Mediterranean Archaeology and Archaeometry, Vol. 18, No 3, (2018), pp. 63-70

DOI: 10.5281/zenodo.1323869

A PRACTICAL METHOD FOR PREPARING $Ca(OH)_2$ NANODISPERSIONS FOR THE CONSOLIDATION OF ARCHAEOLOGICAL CALCAREOUS STONES

E. Caner*[1], E.N. Caner-Saltık[2]

[1]Department of Conservation and Restoration of Cultural Heritage, Pamukkale University, Denizli, Turkey
[2]Materials Conservation Laboratory, Department of Architecture, Middle East Technical University, Ankara, Turkey

Received: 13/07/2018
Accepted: 18/08/2018
**Corresponding author: E. Caner (ecaner@pau.edu.tr)*

ABSTRACT

Exposure to atmospheric conditions results in considerable deterioration of calcareous building stones, lime mortars and plasters in archaeological monuments, requiring several conservation treatments. During the consolidation treatments of the deteriorated calcareous stones, compatibility can best be achieved by introducing a material that would have similar chemical composition and mineralogical structure with the original stone. In recent years, studies on the preparation of $Ca(OH)_2$ nanodispersions for the consolidation of limestone and marble have increased but the preparation processes of these nanodispersions are usually complicated and time consuming. This study aimed to prepare $Ca(OH)_2$ nanodispersions in ethyl alcohol at sufficient concentration levels with a practical method for the consolidation of calcareous archaeological materials.

The preparation of higher concentrations of $Ca(OH)_2$ nanodispersion in ethyl alcohol was done by using nano sized CaO and its dispersion in ethyl alcohol.

Deteriorated marble pieces from Roman Marble Quarry near Pessinus Archaeological site (Ballıhisar, Turkey) were treated with the prepared $Ca(OH)_2$ nanodispersion and kept at high relative humidity (~90%) at room temperature in the laboratory. Efficient penetration of the nanodispersion, and increase in the physicomechanical properties of treated marbles were followed by examinations with polarizing microscope, SEM, XRD and ultrasonic pulse velocity measurements. Carbonation of the dispersion was followed by titrimetric analysis. Calcite was the main polymorph observed after carbonation.

The results showed that consolidation treatments with $Ca(OH)_2$ nanodispersions similar to the one prepared in this study can be used for all calcareous archaeological materials that need improvements in their physical and mechanical properties.

KEYWORDS: archaeological calcareous stone, $Ca(OH)_2$ nanodispersion, consolidation, marble

1. INTRODUCTION

Building materials of historic monuments exposed to atmospheric conditions are subjected to weathering by physical, chemical and biological processes. In time, these weathering processes cause considerable changes in the microstructure of those materials, in their physical and mechanical properties, as well as their chemical composition starting from exterior surfaces towards interiors of the materials.

Those changes are become visible to the eye as changes in color, depositions, detachments as scales and flakes, crack formations, deformations, material losses as powdering, granular disintegration, fragmental disintegration, karstic dissolution, outbursts etc. (Fitzner et al., 1995). While it is important to define the state of deterioration of building material and its major causes, some conservation treatments are also necessary to improve its weathered state. However, most of the conservation treatments prove to be unsatisfactory in time and there is need for the improvements in the field (Teutonico et al., 1997; Sasse and Snethlage, 1997; Wendler, 1997). Physical, chemical and mechanical compatibility with the original building material assures long term durability of conservation treatments (Teutonico et al., 1997; Sasse and Snethlage, 1997; Ambrossi et al., 2001). During the consolidation treatments, compatibility can best be achieved by producing a similar structure to the original material. For the consolidation of calcareous stones lime is the best material to be used for this purpose. However, traditional methods using lime water were found to be inefficient because of the low penetration depth due to the larger size of $Ca(OH)_2$ particles (Price et al.,1988). In the recent studies treatments with $Ca(OH)_2$ nanodispersions to produce calcite network in deteriorated calcareous materials has been promising (Giorgi et al., 2000; Ambrossi et al., 2001; Tiano et al., 2006; Dei and Salvadori, 2006). Other treatments in stone conservation include polysiloxane material with silica nanoparticles (Manoudis et al., 2017) and nanoparticles in pigments (Salama et al., 2018).

During the treatments, the crystallization of calcium carbonate has to occur in the pores and capillaries of decayed calcareous building materials. It can be achieved by treatments with nanodispersions of calcium hydroxide and/or calcium carbonate. The important point for the success of this method is the average size of the applied calcium hydroxide/calcium carbonate particles to be penetrated into the pore structure especially when the matrix of the stone exhibits low porosity (Tiano et al., 2006; Smith et al., 2000; Cölfen, 2003). Therefore, the preparation of a stable nanodispersions with sufficient concentration is an important step in the development of those treatments. In the previous studies, Tiano et.al. (2006) prepared supersaturated nanodispersive (20 nm) calcium carbonate solution by using ammonium carbonate and calcium chloride solution. Feng et al. (2007) prepared calcium carbonate dispersions by passing CO_2 gas through $Ca(OH)_2$ solution. They also tried some additives to control the particle size of calcium carbonate. Seo et al. (2005) formed precipitated calcium carbonate in pure ethanol as the main solvent.

Several $Ca(OH)_2$ nanodispersions were prepared using water, ethanol and isopropyl alcohol as solvent (Tiano et al., 2006; Smith et.al, 2000; Cölfen, 2003; Lopez-Acre et al., 2010). Alcoholic solvents were found to slow down the rate of agglomeration and sedimentation of dispersed calcium hydroxide particles. Ambrosi et.al (2001) formed a stable dispersion of $Ca(OH)_2$ in propan-1-ol having 300-600 nanometers particle size. Dei and Salvadori (2006) have used soluble calcium salts to produce nanodispersion of $Ca(OH)_2$ reaching a concentration of 5g/l calcium hydroxide in propan-2-ol. There are also several recent studies for developing dispersions of $Ca(OH)_2$ with higher concentrations and lower particle sizes and good results have been obtained (Liu et al., 2010; Daniele and Taglieri 2012; Taglieri et al., 2015; Samanta et al. 2016). However these methods are usually complicated and time consuming. For example for producing nanoparticles from micron sized particles, processes such as laser ablation, thermal decomposition, mechanical milling have to be used. On the contrary production of nanoparticles by chemical precipitation involves several techniques such as chemical vapour condensation, hydrogen plasma-metal reaction 4, liquid phases etc. (Otero et al., 2017).

This study propose a practical method for the preparation of $Ca(OH)_2$ nanodispersions that can be easily utilized even with basic equipment i.e. ultrasonic bath and magnetic stirrer.

2. MATERIALS AND METHODS

2.1. *Preliminary test on preparation of calcium hydroxide nanodispersion*

Preparation of nanodispersion was an important step of the conservation treatment. In the light of previous research on the subject, experiments were done to improve the proper calcium hydroxide nanodispersion for the conservation treatment of calcareous building materials. For that purpose, Analar grade chemical compounds such as calcium hydroxide and calcium oxide were used. Water, propanol and ethanol were tried to be used as solvents. Utilization of ultrasonic vibration and vigorous magnetic stirring was necessary to achieve high

concentrations of nano sized calcium hydroxide particles in the dispersion. The results of the trials were evaluated systematically by investigating $Ca(OH)_2$ concentration of the nanodispersion and the stability of the solution in time. Those trials were done systematically by testing the solutions each time for the concentration of nanodispersion and its stability in time using titrimetric analysis.

2.1.1 Determination of Calcium Hydroxide Concentration in Nanodispersion by Titrimetric Analysis

Amount of $Ca(OH)_2$ in the prepared nanodispersion was determined by titrimetric analysis using 0.01 M EDTA solution. It is known that EDTA (Y^{4-}) makes one to one stable complex with metal ions.

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-}$$

Where, Y^{4-} shows the anion of EDTA that forms complex with calcium ion.

10 ml of nanodispersion was treated with 3.0 ml of 5% hydrochloric acid in 100 ml volumetric flask. After the dissolution of calcium compounds, volume was diluted to 100 ml with distilled water. Then 20 ml of this solution was taken and diluted to 100 ml and the pH of the solution was adjusted to 12-13 using few milliliters of 10% NaOH and few milliliters Calcon indicator was added. Calcon indicator solution was prepared by dissolving 0.02 gr Calcon indicator in 100 ml ethanol. Titration was performed by using 0.01M EDTA solution, until the pink color became permanently blue (Black, 1965).

2.1.2 Carbonation Rate Determination of the Nanodispersion

Carbonation of calcium hydroxide nanodispersion were examined determining their carbonation rate under high concentrations of carbon dioxide (5%) and at high relative humidity conditions (~90%). For that purpose about 10-20 ml of solution was put on a watch glass and left to dry and carbonate. Carbonation percentage was determined by the EDTA titration and examination of the XRD traces of the dried powder sample.

2.2. Treatment evaluation

Deteriorated marble pieces taken from Roman Marble Quarry near Pessinus archaeological site (Ballıhisar-Turkey) were used for the treatment trials. Efficiency of treatments were evaluated by the examination of penetration depth of nanodispersion and the changes in the physico-mechanical properties of deteriorated marble samples. Penetration depth was followed by examining thin sections of the treated samples using calcein indicator which made nanodispersed $Ca(OH)_2$ fluorescent under ultraviolet light. A Leica DM4500P polarizing microscope with UV light attachment was used for these examinations. The changes in physicomechanical properties were examined through the measurements of ultrasonic pulse velocity of the samples before and after treatments using a PUNDIT Plus instrument using 220 kHz probes.

The influence of surfactants particularly the use of sodium stearate on the formation of well-shaped calcite crystals was studied by adding 0.025g sodium stearate in the calcium hydroxide nanodispersion (Ukrainczyk, 2009; Tran et al., 2010). After the carbonation of the nanodispersion at high humidity conditions at room temperature, the morphology of the calcite crystals was examined in SEM analysis.

3. RESULTS

3.1. Experiments on the Preparation of Calcium Hydroxide Nanodispersion for the Conservation Treatments

The most efficient calcium hydroxide nanodispersion was prepared by putting 50 gr CaO in 25 ml water and adding 975 ml ethanol followed by magnetic stirring for 24 hours and 3 hours ultrasonic vibration of the solution. CaO was Aldrich calcium oxide nanopowder <160nm (BET) of %98 purity. 31 g of $Ca(OH)_2$ nano particles remained suspended in the dispersion after 16 hours (as shown in Figure 1). Amount of suspended nanoparticles were about 22.9 g/l after the end of 4 days.

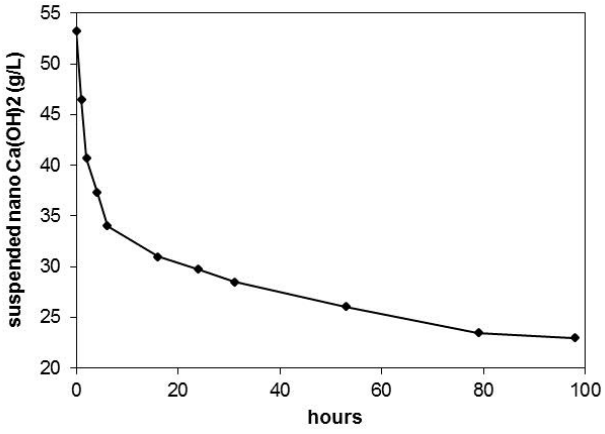

Figure 1. Stability of $Ca(OH)_2$ nanodispersion in time

The particle sizes of the nanodispersed particles were measured by Malvern Nano ZS90 instrument. The average particle size was found to be in the range of 200-300nm (as shown in Figure 2).

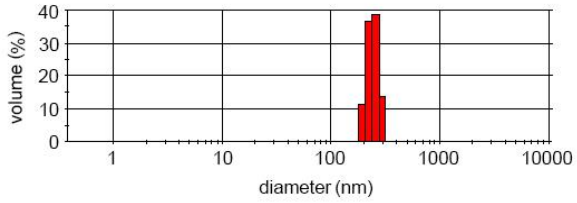

Figure 2. The particle size distribution of $Ca(OH)_2$ nanodispersion

3.2. Treatment of deteriorated marble samples with $Ca(OH)_2$ nanodispersion

Deteriorated marble samples taken from Roman Marble Quarry near Pessinus archaeological site (Ballıhisar-Turkey) were impregnated by calcium hydroxide nanodispersion until saturation. The samples were kept in a high humidity chamber (RH: ~90%) for 28 days.

There was considerable increase (~25-30%) in the ultrasonic pulse velocity measurements of the samples after treatments indicating an increase in physicomechanical properties of marble (as shown in Figure 3).

The penetration of the solution through the fine cracks of deteriorated marble was very efficient. It was observed that fine cracks and pores of 4-6 µm were filled with particles of $Ca(OH)_2$ which were then transformed into calcite (as shown in Figures 4-5).

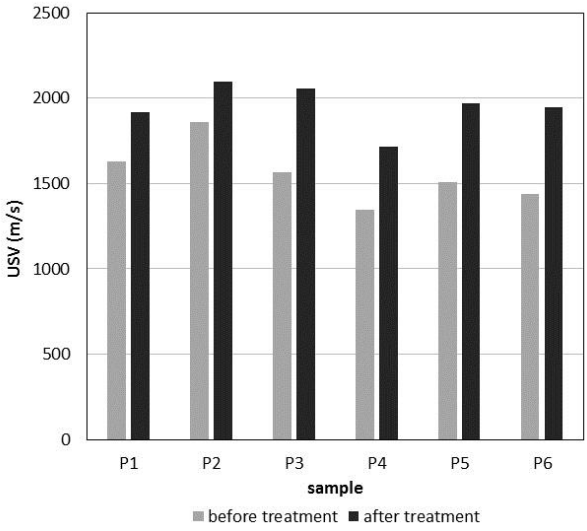

Figure 3. Ultrasonic pulse velocity values of Pessinus marble samples before and after treatment with calcium hydroxide nanodispersion in the laboratory at the end of 28 days.

3.3. Carbonation of $Ca(OH)_2$ nanodispersion

Carbonation of $Ca(OH)_2$ nanodispersion in an atmosphere enriched with CO_2 (5%) and at high relative humidity was found to be about 66% at the end of the 72 hours (as shown in Figure 6). The results show that efficient carbonation of nanodispersion to calcite can be obtained by keeping the samples at high relative humidity and in an atmosphere enriched with CO_2.

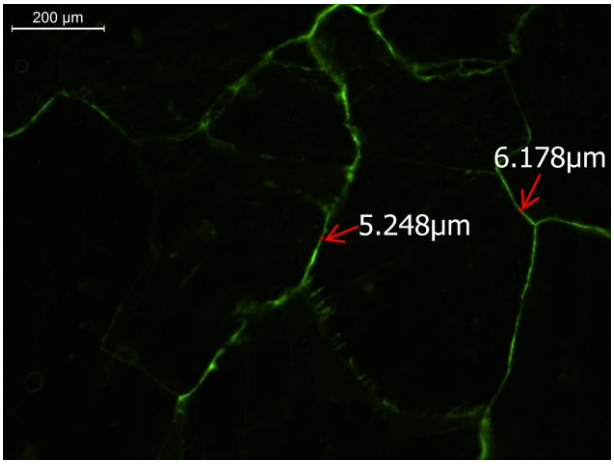

Figure 4. Crack surface of sample from Pessinus ancient quarry treated with fluorescent calcium hydroxide nanodispersion showing the distribution of the calcium hydroxide nanodispersion in the crack.

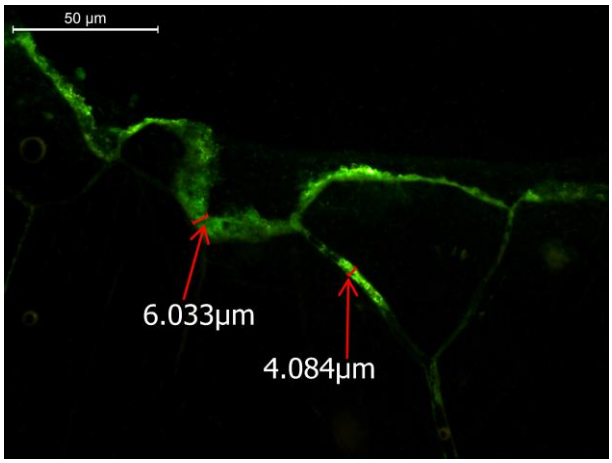

Figure 5. Thin section view of a sample from Pessinus ancient quarry showing penetration of calcium hydroxide nanodispersion through the fine intergranular cracks.

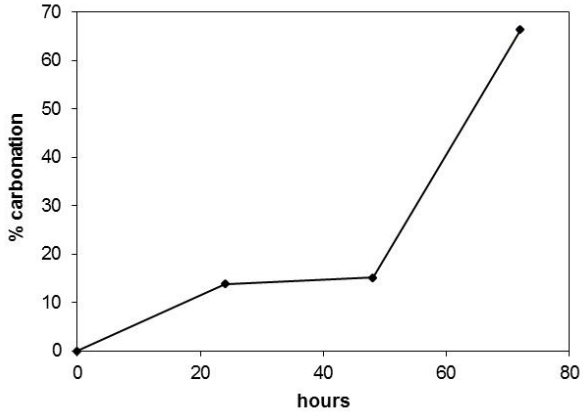

Figure 6. Carbonation of $Ca(OH)_2$ nanodispersion followed by volumetric titration method.

XRD traces of the dried $Ca(OH)_2$ nanodispersion of were taken after 3 days of carbonation. Calcite was the only polymorph detected and portlandite was present (as shown in Figure 7). Percentage of carbonation was estimated by using the ratio of the intensities of portlandite peak at d=2.62A° to calcite peak at d=3.03A°. That ratio was converted to percent calcite by using the standard curve of Perdikatsis for the quantitative calcite-portlandite determination (Perdikatsis, 1996). Percent carbonation at the end of 3 days was found to be about 75% by that method. Carbonation percentages determined by the volumetric titration method and by the calculations through the ratio of peak intensities in XRD traces were in quite good agreement.

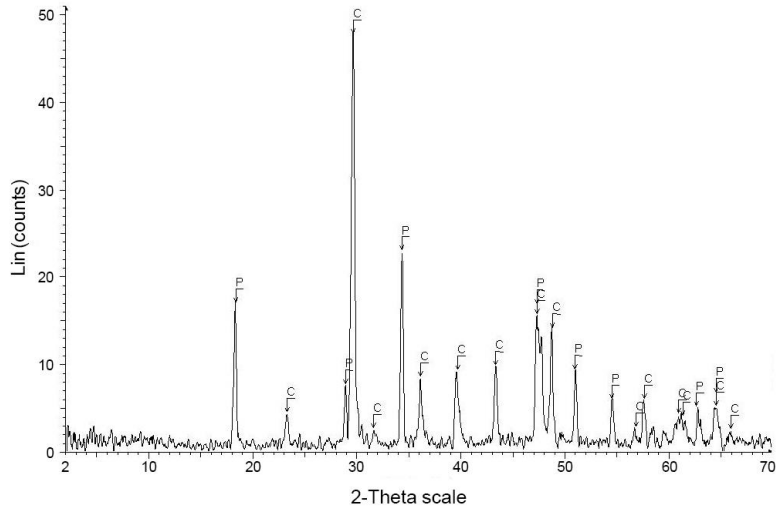

Figure 7. XRD traces of dried the $Ca(OH)_2$ nanodispersion of after 3 days of carbonation. C: Calcite, P: Portlandite

3.4. Use of sodium stearate in $Ca(OH)_2$ nanodispersion

Carbonation of $Ca(OH)_2$ is expected to proceed by surface reaction controlled precipitation of calcite at high pH under high relative humidity conditions. That conclusion is derived from previous studies on dissolution and precipitation of calcite. It is indicated that at pH values higher than 4, calcite dissolution and precipitation reactions are governed by surface reaction controlled mechanisms (Berner and Morse, 1974; Caner and Seeley, 1979; Angwal, 1983; Simon and Snethlage, 1992; Koutsoukos et al., 2001; Morse and Arvidson, 2002). As a consequence, surfactants can have influence in the control of dissolution and precipitation reactions of calcite polymorphs (Ukrainczyk et al., 2009; Kirchgessner and Lorrain, 1987; Wei et al., 1997; Xiang et al., 2002; Cheng et al., 2004; Yu et al., 2004; Xiang et al., 2004). Therefore carbonation reactions can be influenced by the surfactants in terms of crystal size, shape and types of polymorphs. That aspect in carbonation reactions may be an advantage in consolidation treatments with $Ca(OH)_2$ nanodispersion for the control of carbonation reactions products. In this study, the influence of surfactants on the calcite formation during the carbonation was examined by adding 0.025 g of sodium stearate to 1000 ml calcium hydroxide nanodispersion. The formation and the texture of calcite crystals with and without sodium stearate were investigated by SEM.

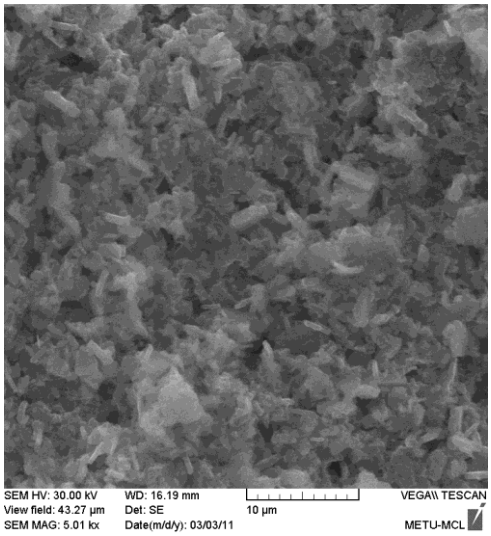

Figure 8. SEM view of crystals carbonated from a calcium hydroxide nanodispersion without any additives.

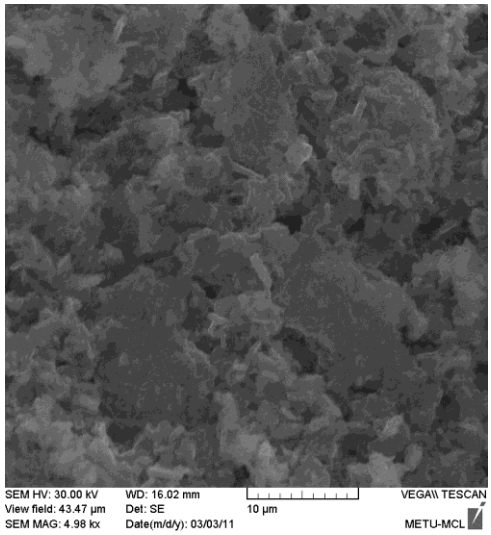

Figure 9. SEM view of larger sized crystal agglomerates carbonated from calcium hydroxide nanodispersion with sodium stearate (0.025 g/L).

The addition of sodium stearate did not change the shape of calcite crystals but the size of the precipitated calcite crystals were increased (as shown in Figures 8-9). Increase of calcite crystal size with the addition of sodium stearate was in agreement with the studies of Ukrainczyk et al. (2009).

Addition of sodium stearate in low concentrations (0.025 g/l) to the calcium hydroxide nanodispersion did not affect the stability of nanodispersion (as shown in Figure 10).

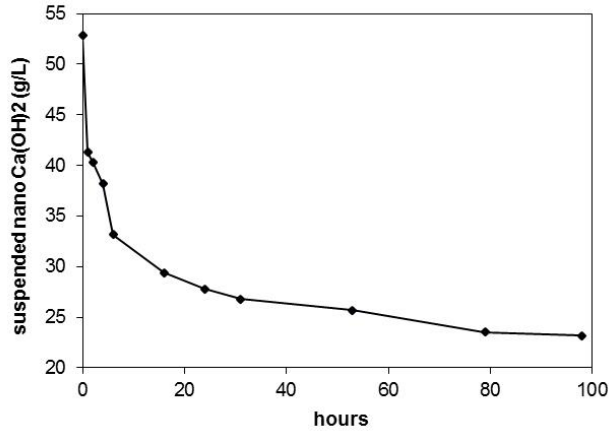

Figure 8. Suspended nano $Ca(OH)_2$ particles (g/L) in time in the sodium stearate added calcium hydroxide nanodispersion.

It was also observed that addition of sodium stearate did not significantly affect the concentration of suspended calcium hydroxide nano particles during the 98 hours of follow up (as shown in Figure 10).

4. CONCLUSIONS

There is a need to prepare stable and concentrated calcium hydroxide nanodispersion for the consolidation of deteriorated archaeological calcareous stones. In this study with the proposed method, the concentration of suspended $Ca(OH)_2$ nanodispersion in ethyl alcohol was about 31g/l after 16 hours of its preparation and about 22.9 g/l after the end of 4 days. The prepared $Ca(OH)_2$ nanodispersion in ethyl alcohol have successfully penetrated into the fine cracks of marbles down to 4-6 µm sizes. Effective carbonation of the nanodispersion can be obtained at high relative humidity (RH: 90%) and under an atmosphere rich in CO_2 (5%). In those conditions, at the end of three days, carbonation was substantial (66%-75%) but not yet complete. Since carbonation of $Ca(OH)_2$ is an irreversible reaction, it will eventually be completed at high relative humidity conditions.

Reaction product of carbonation was found to be mainly calcite. The use of surfactants such as sodium stearate has influence on the crystal size of calcite particles. Since the use of surfactants affect the crystal size, shape and types of polymorphs in carbonation reactions, it can be further studied for the manipulation of carbonation reaction products during the consolidation studies with $Ca(OH)_2$ nanodispersions.

Consolidation treatments with $Ca(OH)_2$ nanodispersions similar to the one prepared in this study can be used for all archaeological calcareous stones that need improvements in their physical and mechanical properties.

ACKNOWLEDGEMENT

Authors would like to acknowledge the support provided to Materials Conservation Laboratory through the EU FP7 Project:-MonumentsLab-206710 that have made this study possible.

REFERENCES

Ambrossi M, Dei L, Giorgi, R, Neto C, Baglioni P. (2001) Colloidal Particles of Ca(OH)$_2$ Properties and Applications to Restoration of Frescoes, *Langmuir*, Vol. 17, pp.4251-4255.

Angwal K. (1983) *Elementary Crystal Growth*, Lublin: Saan Publ.,, pp. 83-176.

Berner RA, Morse JW. (1974) Dissolution kinetics of calcium carbonate in sea water IV. Theory of calcite dissolution. *Am. Jour. Sci.*, Vol.274, pp.108-134.

Black CA, (1965) *Methods of Soil Analysis*, Part 2, American Society of Agronomy, Wisconsin, U.S.A., Madison; 1965, pp. 999-1010.

Caner EN, Seeley NJ. (1979) Dissolution and precipitation of limestone, *Deterioramento e Conservazione della Pietra Fondazione Giorgio Cini*, Venezia, p. 107-129.

Cheng B, Lei M, Yu J, Zhao X. (2004) Preaperation of monodispersed cubic calcium carbonate particles via precipitation reaction, *J Materials Letters,* Vol.58, pp.1565-1570.

Cölfen H. (2003) Precipitation of carbonates: recent progress in controlled production of complex shapes, *J Current Opinion in Colloid and Interface Science,* Vol.8, pp.23-31.

Daniele, V., Taglieri, G. (2012) Synthesis of Ca(OH)2 nanoparticles with the addition of Triton X-100. Protective treatments on natural stones: Preliminary results, *Journal of Cultural Heritage*, Vol.13(1), pp.40–46.

Dei L, Salvadori B. (2006) Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay, *J Cultural Heritage*, 7:110-115.

Feng B, Yong KA, An H. (2007) Effect of various factors on the particle size of calcium carbonate formed in a precipitation process, *Material Science and Engineering,* Vol. A: 445-446, pp.170-179

Fitzner B, Heinrichs K, Kownatzki R. (1995) Weathering Forms-Classification and Mapping. In: Verwitterungsformen-Klassifizierung und Kartierung-Denkmalpflege und Naturwissenschaft, Natursteinkonservierung I, Förderprojekt des Bundesministeriums für Bildung, *Wissenschaft, Forschung und Technologie*, Berlin: Verlag Ernst & Sohn, p. 41-88.

Giorgi R, Dei L, Baglioni P. (2000) A new method for consolidating wall paintings based on dispersion of lime in alcohol. *J Studies in Conservation*, Vol.45, pp.154-161.

Kirchgessner DA, Lorrain JM. (1987) Lignosulfonate-modified calcium hydroxide for sulfur dioxide control, *Ind. Eng. Chem. Res.*, Vol.26, pp.2397-2400.

Kitamura M, Konnob H, Yasuia A, Masuokaa H. (2002) Controlling factors and mechanism of reactive crystallization of calcium carbonate polymorphs from calcium hydroxide suspensions, *J Crystal Growth,* Vol.236, pp.323-332

Koutsoukos PG, Orkoula M, Kanellopoulou D, Kontoyannis CG. (2001) Understanding marble deterioration at a microscobic level, *Proceedings of Eurocare Euromarble*, Vienna, pp. 75-88.

Lopez-Acre P, Gomez-Villalba LS, Pinhp L, Fernandez-Valle ME, Alvarez de Buergo M, Fort R.(2010) Influence of porosity and relative humidity on consolidation of dolostone with calcium hydroxide nanoparticles, Effectiveness assessment with non-destructive techniques, *Material Characterization*, Vol.61, pp.168-184.

Manoudis, P.N, Gemenetzis, D and Karapanagiotis, I (2017) A comparative study of the wetting properties of a superhydrophobic siloxane material and rose petal. *SCIENTIFIC CULTURE*, Vol. 3, No 2, pp. 7-12 (DOI:10.5281/zenodo.438182)

Morse JW, Arvidson RS. (2002) The dissolution kinetics of major sedimentary carbonate minerals, *Earth Science Reviews* Vol.58, pp.51-84.

Otero, J, Charola, A. E., Grissom, C.A. and Starinieri, V. (2017). An overview of nanolime as a consolidation method for calcareous substrates, *Ge-conservación*, Vol.1 (11), pp.71-78.

Perdikatsis V. (1996) Quantitative analysis by X-ray diffraction and calculated curves for binary mineral mixtures. In: Petros G Koutsoukos, Christos G Kontoyannis editors, *Eurocare Euromarble Proceedings*, Patras-Greece, p.128-136.

Price C., Ross K., White G. (1988) A Further Appraisal of the 'Lime Technique' for Limestone Consolidation, Using a Radioactive Tracer, Studies in Conservation, Vol.33(4), pp.178-186

Salama, K Kholod, Mona F.Ali, Said M. El-Sheikh (2018) The different influence of nano-materials on pigments. SCIENTIFIC CULTURE, Vol.4, No.3, 1-17.

Samanta, A., et al., (2016) Synthesis of nano calcium hydroxide in aqueous medium, *Journal American Ceramic Society*, Vol. 795 (37004), pp.787–795.

Sasse HR, Snethlage R. (1997) Methods for the Evaluation of Stone Conservation Treatments. In: N.R. Baer and R. Snethlage, editors. *Saving our Architectural Heritage*. Berlin: John Wiley & Sons, p. 223-243.

Seo K, Hana C, Weeb J, Parkc J, Ahnc J. (2005) Synthesis of calcium carbonate in a pure ethanol and aqueous ethanol solution as the solvent, *J Crystal Growth*, pp.680-687

Simon S, Snethlage R. (1992) The First Stages of Marble Weathering, Preliminary Results After Short-Term Exposure of Nine Months, *Proceedings of Eurocare-Euromarble*, Göteborg, pp. 37-44.

Smith LB, Paloczi GT, Hansma KP, Levine PR. (2000) Discerning nature's mechanisms for making complex biocomposite crystals, *J Crystal Growth*, Vol. 211, pp.116-121.

Taglieri, G., et al. (2015) A new and original method to produce $Ca(OH)_2$ nanoparticles by using an anion exchange resin, *Advances in Nanoparticles*, Vol. 4, pp.17–24.

Teutonico JM (rapporteur), Charola AE, De Witte E, Grassegger G, Koestler RJ, Tabasso ML, Sasse HR, Snethlage R. (1997) Group Report*:* How can we ensure the responsible and effective use of treatments (cleaning, consolidation, protection)? In: N.S. Baer and R. Snethlage, editors. *Saving Our Architectural Heritage: The Conservation of Historic Stone Structures*, Dahlem Workshop Report ES20, New York: Chichester, Wiley, p. 293–313.

Tiano P, Cantisani E, Sutherland I, Paget JM. (2006) Biomediated reinforcement of weathered calcareous stones, *J Cultural Heritage,* Vol.7, pp.49-55.

Tran HV, Tran LD, Vu HD, Thai H. (2010) Facile surface modification of nanoprecipitated calcium carbonate by adsorption of sodium strearate in aqueous solution, *J Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol.366, pp.95-103.

Ukrainczyk M, Kontrec J, Kralj D. (2009) Precipitation of different calcite crystal morphologies in the presence of sodium stearate, *J Colloid and Interface Science,* Vol.329, pp.89-96.

Wei SH, Mahuli SK, Agnihotri R, Fan LS. (1997) High Surface Area Calcium Carbonate: Pore Structural Properties and Sulfation Characteristics, *Ind. Eng. Chem. Res.*, Vol.36, pp.2141-2148.

Wendler E, (1997) New materials and Approaches for the conservation of stone, In: N.R. Baer and R. Snethlage, editors. *Saving Our Cultural Heritage*. Berlin: John Wiley & Sons, p. 181-196.

Xiang L, Xiang Y, Wang ZG, Jin Y. (2002) Influence of chemical additives on the formation of super-fine calcium carbonate, *J Powder Technology*, Vol.126, pp.129-133.

Xiang L, Xiang Y, Wen F, Wei F. (2004) Formation of $CaCO_3$ nanoparticles in the presence of terpineol, *J Materials Letters*, Vol.58, pp.959-965.

Yu J, Lei M, Cheng B, Zhao X. (2004) Facile preparation of calcium carbonate particles with unusual morphologies by precipitation reaction, *Journal of Crystal Growth,* Vol.261, pp.566-570.