Applied Surface Science 358 (2015) 612–618

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Caoxite-hydroxyapatite composition as consolidating material for the chalk stone from Basarabi–Murfatlar churches ensemble

Rodica-Mariana Ion[a,b,*], Daniela Turcanu-Caruţiu[c], Radu-Claudiu Fierăscu[a], Irina Fierăscu[a], Ioana-Raluca Bunghez[a], Mihaela-Lucia Ion[d], Sofia Teodorescu[e], Gabriel Vasilievici[a], Valentin Rădiţoiu[a]

[a] ICECHIM-Bucharest, 202 Splaiul Independentei, 060021 Bucharest, Romania
[b] Valahia University, Faculty of Materials Engineering and Mechanics, 18-20 Blv. Unirii, 13200 Targoviste, Dambovita County, Romania
[c] Ovidius University, Art Faculty, 124 Blvd. Mamaia, 900527 Constanţa, Constanţa County, Romania
[d] Valahia University, History Faculty, Carol I Blvd. no.2, 13200 Targoviste, Dambovita County, Romania
[e] Multidisciplinary Scientific and Technologic Research Institute, "Valahia" University of Targoviste, Carol I Blvd. no.2, 13200 Targoviste, Dambovita County, Romania

ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form 6 August 2015
Accepted 24 August 2015
Available online 28 August 2015

Keywords:
Chalk stone
Caoxite-hydroxyapatite
Accelerated weathering tests
Freeze–thaw
Porosity

ABSTRACT

The development of new composition for surface conservation of some architectural monuments represents now an important research topic. The Basarabi–Murfatlar Ensemble, recognized as the first religious monument from mediaeval Dobrogea (Romania) (from 9th to 11th century), is one of the most impressive archaeological sites of Europe. This ensemble is built from amorphous calcium carbonate, very sensitive to humidity, frost, salts, etc. The aim of this paper is to test on chalk stone samples a new consolidant – hydroxyapatite (HAp) mixed with calcium oxalate trihydrate (caoxite) (COT). Some specific techniques for evaluation its impact on chalk stone surface are used, as follows: petrographical and physical–chemical techniques: SEM, OM, ICP-AES, TGA, FTIR and Raman spectroscopy, chromatic parameters changes, the accelerated weathering tests: heating, freeze–thaw, and their effects on porosity and capillary water uptake by the chalk surface. All these have been evaluated before and after treatment with COT-HAp, putting into evidence the effect of the new composition on the chalk stone surface. HAp induces COT stabilization, and their joint composition can bind weathered stone blocks providing a substantial reinforcement of chalk surface.

1. Introduction

Basarabi–Murfatlar Churches Ensemble is a unique religious monument from mediaeval Dobrudja (from 9th to 11th century), located in the South-East part of Romania, very close to Black Sea [1]. This ensemble is built from amorphous calcium carbonate and very sensitive to external environmental factors: air pollutants, light, temperature changes, humidity and water leak, all these being responsible for its damages. The first research on its conservation was started in the 70-ties of the 20th century, guided by the necessity of the safeguarding of this monument, but without significant results; now the monument is in a state of advanced decay, and new materials and conservation procedures are absolutely necessary for further preservation [2].

It is well known that some inorganic materials, as calcium hydroxide Ca $(OH)_2$, magnesium hydroxide $Mg(OH)_2$, hydroxyapatite (HAp), have already been used as consolidants for different damaged carbonate stones [3–7]. Calcium hydroxide has been used as nanoparticles (130–300 nm) dispersed in alcohols, as nanosols (50–250 nanometres), as "paste-like" in ethanol, and as calcium hydroxide microparticles (1–3 micrometres) (CaLoSiLW-Micro). But, regardless of the form in which is found, due to their low porosity, high moisture content of the substrate, over-saturation of the material and quick evaporation of the solvent, calcium hydroxide is not an optimal option for this monument [8]. That is why it is important to find another optimal materials. Lime-based consolidants, such as lime milk and limewater, introduce lime ($Ca(OH)_2$) inside the pores of the stone. As $Ca(OH)_2$ reacts with atmospheric carbonic dioxide (CO_2), calcium carbonate ($CaCO_3$) is produced and could bond to stone grains and strengthen the stone. But, lime-based treatment has some limitations, such as the reduced penetration

* Corresponding author at: ICECHIM-Bucharest, 202 Splaiul Independentei, 060021 Bucharest, Romania.
E-mail addresses: rodica_ion2000@yahoo.co.uk (R.-M. Ion), d_turcanu2002@yahoo.com (D. Turcanu-Caruţiu), mihaella_ion@yahoo.com (M.-L. Ion), sofiateodorescu@yahoo.com (S. Teodorescu).

http://dx.doi.org/10.1016/j.apsusc.2015.08.196
0169-4332/