa* and Δb*. The difference in total colour is given by the equation $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [15]. Stones blocks (5 x 5 x 5 cm) were cut and the values of the coordinates were averaged from measurements on these five faces. A complete three-way experimental design was implemented: i) type of sample; ii)Treatment; iii) Ageing. The analytical study was complemented with interaction plots, following the ANOVA study, the corresponding contrasts were performed by incorporating a type 1 error-correcting factor.

Consolidation treatments were carried out following slightly modified NORMAL recommendations [16], by immersing the sample in the consolidant fluid (instead of capilar absorption) and using different concentrations (instead of a single one), in order to favour penetration of the product inside the stone sample. Treatment was carried out by immersing the samples in white spirit for 30 min, followed by immersion in white spirit solutions of the reagents at three increasing concentrations: (i) eight hours with a 5% solution, (ii) twenty four hours with a 40% solution and (iii) forty hours with a 75% solution. Cubic (5 x 5 x 5 cm) samples treated as described above were aged through 25 cycles of freezing/thawing and cooling/heating (-20 to 100 °C) in a simulation chamber, following standard recommendations by Tiano and Pecchioni [17].

Samples for salt extraction studies were aged by immersing blocks (5 x 5 x 5 cm) in 0.5 M solutions of $NaCl$, $NaNO_3$ and Na_2SO_4 for 4 days up to a height of 1cm above the base in order to produce total impregnation via capillary uprising. After removing the blocks from the bath they were dried at room temperature, and a salt extraction process was performed using poultices of bentonite or sepiolite. Two extraction protocols were used [18], under D (dry) and W (wet) conditions:

- D *Protocol*: Poultices were prepared by wetting the clays (B or S) with distilled water, and placing the poultice (4 mm thick) on the top surface of three salt-aged blocks. The blocks were placed on a dry surface and the side faces covered with paraffin to avoid evaporation; the blocks were covered with a plastic film to prevent drying of the poultice (when dried, poultices peel off and lose contact with the stone block easily). The plastic film was removed after 3 days and the blocks were allowed to dry at room temperature. The poultice peeled off spontaneously and was analyzed. The same blocks were treated twice more, following the same method, to assess the efficiency of the method.

- *W Protocol* is identical to protocol D, but the blocks were placed on a humid surface for 4 days and then moved to a dry surface for 3 days. The blocks were submitted to two additional cycles of wetting and drying.

After being removed from the blocks, the poultice was dried to constant weight; then, ions were extracted following the NORMAL [19] procedure. Analysis of the different salt species extracted was acccomplished using a Metrohm ion chromatography System, equipped with a CI 709 pump, a CI 732 conductivity detector, a CI 733 separation chamber, and a Metrohm MSM (CI 753) suppressor module, with a CI 752 peristaltic pump.

Results and Discussion

Main decay pathologies

In low air polluted areas, like those studied here (Avila and Salamanca, Spain), climatic conditions determine the different weathering processes that rule the behaviour of a material.

Avila *granites* are easily weathered. Desaggregation and even arenization is observed in very humid areas of the Avila Cathedral. Weathering has been so severe in some vaults in the cloister and some humid walls that it is difficult even to ascertain which stones are original and which come from restorations. In dry areas, without permanent humidity, but submitted to wind and thermal oscillations, weathering consisting of formation of alveolus, scales and slabs is observed.

Villamayor *sandstones* include swellig-contraction of smectites, precipitation of salts in wet areas, and a lack of mechanical resistance when the material is maintained in wet conditions. However, if the stone is in dry areas, and exposed to sunshine, it develops a nice golden patina. These are usually weathered through complete sanding in humid areas. In carved stones and balaustrades a rounding of the shapes can be seen, and in high locations facing SW the formation of alveolus is observed.

Petrophysical Properties

Petrophysical properties for the granite samples are summarized in Table 1. Densities (δ and δ_{ap}) are nearly constant for both natural and treated granites. Total porosity (P_t) remains almost constant after RC70 treatment, but a slight decrease (10-20%) is observed after RC80 treatment. On the contrary, open porosity (P_o) sharply decreases upon these treatments, reaching values even 25% of the original one. As the water absorption coefficient (W_{ac}) is the ratio between P_o and P_t, and this last one shows only minor changes, those observed for W_{ac} follow the same trends as P_o. Studies reported elsewhere [20] have shown that one of the most informative parameters to discriminate the efficiency of different treatments is open porosity.

Data for sandstone samples are given in Table 2. Real density (δ) slightly decreases upon treatment, while δ_{ap} increases. Changes in total porosity are not regular: important decreases (up to 50%) are observed for samples DM and S-I, but decreases amounting 22-24% are observed for samples S-II and S-III. Open porosity sharply decreases to ca. 13% of the original values, whichever the treatment. Consequently, a rather unregular behaviour is observed for parameter Wac, although its decrease is more evident (ca. 90%) for samples S-II and S-III than for samples DM and S-I (ca. 75%).

Table 1.- Physical Properties in Water of Granites

Sample	Apparent Density δ_{ap},*	Density δ, *	Total Porosity P_t ,**	Open Porosity P_o,**	Water Absorption Coefficient W_{ac} ***
M-3	1.77	2.47	28	21	74
M-3-RC-70	1.79	2.47	27	10	37
M-3-RC-80	1.86	2.46	24	5	22
M-4	1.98	2.48	20	13	67
M-4-RC-70	1.99	2.43	19	4	21
M-4-RC-80	1.96	2.43	18	2	12
M-5	1.87	2.37	22	13	57
M-5-RC-70	1.87	2.40	21	11	52
M-5-RC-80	1.90	2.39	18	3	18

*g/cm^3 ref. [12,13]; **% ref. [12,13]; ***% ref. [12,13]

Table 2.- Physical Properties in Water of Sandstones

Sample	Apparent Density δ_{ap},*	Density δ, *	Total Porosity P_t ,**	Open Porosity P_o,**	Water Absorption Coefficient W_{ac} ***
DM	1.86	2.65	30	26	85
DM-RC-70	1.97	2.46	20	4	22
DM-RC-80	1.99	2.28	13	3	24
S-I	1.80	2.66	32	25	76
S-I-RC-70	1.94	2.50	22	4	17
S-I-RC-80	1.92	2.30	17	3	18
S-II	1.69	2.65	36	24	66
S-II-RC-70	1.78	2.53	29	3	10
S-II-RC-80	1.76	2.46	28	2	7
S-III	1.66	2.66	37	26	70
S-III-RC-70	1.74	2.54	31	3	11
S-III-RC-80	1.76	2.46	28	2	9

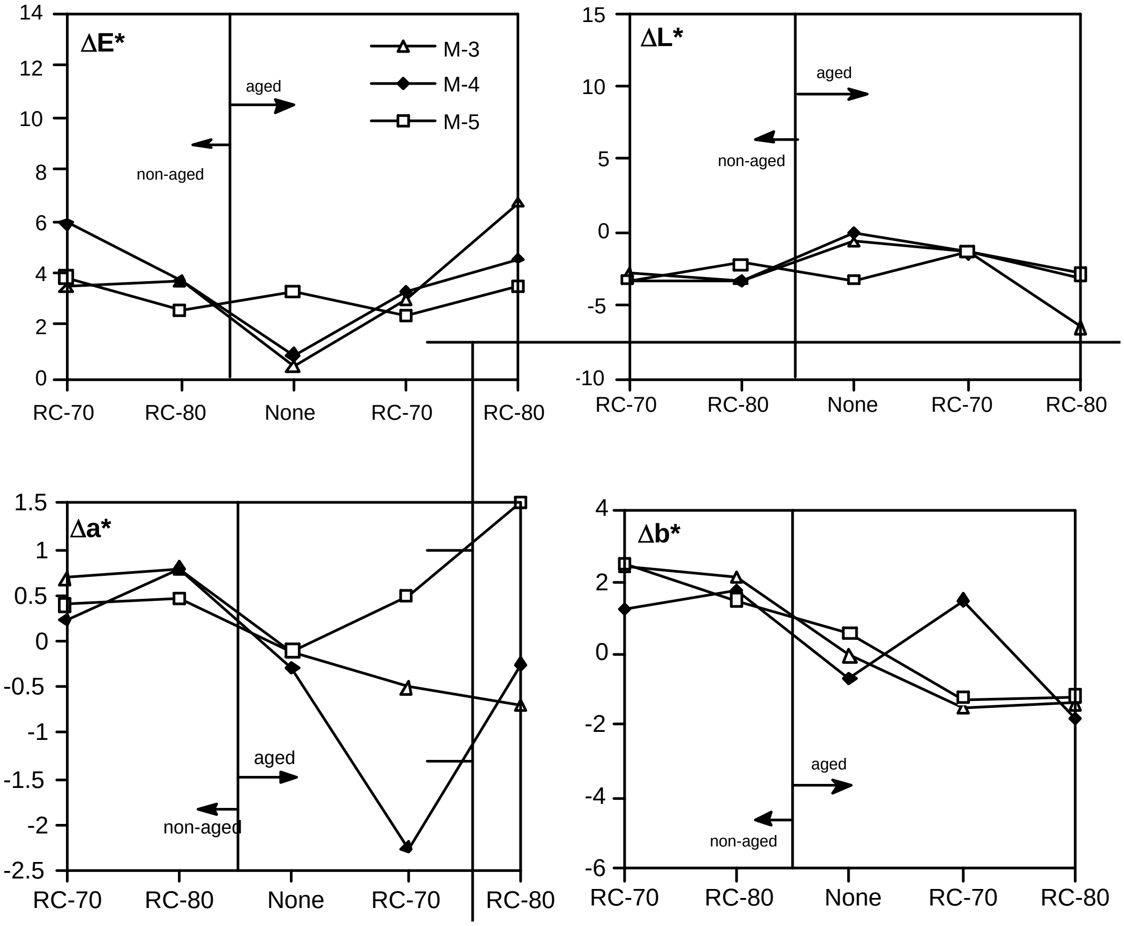
*g/cm^3 ref. [12,13]; **% ref. [12,13]; ***% ref. [12,13]

Colour properties

Colour is one of the parameters currently used to monitore the quality of a conservation treatment of ornamental stones, and its further ageing, well artificially or by decay in the monuments [21].

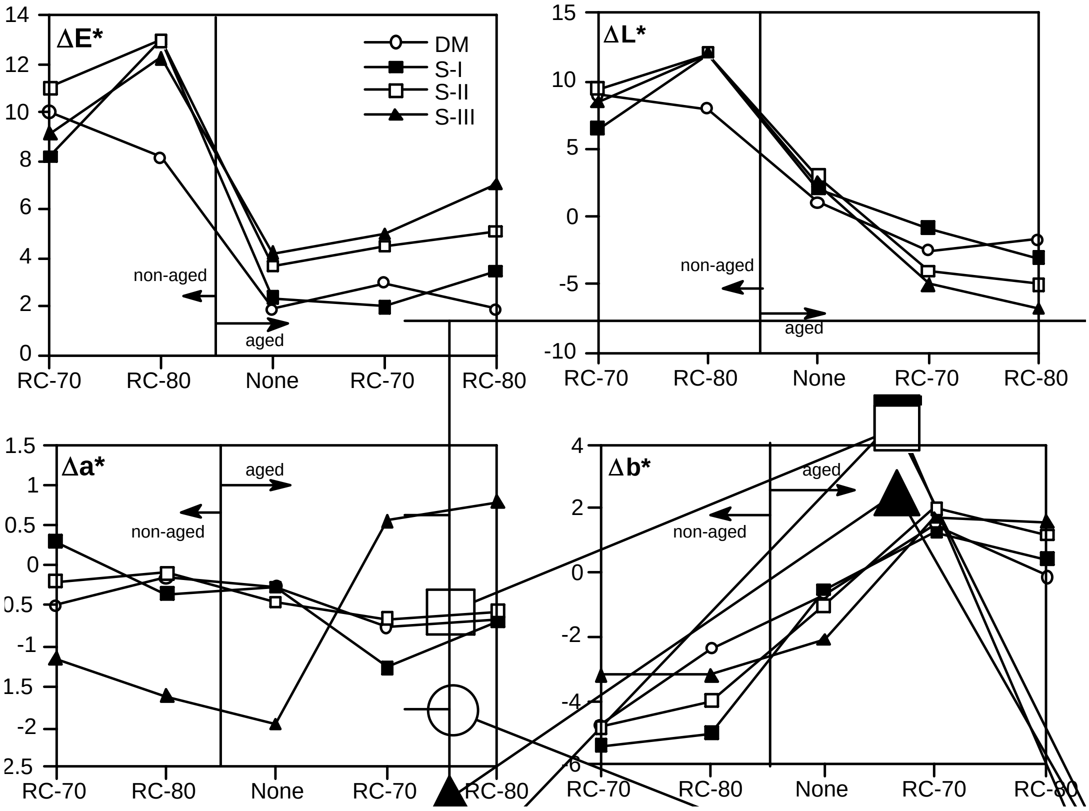
Fig. 1 shows the results of the statistical analysis of changes in colour of the samples upon treatment and ageing. The behaviour observed for the unaged and aged samples seems to be different. Important changes in ΔE* are observed only for sample M-3 and M-4 submitted treatment and ageing. Although darkening (ΔL*<0) is observed in all cases upon treatment and ageing, such an effect is much more pronounced for sample M-3. Chromatric parameters Δa* and Δb* also show minor shifts, but in this case sample M-4 deviates from the other two.

Fig. 1.- Chromatic parameters for granites.
The treatment agent (none, RC-70 and RC-80) is indicated



The results for the ΔE*, ΔL*, Δa*, Δb* parameters corresponding to sandstones are shown in Fig. 2. ΔE* indicates a loss in colour of the treated samples, upon ageing, with respect to the treated ones. Regarding ligthness (through parameter ΔL*), positive values were measured for the unaged samples, but negative values for the aged ones, indicating darkening (ΔL*<0) upon ageing, while unaged samples became lightened upon treatment. The change observed in parameter ΔL* is much larger than that observed in parameters Δa* and Δb*, for which only minor differences are observed upon ageing and/or treatment.

Fig. 2.- Chromatic parameters for sandstones.
The treatment agent (none, RC-70 and RC-80) is indicated



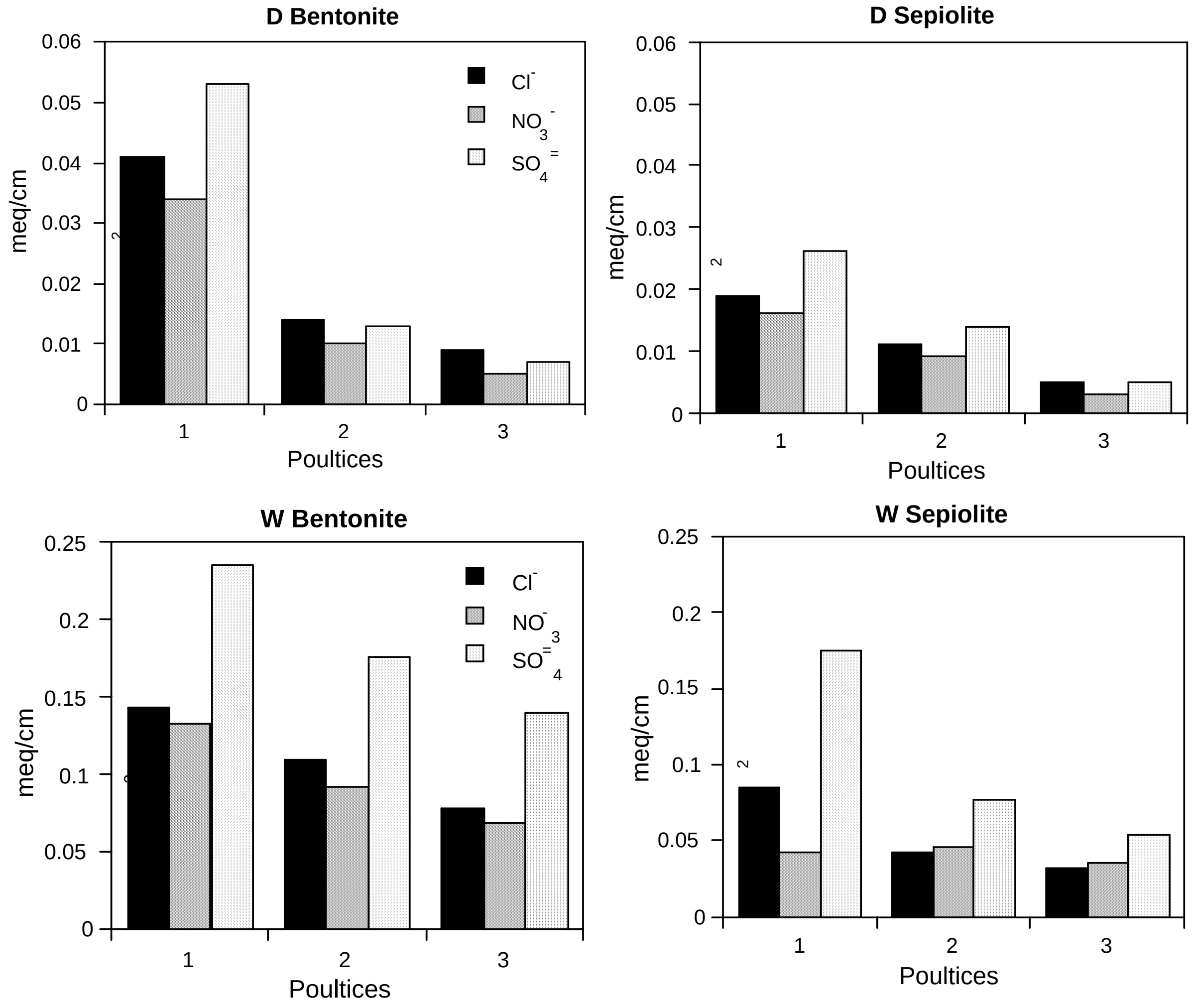
Extraction of salts by poultices

The conditions involved in the use of poultices (e.g. contact time, temperature), the efficiency of the procedure also depends on the nature of the poultices and the type of ions to be removed. No general agreement exists about the beneficial effects of salt removal or the suitability of the use of poultices. [22] addressed the problems arising when the stone is contaminated by mixtures of ions, and they detected an increase in sulfate content and subsequent surface degradation in ornamental stones, following salt extraction by poultices.

Most representative data on salt extraction for ochre granite (sample M-3) are shown in Fig. 3. Obviously, the amount of salts extracted decreases progressively when consecutive extractions are performed on the same sample. However, important differences can be found between the results following both protocols and both extracting clays. Broadly speaking, the amount extracted by the third poultice constitutes only ca. one sixth of the amount extracted by the first one following protocol D, but only one third following protocol W. Under W conditions the ions migrate toward the surface by water flow, while under D conditions, mobilization of ions occurs in the wet part by diffusion from the poultice.

On comparing the extraction ability of bentonite and sepiolite, it seems surprising that bentonite, with a specific surface area ca. one half of that of sepiolite, shows a more powerful extraction ability than this. Such a behaviour can be tentatively related to the different porous system these two clays show: Extremely narrow pores in the sepiolite network provide a high specific surface area, but their diameter is too small to permit an easy free circulation of solutions; on the contrary, the slit-like pores of bentonite, with a larger average diameter, allows fluids circulate freely.

Fig. 3.- Amount of anions extracted (meq/cm^2) by application of three successive poultices of bentonite and sepiolite under dry (D) and wet (W) conditions.



Conclusions

Treatment agent RC80 seems to be more efficient than RC70, probably because the combination of its consolidation and hidrofugation abilities. Upon treatment the water absorption coefficient decreases, so hindering fluids circulation through the stones.

Changes in colour are more evident for sandstones than for granites, especially coordinate ΔL*, leading consequently to major changes in ΔE*, as Δa* and Δb* do not change excessively. Treatment lightness the sandstones, but ageing darkens them. However, the granites become darkner in all cases.

Finally, with respect to salt extraction, protocol D seems to be more adequate than protocol W, as in the first case only salts close to the external surface are extracted, avoiding a continuous circulation of fluids, as it occurs following protocol W. The better behaviour observed for bentonite, despite its lower specific surface area, may be related to the size of the pores existing in these two clays.

Acknowledgments

Authors thank financial support from MCyT (grant MAT2000-0972-C02-01) and Junta de Castilla y León (CSI08/03). JGT and ACI acknowledge I3P grants from CSIC. This work is dedicated to the beloved memory of Dr. M. Angeles Vicente.

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