New Diagnostic Tools for “in situ” Evaluation of Conservative Treatments for Monumental Stones

Piero Tiano, Silvia Rescic
Institute for Conservation and Enhancement of Cultural Heritage, CNR, Florence, Italy (ICVBC)

Emilio Valentini
SINT Technology, Calenzano, Florence, Italy
Performance Tests of Consolidation Treatments (laboratory and in situ tests)

Portable Equipments for “In situ” Tests:
- Drilling Force Measurement System (DRMS) and
- Indentation System (under testing for this type of application)

Laboratory Test Results

Results of “in situ” Tests performed on Monuments:
- the Cathedral of San Leo (DRMS),
- the Abbey of Badia a Passignano (DRMS),
- the Cathedral of Florence (INDENTER)
Laboratory Tests

Evaluation of the performance of conservation products applied during restoration work such as consolidating or protective treatments

LABORATORY TESTS

- Tests on specimens, of the same monumental stone,
  - New stone samples
  - Cores taken from treated monuments

- Minimum sizes for a representative sample should be not less than 5x5x5 cm.

- The laboratory test results should be considered only as a preliminary indication
Evaluation of the performance of conservation products applied during restoration work such as **consolidating** or **protective treatments**

**IN SITU TESTS GIVE THE FOLLOWING BENEFITS**

- The possibility of evaluating the specific state of conservation of the stone material to be treated with its local environmental exposure.
- Determination of actual stone features and properties and the effect of the treatment applied.

*The results of in situ tests are essential input for effective maintenance programming.*
Parameters influencing the effectiveness of consolidation treatment

- **Characteristics of the stone materials**
  - Lithotype
  - Porosity
  - State of conservation etc....

- **Chemical and physical properties of the consolidation product**
  - Molecular weight
  - Functional group
  - Glass transition temperature \((T_g)\) etc......

- **Application Methodology**
  - Solvent
  - Concentration of the solution
  - Application technique, etc............

**Types of consolidating products for stone materials**
- Organic
- Inorganic
## Performance Test Methods of Consolidation Treatments

<table>
<thead>
<tr>
<th>Method</th>
<th>Laboratory</th>
<th>In Situ</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniaxial Compressive Strength (UCS)</td>
<td>yes</td>
<td>no</td>
<td>Not applicable if the treatment affects only the external layer of the stone specimen under test</td>
</tr>
<tr>
<td>Abrasion resistance</td>
<td>yes</td>
<td>no</td>
<td>Standardized testing of paving stone</td>
</tr>
<tr>
<td>Water absorption</td>
<td>yes</td>
<td>yes</td>
<td>Can be done in situ (Karsten tube and Contact sponge)</td>
</tr>
<tr>
<td>Contact Angle of a Water Droplet</td>
<td>yes</td>
<td>no</td>
<td>Best to evaluate water-repellent products</td>
</tr>
<tr>
<td>Chemical analysis (SEM - EDS or FT-IR)</td>
<td>yes</td>
<td>no</td>
<td>The most reliable method for assessing penetration. Not practicable for consolidation</td>
</tr>
<tr>
<td>Staining of stone slices with iodine vapour</td>
<td>yes</td>
<td>no</td>
<td>Method for organic based consolidating products</td>
</tr>
<tr>
<td>Ultrasonic Wave Velocity Measurement</td>
<td>yes</td>
<td>yes</td>
<td>Non destructive method to evaluate the mechanical behaviour of the material</td>
</tr>
</tbody>
</table>
**Portable Equipment for On Site Tests - DRMS**

**Drilling Resistance Measurement System**

- Suitable for both laboratory and “in situ” tests
- It measures the Force necessary to drill the material.
- The mean value of the Drilling Resistance can be correlated with the Uniaxial Compression Strenght (UCS).
- Works at constant operating conditions: Rotation speed (150-1000 RPM) and Penetration rate (5-80 mm/min).
- Records the resistance profile of the first layer of a stone material (up to 50 mm depth),
- Enable quantification of the consolidating effect and the determination of the penetration depth of the consolidating product.
DRMS Principal Features

Drilling Resistance Measurement System

- Fully portable and stand-alone system for “in situ” measurement.
- Battery operated (14 V)
- USB connection between the electronic microdrilling device and the laptop computer
- Load cell for the drilling force measurement (Max. Force 100 N)
- Special diamond drills are used to minimize the wear effect. The standard drill diameter is 5 mm.
- Developed under the Hardrock and DIAS European Projects
Polycrystalline diamond plates inserted at the tip of end mills minimize the effect of abrasivity.
DRMS – Consolidating Evaluation of a Limestone (Pietra di Lecce)

Laboratory Test

Drilling Resistance Measurement on a “Pietra di Lecce” limestone treated with Ethyl Silicate

Material: Limestone (Pietra di Lecce)
Consolidating Product: Ethyl Silicate
**Material:** Decayed Marble

**Consolidating Products:** Fluoroelastomer, Ethyl Silicate
**DRMS - Consolidating Evaluation of a Sandstone (Pietra Forte)**

**Laboratory Test**

Samples treated with 5 consolidating products, were exposed in an external environment for a period of five years.

<table>
<thead>
<tr>
<th>product name</th>
<th>chemical composition</th>
<th>treating solution</th>
<th>manufacturer</th>
<th>acronyms</th>
</tr>
</thead>
<tbody>
<tr>
<td>W290L</td>
<td>siloxane oligomers</td>
<td>white spirit (10%)</td>
<td>Wacker Chemie</td>
<td>W290L</td>
</tr>
<tr>
<td>Silirain 50</td>
<td>methylsiloxane oligomers</td>
<td>white spirit (5%)</td>
<td>Rhône Poulenc</td>
<td>Sil50</td>
</tr>
<tr>
<td>Paraloid B72</td>
<td>(ethyl methacrylate - methyl acrylate) copolymer(70/30)</td>
<td>acetone (5%)</td>
<td>Röhm &amp; Haas</td>
<td>PB72</td>
</tr>
<tr>
<td>Paraloid B67</td>
<td>poly i-butyl methacrylate</td>
<td>acetone (5%)</td>
<td>Röhm &amp; Haas</td>
<td>PB67</td>
</tr>
<tr>
<td>Akeogard CO</td>
<td>hexafluoropropene-vinylidene fluoride copolymer (70/30)</td>
<td>acetone (5%)</td>
<td>Syremont</td>
<td>AKCO</td>
</tr>
</tbody>
</table>

**Only the silica-based treatments**

- **Siloxane oligomers**
- **Methylsiloxane oligomers**

*show a consolidating effect after 60 months*

*Penetration of the products is not very deep*
**DRMS - Consolidating Evaluation of a Limestone (Maastricht Stone)**

### Evaluation with DRMS

**Operating condition**
- **Rotation Speed:** 600 RPM
- **Penetration Rate:** 40 mm/min
- **Depth:** 10 mm
- **Drill Bit (Diamond):** 5 mm.

### Consolidating Treatment

**Product:** FLUORMET CP - 2.5 % Solution in Acetone

*(Blend of fluoroelastomer and ethyl methacrylate -co-methyl acrylate)*

**Application:** Brush

**Time:** Until refusal (50-80 g/m²)
**Cathedral of San Leo, 11th Century (near San Marino)**

**Material:** Sandstone of San Marino

**Different consolidating Products**

<table>
<thead>
<tr>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Silicate</td>
</tr>
<tr>
<td>Alkyl alkoxy silan oligomer (1)</td>
</tr>
<tr>
<td>Alkyl alkoxy silan oligomer (2)</td>
</tr>
<tr>
<td>Blend of fluoroelastomer and ethyl methacrylate -co-methyl acrylate (<em>Fluormet CP</em>)</td>
</tr>
</tbody>
</table>

**Treatment**

| Brush until refusal |
The Sandstone of San Marino is characterized by a high non-homogeneity and by frequent zones with sheetings located at different penetration depths.
The abbey of Badia a Passignano, (11th-12th Century)

Walls of the Cloister

Material: Mortar

The last supper by Domenico Ghirlandaio - (1476)
**DRMS - in situ evaluation of consolidating agents**

<table>
<thead>
<tr>
<th>Material</th>
<th>Consolidating Product</th>
<th>Application mode</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar</td>
<td>Saturated ammonium oxalate solution</td>
<td>Slow absorption (Flebo)</td>
<td>1 week</td>
</tr>
<tr>
<td>Mortar</td>
<td>Saturated barium hydroxide solution</td>
<td>Slow absorption (Flebo)</td>
<td>1 week  2nd appl. after 1month</td>
</tr>
</tbody>
</table>

**Barium Hydroxide**

**Ammonium Oxalate**
**DRMS – On site evaluation of consolidating treatment - Column**

<table>
<thead>
<tr>
<th>Material</th>
<th>Consolidating Product</th>
<th>Application mode</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decayed Marble</td>
<td>Lime water + Saturated solution of ammonium oxalate</td>
<td>Arbocel BC 200 pack 2 of Arbocel BC 1000 + 1 of Arbocel BC 200 pack</td>
<td>10 days 16 hours 2nd applicat. After 1 week</td>
</tr>
</tbody>
</table>

*Abbey of Badia a Passignano*

**Before treatment**

heavy decayed fragment of a marble column

**After treatment**
Portable Equipment for In Situ Tests

**Indentation System**

- Portable instrumentation. Suitable for both laboratory and “in situ” tests
- Automatic indentation sequence.
- Continuous measurement of drilling force and indentation depth
- The superficial indentation hardness and the modulus of elasticity of stone can be evaluated.
- Hardness related to UCS Strength

![Typical indentation curve](image)
Evaluation of the material hardness

- Use of spherical indenters (2.5 or 5 mm)
- Indentation forces up to 600 – 800 N (with marbles)
- Disadvantage: Need of a constraint to be fixed for the in situ tests
- Constant displacement Rate

Loading Period: The indenter is pressed into the specimen with a constant loading displacement rate.

Hold Period: The maximum load is held for a short period of time.

Unloading Period: The indenter is removed from the specimen with a constant unloading displacement rate.
Superposition of 6 indentation tests on a Sander Sandstone

Sphere of 2.5 mm diameter

The indentation hardness is related to slope of the loading curve

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>AVERAGE</th>
<th>STD DEV</th>
<th>STD DEV%</th>
</tr>
</thead>
<tbody>
<tr>
<td>INDENTATION MODULUS</td>
<td>GPa</td>
<td>39</td>
<td>1.9</td>
<td>4.97%</td>
</tr>
<tr>
<td>INDENTATION HARDNESS</td>
<td>MPa</td>
<td>794</td>
<td>33.1</td>
<td>4.17%</td>
</tr>
<tr>
<td>DEFORMATION WORK</td>
<td>Nmm</td>
<td>37</td>
<td>3.7</td>
<td>9.92%</td>
</tr>
<tr>
<td>MAX FORCE</td>
<td>N</td>
<td>588</td>
<td>20.0</td>
<td>3.40%</td>
</tr>
<tr>
<td>SINT HARDNESS (Slope)</td>
<td>MPa</td>
<td>927</td>
<td>53.7</td>
<td>5.80%</td>
</tr>
<tr>
<td>SINT HARDNESS (Max load slope)</td>
<td>MPa</td>
<td>946</td>
<td>32.1</td>
<td>3.39%</td>
</tr>
</tbody>
</table>
**Indentation Laboratory test – Limestone**

*(Maastricht Stone)*

---

**INDENTATION Results**

<table>
<thead>
<tr>
<th>HIT</th>
<th>Max Force</th>
<th>Slope @ 40 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 43.8%</td>
<td>+ 30.6%</td>
<td>+ 10.6%</td>
</tr>
</tbody>
</table>

**TREATMENT**

*Product*: FLUORMET CP - 2.5 % Solution in Acetone (Blend of fluoroelastomer and ethyl methacrylate -co-methyl acrylate )

*Application*: Brush

*Time*: Until refusal (50-80 g/m²)

---

**DRMS Measurements**

Consolidating evaluation on Maastricht stone

---

![Graph showing DRMS Measurements](image-url)
INDENTER “in situ” test results
the Cathedral of Florence

Cupola of Brunelleschi

Mounting Plate

Test location
The loading curve slope and the maximum force are strongly dependent upon the condition of the surface:

- Consistency of the surface layer
- Roughness of the surface layer

ADVICE: The surface patina must be removed mechanically (i.e. sand papering) to obtain a satisfactory surface roughness in order to compare loading curve data.

The slopes of the unloading curves are very similar. The low consistency surface layer is compacted by the indentation and has no influence.

It is possible to calculate the hardness and modulus of elasticity by comparing the slopes at a particular force level (for example 350 N).
The presence of a “low resistance” superficial layer can be detected by observing the slope of the indentation loading curve (derivative analysis).

**Carrara Marble**
- Material homogeneous through the thickness

**Weathered Marble**
- Material with a “low resistance” superficial layer

---

### Derivative function of the loading curve

[Slope graphs for Carrara and Weathered Marble]
New Diagnostic Tools for “In situ” Evaluation of Conservative Treatments for Monumental Stones

Thank you for your attention

Emilio Valentini
emilio.valentini@sintechnology.com

www.sintechnology.com