Conservation of sugaring marble by hydroxyapatite: some recent developments on producing and treating decayed samples

Enrico Sassoni¹,², Gabriela Graziani¹, Elisa Franzoni¹, George W. Scherer²

¹ Dept. Civil, Chemical, Environmental & Materials Engineering (DICAM), University of Bologna, Italy
² Dept. Civil & Environmental Engineering (CEE), Princeton University, USA

enrico.sassoni2@unibo.it, Website: https://events.unibo.it/hap4marble/

**BACKGROUND**

Architectural decorations and sculptures made of marble, when they are exposed outdoor, deteriorate because:

- Temperature variations cause the opening of cracks between calcite grains, so that grains detach and fall
- Rain causes the dissolution of calcite grains, so that the marble carved surface is lost

The products currently available are not effective and/or durable in preserving marble against these deterioration causes

In 2011, we proposed the use of hydroxyapatite (HAP) to preserve carbonate stones [1]

HAP can be formed directly inside marble and over marble surface, from the reaction between calcite and an aqueous solution of diammonium hydrogen phosphate (DAP) in mild conditions

![HAP Formation Diagram](Image)

**RESEARCH AIMS**

1. **Accelerated ageing**
   - To study the consolidating efficacy of the HAP treatment, artificially aged samples with characteristics similar to naturally sugaring marble (i.e. micro-cracks more diffused near the surface) are needed

2. **Treatment parameters**
   - The treatment parameters need to be optimized to reduce the porosity of the HAP layer, increase the surface coverage and prevent the formation of soluble calcium phosphate phases

3. **Consolidation**
   - The ability of the HAP treatment to re-establish cohesion between calcite grains and restore the strength of weathered marble, without causing over-consolidation, needs to be investigated

4. **Protection**
   - The ability of the HAP treatment to prevent the dissolution of marble surface in rain, by formation of a dense coating with low solubility, needs to be investigated

**MATERIALS AND METHODS**

1. **Ageing**
   - Ageing was produced by heating samples over a hot plate, the temperature and time of heating being calculated by a theoretical model. Damage was assessed by measuring the modulus Eσ

2. **Treatment parameters**
   - The influence of several treatment parameters (ethanol addition, pH control, double treatments [2]) was investigated and the effects evaluated by SEM-FIB

3. **Consolidation**
   - The increase in marble cohesion after consolidation was assessed by measuring the increase in modulus Eσ and observing the new phosphate phases by ESEM

4. **Protection**
   - The resistance to dissolution was assessed by measuring the increase in pH vs time of an aqueous solution of HNO₃ initially at pH=5 (simulating slightly acid rain)

**RESULTS AND DISCUSSION**

- **Heat treatment**
  - Heating at 200 °C for 20 sec was predicted to cause an average ΔEσ = -35% in the first 1 cm from the surface, leaving the rest undamaged. Experimental results confirmed the prediction

- **Ethanol addition**
  - Ethanol addition favors marble surface coverage and helps reduce the porosity of the HAP layer, as it weakens the hydration shell of the phosphate ions in solution

- **Double application**
  - Double application of the HAP treatment with 10 vol% ethanol was able to fully restore the Eσ thanks to HAP formation inside cracks formed by artificial ageing

- **HAP coating**
  - The HAP coating was able to reduce marble dissolution, even if cracks appeared after the test. The orientation of the underlying calcite grains influences the film durability

**CONCLUSIONS AND FUTURE WORK**

- The developed model allows to produce samples with a desired level of damage.
- The addition of ethanol is effective in promoting HAP formation and reducing the film porosity, thus allowing to achieve a good consolidating and protecting ability
- Ethanol has a competitive effect, as it weakens the hydration shell of the phosphate ions in the solution but it is adsorbed on calcite surface.
- Future research will be aimed at identifying by NMR possible alternative solvents that may weaken the hydration shell without being adsorbed on calcite

**ACKNOWLEDGEMENTS**

This project has received funding from the European Union’s Horizon 2020 programme through the Maria Skłodowska-Curie HAP4MARBLE Project (Multi-functionalization of hydroxyapatite for the restoration and preventive conservation of marble artworks, grant agreement No 655239)

**REFERENCES**