THERMAL AND CHROMATIC PARAMETERS AS DAMAGING INDICATORS OF STUCCO DECORATIONS

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Abstract: The stuccoes weathering varies depending on the environment and building materials involved, the basic conditions associated with the deterioration of stucco being: biological growth, blistering, cracking, delaminating, detachment, disaggregation, flaking and loss. For evaluating the damaging mechanism of the stucco,, some models have been created in the laboratory and the effect of high temperature on them have been evaluated. Also, all of them have been analyzed and discussed, based on the analytical investigations (FTIR, XRD and chromatic parameters). The chromatic parameters (L*,a*, b*, C*, *H** and *E** and their differences) before and after treatment have been correlated with the species generated from gypsum and lime. A comparative study of these parameters and the original color of the stuccoes were carried out. A comparative study of these parameters and the original color of the stuccoes were carried out.

Keywords: *stucco decorations, thermal treatment; chromatic parameters, XRD, FTIR*

1. INTRODUCTION

Many of the historical stucco decorations have today have undergone some chemical and physical changes. Most of these historical artefacts have been lost due to the fragile nature of the material [1].

During time, the stuccoes supported some changes, and for their preservation, it is important to understand the structure and chemistry of stucco. Typically, stucco is painted in an effort to improve its water resistance. Paint observed in many installations, however, was found to have defects such as cracking, particularly after several years of service and particularly on orientations with direct sun exposure. In these locations, paint and sealants develop defects such as cracks and checks. Paint was also observed to have cracked as the stucco beneath the paint developed cracks, thus making the paint ineffective in preventing water intrusion [2]. The decoration is made of plaster facades in stucco, brick less apparent. Original decorations for the buildings have valuable artistic components inside (balustrade, mosaic floors, and stucco decorations), need works of conservation and restoration, very important for maintenance of the building: roof structure, artistic components: stucco facades, gates, joinery, fittings [3]. Traditional stuccos involved a binder (traditionally slaked lime), an aggregate (often a locally available sand), and some additives which some characteristics. The lime-based stuccos provided a protective coat (elastic, vapor permeable and low in strength) adequate for stucco. Inorganic additives such as brick dust or natural cements gave a mix a hydraulic or quick set. As organic additives human used animal hair, blood, urine, linseed oil, eggs, and beer. Their color and texture came from the sand, and some stuccoes could be pigmented to add color [4]. The weathering depends on the environment and building materials involved, the main deterioration processes of stuccoes are: blistering, cracking, delaminating, detachment, disaggregation, flaking and loss [5]. Most often, water causes all these conditions. The traditional stuccoes contain acid-soluble lime, making them susceptible to disaggregation when exposed to acid rain. When salts are formed on the stucco surface, under cyclical alternating wetting and drying processes, a damaging efflorescence could favors the expansion of stone, and attract more moisture. Also, by repeated freezing and thawing processes, an internal deterioration, detachment of stucco from the substrate, and delamination of the stucco’s layers, can occur. In order to evaluate the damaging mechanism of the stuccoes, some models have been created in the laboratory and the effect of high temperature on them have been analyzed based on the analytical investigations (FTIR, Raman, XRD, chromatic parameters).

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Fig.1. The stucco models

The first samples set has been prepared by adding 10 ml of water to 100 g of gypsum. After stirring, a homogeneous pasta has been put into special shapes (Fig.1.) and dryed in a special oven in air flux.

The second samples set has been prepared in a similar manner by mixing lime with gypsum and water in the following ratio: 37%-53%-10%. The others operations were similar as above.

2.2 Characterization techniques

The FTIR spectra have been recorded by Attenuated Total Reflectance, ATR, with a Perkin Elmer Spectrum GX spectrometer (PerkinElmer Ltd., UK), in the following conditions: range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}.

X-ray diffractions (XRD) analyses were performed using a Rigaku SmartLab equipment, operating at 45 kV and 200 mA, using Cu Kα radiation (1.54059 Å), in parallel beam configuration (2theta/theta scan mode), from 3 to 90 2θ degrees; the components were identified using the Rigaku Data Analysis Software PDXL 2, database provided by ICDD.

Color measurements, achieved with a spectrophotometer (Carl Zeiss Jena M40) under a D65 light source and an observer angle of 10^{O}. The CIELAB color parameters clarity (L*), red/green colour component (a*) and yellow/blue colour component (b*) and their derived magnititudes: chroma (C*) and tone (H*). Also, were calculated the differences in ΔL^*, Δa^*, Δb^* and color differences ΔE^*.

2. RESULTS AND DISCUSSIONS

Gypsum (calcium sulfate dihydrate) is a crystalline mineral which has the chemical formula of $CaSO_4 \cdot 2H_2O$. The gypsum is calcium sulfate (79.1%) with 20.9% chemically-bound water. A small amount of free water may also exist in the compound [6,7].

In a non-heated state gypsum is chemically very stable. By slowly heating, gypsum crystals undergo a phase change into an orthorhombic formation, even prior to the release of chemically combined water, Figs.2a,b., process which occurs at temperatures higher than 80° C, and only for the samples where is present lime (2b), in good agreement with literature [8, 9].

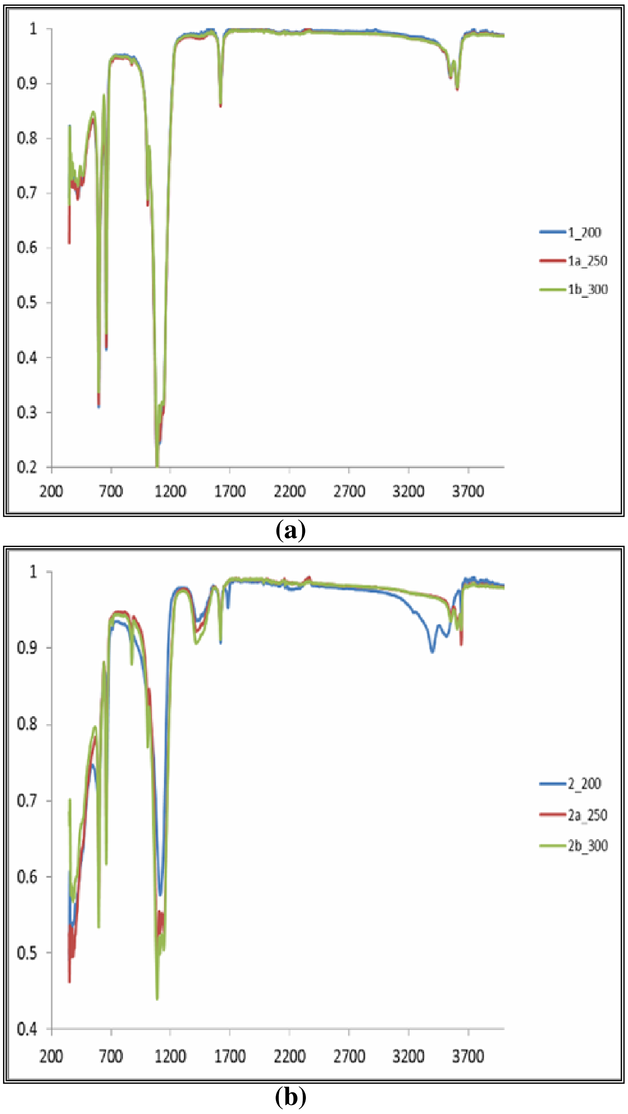

Fig.2. The FTIR spectra of 1st samples set (a) and 2nd samples set (b)

When the gypsum is heated above 80° C, some of the chemically combined water disassociates ($CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0.5\ H_2O$) resulting in the formation of hemihydrate (Bassinite), process known as "calcination" [10-13]. In the range from 98° to 130° C gypsum has fully transformed to hemihydrate [10]. There are two forms of hemihydrate: α (T< 110°C) and β (T>110° C to 115° C) [14, 15]. When subjected to additional heating (greater than 130° C), β hemihydrate undergoes continued thermal decomposition and forms a soluble anhydrate (α - $CaSO_4$) · (0.5 → 0.001) H_20. At higher temperatures than 200° C, the soluble anhydrate progressively is transforming into insoluble anhydrate (β-$CaSO_4 \cdot < 0.001\ H_20$) [16].

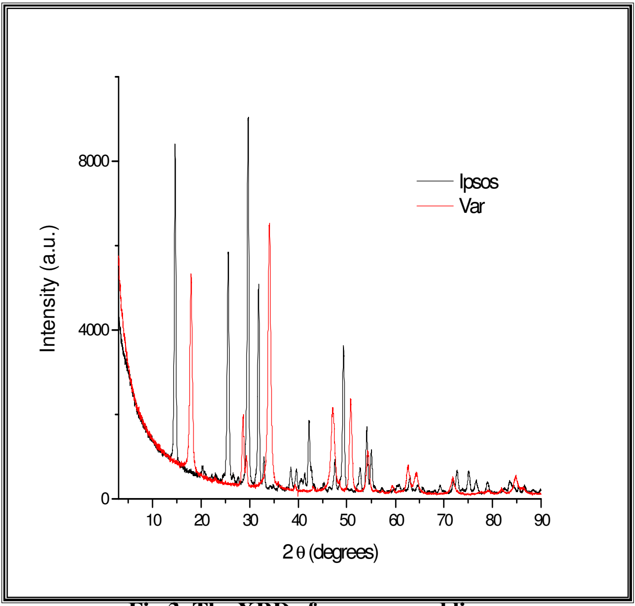

Fig.3. The XRD of gypsum and lime

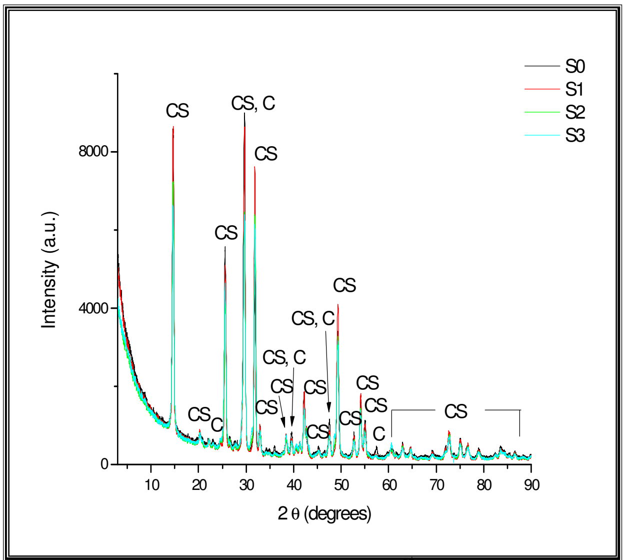

Fig.4. The XRD diagramm of 1st samples set

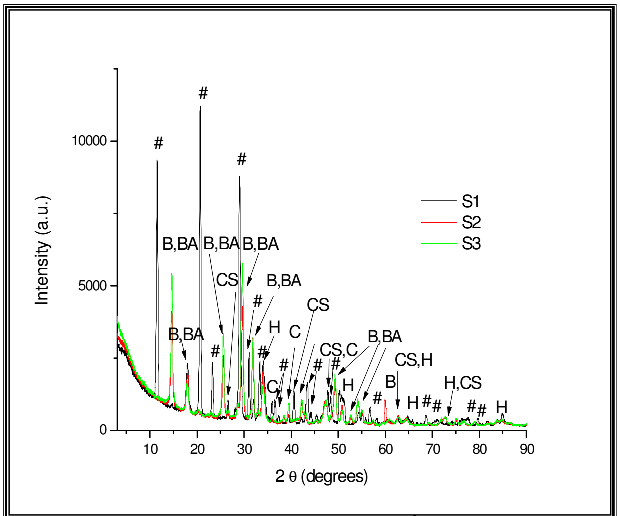

Fig.5. The XRD diagramm of 2nd samples set

S0 – reference gypsum; S1 –200 C 2h; S2 –250 C 2h; S3 –300 C 2h; CS- Calcium sulfate(VI) hemihydrate, 01-076-6905; C – calcite, 00-001-0837; # - Calcium Sulfate Hydrate - 01-078-6179; B - Bassanite - 01-080-7957; BA- Calcium Sulfate Hydrate–01-081-1848 ; H - $Ca(OH)_2$ –00-044-1481; CS - Calcium sulfate (VI) hemihydrate –01-076-6905; C - Calcite –00-001-0837.

Colorimetric measurements (CIELab) were performed to verify the colour modification ($\Delta E^* = \sqrt{\Delta L^*} + \Delta a^* + \Delta b^*$), where L*, a* and b* are the brightness (0 for black – 100 for white), the red–green component (positive for red and negative for green) and the yellow–blue component (positive for yellow and negative for blue), respectively. and their derived magnitudides: chroma (C*) and tone (H*).

The differences between treated and non-treated samples have been calculated, too (ΔH*, ΔC*), correlated with the overall colorimetric difference between non-treated and treated samples: ΔE*: the difference beween treated and non-treated samples, the results indicated: the color properties are in direct relation to aging, i.e., the lightness of stucco decreases and the hue is shifted slightly to red colour.

From the calculus, have been observed the following results for the stucco 1:

1_200 °C: ΔL= 0.59; ΔC = 0.27; ΔH = 0.14 and ΔE=0.66;

1_250 °C: ΔL= -0.66; ΔC = 0.12; ΔH = 0.30 and ΔE=0.73;

1_300 °C: ΔL= 0.05; ΔC = 0.12; ΔH = 0.94 and ΔE=0.95;

From the calculus, have been observed the following results for stucco 2:

2_200 °C: ΔL= -7.00; ΔC = 0.55; ΔH = 0.56 and ΔE=7.04;

2_250 °C: ΔL= 1.20; ΔC = -0.75; ΔH = 0.62 and ΔE=1.55;

2_300 °C: ΔL= 0.49; ΔC = -0.64; ΔH = 1.11 and ΔE=1.37;

Increasing the temperature, there is a variation for ΔL from negative values to positive ones, as a proof for a change from lighten to darken aspects. Also, chroma (C*) changes from positive to negative values, and tone (H*) is increading constantly. All these results are in good agreement with the literature data [17].

4. CONCLUSIONS

For evaluating the damaging mechanism of the stucco,, some models have been created in the laboratory and the effect of high temperature on them have been evaluated. Also, all of them have been analyzed and discussed, based on the analytical investigations (FTIR, XRD and chromatic parameters). The chromatic parameters (L*,a*, b*, C*, *H** and *E** and their differences) before and after treatment have been correlated with the species generated from gypsum and lime. A comparative study of these parameters and the original color of the stuccoes were carried out.

5. ACKNOWLEDGEMENTS

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