

ELARCH Project: the use of innovative product based on nanotechnologies for the protection of architectural heritage

Graziella BERNARDO¹, Michelangelo LATERZA¹, Michele D'AMATO¹, Giuseppe ANDRISANI⁴, Daniela DIAZ⁵,
Edgar LAGUNA⁶

(1,2,3,4,5,6) DICEM, Department of European and Mediterranean Cultures (Architecture, Environment and Cultural Heritage) - University of Basilicata, Matera, Italy

(1) Assistant Professor, graziella.bernardo@unibas.it

(2) Professor, michelangelo.laterza@unibas.it

(1) Assistant Professor, michele.damato@unibas.it

(1) Assistant Professor, andrisanigiuseppe@gmail.com

(5) PhD Student, daniela.diaz@unibas.it

(6) PhD Student, edgar.laguna@unibas.it

Abstract: Most of the world's architectural heritage consists of constructions in stone materials. These materials conditioned to the architectural styles of the past and marked connotative characters of entire ancient cities. There is a huge variety of stone materials that have substantially different characteristics depending on the type of sourced rocks from which they are extracted. Limestone rocks of biochemical origin are widespread in all over the countries both of Latin America and Mediterranean area, where they are often known with the local denominations, such as calcarenites or tuffs of Matera, Lecce, Agrigento, Malta, etc. These materials are affected by synergistic chemical, physical and biological degradation phenomena caused by the complex interaction between the materials and the environment that surrounds them, i.e. exposure environment. The degradation of materials can compromise the structural behavior of the construction, increasing its seismic vulnerability. The preservation of the architectural heritage built with stone materials requires restoration works able to neutralize or, at least, to reduce the degradation phenomena of these extremely vulnerable materials. The choice of the consolidating and protective products plays a key role in the effectiveness of restorations: their wrong choice can determine the uselessness of restoration works, but it can also worsen the diseases of the stones and irreparably damage architectural heritage. However, the effectiveness of these products is highly dependent on the stone characteristics and on the many interactions that occur among the stone, the product and the exposure environment over the short and long time after the restoration treatment. This paper illustrates a multidisciplinary research activity on the use of innovative product based on lime and nanoparticles of graphene in restoration and seismic retrofit of masonry constructions in limestone materials. The use of graphene as nanotechnological component overcomes the drawbacks of traditional products based on lime, providing extraordinary physical properties (hardness, strength and flexibility) to the investigated product. This is translated to more durability, less maintenance costs of the repair and restoration works.

Keywords: limestone materials, nanotechnologies, graphene, lime, seismic retrofit

1. Introduction

The stone materials are the main material used in the architectural and sculpture heritage. They are characterized by a great variability depending on the type of rock from which they are quarried. Limestone is widespread in all over the countries of both Latin America and the Mediterranean area. Due to the characteristics of durability, strength, workability and fire resistance, limestone was widely used in ancient times worldwide for churches and temples in the Mediterranean area, the Maya pyramids in Mexico or the Underground City of Cappadocia in Turkey. The limestone rocks of biochemical origin are often known with the local denominations, such as calcarenites or tuffs of Matera, Lecce, Agrigento, Malta, and *calizas* in Latin America. They have different microstructural characteristics depending on the size grains and the quantity

of cement. Consequently, their technological properties, such the mechanical strength and durability, have a high variability (Bernardo and Guida, 2015).

The calcarenites are affected by severe chemical, physical and biological degradation phenomena, due to their high open porosity that allows the entry into the materials of aggressive agents present in the exposure environment. The two most frequent and aggressive chemical process are caused by the environmental pollution arising from the use of fossil fuels. The first one is the interaction between sulphuric acid and calcium carbonate that forms black crust on the surfaces and gypsum crystallization within the pores of the material causing internal stress and fractures of the stone. The second one is the attack by water containing carbon dioxide that transforms the insoluble carbonate into soluble bicarbonate, which can corrode the surface of the material. In certain conditions, the calcium carbonate may recrystallize in the form of a crust harder and compact than the previous carbonate, causing detachments due to mechanical and thermal stress (Bernardo and Guida 2015).

Another frequent physical degradation phenomenon that affects the calcarenitic materials is the crystallization of soluble salts, which together to the wind erosion determine the alveolization phenomenon. As regards the biological degradation phenomena, it is mainly due to the action of different species of bacteria, algae and lichens (Bernardo and Guida 2015). All the degradation processes imply microstructural changes, and in some cases the physical loss of material, which leads to the loss of historic and cultural value of the architectural or decorative heritage.

On the other hand, masonry walls are vulnerable to the seismic action, mainly due to the absent tensile strength and also due to technological-constructive reasons. The frequent lack of effective connections between the building parts (walls, horizontal structures and roofing) creates local-response mechanisms, which, very often, generate partial collapse situations due to the loss of stability of the weaker macro-elements, acting independently to the seismic stress and not performing a box-behavior. Limestone masonry walls are even more vulnerable to the seismic action, because the stones react as rigid and fragile materials, performing an effective behavior to compression strength, but having a limited capacity to tensile, flexural and shear strength (Lazzarini and Laurenzi 2010). Moreover, the mechanical capacity of the walls may decrease due to the loss of material of the limestone masonry by chemical or physical degradation processes. The limestone is also vulnerable to the interaction with incompatible materials, which turns simple conservation actions, such as the repointing of mortar joints or the re-plastering, to a critical intervention that may worsen the previous condition.

The structural function of the mortar joints in masonry walls is to ensure the continuity between the stones, avoiding the concentration of stresses under the seismic action. Therefore, the repointing of joints, which is a common consolidation action, might be improved by the use of an appropriate technique, searching to achieve a suitable seismic retrofit for limestone masonry.

Nanoscience deals with a large diversity of research fields and applications, due to the modification or improvement of the nanomaterials properties by the effect of the reduction in the size of the particles. The graphene is a nanoparticle discovered in 2004 by Konstantin Novoselov and Andre Geim, for which they won the Nobel Prize in Physics in 2010. The graphene is a flat sheet of monatomic carbon atoms linked by covalent bonds (Solís Fernández, 2011), it is the thinnest possible 2D membrane in nature, and among other features, it has the highest stiffness and strength ever recorded (Lee et al, 2009). These nanoparticles have an ultimate tensile strength of 130 GPa, compared to the 400 MPa of A36 structural steel, they have elastic properties and are very light as well, weighting 0.77 mg/m².

The nanotechnology has provided new products for the conservation of architectural heritage, which has enhanced the properties for protection and consolidation of the traditional materials. For instance, nanoparticles of calcium hydroxide have been used with good results for consolidating limestone with a product developed in the University of Florence, the Nanorestore[®], and the German Institute developed the CaLosil[®], another product with similar results (Gómez-Villalba *et al* 2011). The lime nanoparticles have been used as a consolidating material of limestone, improving the penetration of the product in the stone

substrate, increasing the cohesion of stone components, avoiding the microorganism colonization and increasing the durability of the intervention.

Considering that one of the main scopes in the conservation of architectural heritage is to minimize the interventions for repairing or consolidating, this paper illustrates a multidisciplinary research activity on the use of an innovative product based on lime and nanoparticles of graphene in restoration and seismic retrofit of masonry constructions in calcarenites.

2. Seismic reinforcement criteria and intervention techniques in masonry Cultural Heritage

The seismic reinforcement of architectural heritage requires the historical and constructive knowledge of the building, which is pursued through interdisciplinary investigations and geometric survey. In order to balance the necessity of conservation with the improvement of the structural behavior, the Italian Guidelines for the seismic risk evaluation and reduction for the Cultural Heritage aligned with NTC 2008, give indications for the seismic improvement by using traditional techniques and innovative materials. In any case, interventions must be accurately evaluated, taking into account the effects of changes in stiffness and resistance of the structure's elements. Moreover, they must be contained in number, compatible with the conservation criteria, preserving the esthetical and technological value of the construction (DCCM 2011).

The possible actions for reducing the degradation phenomena of the masonry constructions and/or their seismic vulnerability are generally more than one, with different characteristics in terms of effectiveness, invasiveness, reversibility, compatibility, durability and cost. The common intervention techniques, suggested also by the Italian Ministry of Culture (DCCM, 2011), allow to obtain the following effects: a) the reduction of the connections deficiencies between walls, or between floors and walls; b) the reduction of the thrusts of the roofing, arches and vaults through metal chains compensating the pressures; c) the reduction of the excessive deformation of the floors and their consolidation; d) the linking of the roofing with the top of the walls; e) the consolidation of pillars, columns and foundations; f) the increase of the masonry elements resistance.

Regarding the consolidation and repair of damaged masonry walls, some interventions that integrate new elements are: the change of damaged stones with similar stone blocks; the insertion of diatons, for making transversal connections; and the strengthening with textiles or fiber-reinforced materials.

On the other hand, some mortar-based consolidation techniques are: the joint repointing; the injection of mortar grout inside the three-leaf masonry walls; and the jacketing with reinforced mortar. These types of consolidations require the choice of a mortar suitable to the construction system, for example, in the case of injection of mortar grout, the use of cement-based mortar may produce saline efflorescence that will arrive to the surface of the wall, affecting frescoes or ornaments. As regards the intervention of joints repointing, if carried out in depth on both sides of not very thick walls, it may improve the mechanical characteristics of the masonry.

However, the Italian Ministry for Cultural Heritage and Landscape considers the jacketing of walls with plaster reinforced with steel nets, glass or basalt fibers as an invasive intervention not consistent with the principles of conservation for the loss of authenticity, adding that it is only effective when is made on both sides of the wall and connected transversally by bars. Therefore, it should only be considered in limited sections of the building (DCCM, 2011: 117). Besides, the reinforced plaster was usually made with cement-based mortar, which might be the main incompatibility. On the other hand, lime-based mortars have been used in the past as a protective finishing of masonry walls and for repointing the joints in restoration as well with positives results in terms of material compatibility. However, lime mortars have a weakness due to its low mechanical strength and virtually no tensile strength, as Lazzarini and Laurenzi (2010) said: "these finishes in lime, however, can obviously not be confused with a consolidation method".

Therefore, this work has the aim to evaluate the possibility of increasing the mechanical strength of the lime with the use of graphene, for developing a most suitable mortar for the consolidation of the masonry by the injection of grout mortar, joint repointing or reinforced plasters.

3. Mortar-based consolidation in masonry Cultural Heritage

There are important vulnerabilities of historical masonry buildings regarding seismic behavior, such as the low mechanical properties of the unreinforced masonry walls and even less in the poor quality ones, and the lack of connection between the walls and with the horizontal structures, but invasive interventions cannot be done due to their cultural value. Therefore, it is necessary to find solutions capable to improving the structural security but taking into account the conservation criteria of Cultural Heritage as well. Often, the aim of the retrofitting of historic masonry is to increase the shear strength of the walls for achieving a better global behavior under seismic actions.

In recent years, the procedure of strengthening masonry walls with the jacketing technique based on steel, GFRP (Glass Fiber Reinforced Polymer) or basalt with different mortars has been investigated and reported, based on the advantages of the meshes due to their high tensile strength and low unit weight. This technique consists in bonding both wall surfaces with the mesh, joined by transversal connectors of the same material to avoid the detachment, and fixed to the masonry wall by epoxy paste or mortar, with the aim of providing tensile strength and restraining the opening of cracks.

Although the research results have revealed that shear and flexural strength in masonry walls can be increased through the use of steel, basalt and FRP composites, some problems have been highlighted: difficulty in the removal of the reinforcement; poor behavior of epoxy resins at high temperatures; high cost of epoxies, basalt and FRP composites; long term behavior of organic protectives and their difficulty to allow the water-vapor permeability of the wall; and the low resistance of the steel to environmental conditions (Borri et al, 2014).

On the other hand, a system for improving the out-of-plane flexural strengthening of historic masonry walls was recently proposed by Csikai et al (2014) called “reticolatus”. The method consists in a reinforced repointing for improving regular and irregular masonry behavior, which is reversible and suitable for fair-face walls of historical buildings, and consists in an irregular net of thin stainless steel cords able to work in tension, fixed into the mortar joints following the joint texture. Nevertheless, this technique is currently being developed, its application on test walls highlighted the improvement of the stiffness, the resilient force at cracking and at the bending force, helping the generation of a more distributed crack-map in all the tests, allowing a greater energy dissipation during earthquakes (Csikai et al, 2014).

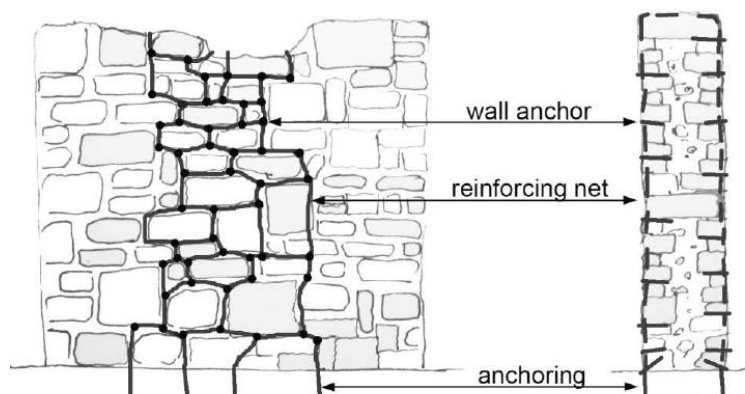


Figure 1- Implementation of “reticolatus” as flexural strengthening technique (Csikai et al, 2014).

Furthermore, the “reticolatus” technique in the repointing of joints has been also tested by Borri by using a net made of Ultra High Tensile Strength Steel fixed to the wall by galvanized steel bars, and then covered with the repointing mortar, which may be cement-based or lime-based. Moreover, the steel bars may be

dimensioned to work as an artificial diatom able to increase the monolithic behavior of the wall panel by avoiding the vertical detachment in three-leaf walls. The outcomes highlighted that the technique increased the compression, shear and flexural strength, and the capacity to withstand tensile stresses. Besides, the small size of the reinforcement cords allow to applying this technique on an extensive area, avoiding the concentrations of stress.

One of the main issues regarding the compatibility and adherence of each technique and the masonry walls is the choice of the mortar. Cement-based mortars and specifically Portland cement was highly used in the 19th century, but nowadays it is known their scarce performance for producing saline efflorescence, and in terms of material compatibility and water-vapor permeability. Thus, considering the successful performance of the lime based historical mortars, it is necessary to develop retrofitting solutions based on this compatible material.

However, as lime mortars has relatively low mechanical strength, recently, another experimental study (Tuncel et al, 2014) tested glass and basalt textile reinforcements with a hydraulic lime-sand-pozzolan mortar, in order to improve the flexural characteristics and toughness of the lime mortar. The results of this study highlighted the better performance of the basalt textile with lime composites, in comparison with the glass textile reinforced ones, but evidenced problems related with the lack of adherence mortar-textile as well, thus, further research is necessary.

On the other hand, an experimental study have been developed (Manoledaki and Vintzileou, 2014) regarding the seismic response effect of hydraulic lime pozzolanic grout injections in three-leaf masonry walls, or two load-bearing external leaves and a poor quality incoherent inner leaf, with no transversal connection. Thus, grout injections combined with joint repointing aim to consolidating the masonry cross-section by filling the existing voids and cracks, seeking for increase the internal cohesion, where material compatibility is one of the most important characteristics, since it is an irreversible technique. The results showed that the rehabilitation with natural hydraulic lime pozzolanic grout injections is highly effective, as it led to substantial improvement of the out-of-plane strength, crack formation was clearly delayed and the wall's failure mechanisms were not modified (Manoledaki and Vintzileou, 2014).

A topic that has not been considered in the retrofitting experimentation above mentioned is the degradation of materials, which may compromise the structural behavior of the construction, increasing its seismic vulnerability. The most often degradation in masonry buildings is the loss of mortar due to weathering, which provokes the disconnection between the masonry blocks, making a discontinuity in the wall even worse in irregular masonry, and provoking the concentration of stresses, which may cause the cracking under seismic action.

The choice of the consolidating products, and specifically the mortar, plays a key role in the effectiveness and durability of restorations. First, they must fulfill the requirement of the compatibility. Mortars based on Portland cement can worsen the decay of the stones due to weathering and efflorescence. They must ensure the durability of the intervention because the loss of mortar provoke the concentration of stresses. Finally, they must provide tensile strength, which is the main weakness of masonry walls.

Recently, the graphene as nanotechnological component mixed with lime has been used in Spain as a painting and restoration material, providing extraordinary physical properties to the mortar as hardness, strength and flexibility, which is linked with more durability. However, the possibility of the use of graphene-lime mortar as a tensile strengthening technique has not been investigated yet. Therefore, we propose to start this research in an interdisciplinary work, by studying the mechanical and physical capacities of the material aiming to apply it in restoration interventions as repointing of joints, which might be more compatible, more durable if affected by weathering, and with the capacity to withstand tensile stresses due to seismic action.

4. Properties of the graphene-lime composite and current use

4.1 The traditional process of the lime since Vitruvius

The term lime refers both to calcium oxide or quicklime, the product of the calcination of calcium carbonate, and to the compound obtained after the hydration of the oxide, i.e. calcium hydroxide the mineral portlandite, also known as slaked lime or hydrated lime (Boyton, 1980). This term also applies to the products of the hydration of Ca and Mg oxides formed after the calcination of magnesium limestone and, in particular, dolomite. Calcitic lime is commonly known as fat lime, while dolomitic or magnesian limes are commonly called magre limes (Rodríguez Navarro, 2004, p. 96).

Historically, lime has been one of the most important binders, and early examples of its use have been found in Palestine and Turkey, dated c. 12,000 BC. Other ancient civilizations, such as India, China and the different cultures of pre-Columbian America (e.g., Mayans and Aztecs) systematically used lime as a building material (Rodríguez Navarro, 2004).

The type of lime first used hardened when exposed to air, and was called air lime. The Greek and Roman civilizations discovered that calcination of marly limestones, i.e., with a concentration of aluminosilicates (clays) > 10 wt %, yielded a binding material that hardened underwater (hydraulic setting) and had improved mechanical properties (Malinowski, 1981). The natural hydraulic limes are obtained from the calcination of impure limestones and clays, which dehydroxylate at 400 to 600°C. The resulting silica and alumina are combined with calcium oxide, formed after the decomposition of calcium carbonate at 950 to 1250° C, to produce calcium aluminates and silicates (Callebaut et al, 2001). Dicalcium silicate is the main phase that reacts with water causing their hydraulic setting, unlike in the case of cement where tricalcium silicate is the main hydraulic phase (Callebaut et al, 2001).

On the other hand, the artificial hydraulic limes, which were discovered by the Phoenicians and perfected by the Greeks and the Romans, were obtained by mixing lime with a pozzolanic material extracted from a tuff with high hydraulic capacity in Puzzoli, Italy. A pozzolanic material contains highly reactive silica and alumina. When it is combined with calcium hydroxide in the presence of water generates new products, mainly hydrated calcium silicates and aluminates, with superior binding or cementing properties (Mertens , et al., 2009).

The Romans used lime in construction since the last two centuries of the Republic (200-100 BC). In addition to air lime, they routinely used lime mixed with either natural (pozzolana s.s.) or artificial (brick powder) pozzolanic materials, thus obtaining the *opus caementitium* and the *cocciopesto* described by Vitruvius (30 BC). After the fall of the Roman Empire, natural and artificial hydraulic limes, including Roman cement, together with traditional air lime were the most common mortar in construction since byzantine time, though the Middle ages, Renaissance and Baroque, until the discovery of Portland cement in the early 19th century by Aspdin (Rodríguez Navarro, 2004).

In recent years, a revival of lime mortar application for the repair of historic buildings has taken place, due to the recognition of the unfavorable properties of Portland cement mortars, including brittleness, high strength, and a thermal expansion coefficient which can be twice as large as that of lime mortars and most types of brick and stone. Lime mortar, on the other hand, has a low efflorescence potential due to its relatively high chemical purity (Elert et al, 2002). Additionally, it has the advantage of allowing flexible but limited movement within the mortar joints.

An important factor to keep in mind when speaking of cultural heritage is determining the process of obtaining lime, Rodríguez Navarro showed that the properties of the phases of obtaining lime predetermine the properties of the phases of products, This has profound consequences in the final set performance material (Rodríguez Navarro, 2004).

Unlike the current production process, the traditional method is characterized by mixing fuel (wood) with limestone and reduce the calcination temperature. The crystals of calcium carbonate formed at low temperatures after a short calcination become nanoparticle, and they show a highly porous and highly reactive structure, which improve surface characteristics, reactivity, dynamic viscosity and plasticity lime (Rodriguez Navarro, 2004).

4.2 Mechanical properties of graphene

Owing to difficulties associated with the handling of monolayer graphene of monoatomic thickness and the extremely low forces required for axial loading, only a few experimental works have been reported in the open literature. Even those are burdened to some extent by the necessity of approximation, because the actual thickness of the atomically thin layer is not known, so a comparison to bulk materials is very difficult (Costas et al, 2015). The first report on the analysis of Young's modulus of graphene ruled that its intrinsic strength reached 300 GPa for monolayer graphene and were obtained by performing nanoindentation measurements using an atomic force microscope (Lee et al, 2009), The results can be seen in Figure 2.

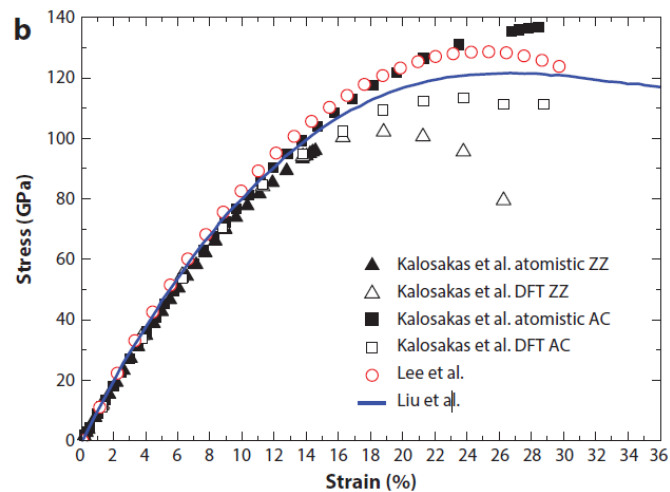


Figure 2- Stress-strain curves for pristine graphene (Costas et al, 2015).

These results were compared with some atomic material models, and it was concluded that both experimental results and atomistic modeling have confirmed unequivocally the high stiffness, of the order of 1 TPa, of exfoliated graphene. Bending experiments, if converted to tensile data by suitable modeling, have also shown that a tensile strength of the order of 130 GPa can be attained at a strain to failure of approximately 30%. These predictions, however, must be confirmed by direct axial measurements in air to failure, which are still lacking. Also, they must be confirmed in commercial CVD-grown films of monolayer graphene (Costas et al, 2015).

4.3 The graphene with the cement.

Cementitious materials have been widely used in constructing architectural structures. Traditionally, mortar or concrete structures have been composed of cement, fine/coarse aggregate, water, some inorganic additives, and chemical agents. Concrete structures, however, are brittle and have low tensile strength, and multiple crack formations develop under mechanical and environmental loads, limiting their durability and contributing to increase maintenance costs (Inkyu, et al 2015). The durability of concrete structures is strongly influenced by its transport properties to the harmful agents such as water, CO₂, chloride, etc. (Sahmaran M. & Li, 2007). Existing durability enhancement methods that are commonly used include

lowering water–cement ratio with the aid of superplasticizers, adding supplementary cementitious materials and using chemical admixtures (P.C, 2005).

On other hand, the use of graphene nanoplatelet (GNP) consists of several layers of graphene with a total thickness of less than 100 nm and a diameter of several micrometers. Hongjian and Dai, demonstrated that the application of nanoparticles GNP low cost refines the pore structure of cement mortar, as revealed by the mercury intrusion porosimetry (MIP), due to their high aspect ratio and layer structure, and barrier properties. Also improves the strength of cement mortar to water permeability, and diffusion of chloride. With the addition of GNP that are higher than those reported in the literature for compounds containing cement nanosize spherical particles as nano-SiO₂ or nano TiO₂ (Hongjian & Dai, 2015).

Another use of graphene with cement was graphene oxide (GO), which is an intermediate product in graphene preparation, which has many advantages as a reinforcing material such as ambiphilicity, excellent mechanical, electrical and thermal properties (Yang et al, 2008). (Wang et al., 2015) made an experimentation with it, a paste of cement and GO (0.05wt %), studying the changes in the physics properties of the mix, the results showed that the addition of GO increases the viscosity, decreases the fluidity and shortens the setting time of the mortar. It also reduces the heat of hydration of the cement. The compressive and flexural strengths of the hardened cement paste at different times are increased by the addition of GO. The flexural strength was greater in 86.1, 68.5 and 90.5% after 3, 7 and 18 days, respectively, and the corresponding compressive strength increased in 52.4, 46.4 and 40.4%. The addition of GO promotes hydration, decreases pore volume, accelerates crystallite formation and causes the crystallites to align, which increases the tightness of both the hardened cement paste and mortar (Wang, et al., 2015).

4.4 The graphene with the lime.

As seen in the previous point, the strength properties, permeability and durability of concrete improve significantly with small additions of graphene, however, when we talk about cultural heritage, mixtures derived from cement are not their best allies because to aesthetic characteristics, running together or simply interaction between the old material and cement mixes.

Instead, the lime mortar is a material widely used in conservation of cultural property, and it has been currently tested in Spain combined with graphene, mainly in paintings and coatings, obtaining an improvement on moisture conditions, permeability and resistance to threats of biological and environmental type (Graphenstone, 2016). Moreover, this nanocomposite made of lime and graphene has the property to be water repellent without reducing the moisture evaporation from the stone, which are properties that every stone protective treatment must have (Bernardo and Guida 2015).

On the other hand, considering the behavior that should have limestone masonry, together with the improvement that has been obtained in tensile strength of the concrete mixed with graphene, comes into consideration to evaluate this feature in the mixture of lime and graphene, aiming to evaluate on a bigger scale this new material.

According to the recent studies regarding seismic retrofit of masonry buildings, which proposed the “reticulatus” as a repointing of joints improved by the tensile strength of the steel, and considering the possible improvement of the tensile strength of the lime by the mixing with the graphene, we propose this new material as a unique seismic reinforcement composite. The first step, however, is to test if the tensile properties of lime-graphene mortar are effectively improved, and then if the composite guarantees an enhancement in the seismic resistance of limestone masonry buildings.

5. Conclusions

The limestone rocks of biochemical origin have been widely used since ancient times in all over the countries both of Latin America and the Mediterranean area, due to their characteristics of durability, strength, workability and fire resistance. However, the calcarenites are affected by severe degradation phenomena

due to their high open porosity that allows the entry into the materials of aggressive agents present in the exposure environment, which causes the loss of material by disintegration, detachment or alveolization. On the other hand, limestone masonry walls are vulnerable to the seismic action, due to the absence of tensile strength of the constructive system and the low capacity of the stones to tensile, flexural and shear strength, mechanical capacity that may decrease due to the loss of material by chemical or physical processes.

Nowadays, there are several techniques of structural seismic retrofit for limestone masonry architectural heritage, such as the polymeric, glass or basalt fibers, however, they have limitations as the necessity of their use in both faces of the wall, and the interactions of the limestone with non-traditional materials as epoxies. Therefore, the proposal of new techniques is required, which allows a better interaction with the original materials of the architectural heritage. On the other hand, throughout the time, researches have proved the compatibility of lime mortars for the conservation and restoration of limestone masonry heritage, however, its low resistance to compression, tensile and flexural strength regarding the seismic action has been tested.

The hypothesis of the improvement of the tensile strength of the traditional lime by using nanoparticles of graphene, allow us to propose a new composite that combine tradition and innovation. To analyze and verify the benefits of this new composite, we will address this general work plan: determination of the physical characteristics of the lime mortar; test the commercial lime-graphene mortar produced in Spain for determine its physical characteristics; and comparative analysis of the results.

The next steps of the research will be to apply the composite in the repointing of joints in testing walls and then compare the outcomes of resistance with the most recent techniques of reinforcement of masonry walls and restoration.

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Bibliography

- Borri, A., Corradi, M., Castori, G. and Sisti, R. (2014). Reinforcement of masonry panels with GFRP grids, in *SAHC2014 – 9th International Conference on Structural Analysis of Historical Constructions*, F. Peña & M. Chávez (eds.), Mexico City.
- Csikai B., Ramos L., Basto P., Susana Moreira, Paulo B. Lourenço, 2014. Flexural out-of-plane retrofitting technique for masonry walls in historical constructions, in *SAHC2014 – 9th International Conference on Structural Analysis of Historical Constructions*, F. Peña & M. Chávez (eds.), Mexico City.
- Bernardo, G. & Guida, A. (2016). Heritages of stone: materials degradation and restoration works. *Proceedings of ReUSO*. Valencia- Spain.
- Callebaut, K., Van Balen, K., & Viaene, W. (2001). Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium): Natural hydraulic lime or cement? *Cement Concrete Res.* 31, 397-403.
- Costas, G., Otakar, F., Koukaras, E., & Dimitris, S. (2015). Graphene Mechanics: Current status and perspectives. *The Annual Review of Chemical and Biomolecular*, 121-136.
- Csikai, B., Ramos, L., Basto, P., Moreira, S., Lourenço, P. (2014). Flexural out-of-plane retrofitting technique for masonry walls in historical constructions, in *SAHC2014 – 9th International Conference on Structural Analysis of Historical Constructions*, F. Peña & M. Chávez (eds.), Mexico City.

- Elert, K., Rodriguez Navarro, C., Pardo, E., Hansen, E., & Cazalla, O. (2002). Lime Mortars for the conservation of historic buildings. *Studies in Conservation Vol 47*, 62-75.
- DCCM 2011 - Directive of the Chairman of the Council of Ministers, Guidelines for the evaluation and reduction of the seismic risk of Cultural Property, in alignment with the Technical Rules for Constructions (Linee Guida per la valutazione e riduzione del rischio sismico del patrimonio culturale allineate alle nuove Norme tecniche per le costruzioni (d.m. 14 gennaio 2008), pubblicata nel supplemento ordinario n. 25 della gazzetta ufficiale n. 24 del 29 gennaio 2008, data ultimo aggiornamento: 19 gennaio 2011).
- Gómez-Villalba, L., López-Arce, P., Fort, R., Álvarez de Buergo, M. and Zornoza, A. (2011). Aplicación de nanopartículas a la consolidación del patrimonio pétreo, La Ciencia y el Arte III: Ciencias experimentales y conservación del patrimonio. Madrid: Ministerio de Cultura, 39-57.
- Graphenstone. (2016, 06 09). *Graphenstone*. Retrieved from www.graphenstone.us
- Hongjian, D., & Dai, P. (2015). Enhancement of barrier properties of cement mortar with graphene nanoplatelet. *ELSEVIER*, 10-19.
- Inkyu, R., Yoong Ahm, K., Gun-Ok, S., Ji Hoon, K., & Hirovuki, M. (2015). Compressive strength sensitivity of cement mortar using rice husk-derived graphene with a high specific surface area. *ELSEVIER*, 189-197.
- Lazzarini, Lorenzo e Laurenzi, Marisa, (2010). Il restauro della pietra, UTET Scienze Tecniche, Torino
- Lee, Wei XD., Kysar JW, & Hone J. (2009). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321-385.
- Malinowski, R. (1981). Ancient mortars and concretes. *ICCROM Symposium, Rome*, 341-349.
- Mertens, G., Snellings, R., Van Balen, K., Bicer-Simsir, B., Verlooy, P., & Elsen, J. (2009). Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity. *Cement Concrete Res.* 39, 233-240.
- P.C, A. (2005). The durability characteristics of high performance concrete: a review. *Cem, Concr. Compos*, 409-420.
- Rodriguez Navarro, C. (2004). Binders in historical buildings: Traditional lime in conservation. *Seminario SEM 09*, 92-111.
- Sahmaran M., & Li, V. (2007). Transport properties of engineered cementitious composites under chloride exposure. *ACI Mater J.* 104, 604-611.
- Solís Fernández, P. (2011). *Modificación superficial de materiales de carbono: Grafito y grafeno*. Oviedo: Universidad de Oviedo.
- Tuncel, E., Polat-Pekmezci, I., and Pekmezci, B. (2014). Behavior of textile reinforced lime composites under flexural loads, in *SAHC2014 – 9th International Conference on Structural Analysis of Historical Constructions*, F. Peña & M. Chávez (eds.), Mexico City.
- Wang, Q., Wang, J., Chun-xiang, L., Bo-wei, L., Kun, Z., & Chong-zhi, L. (2015). Influence of graphene oxide additions on the microstructure and mechanical strength of cement. *New Carbon Materials* 30 (4), 349-356.
- Yang, Y., Chen, C. M., & Wen, Y. F. (2008). Oxidized graphene and graphene based polymer composites. *New Carbon Materials*, 23 (3), 193-200.