Journal of
Powder Metallurgy & Mining

Editorial Open Access

Marble Consolidation: Can Nanomaterials Help?

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Editorial

In spite of the huge literature delivered in last decades about stone protection and conservation, marble consolidation remains a quite delicate problem. In the last 10 years, more than 400 papers about stone consolidants have been delivered, only 10% of which specifically devoted to marbles; if we have a look to the Countries involved in these researches, more than 60% of published data are released by Italian Institutes, followed by Spain, Greece, and Belgium, revealing an Europe-centrism of this topic (statistical data from SciVal 2005-2016). Effectively, in the same time lap, EU financed almost eight Projects devoted to produce new materials for stone consolidations [1,2], three of which specifically finalized to support transnational access and networking among conservator scientists (*e.g.*: Stonecore, Nanomatch, Nanoforart, Nanorestart, NanoCathedral, Eu-Artech, Charisma, Iperion CH.it).

From these drawbacks, appears quite clear that the problem of suitable consolidant selection for building materials in is the light of the current research, even if, especially for marbles, no valid conclusions seem to be addressed [3,4]. In fact, differently than with other building materials, the choice of a suitable consolidant for marble is a not so trivial, as its low porosity often prevent the efficient penetration of products. Before to test new materials on built heritage, laboratory tests have to be carried out to evaluate the efficacy and the harmfully of products against the substrate. However, also this aspect suffers of a lot of gaps, as no univocal methods have been practically proposed to artificially degrade stone samples, to perform consolidating tests, to assess the treatment method and, finally, to properly evaluate efficacy, durability and harmfulness. All the aforementioned arguments are quite remarkable, as the outputs of tests greatly influence the possibility to transpose the laboratory routines to the real practices.

Regarding the first point (i.e.: how to degrade marble for consolidation test?), numerous recommendations can be found; some authors propose to prepare dummies or sandwiches made by mixing crushed stones and consolidant to mimic high damaged substrates [5]; other authors suggest to heat samples, expecting to produce anisotropic deformation and cracking, or to attack them by acid solutions, reproducing the effects of acid rain attack, or, finally, to induce mechanical pre-stress, producing microcracks in the stone [6,7]. In the case of marbles, thermal aging seems to be the most appropriate method, even if different temperature ranges as well number of cycles are proposed [8]. Also the product application method is not univocal established, as greatly depend on the characteristic of the products (namely concentration, solvent type, and contact time); generally, brushing is preferred assuring a good control of product application [9,10]. Finally, how to evaluate efficacy? Some authors propose ranges of acceptability for some measured parameters [11], other elaborate compatibility indexes [12], others more focus their attention on results obtained from field exposure tests [13].

The current researches are therefore moving, more and more, through testing products and procedures, taking advantages from the new technologies and soft-matter chemistry methods. In this sense, a quite valuable effort seems to be provided by nanotechnologies and nanomaterials, recently successfully employed also for stone conservation issues [14]. Among nanoparticles (NPs) based products tested on marbles, nanolime stand out; both commercial and research products have been tested on marbles by monitoring its efficacy both in laboratory condition [5,15,16] and in situ [13,17]. Results suggest general positive effects in term of absorption and mechanical proprieties, even if low penetration depth, slow kinetic, influence of environmental and substrate condition during application and curing, and type of solvent in which NPs are dispersed have been highlighted. Moreover, some authors indicate that it could be necessary to repeat the application for 30-40 times [18], a routine absolutely impracticable in real practice. Another class of NPs-based product is represented by nanosilica dispersions; also in this case, some tests have been performed on marbles, even if a lot of questions are currently opened the effective compatibility of silica particles with a carbonate substrate, the appropriate control of humidity conditions, the relative humidity of substrate, the dispersion of particles in different solvent, the curing conditions. The literature suggests, however, that the potential use of SiO_2 NPs needs more and more researches finalized to better evaluate all the variable affecting efficacy of this product, available both as commercial and research product [19]. Beside the promising results obtained by applying these products, alkoxysilanes (TEOS and MTMOS) continue to be used in consolidating marble substrates, even if the well-known disadvantages related to shrinkage, cracking, low chemical compatibility and limited long term performances of these products. For these reasons, researches are widely focused on ameliorating TEOS long performances with the addition of NPs; preliminary results have demonstrated an improvement in cracking and shrinkage of TEOS, allowing to obtain "tunable" products [20].

Apart from nanoparticle-based products, the current studies are focused on the synthesis and testing of new alternative solutions for marbles, including for example alkoxides [17], hydroxyapatite [21] and oxalates [22]. However, due to the absence of standards on the evaluation and choice/selection of the methods, products performance and operating conditions in relation to the restoration, repair, maintenance and preventive conservation of stone materials, the final assessment of good practices and suitable products is far from its end. This statement has to not discourage researchers, who are therefore exhorted to push studies toward more and more high challenges.

Acknowledgements

Studies supported and scientific issues debated in the framework of the European project Nanocathedral, n. 646178.

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Received October 18, 2017; **Accepted** October 20, 2017; **Published** October 31, 2017

Citation: Raneri S, Lezzerini M (2017) Marble Consolidation: Can Nanomaterials Help? J Powder Metall Min 6: e137. doi:10.4172/2168-9806.1000e137

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