INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE
ISSN: 2067-533X Volume 11, Issue 2, April-June 2020: 531-538 www.ijcs.ro

HANDY AND SUSTAINABLE METHOD OF NANO-$Ca(OH)_2$ SYNTHESIS USED IN CONSERVATION AND CONSOLIDATION WORKS

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Abstract

The heritage conservation always remains a scientific and complex task. Either used for preservation of cellulose-based artifacts or as limestone consolidant, the nano-$Ca(OH)_2$ is often associated with its carbonation process. The use of waste materials for nano-$Ca(OH)_2$ synthesis transforms the entire process into a handy and sustainable one. Within this study, the calcium hydroxide nanoparticles have been synthesized from eggshell wastes through the precipitation method. For this purpose the raw eggshells were washed for organic traces removal and disolved in concentrated HCl solution to form $CaCl_2$. The nano-$Ca(OH)_2$ was obtained by adding into the chemical reaction media a solution of NaOH, the white precipitate being afterwards dried at 100°C for two hours. The synthesized nanoparticles were characterized by X-Ray fluorescence (XRF), scanning electron microscope (SEM), X-Ray diffraction (XRD), thermal analyses (DTA-TG) and laser granulometry using as comparative specimen a commercial calcium hydroxide. The granulometer analyses showed that the particle size of the obtained nano-$Ca(OH)_2$ was in the range 10 – 150nm, these results being also confirmed by SEM images.

Keywords*: Nano-$Ca(OH)_2$; Eggshell wastes; Consolidation works; granulometer analyses*

Introduction

Solid waste management is now a challenge for a sustainable world, the huge amounts of wastes generated worldwide leading to public health and environment related problems. The eggshells wastes have an important contribution to the environmental degradation, due to their landfill or incineration [1]. A targeted goal for the eggshells use is the synthesis of green calcium hydroxide nanoparticles, which may be a valuable candidate for the conservation and consolidation of historical monuments [2, 3].

The typical composition of historic mortars and plasters consists of hydraulic lime and calcium sulphate and the conservation of historical buildings, sculptures or even wall paintings require materials which are compatible with the components used for the original construction. It means that the used materials should not interfere and therefore change the specific properties of the historical monument in terms of porosity, stability or retreatability. However, many materials used nowadays (e.g. polymeric organic materials) are not suitable for this action, causing even additional damages [4-6].

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In order to eliminate these restraints, calcium hydroxide nanoparticles can be synthesised and used as an alternative to the traditional lime, considering that the nanosized particles allows a faster carbonation at the contact with the atmospheric air. Moreover, the advanced properties of nanolime consisting of nanometric dimensions and high specific surface area at volume ratios facilitate the infiltration into the damaged zones regardless of their dimensions [7, 8].

The application of nanotechnology to the conservation of architectural heritage gained a high interest in recent years [9], and different methods of calcium hydroxide nanoparticles synthesis have been developed for conservation purposes [10-12]. A type of green calcium hydroxide nanoparticles was reported by *M.D. Khana et al.* [2]. They synthesized nanolime plates from oyster shells wastes in an aqueous medium without using any additive or extreme experimental conditions. The as-synthesised nanoparticles had similar characteristics with those conventionally obtained with hazardous chemicals or polymeric agents.

Regarding the green development of calcium hydroxide nanoparticles there is a lack of scientific data which leads to the necessity of new researches in order to identify suitable solid wastes with adequate compositions, which can be further used for heritage conservation. Therefore, in this study, eggshells derived from agroindustrial waste has been used to obtain nano-$Ca(OH)_2$ whose advanced properties are so appreciated in conservation activities, also contributing to reducing the environmental impact.

Experimental

Materials

In order to obtain nano-$Ca(OH)_2$, pure chemical regeants were used, namely hydrochloric acid with 9 – 14% concentration and sodium hydroxide 10 - 15M, as well as the eggshell wastes. Additionaly, to compare the obtained results, commercial hydrated lime (CHL) was used. The eggshells' chemical composition and that of the CHL was determined by X-ray fluorescence (XRF), using a RIGAKU SUPERMINI spectrometer, the results being presented in Table 1. As it can be observed the XRF results highlight the advantage of using eggshells as precursor for $Ca(OH)_2$ obtaining, since its CaO content (95.7%) is comparative with that of the CHL (96.43%), increasing thus their recovery potential.

Table 1. The eggshells and CHL chemical composition

Materials	Chemical composition [% by mass]									
	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	BaO	Fe_2O_3
Eggshell	1.61	0.51	0.62	0.96	0.40	0.11	95.7	-	-	0.09
Nano-$Ca(OH)_2$	0.44	-	1.38	0,43	-	-	96.1	-	1.5	0.14
CHL	1.43	0.24	0.78	0.17	0.06	0.04	96.43	0.44	-	0.41

Synthesis of nano-$Ca(OH)_2$

The synthesis of $Ca(OH)_2$ nanoparticle by precipitation method was carried out in three stages. Thus, in the first stage it was pursued to obtain the concentrated solution of $CaCl_2$ by dissolving solid $CaCO_3$ in HCl as shown in Equation 1. For this purpose the eggshells were washed to eliminate the organic residues, dried and crumbled so that the solubilisation process with 9% of HCl solution to be carried out more accurate.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_2\uparrow + H_2O_{(l)} \quad (1)$$

The $CaCO_3$ dissolution kinetic depends on the solution pH, thus during this chemical process the pH value was ranged beween 2 and 4 (strong acid – s.a. and week acid – w.a.).

When the total amount of $CaCO_3$ was dissolved, the $CaCl_2$ solution was filtered under vacuum to remove the inner membranes of the eggshells.

The second stage debuts with the preparation of NaOH 12M solution used for $Ca(OH)_2$ precipitation, as can be seen in Equation 2.

$$CaCl_{2(aq)} + 2NaOH_{(aq)} \rightarrow Ca(OH)_{2(s)} + 2NaCl_{(aq)} \quad (2)$$

The NaOH solution was added in low ammounts to enable a low rate of nucleation, preventing thus the sudden formation and in large quantity of $Ca(OH)_2$. The resulted precipitate was filtered under vacuum and washed with distilled water in excess to remove the NaCl and potential traces of reagents. Afterwards the translucent precipitate was dried in oven at 100°C for two hours transforming it in a very fine and silky white powder with a total amount of CaO of 96.1% (Table 1).

In the third stage, the silky white powder was characterized and compared with CHL in terms of chemical and microstructural particularities.

The chemical and microstructural characterization of nano-$Ca(OH)_2$

The nano-$Ca(OH)_2$ characterization was performed by using a full range of techniques available for an accurate qualitative and quantitative determination of their intrinsec microstructural features. Thus, the particle-size distribution was determined for both nano-$Ca(OH)_2$ powders (*s.a.* and *w.a.*), as well as for CHL for comparison, by using a laser particle sizer, ANALYSETTE 22 NanoTec from FRITSCH, with measuring range of 0.01 – 2100μm in the wet dispersion unit. Since calcium hydroxide is not soluble in ethanol, ethanol/nano-$Ca(OH)_2$ and ethanol/CHL suspensions were prepared to prevent agglomeration and to obtain more accurate representations.

The crystalinity and phase identification was determined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, with a step of 0.02grade/min. The mass changes of the samples and the thermal changes which occur during heating were investigated by thermal analysis (DTA - TG), using a NETZSCH STA-TG analyzer. The powder samples were heated up to 1000°C, at a rate of 10°C/min in nitrogen atmosphere. The morphology of both nano-$Ca(OH)_2$ s.a. and CHL powders, was investigated by scanning electron microscopy (SEM) using a HITACHI SU 70 microscope.

Results and discussion

Since the $Ca(OH)_2$ nanoparticles represent an effective conservation material for the consolidation of stone, mortars and plasters present in old masonry and/or mural paintings, regardless of the synthesis route or the material from which it starts, is necessary to obtain nanometric sizes. Thus, the results of the particle-size distribution, determined for $Ca(OH)_2$ powders synthetised within this work as well as for the CHL are presented in Figure 1.

As it can be observed the powder obtained by using strong acidified solution (Fig. 1a) has most of the grain sizes ranging between 10 – 100nm. However, the distribution also presents population of grains with particle diameters ranging between 100nm – 4μm, which represent the fine particles of $Ca(OH)_2$ agglomerated in clusters. A higher pH of $CaCl_2$ solution determines an increase of $Ca(OH)_2$ grain sizes so that the diameter of the powder obtained by precipitation from weak acid solution ranges between 50nm – 10μm (Fig. 1b). This variation is similar to that of the commercial hydrated lime (Fig. 1c).

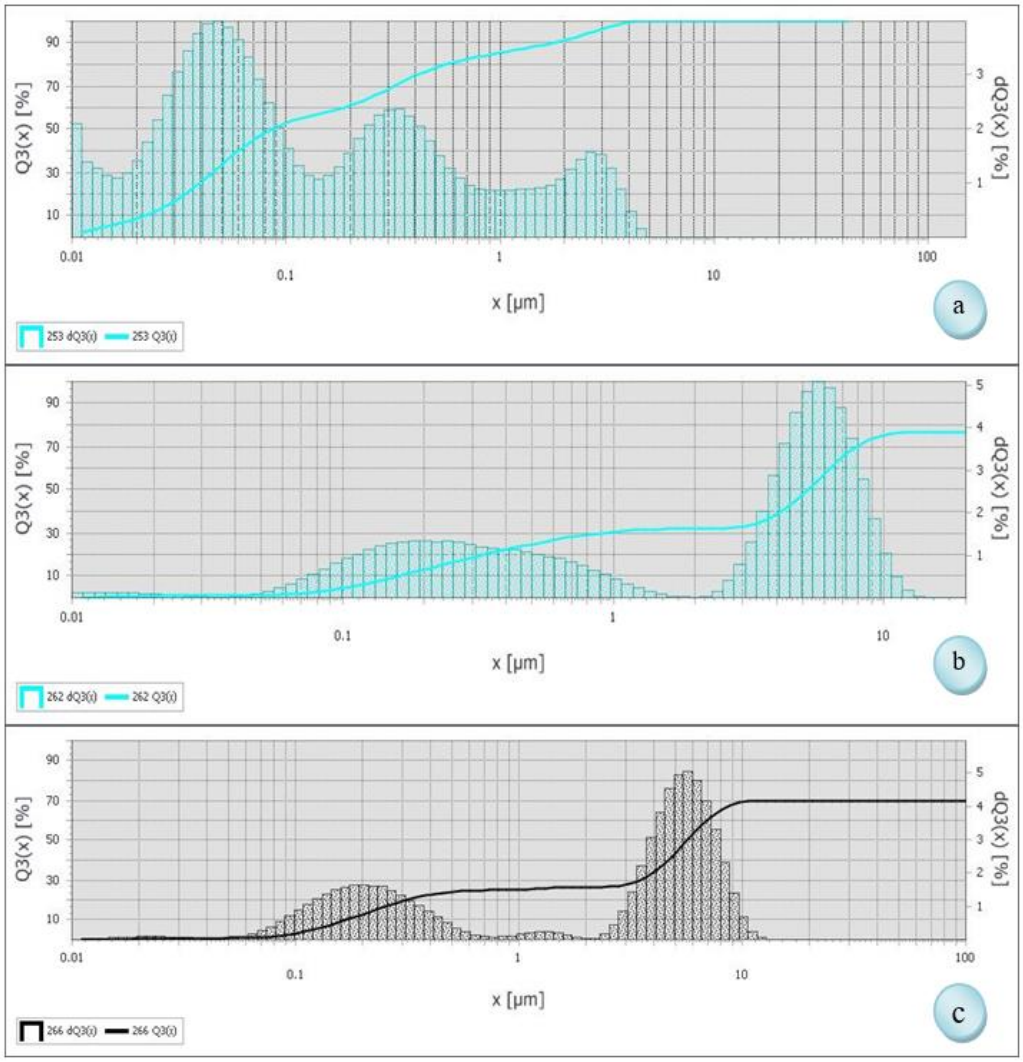

Fig. 1 Particle-size distribution of nano-$Ca(OH)_2$ synthetised from strong acid media (a), week acid media (b) and comercial hydrated lime (c)

Figure 2 depicts the XRD patterns of synthesized calcium hydroxide $Ca(OH)_2$, from both strong and weak acidified solutions, dried at 100°C. The XRD patterns show well-defined peaks at 2θ = 18°, 29°, 34°, 47°, 50° and 54° typical of $Ca(OH)_2$.

Although the XRD patterns highlight an obvious similitude in terms of chemical composition, there are some small diffrences among peaks intensities indicating the nanometre scale of $Ca(OH)_2$. In order to determine the crystallite size of nano-$Ca(OH)_2$, the Scherrer equation was used, as it is usually most effective for crystallite sizes of 200 nm or less: $D = (k \times \lambda)/(FWHM \times \cos \theta)$, where D is the crystallite size, k is the shape constant, FWHM is the full width at half intensity of the diffraction peak and θ is the Bragg angle. The shape constant is typically = 1.24 for FWHM of crystals with hexagonal symmetry [13]. Thus, for the $Ca(OH)_2$

obtained from strong acidified solution the calculated crystallite size was 12nm while for that obtained from weak acid solutions the crystallite' dimension was 17nm.

The complex thermal analyzes results performed on the precipitated calcium hydroxide from the two solutions with different pH are shown in figure 3.

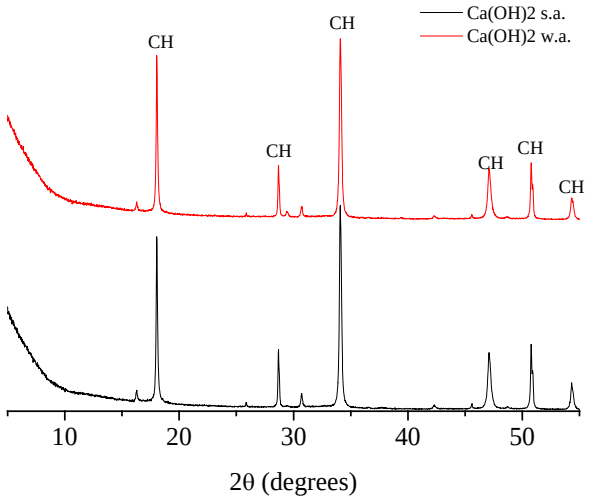

Fig. 2 XRD patterns of $Ca(OH)_2$ obtained from both strong and weak acidified solutions

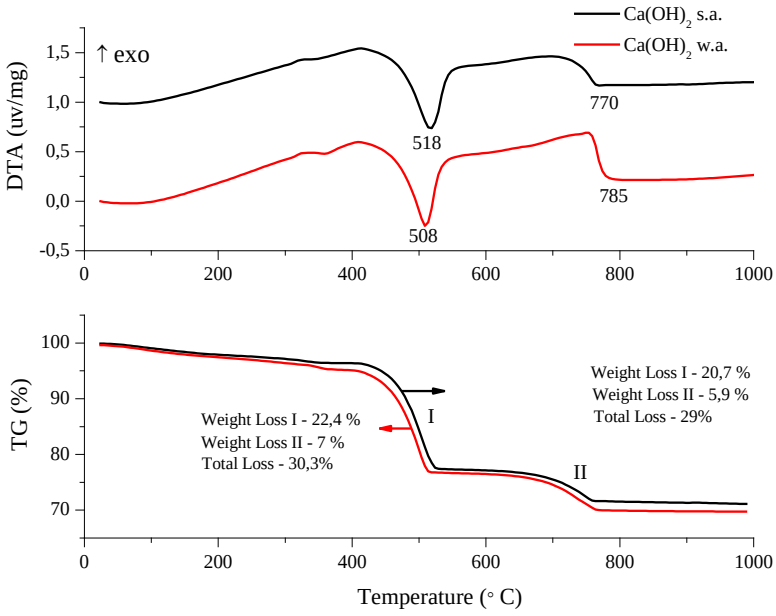

Fig. 3 DTA / TG curves of $Ca(OH)_2$ obtained by precipitation from strong acid medium ($Ca(OH)_2$ s.a.) and weak acid medium ($Ca(OH)_2$ w.a.)

There are two endothermic effects emphasized by the DTA curves for both powders, recorded at T = 508ºC and T = 518ºC, correlated with $Ca(OH)_2$ dehydroxylation, a process to which it corresponds a mass loss of 22.4% and 20.7% respectivelly. The decomposition temperature of pure $Ca(OH)_2$ is 512ºC, therefore the differences between this value and those experimentally recorded could be explained by the presence of minor impurities. The endothermic effect recorded around 800ºC (at T = 770ºC and T = 785ºC) coresponds to the CaO syntering, when the analysed powders lose 6 – 7% of the total mass. This behavior is similar to that observed by *Mirghiasi et. al.* [14] when preparing CaO nanoparticles from $Ca(OH)_2$ by direct thermal decomposition method.

In order to study the $Ca(OH)_2$ morphology and dimensions, SEM analyses were performed on $Ca(OH)_2$ s.a. and for comparison the CHL was also investigated, the results being presented in figure 4.

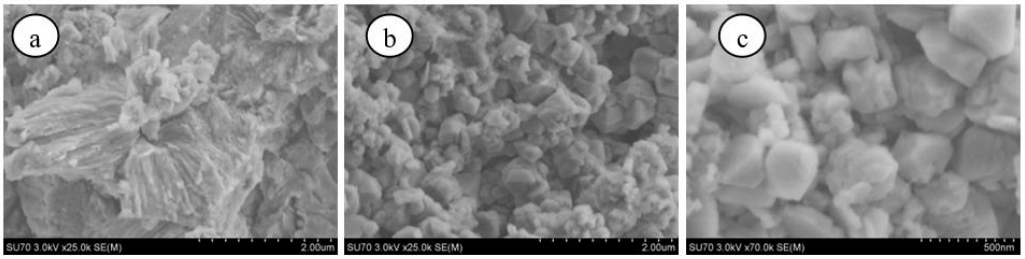

Fig. 4 SEM images of CHL (a) and $Ca(OH)_2$ obtained by eggshells valorisation from strong acidified solution (b and c)

The CHL's morphology highlights irregular and fibrous-looking crystalline formations (Fig. 4a) while for the same magnification (2μm) the SEM images of the obtained $Ca(OH)_2$ underline overlapped hexagonally and regularly shaped particles with dimensions lower then 500nm (Fig. 4b and c), which could be due to the reaction time for the formation of $Ca(OH)_2$. The SEM images are in good agreement with the particle size analysis, these determinations confirming the obtaining of nano-$Ca(OH)_2$, which is a valuable component involved in conservation works.

Conclusions

Nano-$Ca(OH)_2$ was synthetised by a simple and handy method starting from the eggshell wastes. The subsequent investigations were conducted so that the synthesized $Ca(OH)_2$ powders to be compared with a comercial hydrated lime obtained by classical routes, in terms of chemical composition, particle-size distribution and crystals morphology.

The XRD patterns showed the existence of main $Ca(OH)_2$ interferences, with slightly differences between the two obtained powders in terms of peaks intensity. The DTA-TG curves presented two endothermic effects corresponding to $Ca(OH)_2$ dihydroxylation and CaO syntering with a total mass loss ranging between 26.6 – 29.4%.

The particle size analyses correlated with the SEM images demonstrated the nanometric sizes of the obtained powders with hexagonal and regular shaped particles characteristic to the $Ca(OH)_2$ crystals, embeded in clusters.

Acknowledgements

This work was financially supported by the Romanian Ministry of Education and Research through the Core Program, contract number 39N/2019, within PN 19 43 05 01 project, *Innovative ecological materials such as nanostructured materials and inorganic binders, with applicability in environmental protection*.

References

[1] Gy. Deák, A.M. Panait, M.A. Moncea, F.D. Dumitru, M. Boboc, M. Matei, M.V. Olteanu, *Influence of water to binder ratio on mechanical properties of blended cements with brick powder waste*, **AIP Conference Proceedings**, **2129**, 2019, p. 020091.

[2] M. Khana, J. Ahnb, G. Namb, *Environmental benign synthesis, characterization and mechanism studies of green calcium hydroxide nano-plates derived from waste oyster shells*, **Journal of Environmental Management**, **223**, 2018, pp. 947-951.

[3] L. Habte, N. Shiferaw, D. Mulatu, T. Thenepalli, R. Chilakala, J. Ahn, *Synthesis of nano-Calcium Oxide from waste eggshell by sol-gel method*, **Sustainability**, **11**, 2019, p. 3196.

[4] A. Daehne, C. Herm, *Calcium hydroxide nanosols for the consolidation of porous building materials - results from EU-STONECORE*, **Heritage Science**, **11**, 2013, https://doi.org/10.1186/2050-7445-1-11.

[5] E. Carretti, D. Chelazzi, G. Rocchigiani, P. Baglioni, G. Poggi, L. Dei, *Interactions between nanostructured calcium hydroxide and acrylate copolymers: implications in cultural heritage conservation*, ***Langmuir***, **29**, 2013, p. 9881−9890.

[6] G. Ziegenblag, K. Brummer, J. Pianski, „*Nano-lime - a new material for the consolidation and conservation of historic mortars*," **HMC2010 Conference Proceedings** , RILEM TC 203-RHM, 2010, pp. 1301-1309.

[7] V. Daniele, G. Taglieri, R. Quaresima, *The nanolimes in cultural heritage conservation: Characterisation and analisys of the carbonatation process*, **Journal of Cultural Heritage**, **9**, 2008, pp. 294-301.

[8] M. El Bakkari, V. Bindiganavile, Y. Boluk, *Facile synthesis of calcium hydroxide nanoparticles onto TEMPO oxidized cellulose nanofibers for heritage conservation*," **ACS Omega**, **4**, 2019, p. 20606−20611.

[9] E. Semenzin, E. Giubilato, E. Badetti, M. Picone, A. Volpi Ghirardini, D. Hristozov, A. Brunelli, A. Marcomini, *Guiding the development of sustainable nano-enabled products for the conservation of works of art: proposal for a framework implementing the safe by design concept*, **Environmental Science and Pollution Research** , **26**, 2019, pp. 26146–26158.

[10] A. Arizzi, L. Gomez-Villalba, P. Lopez-Arce, G. Cultrone, R. Fort, *Lime mortar consolidation with nanostructured calcium hydroxide dispersions: the efficacy of different consolidating products for heritage conservation*, **European Journal of Mineralogy**, **27**, 2015, p. 311–323.

[11] N. T. Ali, R. K. Abrahim, H. F. Saad, N. K. Jabr, S. S. Hindal, D. R. Hussain, A. M. Sekp, *Synthesis of calcium hydroxide for heritage conservation*, **Journal of Physics Conference Series** , **1234**, 2019, p. 012021.

[12] A.M. Panait, M.A. Moncea, F.D. Dumitru, Gy. Deak, *Method of obtaining the calcium hydroxide nanopowder by recycling the eggshells wastes derived from agroindustrial activities*, **Romanian Official Bulletin of Industrial Property**, A/00226, 2020, p. 44.

[13] W.H. Qi, M.P. Wang, Q.H. Liu, *Shape factor of nonspherical nanoparticles*, **Journal of Materials Science**, **40**, 2005, pp. 2737–2739.
[14] Z. Mirghiasi, F. Bakhtiari, E. Darezereshki, E. Esmaeilzadeh, *Preparation and characterization of CaO nanoparticles from $Ca(OH)_2$ by direct thermal decomposition method*, **Journal of Industrial and Engineering Chemistry, 20**, 2014, pp. 113-117.

Received: April 10, 2019
Accepted: May 12, 2020