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SYNTHESIS AND CHARACTERIZATION OF AN ECO-FRIENDLY MATERIAL FOR STONE MONUMENTS PREZERVATION STARTING FROM THE EGGSHELLS

György DEÁK[1], Mihaela-Andreea MONCEA[1*], Ion SANDU[1,2,3,4], Mădălina BOBOC[1], Florina-Diana DUMITRU[1], Gina GHIȚĂ[1], Ioan Gabriel SANDU[4,5*]

[1] National Institute for Research and Development in Environmental Protection, 294 Splaiul Independentei, District 6, 060031 Bucharest, Romania;
[2]Academy of Romanian Scientists (AOSR), 54 Splaiul Independentei St., Sect. 5, 050094 Bucharest, Romania;
[3]Alexandru Ioan Cuza University, Institute of Interdisciplinary Research, 22 Carol I Blvd., 700506 Iasi, Romania;
[4] Romanian Inventors Forum, 3 Sf. P. Movila Street, Bloc L11, Sc. A, III/3, 700089 Iasi, Romania;
[5] Gheorghe Asachi Technical University of Iași, Faculty of Materials Science and Engineering, 41 Dumitru Mangeron Blvd., 700050, Iasi, Romania;

Abstract

Conservation and restoration of heritage structures represents a highlighted issue, the main challenge being to bring the cultural objective to its original state, or as close as possible to it by using eco-friendly materials with lover impact on the environment and human health. Within this study, the calcium zincate nanoparticles have been synthesized starting from the eggshels 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 $Ca(Zn(OH)_3)_2 \bullet 2H_2O$ was obtained by adding into the chemical reaction media a solution of zinc acetate dihydrate previously dissolved in 100mL of methanol under vigorous stirring at room temperature and precipitating with NaOH 12M solution. The white precipitate was characterized by field emmision scanning electron microscope (SEM), X-Ray diffraction (XRD) and thermal analyses (DTA-TG). The Scherrer equation result showed the nanometric size of calcium zincate crystallite, about 23nm.

Keywords*: Calcium zincate; Eggshell wastes; Consolidation; Preservation works*

Introduction

Conservation and restoration of heritage structures represent a topical issue, the diagnosis of building pathology and proper consolidation measures adoption to reinstate the initial sound condition of the system being fundamental actions. The most important link in all this conservation and restoration chain is represented by materials.

Eighter is about cleaning materials (a wide palette of natural materials, edible ingredients or ash and rudimental soaps up to most recently, nanomaterials which have revolutionized the cleaning of works of art) [1-3], or advanced materials for consolidation of cultural heritage (which display a significant worsening of their mechanical properties as a result of flaking and powdering of pictorial layers, blistering, delamination, and cracks in mortars, stones, and cements) [4, 5] or materials for surface protection (nanosized materials, such as nanoparticles of titanium dioxide, silver and zinc oxide, have been explored over the years to hinder microbial colonization on

* Corresponding authors: moncea.andreea@gmail.com and gisandu@yahoo.com

heritage substrate materials) [6, 7], the main challenge is to bring the cultural objective to its original state, or as close as possible to it by using eco-friendly materials that endanger the environment as little as possible.

In recent years, nano calcium hydroxide finds its potential applications in conservation and restoration of heritage structures due to its properties (quick transformation of lime into calcium carbonate) [8-14]. In other works the use of zinc hydroxide dihydrate, $Ca[Zn(OH)_3]_2\times2H_2O$ as a material for the limestone protection against biodeterioration caused by fungi was studied. The ideea started from combining the compatibility of $Ca(OH)_2$ and the antifungal activity of ZnO or Zn^{2+} ions in one material [15-17]. In the present study calcium zincate powder was synthesized for surface treatment of limestone monuments by using a simple and novel methods starting from the eggshells wastes. In order to obtain the accurate results, the chemical and microstructural characterization of calcium zincate was performed by using X-ray diffraction, thermal analysis and field emission scanning electron microscopy.

Experimental part

Materials

In order to obtain $Ca(Zn(OH)_3)_2\cdot2H_2O$, pure chemical regeants were used, namely hydrochloric acid, 9% concentration, sodium hydroxide solution of 12M, zinc acetate dehydrate, methanol as well as the eggshell wastes. The eggshells' chemical composition was determined by X-ray fluorescence (XRF), using a RIGAKU SUPERMINI spectrometer, the results being presented in Table 1. As can be observed the XRF results highlight the advantage of using eggshells as precursor for $Ca(Zn(OH)_3)_2\cdot2H_2O$ obtaining, since its CaO content is 96%.

Table 1. The chemical composition of materials determined by XRF analyses

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

Synthesis of nano - $Ca(Zn(OH)_3)_2\times2H_2O$

The synthesis of $Ca(Zn(OH)_3)_2\cdot2H_2O$ nanoparticle was carried out in two steps. The first step assumed the eggshell dissolving in 9% HCl solution 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 to be carry more rappid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2\uparrow + H_2O(l) \quad (1)$$

The $CaCO_3$ dissolution kinetic depends on the solution pH, thus during the solubilisation process its value was keeept constant at 2. When the eggshell powder was completelley dissolved the $CaCl_2$ solution was filtered under vacuum to remove the organic membranes. In the second step 12g of zinc acetate dihydrate ($Zn(Ac)_2\cdot2H_2O$) were dissolved in 100mL of methanol under vigorous stirring at room temperature and atmospheric pressure, a clear and transparent solution being obtained. This solution was mixed with 100mL of $CaCl_2$ sollution by vigourous stirring for 1 hour. Meanwhile, a NaOH 12M solution used forward for precipitation, was prepared and added in dropwise to enable a low rate of nucleation, preventing thus the sudden formation and in large quantity of $Ca(Zn(OH)_3)_2\cdot2H_2O$. The resulted wihte precipitate was filtered under vacuum and washed with excess of distilled water:alcohol, 1:1 volumetric report, in order to remove the secondary reaction products. Afterwards the white precipitate was dried in oven at 100ºC for two hours transforming it in a very fine and silky powder, which were forward characterized in terms of chemical and microstructural particularities.

The chemical and microstructural characterization of calcium zincate

The $Ca(Zn(OH)_3)_2 \times 2H_2O$ characterization was performed by using a full range of available techniques for accurate analysis. The mineralogy determination and crystalinity degree was carried by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, with step of 0.02 grade/min. The mass changes of the powdered sample and the thermal effects which occur in the temperature range 22 – 1000ºC were investigated by thermal analysis (DTA - TG), using a NETZSCH STA-TG analyzer. The powder samples were heated up to 1000ºC, at a rate of 10ºC/min in nitrogen atmosphere. The morphology of calcium zincate powder was investigated by field emission scanning electron microscopy (FE-SEM) coupled with Energy dispersive X-ray (EDS) spectroscopy using a HITACHI SU 70 microscope.

Results and discussion

In figure 1 is presented the X-ray diffractometry (XRD) spectrum of calcium zincate powder obtained under the above presented experimental conditions.

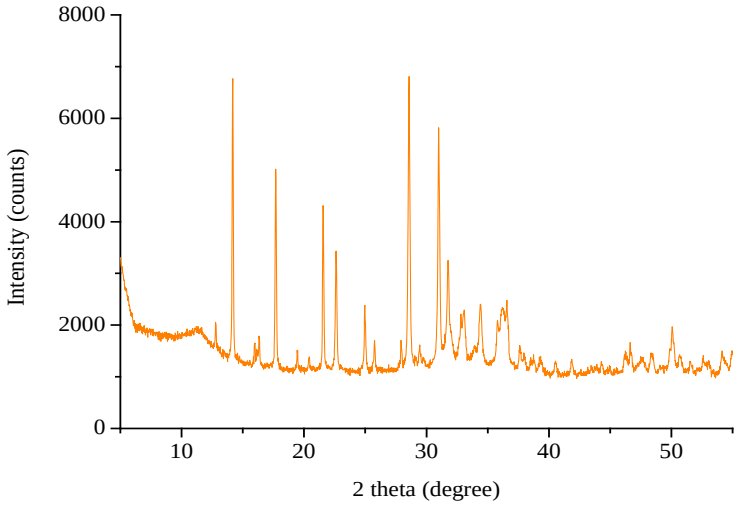

Fig. 1. XRD patterns of calcium zincate crystals

As can be observed the calcium zincates were indexed as main phase, monoclinic crystal system, (space group P21/c with a = 6.3840Å, b = 10.9770Å, c = 5.7560Å, α = 90.0000Å, β = 78.0200Å, γ = 90.0000Å) at specific interferences of 2θ = 14.28, 17.7, 21.63, 22.63, 25.05, 28.53, 31.07, 31.79, 34.42 and 50.14, similar results being presented in the literature [18]. The XRD peaks are characterized by high intensity and narrow line width being an indicative of the good crystallinity of the synthesized calcium zincates particles. The crystallite size was determined from the diffraction patterns by using the Scherrer equation:

$$D = (k \times \lambda) \cdot (FWHM \times \cos\theta)^{-1} \quad (1)$$

in which 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 [19]. The shape constant used in the equation was 1.49, which was the value recommended for tetrahedral particles [20]. Based on equation (1) the average crystallite size for calcium zincate particles was established for the 6 most intense peaks corresponding to the XRD spectra, as it can be seen in table 2.

Table 2. Crystallite sizes for the obtained calcium zincate particles

2θ, degrees	Crystalite size	
	D, (nm)	D avarage, (nm)
14.28	22.87	22.31
17.67	31.72	
21.63	23.93	
22.63	19.45	
28.53	19.40	
31.07	16.46	

The results presented in table highlight the nanometric size of the obtained calcium zincate with an average crystallite size of 22nm.

Figure 2 shows the thermogravimetric analysis results of calcium zincate sample.

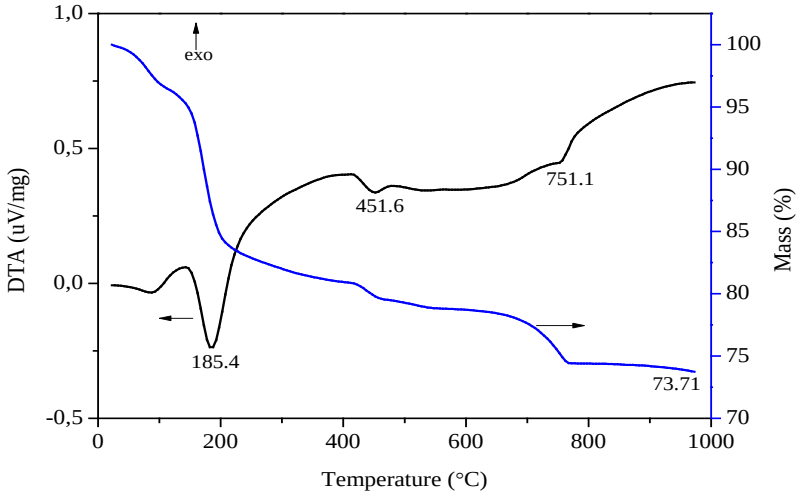

Fig. 2. Thermogravimetric analysis of calcium zincate sample

On DTA-TG curves of the sample, can be observed three endothermic peaks at about 185, 450 and 750ºC. The steep TGA weight loss (aprox. 15%) between 130 and 180°C and the endothermic DTA transition at the same temperature corresponds to dehydration of $Zn(OH)_2$ to form ZnO [21]. The endothermic effects emphasized by the DTA curve recorded at T = 451ºC is associated with $Ca(OH)_2$ dehydroxylation, ($Ca(OH)_2 \rightarrow CaO+H_2O$), a process to which it corresponds a mass loss of 3.3%. The third endothermic effect recorded around 800ºC (at T = 751ºC) coresponds to the CaO syntering, when the analysed powders lose about 5% of the total mass. This behavior is similar to that observed in paper [8] when preparing $Ca(OH)_2$ nanoparticles starting from the eggshells. The residual mass at the end of thermal treatment was around 74%.

In order to study the calcium zincate morphology, FE-SEM analyses cupled with EDS were performed the results being presented in figures 3, 4 and 5.

The FE-SEM images highlight formation of thin crystals of calcium zincate in tetragonal shape [22-26], one of them overlaped (Fig. 3a and b), which after the thermal treatment at 1000ºC they get a melted appearance (with rounded edges) due to the syntering process (Fig. 3c and d).

The EDS spectrum together with the elemental maps confirms all the other presented analysis by evidencing the presence of Ca and Zn as main elements in the analysed powdered sample.

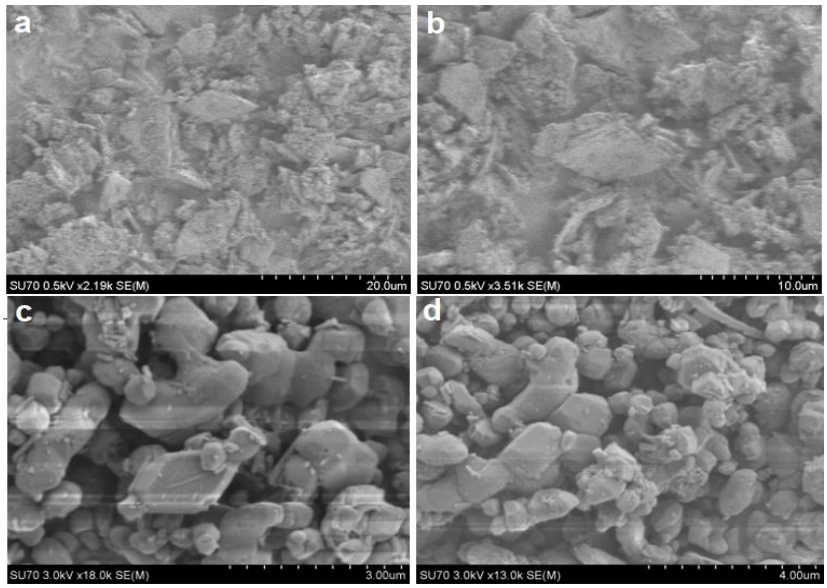

Fig. 3. FE-SEM images of raw calcium zincate sample (a and b) and after the thermal treatment at 1000ºC respectively (c and d)

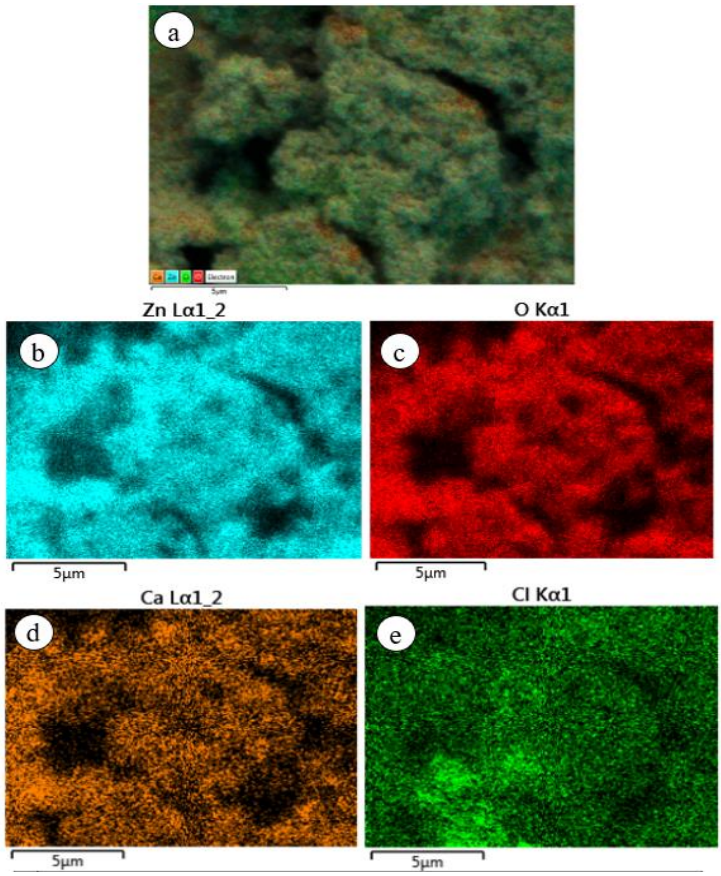

Fig. 4. The elemental maping of calcium zincate samples

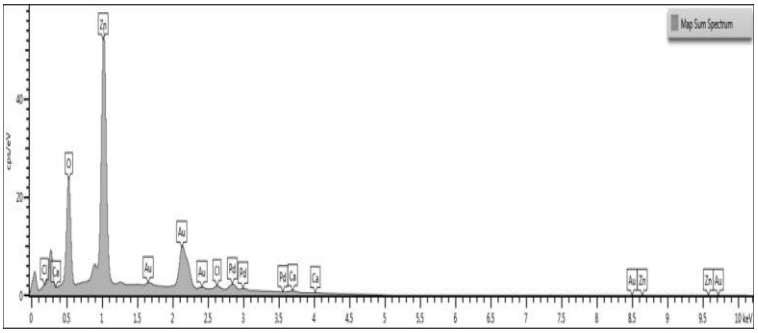

Fig. 5. The EDS spectrum

Conclusions

Calcium zincate, used in preservation works of limestone monuments, was synthetised by precipitation method starting from the eggshell wastes and zinc acetate. The subsequent researches showed its formation so thus the simple synthesis routes by using ecological materials represents a novelty in the field. The XRD pattern showed the existence of main calcium zincate interferences, with very intens and sharp peaks and the Scherrer equation results showed the nanometric size of calcium zincate crystallite. The DTA-TG curves presented three endothermic effects corresponding to dehydration of $Zn(OH)_2$ to form ZnO, $Ca(OH)_2$ dihydroxylation and CaO sintering with a total mass loss of 24%. The FE-SEM images highlight formation of thin crystals of calcium zincate in tetragonal shape and the EDS spectrum together with the elemental maps confirms the presence of Ca and Zn as main elements in the analysed powdered sample.

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