PRE-RESTORATION INVESTIGATIONS OF THE BASARABI CHALK MONUMENT DIAGNOSIS, TREATMENT AND IMPLICATIONS

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Abstract

This paper will sumarize several important aspects of the material research of chalk stone monument that is affected by various weathering/decay processes. Diagnosis of materials on monument should offer the necessary informations about the nature (genesis, composition) of materials and their states - intact and/or altered state. Detection of the major damage processes located on the studied monument can elucidate what are the factors contributing to the damage. Depending of the above results, will be established the managing restoration steps: selection of methodology of research, sampling strategy, analytical procedures and the time issue. Atmospheric pollution and acid deposition materials are recognized as the most important and common causes of decay the heritage monuments. Studies on chemical-mineralogical-physical changes in Basarabi chalk monument caused by weathering will also make a part of the paper. Discovered on 1957, the Basarabi – chalk church is one of the most impressive archaeological sites of Europe, consisting of churches dated from $9^{th} - 11^{th}$ century. Situated in the cliff of a chalk stone hill, this church is built from amorphous calcium carbonate and is very sensitive to humidity, frost, salts etc. The studies called 'pre-restoration material investigation' is in fact, 'in-between two interventions' - past one and future one. Only our deep understanding of these changes, together with recent material properties and their possible future development can make the material investigation of stone monuments a strong tool that improves the restoration itself.

Keywords: Basarabi Church, chalk stone, restoration, consolidation

Introduction

Building materials on the surface of architectural monuments are prone to degradation phenomena, aesthetic, and functional. Historical monuments suffer various forms of degradation, the most common being:

a) detachment of plaster or masonry substrates wall decorations. Causes detachment supported are: capillary moisture infiltration combined with migration and crystallization of salts, improper works on architecture structure, vibrations caused by blasting, traffic.

b) Cracks in the substrate, corresponding dislocations facing and contraction cracks as a fine network of cracks, due to the contraction of unsuitable materials introduced into the original substrate, technical flaws, the inadequate restoration (refurbishment) [12].

c) Migration and crystallization of salts in the plaster layer, the phenomenon of Freezethaw, air pollution in the presence of humidity and temperature variations, technical defects may result to a friable mortar, resulting in a powdery surface of the plaster, not resistant to mechanical action. d) deposits adhering impurities (dust, smoke, soot, cobwebs - and adhesion (smoke, tar, bird droppings), due to air pollution, improper maintenance of the monument.

e) soluble efflorescence, poorly soluble or insoluble - are due salts (nitrate, sulfate, chloride, carbonate) which crystallizes in certain conditions of temperature and humidity on architectural surfaces.

f) degradations due to the action of microorganisms that thrive in conditions of microclimate: humidity, temperature, light, air pollution.

In order to evaluate all the effects of the application of any used consolidant, changes in the chemical and physical properties (e.g. strength, porosity, liquid-water and water-vapor transport, and hygroscopicity) of the substrate must be determined. This involves the depth of penetration, material-strength profile and the concentration profile of the consolidant. Also, the changes that appear (e.g. whitening and added gloss) should also be quantified. Never the less, the historic transformation of the historical building is essential and for this is necessary the diagnostic procedures and protocols used on the investigated buildings.

In this paper, some important aspects about the diagnostics on materials involved in the architectural restoration are analyzed. The materials microstructure as: consolidating value, depth of penetration, effect on appearance, compatibility of consolidant with substrate, durability of treatment, effect on liquid water and vapor permeability, biological resistance, ease of application and health and safety issues, are discussed for Basarabi Chalk Church in particular. Causes of stone deterioration, mechanisms, characterization of building materials, in terms chemical and mineralogical composition, the physical, chemical and mechanical properties, have been studied in this paper. Also, the composition will be decelated by petrographic analysis, and analytical techniques: X-ray diffraction (XRD), thermal analysis, scaning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR) and energy-dispersive X-ray fluorescence (EDXRF). The materials compatibility restoration conservation of the monument will be made by techniques such as zoom microscopy, SEM, relative kinetic stability. Mechanical properties as compressive strength and capillary water uptake test, have been evaluated and discussed, comparing the model-smaples with chalk samples, treated as shown above.

Experimental part

Specimens samples preparation

The samples prelevated from Basarabi Church (samples collected from the exterior of the monument, without any value for this church. Samples were obtained by taking a minimum part of the archaeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. Being detached from the Church's wall, all the samples, have the same constitution as the wall and the same composition.

Consolidants

Nanosuspension of $Ca(OH)_2$ dispersed in ethanol, is synthesized in the lab (Ion, 2010). By comparison, has been used CaLoSiL E25 composed of lime nanoparticles suspended in alcohol [15, 16,17]. It is supplied as CaLoSiL E25 consisting of 25g particles per litre of ethanol. Each type of mortar substrates was treated by three different consolidants.

Application of consolidants

The application of all types of consolidant was carried out by immersion. After the each cycle the all samples were covered for one day by a slightly opened cover to avoid quick evaporation of solvent. Next day the cover was removed and the specimens were exposed to

laboratory conditions to get dry. The following application cycle was done when the specimens became completely dry.

Characterization techniques

The samples were analyzed by using the following techniques:

Ion Chromatography, performed on a DIONEX DX-500 Chromatograph, was used to identify the soluble salts as cations and anions present in the samples. The eluent was sodium carbonate and sodium bicarbonate with a flow rate of 2 ml/min, and a 4 mm column for the separation of anions.

The diffraction analysis has been carried out in a DRON UM1 diffractometer using an iron filter for the CoK_{α} radiation (1.79021Å) and also, with a XRD, Philips Diffractometer PW 1840, 40kV/20mA, Cu K α radiation).

DSC was performed on a Metter-Toledo Instrument DSC 823^{e} . Samples (1-2 mg) were loaded into sealed aluminum pans with lids and heated to 600° C at a heating rate of 10° C min ⁻¹ in oxygen flux (100 ml min ⁻¹).

X-ray fluorescence analysis was performed with an energy dispersive instrument, EDXRF PW4025, type Minipal- Panalytical, with a Si(Li)-detector of 150 eV resolution at 5.89 keV (Mn-Ka-line). A Rh-tube with an acceleration voltage of 50 kV and a primary filter of Pd with 0.05mm thickness were used for excitation.

For evaluating the effectiveness of the consolidating treatments, the **relative kinetic stability** of the dispersion of nanomaterials, was defined as ξ , which is calculated using eq.1 [18].

The particles size and theirs size distribution have been measured by **Dynamic Light Scattering** (DLS) technique.

Scanning electron microscopy (SEM) produces high resolution images of a sample surface. The Quanta 200 Scanning Electron Microscope (SEM) was used to produce enlarged images of a variety of specimens, achieving magnifications of over 100000x providing high resolution imaging in a digital format.

Atomic force microscopy (AFM) investigations were carried out with an Agilent 5500 SPM system, described by PicoSPM controlled by a MAC Mode module and interfaced with a PicoScan controller from Agilent Technologies, Tempe, AZ, USA (formally Molecular Imaging). The original images for the samples, the 3D topographical images and section analysis over the articles were performed using the PicoView SPM Software, version 1.6.2, Molecular Imaging. Height image data obtained by the AFM is three-dimensional.

The conservation efficiency of the consolidant was estimated:

- by compressive strength, with Silver Schmidt Hammer L, with a compressive range 5-30 N/mm^2 and 0.735 Nmm impact energy (EN 12 504-2).

- by capillary water uptake tests, determined according to the method according to EN ISO 15148 .

Results and discussion

Historical aspects

The assembly is part of a career "of Roman", a cliff named Tibişir hill on the outskirts of Murfatlar (Basarabi), 20 km far from Constanta. The rock, chalk, amorphous calcium carbonate, almost pure, soft, with high porosity, very hygroscopic and capillary. During the massive extraction operation from career, were excavated several chapels (small churches), vaults, etc. branched galleries. The first chappel has been discovered, on June 11, 1957, in the works of opening a contemporary rock mining. The new operation was stopped and follow work archaeological research. Thus, a whole set of religious cave came to light, after being released by sterile deposits of chalk, various concentrations and soil accumulated over approximately in a millennium.

The main causes of degradation are :

- Water accumulation, before 1977 to 2007, due to the defects of the old temporary buildings, frequent freeze-thaw sequences lead to fragmentation (disintegration) masses of rock and degradation surfaces, the composition of the causes of pathology is essentially reduced in 2006, the rehabilitation of temporary protective structure.

- Crystallization of salts has a similar, somewhat to that of frost: crystal formation is a huge mechanical force and break porous structure of the rock when the humidity is reduced and salts are solid, moisture variation alternative sequences are basically the same harmful as variations in temperature around the freezing point.

This component causes pathology is essentially reduced in 2006, the rehabilitation of temporary protective structure, but are essentially required for degradation of existing symptomatic treatments and developing.

- Soluble salts and crystalline certainly come from the masses of concrete made the structural system in the years 1960-1977, when these phenomena incompatibility does not appear to have been known. We study methods to stop these potentially harmful chemicals, and flow control them through masses of chalk and surfaces.

- Other salts come under investigations already carried out, the waters of Lake the nearby soil, the main source being the "mountain of garbage " located in near which, stupidly, increases very day.

- Proliferation of massive biological gone, after decomposition, the accumulation of the nitrate salts which are also crystalline and are soluble and regress solid after rehabilitation (the "unhealthy" conducive to such bodies changed, and largely left alone without waiting for treatment biocides).

In conclusion, it is essential for the future of environmental control, and treatment existing damages at all stages, as in medicine: emergency treatment causally symptomatic background maintenance.

Stone characterization

Stone materials are characterized by a mineral-inorganic nature, and by hydrophilic properties, both these aspects being very important when choosing the treatments for their conservation. Two main causes for stone deterioration have to be mentioned: acid attack (caused by rains and humidity condense in polluted urban atmospheres) and soluble salts cyclic crystallization [1]. The first mechanism (acids) induces corrosion to carbonatic materials such as calcium and/or magnesium carbonates based stones while silicatic stones are only poorly affected. The second mechanism (salts) is mainly active towards porous stones, independently of their nature. Also, important is the effect on low porosity stones. This is important for the consolidation of natural stone such as limestone, marble or sandstone as well as for mortar and plaster [2].

It should take into acount that decay agents can reach the surface both from outside (acid attack and salts deposits) and inside (soluble salts), in case of porous materials [3,4].

Some studies on environmental influences on degradation stone monuments, considering the factors such as temperature (average, minimum, maximum), number of days of frost and sunny days, humidity annual average rainfall amount and chemical composition, currents air, will be evaluated, too, knowing that carbonates have been detected as the predominant in the body of the church with sulphates impurities [5].

Usually, calcium carbonate is occurring as limestone, chalk and biomaterials. It is known that some nonaqueous dispersions of calcium, barium or magnesium hydroxide nanoparticles started to be tested and used as new possible consolidants for calcareous material [19]. Gypsum is, as lime, one of the important component used as binder alone or together with lime for the production of plaster and mortars [20, 21]. In order to evaluate the

efficiency of the new treatment method, based on nanomaterials, first of all the characteristics of the substrates and chalk wall, have been evaluated.

Many literature sources rank magnesium sulfate among the most damaging salts. [4,5]

The alteration of stone is a natural and irreversible process. Crystallization of soluble salts in the construction materials, is considered today one of the most important decay process. These soluble salts induce the rock fabric, when efflorescence appear, especially, and induce crystallization within the pores causing the stone damage. All the damage processes from the stone surface is due to high level of sulphates, chlorides, nitrates, detected by ion chromatography and Ca, Na, K and Mg. Deterioration of mortar can be rarely attributed to the presence of only one salt. The most abundant salts are chlorides, sulphates or nitrates, of calcium, sodium, potassium, magnesium and sometimes also ammonium kations. Source of chlorides are usually deicing agents, nitrates are of organic origin. Sulphates are usually rising from groundwater but may be also a product of calcium carbonate corrosion reaction with sulphur oxides. Nitrates and sulphates can be also product of an action of some bacteria.

By ICP-MS all the metals constituents of the chalk sample, have been identified, Table 1.

Metal	Concentration (ppm)	Metal	Concentration (ppm)
Ti	75.19	Cu	42.69
Sr	857.69	K	2600
Ba	136.92	Al	8100
Mn	272.115	Fe	4800
Bi	191.69	Mg	2300
Sn	152.115	Na	8600
Si	14400	Li	34.61
Ca	241200	Zr	10.77

Table 1. The metal composition of the chalk stone sample.

Divalent metal ions of similar ionic radius as Ca^{2+} may be incorporated as impurities into calcite during mineral precipitation. In agreement with the literature data, these results indicate the presence of Sr, which is favouring the calcite stability by precipitation/adsorption of SrCO₃ and the dissolution of CaCO₃ is occurring at these sites [25]. On the other hand, Gutjahr and co-workers have shown that Sr^{2+} causes a significant reduction in the growth and dissolution rates of aragonite. This was attributed to reversible adsorption of Sr^{2+} ions at growth sites (kinks) [26]. Cu^{2+} and Zn^{2+} could form soluble oxides and carbonated over the calcite surface, [27].

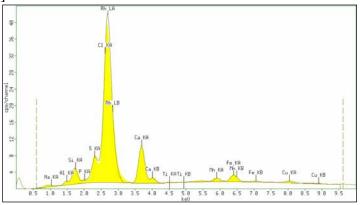


Figure 1. EDXRF spectrum of the chalk sample

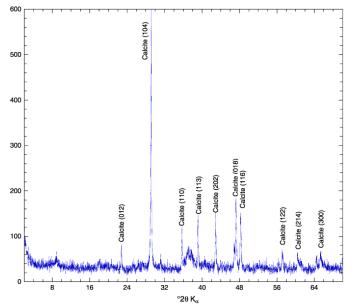


Figure 2. XRD of calcite

Magnesium sulfate tends to precipitate within a wider crystallization front and in pores of different size, while sodium sulfate is mainly concentrated close to the surface and in large pores. The goal of the DSC experiments was to determine the composition of the salt mixture that forms by drying a magnesium sulfate solution. [6-8]. By DSC techniques is important to detect the soluble salts arising from the degradation, because the soluble salts are usually hydrated, so they undergo changes at low temperatures, less than 100 $^{\rm O}$ C. Is important to identify them by DSC techniques, so: CaSO₄ • 2H₂O, KNO₃, Mg(SO₄)₂, NaSO₄. If we compare the temperatures corresponding to the minimum of the peaks in DSC curves for each sample with the data listed in Table 1, we can see that CaSO₄ • 2H₂O is present in all type of deteriorated materials; KNO₃ is always present in salt efflorescences and scarcely in patinas and crusts. Hydrous or anhydrous Mg and Na sulphates are also frequent. Hence, the most abundant anions are nitrates and sulphates and cations are Ca, Na, K and Mg.

Soluble salts	Temperature (⁰ C)			
	Dehydration	Phase transition	Melting point	Decomposition point
$CaSO_4 \bullet 2H_2O$	143			
Na ₂ SO ₄		257		
$Na_2SO_4 \bullet 10H_2O$	40	251		
K ₂ SO ₄		583		
MgSO ₄		352		
$MgSO_4 \bullet 7H2O$				
$MgSO_4 \bullet 6H2O$				
MgSO ₄ • H2O	76	345		
$(NH_4)_2SO_4$		355	505	
NaNO ₃			275	308
KNO ₃		133	334	
NH ₄ NO ₃				267
$Mg(NO_3)_2 \bullet 6H_2O$	93			423
$Ca(NO_3) \bullet 4H_2O$	49			549

Table 1. Decomposition temperature of the salts which appear as products of the monumental rocks degradation

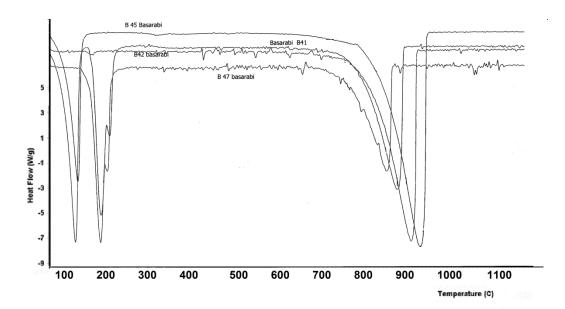


Figure 3. The DSC diagrammes for different church walls (left ordonate, mg; right ordonate, mg/Celsius degree). [B41 = stone dislocated from inside West wall; B42 = wall efflorescence dislocated from the inside wall surface; B45 = wall sample from inside East wall; B47 = dust from the dome surface]

Efflorescence is well known as the unsightly white deposits or stains that sometimes appear on the surfaces of concrete or brickwork on buildings. Three categorites of efflorescence are known: Lime bloom, Lime weeping, Crystallization of soluble salts.

Primary efflorescence observed with lime bloom and lime weeping refers to uniform calcite deposits $CaCO_3$ arising from transport of calcium hydroxide $Ca(OH)_2$ in solution through capillaries within the structure to the external surface. The solution evaporates and leaves behind deposits of solid white calcium hydroxide. These in turn react with atmospheric carbon dioxide CO_2 to form white deposits of calcite, the normal end product. Secondary efflorescence arises where water penetrates the surfaces and dissolves soluble calcium salts in a basically patchy way. The main chemical reaction is the same as that in primary efflorescence, namely conversion of calcium hydroxide to calcite. Secondary efflorescence originates from reaction in solution, usually caused by rain or condensation, whereas primary efflorescence is caused by evaporation leaving behind the deposited salts.

Consolidation options

Nanotechnology applied to building materials represents an example of how innovation increasingly combines dematerialization, eco- efficiency and knowledge-based approach to develop new classes of products – often substitute of conventional technologies – with the aim of opening new market sectors based on the paradigm of the green high-tech.

Recent innovations in construction materials driven by nanotechnologies application are based on the design of material properties in order to obtain the required performances, developing sophisticated transformation processes that allow to realize custom-fit products for specific architectural applications. The development of "designable" materials and components marked the evolution of architectural languages, evolving from a "muscular" exhibition of technology (typical of the "high-tech" architecture of the past decades) to a widespread microinnovation not always visible to the naked eye. Historically, limestone objects, lime-based renders and wall paintings have been treated with solutions that resulted ultimately in the deposition of calcium carbonate. A saturated solution of calcium hydroxide in water (often referred to as 'limewater') was one of the earliest treatments for building materials and was well documented in the classical literature by authors such as Vitruvius (c. 70-25 BC) [Vitruvius, 1970].

Calcium hydroxide readily reacts to form calcium carbonate when exposed to atmospheric carbon dioxide under moist conditions. The rate and extent of carbonation may vary, prompting attempts to hasten or supplement the transformation of the calcium hydroxide. For chalk consolidation, calcium hydroxide has been used, due to theie similarities of the lattice parameters, Table 2.

Table 2. Lattice parameters of calculateria and calculateria indication involved [42, 14]Mineral a (Å) b (Å) c (Å)			
Calcite	9.98	9.98	33.82
Calcium hydroxide	12.59	29.27	20.34

Table 2: Lattice parameters of calcite and calcium hydroxide [42, 14]

However, a humid environment and a higher and larger porosity of the stone favour the consolidation with time, being these conditions necessary to take into account when Ca(OH)₂ nanoparticles are used to consolidate carbonate stones [46].

First of all, we determined the relative kinetic stability for every type of nanomaterial. Despite the fact that calcium hydroxide has a bigger size (408.9 nm, determined by DLS), it has a good kinetic stability followed by hydroxyapatite with a very small size (30 nm) and its mixture with calcium hydroxide, Figures 8-10.

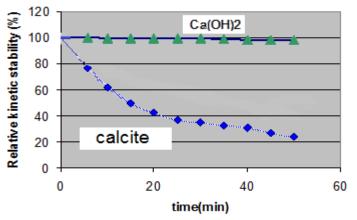


Figure 8. The relative kinetic stability of nanomaterials

Optical and Scanning electron microscopy research was performed to investigate microstructure characteristic of the specimens. Special attention was paid to the effectiveness of consolidation treatment observable namely in the pores and cracks. It is mostly the size of pore openings and the chemical/ mineralogical nature of the pore walls which are of relevance to the treatment by consolidant.

The nanoparticles of Ca(OH)₂ have been synthesized as previously reported [47, 48].

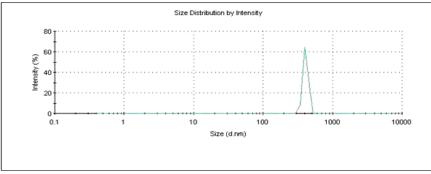
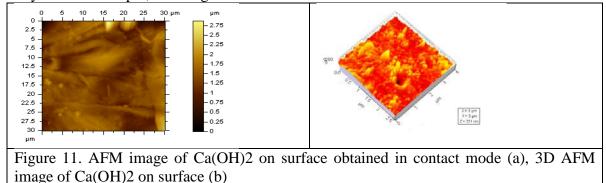
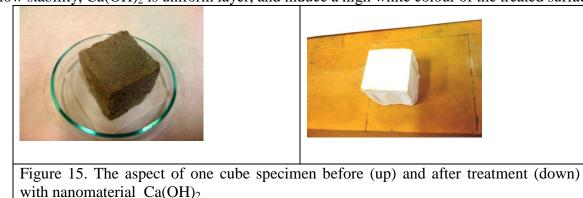


Figure 9. Size distribution for Ca(OH)₂ nanoparticles dispersed in 2-propanol

Besides detail structural features AFM can provide important information on surface forces (adhesion, friction, electrostatic, van der Waals, etc). By spraying on a cubic piece, less white deposits of Ca(OH)₂, although the same concentration and the same volume of suspension has been applied on the same type of stone. AFM revealed a rough surface architecture for HAp, the predominant size of grains being in the range of 90-100nm. The light part of the image can be the consequence of the presence of a thick part of sizing material, possibly to an aggregate form [49, 50]. For Ca(OH)₂ a higher magnified of 5000x has been used to provide a great depth field and to aid to morphological and topographical analysis of the sample, as in Figures 11.



Three specimens of cube shape (4x4x4 cm3) of each type of substrate were used for measurement. Before testing, all samples were dried up to constant weight at 80 °C in a drying chamber for 24 hours. After the drying process the substrates were left to get cold for two hours in a dessicator and their aspect was measured, Figure . Despite of its relatively low stability, Ca(OH)₂ is uniform layer, and induce a high white colour of the treated surface.



For the model-samples, the compressive strength determined with Silver-Schmidt Hammer, indicated that the most effective treated sample has a compressive strength of 40 MPa and is that treated with Ca(OH)₂. In the case of Ca(OH)₂, we have to take into acount the non-uniform thickness of the consolidant, due to the aggregation tendency of Ca(OH)₂. For chalk samples, the values are bigger, but the order is the same, most probably due to the inhomogeneity of the chalk strone. The drilling resistance measurement system is measuring the penetration force versus depth and can detect fluctuations in the drilling resistance with depth, attributed to non-homogeneities in the material (sedimentation layers, different grain size and resistance, micro and macro cracks). The results are shown in Table 3.

Sample	Treatment	Drilling resistance	Compressive strength
		Mean (N)	(Silver Schmidt) (MPa)
		(10 mm)	(5 mm)
Model-sample	Not treated	6.2±1.73	11±4.0
	Ca(OH) ₂	9.63±2.31	13.33±3
Chalk sample	Not treated	13.19±1.83	20±3.2
	Ca(OH) ₂	6.18±2.52	40±2.3

Table 3. Drilling resistance tests for the studied samples

For chalk samples, the treatment with $Ca(OH)_2$ do not cause any increase in cohesion, rather a decrease. In this case we should take into account the considerable moisture that characterizes the area, which lowered the average value of drilling resistance of this area. The capillary water uptake of the test blocks is decreased after the treatment with consolidants, concluding that the treatment makes the stone samples more compact and less permeable to water, Table 4. Low capillary action can protect the stone against erosion by water and soluble salts or bases [53]. The area treated with $Ca(OH)_2$ shows an absorption capacity similar to the untreated zone. A possible explanation of this behaviour is the inhomogeneity of the chalk.

Table 4. Water absorption tests for samples

Sample	Treatment	Water absorbed (cc/cm ² s)
Sample model	Not treated	2.87±0.09
	Ca(OH) ₂	2.53±0.08
Chalk sample	Not treated	2.22±0.10
	Ca(OH) ₂	2.25±0.22

Conclusion

In this paper has been treated the structural, morphological and compositional aspects of chalk stone sample prelevated from Basarabi Chalk Church (Romania), for which a new method based on nanoparticles Ca(OH)₂:HAp has been tested.

A complex collection of petrographic (stereozoom microscopy) and analytical techniques ((Dynamic Light Scattering (DLS), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Energy-dispersed X-ray fluorescence (EDXRF), ion chromatography, thermal analysis, X-ray diffraction (XRD), relative kinetic stability parameter (ξ), have been used in order to identify the major constituents of chalk stone (metals, anions, type of calcium carbonate), the influence of environmental salts (MgSO₄ • 7H₂O and MgSO₄ • 6H₂O, Na₂SO₄ • 10H₂O and Na₂SO₄) on this monuments, all these being useful for subsequently method of restoration. The mechanical parameter compressive strength either determined by DRMS, or by Silver Schmidt hammer, indicated us a resonable value for Ca(OH)2, most probably due to the aggregation tendency of Ca(OH)₂, the inhomogeneity of the chalk strone, and the humidity, determined here by cappilarity water uptake.

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