

# CONSOLIDATION OF GLOBIGERINA LIMESTONE (MALTA) BY MEANS OF INORGANIC TREATMENTS: PRELIMINARY RESULTS

**Paola Croveri\*** *Diagnostic Science Laboratories, Malta Centre for Restoration, Bighi, Kalkara, CSP12, Malta, Tel. : (+356) 21807675/ 6, Fax: (+356) 21674457 e-mail. [croveri@mcr.edu.mt](mailto:croveri@mcr.edu.mt), [croveriopd@hotmail.com](mailto:croveriopd@hotmail.com)*

**Luigi Dei , Rodorico Giorgi and Barbara Salvadori** *Department of Chemistry and CSGI, University of Florence, via della Lastruccia, 3 ,I-50019 Sesto Fiorentino (FI), Italy Tel. direct + 39 – 0554573045 Fax + 39 – 0554573036 e-mail: [dei@csgi.unifi.it](mailto:dei@csgi.unifi.it), [giorgi@csgi.unifi.it](mailto:giorgi@csgi.unifi.it), [salvadori@csgi.unifi.it](mailto:salvadori@csgi.unifi.it)*

## Abstract

Soft limestones used as building materials in marine environment undergo fast and peculiar deterioration processes that seriously damage the historical and architectural cultural heritage of Mediterranean cities. The aim of the present work was to evaluate the effectiveness of inorganic compatible treatments on *Globigerina Limestone* (the local limestone of the Maltese islands) to assess their suitability for the conservation of stone. Barium hydroxide,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , ammonium oxalate,  $(\text{NH}_4)_2 \cdot (\text{COO})_2 \cdot \text{H}_2\text{O}$ , and dispersion of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in alcoholic medium were tested in the laboratory on two different qualities of limestone, the easily perishable *Globigerina Soll* and on the more durable *Globigerina Franka*. Changes in water-interaction properties were investigated through water absorption by capillarity and water vapour permeability tests. Colorimetric analyses were performed before and after the application of products. Morphology and distribution in the porous substrate of deposited phases were investigated by SEM-EDX and analysis of surface area (BET). Re-aggregating properties were evaluated by means of a microdrilling system.

**Keywords:** stone consolidation, inorganic treatments, calcium hydroxide dispersion, barium hydroxide, oxalates, *Globigerina Limestone*, Malta.

## 1. Introduction

The *Globigerina Limestone* is a soft, highly porous sedimentary stone widely used as building material in the archipelago of Maltese islands. Starting from prehistoric times, when it was first quarried to erect the megalithic temples (4000-2500 BC), the limestone was directly exposed to aggressive conditions typical of the Mediterranean marine environment (Vannucci et al. 1994). The combination of intrinsic factors (texture and physico-chemical properties of constituent materials) and extrinsic factors (seaside region, specific microclimate, today worsened by heavy local pollution) give rise to dramatic decay phenomena that put at risk the permanence of cultural memory of the past ages.

One of the fundamental aims for the conservation scientist is to find suitable and compatible methodologies to slow down the natural phenomena of deterioration. With this purpose, the efficacy of inorganic treatments was investigated in order to understand mechanisms and effects of consolidation and to assess the suitability of these classes of substances for the conservation of porous materials in aggressive environmental conditions.

\* Author to whom correspondence should be addressed.

Preliminary testing of three different methodologies that allow the formation of a mineral phase in the porous matrix of the stone was carried out in the laboratory on unweathered quarry samples:

- 1- "Barium method" - aqueous solution of barium hydroxide applied by cellulose poultice.
- 2- "Artificial calcium oxalate method" - aqueous solution of ammonium oxalate applied by cellulose poultice.
- 3- "Dispersion of  $\text{Ca}(\text{OH})_2$  method" - application of a dispersion of micro- and nano-particles of calcium hydroxide in alcoholic medium, by brush.

Treatments of calcareous stone with barium hydroxide have been experimented since the second half of the 19<sup>th</sup> century and improved at the end of the sixties for mural painting conservation (Ferroni and Dini 1977), while the oxalate method was evaluated mainly at the laboratories of the Opificio delle Pietre Dure (Florence) in the nineties (Matteini M. et al. 1994)

The last innovative method was developed at the University of Florence (CSGI Consortium at Department of Chemistry) since 1996 in order to find a solution for the low solubility of calcium hydroxide in water (1.7 g/l) limiting the amount of the deposited consolidating phase (Giorgi et al. 2000; Ambrosi et al. 2001). The method, initially based on the use of commercial slaked lime dispersed in short-chain aliphatic alcohols (micron-sized calcium hydroxide particles), was afterwards improved by reducing the average size of the consolidating particles to the nanometric scale in a synthetic path (Salvadori and Dei 2001). Submicrometer calcium hydroxide particles are more effective than slaked lime in consolidation of porous materials in terms of higher penetration efficacy, stability and very weak white glazing of the stone surface after application.

## 2. Materials and Methods

Samples of stone of two different qualities, the easily perishable *Globigerina Soll* and the more durable *Globigerina Franka*, were cut from separate sedimentation layers of a local quarry (Mqabba, Malta) and characterized by SEM-EDX, BET and calcimetric analysis (Dietrich-Frühling method).

Treatments were carried out with aqueous saturated solutions of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$  (AmOx) in cellulose poultice (Arbocel BC1000) with a contact time of 5 and 6 hours, respectively. A 2-propanol dispersion [0.06 M] of nanosized calcium hydroxide particles (Salvadori and Dei 2001) was applied by brush (350 ml/m<sup>2</sup>). Samples (5x5x2 cm and 5x5x1 cm) were first conditioned following the UNI 10921 standard and then treated on one surface only.

The evaluation of the effectiveness of the conservation treatments was performed according to the methods adopted by the UNI-NORMAL Commission. (AA.VV. Raccomandazioni NORMAL 1981-1985-1989-1993, UNI 10921 Norma Italiana 2001, UNI 10859 Norma Italiana, 2000). Changes on water-interaction properties were investigated through water absorption by capillarity and by water vapour permeability test. All tests were carried out before treatment, and then repeated after one month on the same samples. At least three samples were employed for each test.

Colorimetric analyses were performed with a Minolta CM-500i equipped with a pulsed xenon arc lamp and an integrating sphere to illuminate diffusely the specimen surface (d/2 geometry, D<sub>65</sub> illuminant source). Morphology and distribution in the porous substrate of deposited mineral phases were investigated by SEM-EDX (LEO 1430,

Oxford Link spectrometer with an ATW2 window for the detection of light elements), EDX analyses were performed on cross sections and on treated surfaces. Analyses of superficial area and pore-size distribution were carried out with a surface analyzer Coulter SA3100 according to the BET model and BJH calculation. In order to compare the results of pore size distribution, the experimental data were normalized using the following formula (1):

$$V\%_N = V\% * (BJH\ tot_{TR} * W_{TR}) / (BJH\ tot_{NT} * W_{NT}) \quad (1)$$

where BJH tot: Total volume of pores (mm<sup>3</sup>/g)  
W: weight of the sample (g)  
TR: treated sample NT: not treated sample

Surface re-aggregating properties were evaluated by means of a Drilling Force Measurement System (DFMS) HARDROCK. Drilling conditions: 300 rpm, 20 mm/min, depth 15 mm (Tiano *et al* 2000).

### 3. Results and discussion

#### 3.1 Globigerina Limestone

*Globigerina Limestone* shows many similarities to other stone materials present in the Mediterranean Basin (“Pietra di Lecce” and “Biocalcarenite di Noto”) regarding both physico-chemical properties and deterioration phenomenology.

*Franka* and *Soll* facies of the *Lower Globigerina Limestone* formation are visually indistinguishable in the unweathered state but the different behaviour to decay results in slight differences in chemical and physical properties (Cassar *et al.* 2003, Vella *et al.* 1997). The *Franka* stone used for the present research is characterized by a superficial area of 6.2 m<sup>2</sup>/g (standard deviation  $\sigma = 0.1$ ) and a CaCO<sub>3</sub> content of 91% ( $\sigma = 0.5$ ). *Soll* samples have a CaCO<sub>3</sub> content of 88% ( $\sigma = 0.5$ ) and a superficial area of 6.2 m<sup>2</sup>/g ( $\sigma = 0.1$ ). EDX microanalysis results for *Franka* and *Soll*, shown in Table 2, are in agreement with those from calcimetric analysis. The *Soll* lithotype has a higher silicon content (Cassar *et al.* 2003, Vella *et al.* 1997). Figure 4 shows the pore size distribution, in the mesopore range, for *Globigerina Soll*. The graph for *Franka* stone is similar, showing more mesopores with  $\varnothing < 6$  nm and less mesopores with  $\varnothing > 80$  nm. For both *facies*, of the total porosity, more than 40% lies within the 20-80 nm diameter range.

The behaviour towards water absorption by capillarity can also differentiate between the two stones studied: *Soll* absorbs more water than *Franka*, at a slower rate (Figure 1 and Figure 2). The asymptote value of absorption M\* (AA.VV. Rac. Normal 11/85) is reached after 7 days for both the materials and is equal 573 mg/cm<sup>2</sup> for *Franka* and 641 mg/cm<sup>2</sup> for *Soll*, the coefficient of average absorption (C.A) is, respectively, 20 mg/cm<sup>2</sup>\*s<sup>-1/2</sup> and 15 mg/cm<sup>2</sup>\*s<sup>-1/2</sup>. As a reference, values obtained for Lecce Stone are M\* = 740 mg/cm<sup>2</sup> and C.A. = 12 mg/cm<sup>2</sup>\*s<sup>-1/2</sup> (Croveri *et al.* 2000)

#### 3.2 Mineral treatments on Globigerina Limestone

The application of consolidating products to the stone surface does not produce any colorimetric change visible to the naked eye (Table 1). Weight variations after treatments are significant for Ba(OH)<sub>2</sub>, being 151 g/m<sup>2</sup> for *Franka* and 182 g/m<sup>2</sup> for *Soll*, moderate for AmOx, being 81 g/m<sup>2</sup> for *Franka* and 84 g/m<sup>2</sup> for *Soll*, and negligible for Ca(OH)<sub>2</sub>, equal to 4 g/m<sup>2</sup> for both substrates.

Table 1: Colorimetric changes after mineral treatments (standard deviation in brackets)

|                        | $\Delta E$ |                       | $\Delta E$ |
|------------------------|------------|-----------------------|------------|
| F-Ba(OH) <sub>2</sub>  | 1.9 (0.8)  | S-Ba(OH) <sub>2</sub> | 1.2 (0.4)  |
| F-AmOx                 | 1.7 (0.4)  | S-AmOx                | 2.5 (0.5)  |
| F- Ca(OH) <sub>2</sub> | 2.0 (0.5)  | S-Ca(OH) <sub>2</sub> | 3.9 (1.4)  |

F: Franka S: Soll

Water absorption tests by capillarity were carried out on 5 samples measuring 5x5x2 cm for each set of treated limestone. Figures 1 and 2 show the curves obtained for *Franka* and *Soll* lithotypes, respectively.

Water absorption by capillarity *Globigerina* Franka

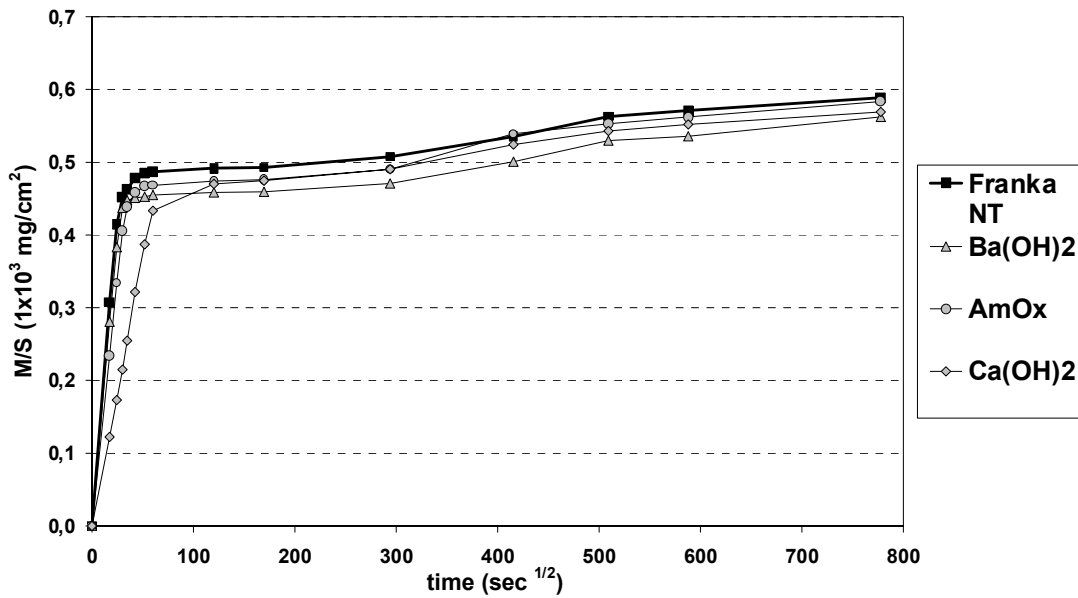


Figure 1: Water absorption by capillarity for untreated (NT) and treated *Globigerina* *Franka* samples

Water absorption by capillarity *Globigerina* Soll

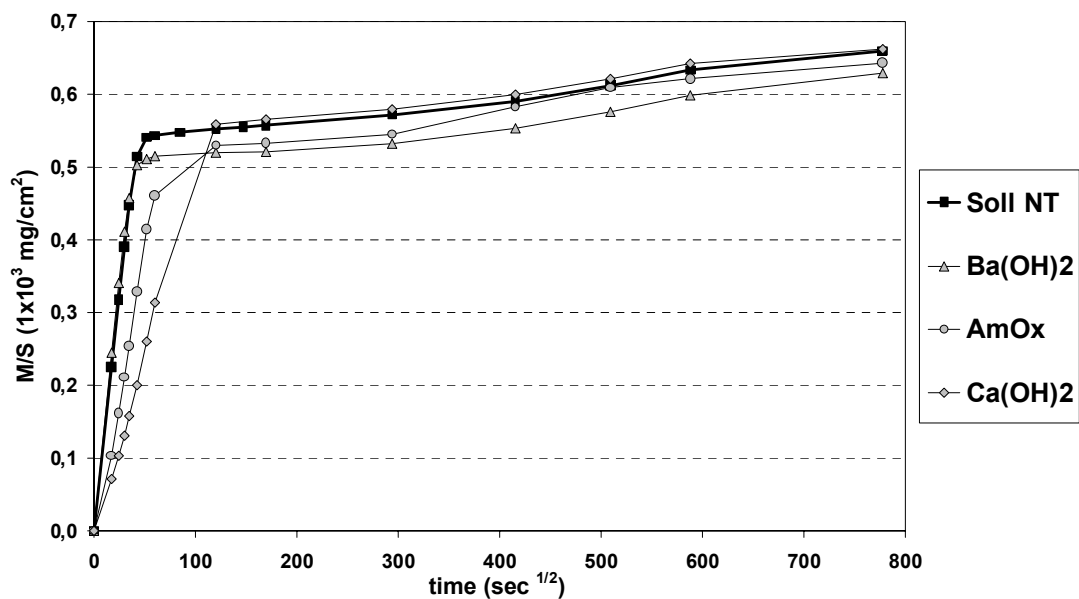


Figure 2: Water absorption by capillarity for untreated (NT) and treated *Globigerina* *Soll* samples

Barium hydroxide treatments affected only slightly the kinetics of capillarity suction during the first 30' minutes ( $C.A.F = 19 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ,  $C.A.S = 14 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ) but treated samples show a slight decrease in water absorption for longer times ( $M^*_F = 562 \text{ mg/cm}^2$ ,  $M^*_S = 629 \text{ mg/cm}^2$ ). *Franka* lithotype treated with AmOx does not show great variations in water absorption, while for the *Soll* treated with the same product a decrease in suction during the first 4h of the test was evident ( $C.A.F = 17 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ,  $C.A.S = 8 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ).

Despite the very small amount of product applied,  $\text{Ca(OH)}_2$  treatment seems to be the most effective one for both substrates, resulting in a remarkable change in the kinetics of short time capillarity rise ( $C.A.F = 8 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ,  $C.A.S = 5 \text{ mg/cm}^2 \cdot \text{s}^{-1/2}$ ).

Water vapour permeability tests, carried out in compliance with Rac. Normal 21/85, indicate that no important changes in transpiration of the materials occurred following consolidation.

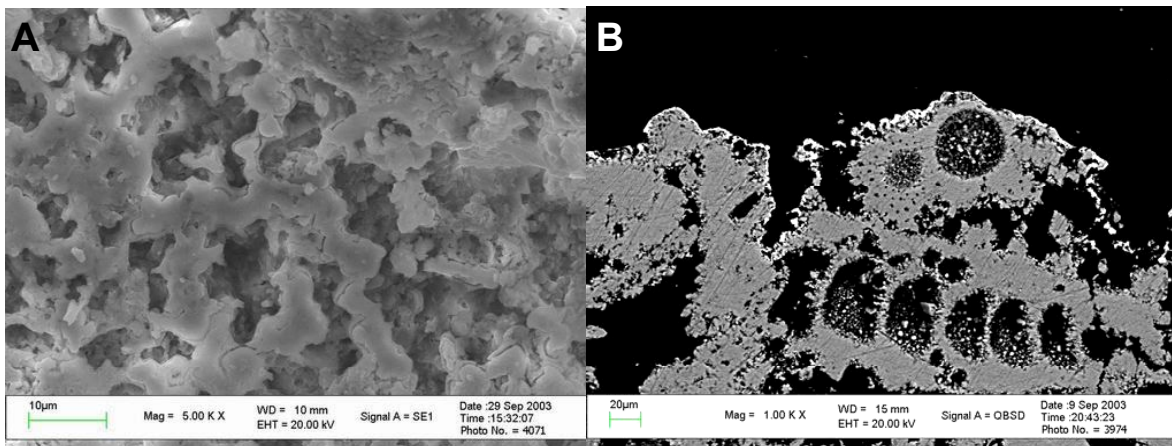


Figure 3: SEM micrographs– **A**- Surface morphology of *Globigerina Soll* treated with  $\text{Ba(OH)}_2$ , SE (scale indicates 10  $\mu\text{m}$ ). **B**- Cross section of *Globigerina Franka* treated with  $\text{Ba(OH)}_2$ , QBSD (scale indicates 20  $\mu\text{m}$ ).

Table 2: EDX microanalysis for treated and untreated surfaces of *Franka* and *Soll* samples. Results are mean values (standard deviation in brackets) expressed as percentage of oxide

|                             | CaO        | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO       | K <sub>2</sub> O | FeO       | BaO        |
|-----------------------------|------------|------------------|--------------------------------|-----------|------------------|-----------|------------|
| <b>Franka</b>               | 91.0 (1.5) | 4.8 (0.6)        | 1.9 (0.3)                      | 0.9 (0.1) | -                | 1.7 (0.4) | -          |
| <b>F-Ba(OH)<sub>2</sub></b> | 60.3 (2.5) | 3.7 (0.6)        | 1.6 (0.2)                      | 0.9 (0.0) | -                | 1.3 (0.2) | 33.2 (2.4) |
| <b>F-AmOx</b>               | 90.9 (1.6) | 4.8 (0.9)        | 2.1 (0.3)                      | 1.0 (0.1) | 0.8 (0.3)        | 1.5 (0.3) | -          |
| <b>F-Ca(OH)<sub>2</sub></b> | 92.6 (1.2) | 3.8 (0.7)        | 1.6 (0.3)                      | 0.8 (0.1) | -                | 1.4 (0.2) | -          |
| <b>Soll</b>                 | 89.4 (1.0) | 6.0 (0.8)        | 2.0 (0.2)                      | 1.1 (0.2) | 0.5 (0.1)        | 1.7 (0.4) | -          |
| <b>S-Ba(OH)<sub>2</sub></b> | 49.4 (4.2) | 4.2 (0.6)        | 1.9 (0.2)                      | 0.8 (0.1) | -                | 1.0 (0.2) | 43.5 (4.6) |
| <b>S-AmOx</b>               | 85.4 (1.5) | 8.5 (1.0)        | 2.9 (0.4)                      | 0.8 (0.1) | 0.6 (0.1)        | 1.9 (0.2) | -          |
| <b>S-Ca(OH)<sub>2</sub></b> | 86.6 (4.2) | 7.9 (2.8)        | 2.6 (0.8)                      | 1.0 (0.2) | 0.5 (0.1)        | 1.7 (0.4) | -          |

SEM observations on  $\text{Ca(OH)}_2$  treated samples do not reveal any modification in the morphology of exposed surfaces. Application of AmOx seems to create a more compact external layer (patina) but the new calcium oxalate phase developed can hardly be distinguished from the matrix. At higher magnification extended rod-shaped microcrystals of maximum length 1 $\mu\text{m}$  are visible on the *Soll* facies, probably whewellite  $\text{Ca(COO)}_2 \cdot \text{H}_2\text{O}$ .

Barium hydroxide treatments totally change the surface appearance by creating a superimposed indented structure (Figure 3-A) made up of elongate olive-like crystals of  $\text{BaCO}_3$ . The thickness of this external layer ranges from 1  $\mu\text{m}$  to 3  $\mu\text{m}$  and it appears to be homogeneously distributed (Figure 3-B). Moreover, EDX microanalysis indicates a higher content of Ba deposited on the *Soll* substrate (S- $\text{Ba}(\text{OH})_2$   $\text{BaO}\% = 43.5$  , F- $\text{Ba}(\text{OH})_2$   $\text{BaO}\% = 33.2$ ) suggesting the formation of a more compact surface structure (Table 2).

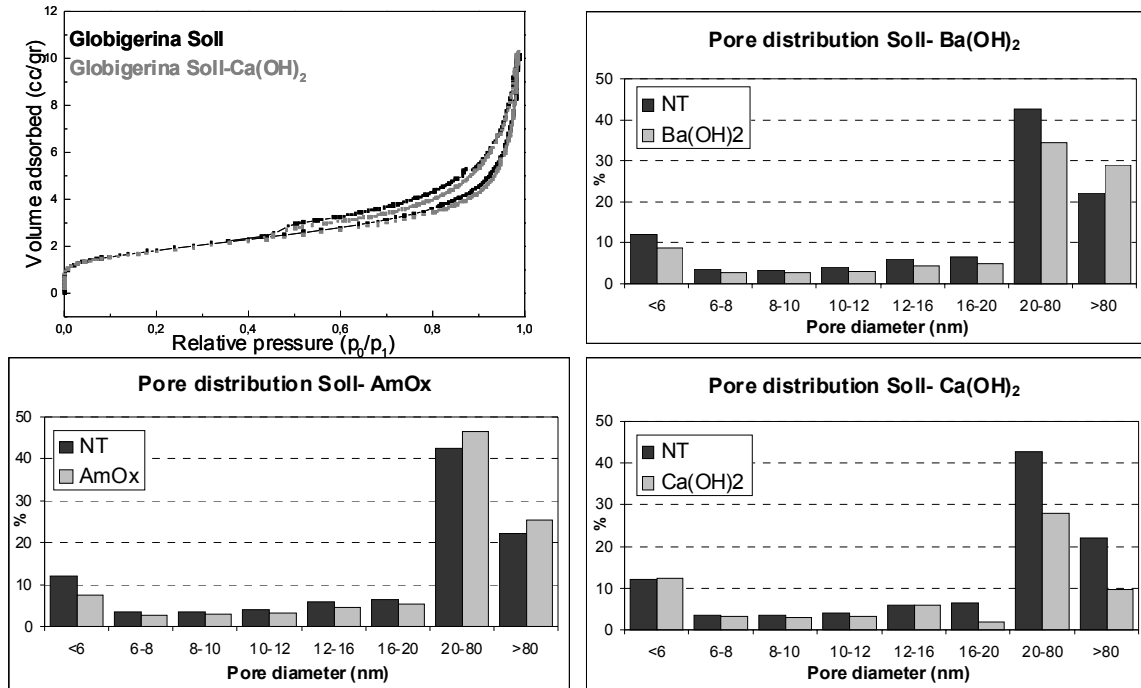


Figure 4: BET analysis. Isotherm and pore size distribution of treated *Globigerina Soll* samples in comparison with that one of the untreated substrate

Modifications of total superficial area and internal porosity due to treatments were then investigated, since these parameters play an important role in determining the resistance of the new created structure to the main sources of deterioration, such as pollutants in gaseous phase, migration and crystallization of soluble salts, absorption and circulation of water solutions inside the materials.

Analyses on the *Soll* lithotype were performed by sampling a layer of 3 mm depth from the treated stone surface.

Untreated *Soll* has a superficial area of 6.2  $\text{m}^2/\text{g}$  that does not undergo significant variation following consolidation treatments: S- $\text{Ba}(\text{OH})_2$  6.0  $\text{m}^2/\text{g}$ , S- $\text{AmOx}$  5.9  $\text{m}^2/\text{g}$ , S- $\text{Ca}(\text{OH})_2$  6.6  $\text{m}^2/\text{g}$ . These apparent changes, indeed, are within the range of the experimental error.

Histograms of pore size distributions of treated and untreated *Globigerina Soll* are shown in Figure 4. Since instrumental output data were expressed as percentages, results were normalized with reference to untreated sample, following the formula (1), in order to get comparable values.

After  $\text{Ba}(\text{OH})_2$  application the stone substrate showed a decrease in pores with  $\varnothing < 80$  nm and an increase in pores with  $\varnothing > 80$ , while after  $\text{AmOx}$  treatment an increasing of percentage of pores was noted starting to 20 nm diameter. The increase of one dimensional class of pores can be explained by the partial filling of cavities of greater size with the formation of smaller porosities.

A significant decrease in pores with  $\varnothing > 16$  nm is evident in the histogram of *Soll* stone

treated with  $\text{Ca}(\text{OH})_2$ , indicating that the deposition of consolidating phase occurred mainly in these empty porosities.

Surface reaggregation efficacy of mineral products was investigated with a Drilling Force system to detect any modification of mechanical properties of treated surfaces. The drilling force profile obtained from tests on *Globigerina Soll* treated with AmOx shows an increase in resistance of 3 units (N) in the first 2 mm from the surface, if compared with the same plot for the untreated stone. This result proves an effective consolidating effect of the AmOx treatment. All the other profiles recorded for *Franka* and *Soll* treated samples do not show any significant variations, probably due to the extreme thinness of consolidated stone layer, not detectable with this technique.

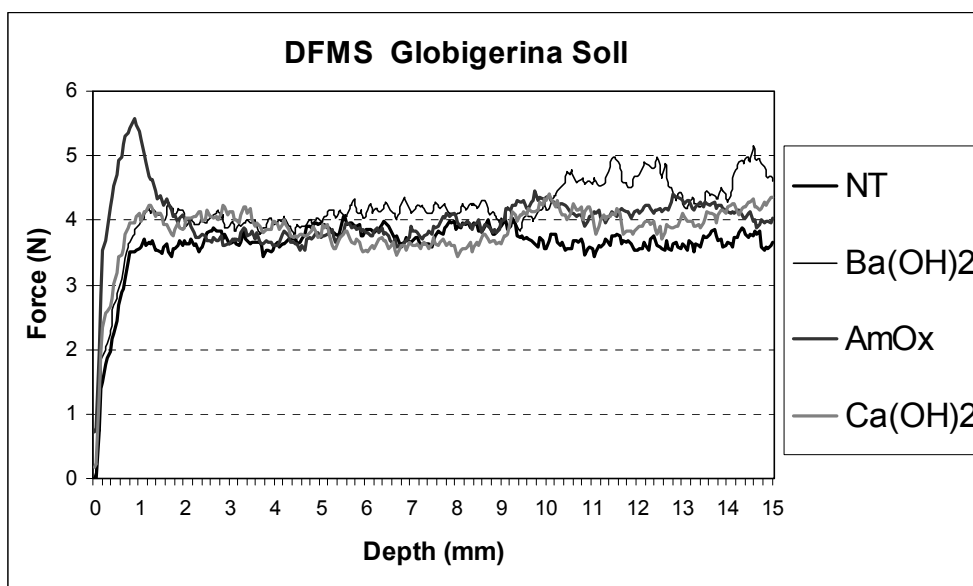


Figure 5: Drilling Force measurements of *Globigerina Soll* (average curves).

#### 4. Conclusions

Preliminary results of the research indicate that the methodologies tested for the consolidation of the Maltese *Globigerina Limestone* are promising. The application of compatible mineral products on *Franka* and *Soll* lithotypes does not produce any harmful dramatic change in their physico-chemical properties. In particular, water absorption properties and pore size distribution analysis show remarkable effects on the surface features of the treated materials. It is worthwhile to underline that the calcium hydroxide method provides the most positive results concerning the reinforcement of the surface layers.

The resistance to marine aggressive environment of the treated calcareous materials and application of these methodologies to real weathered substrates would be further areas of study. In particular, investigations on the effect of soluble salts on the untreated and treated limestone and on the effectiveness of treatments carried out in their presence are interesting correlated research topics.

#### 5. Acknowledgement

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## 7. Materials

Cellulose poultice Arbocel BC1100 - Barium idroside  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  purity  $\geq 98\%$ , CTS S.r.l. Via Piave 20/22 36077 Altavilla Vicentina (VI) Italy, Tel +39-0444349088 Fax +39-0444349039 e-mail: [info@ctseurope.com](mailto:info@ctseurope.com)

Ammonium oxalate  $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$ , BDH Laboratory Supplies Poole, BH15 1TD, England Tel (01202)669700

2-propanol pro analysis, Merck, Darmstadt, Germany, supplied by Laborchimica, via B. Marcello, 15 50144 Firenze, Italy tel. + 39 – 055352917; fax + 39 – 055365619; e-mail: [info@laborchimica.com](mailto:info@laborchimica.com)

Calcium hydroxide nanoparticles, synthesized in the CSGI Laboratory according to the procedure reported in ref. Salvadori and Dei 2001.