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SHORT STUDY ABOUT REMOVING THE BLACK CRUST FORMED BY THE INFLUENCE OF SO_2, NO_X, CO_2 ON SAINT MICHAEL'S CHURCH MASONRY IN CLUJ-NAPOCA, ROMANIA, BY CHEMICAL AND PHYSICAL METHODS

[1]Elena Maria Pică*, [1]Ioana Popişter, [2]Zuzana Slížková, [1]Valer Micle

[1]Technical University of Cluj-Napoca -UTCN, Romania

[2]*Institute of Theoretical and Applied Mechanics, AS CR, v.v.i., Prosecká 809/76, Prague 9, 190 00, Czech Republic.*

Abstract-A short study of the SO_2, NO_x, CO_2 influence on cultural heritage, as in the case of Sf. Michael's Church Masonry in Cluj-Napoca, Romania is presented; special attention is given to the black crust formation. The composition of the black crust was determined; the black crust was then cleaned with the laser-based chemical method and with the physical method of cellulose plaster soaked in ammonium hydrogen carbonates [$NH_4(HCO_3)$].

Keywords-Air pollution: SO_2, NO_x, CO_2; Black crust; St. Michael's Church, Cluj-Napoca, Romania

I. INTRODUCTION

Historical heritage is very important for any nation, being a source for the development of the tourism and its competitiveness. Cultural tourism and historical heritage management operate as parallel activities in most places, with remarkably little dialogue between the two [1]. The purpose of this study is to determine the effect of the polluted environment on building materials used in monuments, such as St. Michael's Church in Cluj-Napoca, Romania, by forming a black crust and of the methods of removing it.

The influence of CO_2 concentration was presented in 2012 [2].

According to Charola [3], the conservation methods used for monuments in cultural heritage can be divided into four wide categories: *cleaning*, *desalination*, *strengthening* and *disinfection*. Each of these categories can be further subdivided, related to the type of intervention and kind of material. The principles at the basis of any conservation intervention are: surface reversibility/retreatability; compatibility; minimal intervention.

The cleaning procedure can be either *physical*, for instance with steam jet or *cellulose plaster*, respectively *chemical*, as in the case of *laser*. For the salt efflorescence present on the surface of the rocks preference is given to desalination. The cleaning methods are selected according to the criteria specified by Cooper [4] or Sidraba [5].

The laser-based removing procedure is the most efficient as its potential increases gradually and it is accurate and selective. The physical process involved consists in laser-based ablation of inorganic layers (sometimes of organic layers, too) that form the damaging crust. The most important features of cleaning can be found [6-9].

The plaster method was described by Ashurst [10] and Voronina [11], where the Woolfitt and Abrey medical term was used as a model [12].

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II. MATERIALS AND METHODS

The materials used in this study were: cellulose poultice and ammonium hydrogen carbonate [$NH_4(HCO_3)$].

The methods used were based on: Energy Dispersive Spectroscopy (EDS) and Energy Dispersive X-ray, technique [13], for the black crust. EDS analysis has executed with Si Detector and Be window (30 s, spot- size 1μm, the high work voltage used was 15.0 kV), from "Babeş-Bolyai" University, Cluj-Napoca, Romania. EDX analysis has executed with Thunder ART, apparatus from Institute of Theoretical and Applied Mechanics and Institute of Rock Structure and Mechanics from Prague-Czech Republic. The high work voltage (HV) used was 15.0 kV, both for the witness sample and test sample; The frequency or pulsation of impulses was 2.7 kcps (kilo-cycles per second) for the witness sample and 11.37 kcps for the test sample.

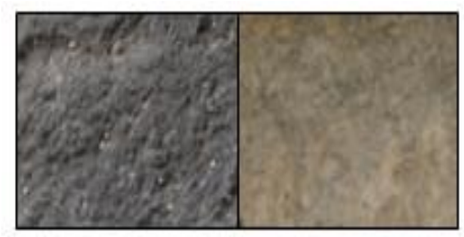
For Laser cleaning used Ultrapulse Fractional Laser CO_2 (LUMENIS), with optimal ablation, 225 mJ, "Babeş - Bolyai" University, from Cluj-Napoca, Romania.

The size of the black crust film was found with the Stereo Optika Vision Microscope (with a 40x lens), then the

samples were cleaned by the laser device from the Materials Science and Engineering Department in the Faculty of Materials and Environmental Engineering of the Technical University of Cluj-Napoca, Romania.

III. RESULTS

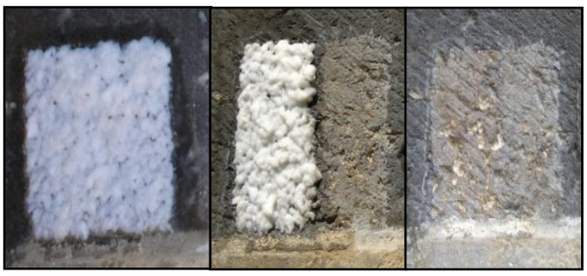
The effect of laser cleaning of one of the samples used for the research is given in Figure 1a and 1b.



a) b)

Fig. 1 The St. Michael's Church sample appearance: before (a) and after laser cleaning (b)

The effect of cellulose poultice cleaning (Figure 2) was watched after 12 hours (b) and after 24 hours (c). The effect aimed at was seen after 24 hours.



a) b) c)

Fig. 2 The appearance of cleaning obtained afterthe applicationof the CELLULOSE poultice:

initially (a); after 12 hours (b); after 24 hours (c)

The results of the EDX spectrum analysis in the sample from St. Michael's Church are given before cleaning (in Figure 3), respectively after laser cleaning (Figure4) and after using the cellulose poultice (Figure 5).

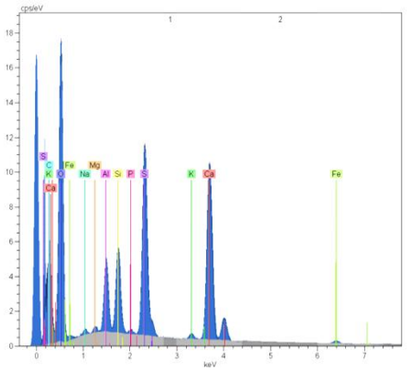


Fig. 3 EDX spectrum of the black crust, before cleaning

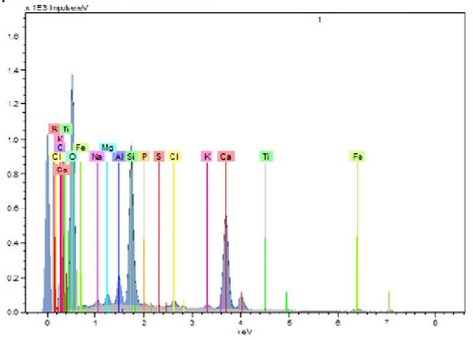


Fig. 4 EDX spectrum of the black crust, after laser cleaning

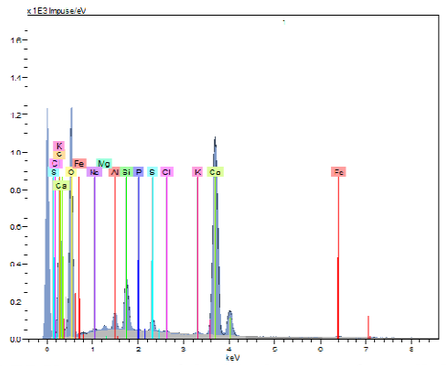


Fig. 5 EDX spectrum of the black crust, after cellulose poultice cleaning

The analyses on the sample collected from the church (Figure 4) point out that after cleaning all the chemical elements at the surface of the sample can be found in larger amounts that in the sample before subject to the laser intervention (Figure 3). The basic gypsum-based of the black crust were not removed entirely; only a part of the polluting chemical elements were removed, namely those black colouring the crust, as it is also shown in Table 1.

The results of the analyses of the cellulose cleaned sample from St. Michael's Church (Figure 5) indicate a diminishing of the amount of the following elements: potassium, aluminium, silicon, sodium, sulphur, phosphorus; a considerable difference among the identified elements is also visible according to the data in Table 1, which presents cellulose cleaning results in comparison with the laser cleaning results.

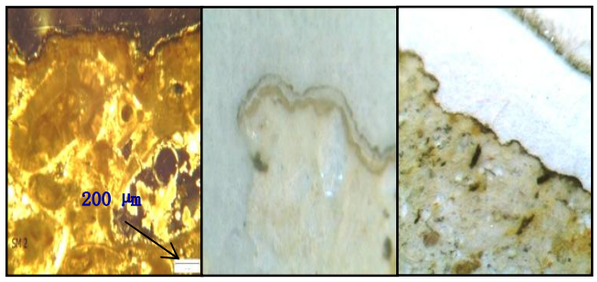
TABLE 1 COMPARATIVE RESULTS OF THE ELEMENTS IDENTIFIED IN THE SAMPLE OF BLACK CRUST, BEFORE AND AFTER LASER AND CELLULOSE CLEANING, WITH EDX/EDS METHODS

Chemical elements	Before cleaning		After LASER cleaning		After CELLULOSE cleaning	
	EDX	EDS	EDX	EDS	EDX	EDS
Silicon	4.25	4.23	14.43	14.44	3.66	3.65
Aluminium	3.62	3.60	2.77	2.79	1.29	1.28
Calcium	18.18	18.17	18.32	18.31	28.70	28.69

Titanium	N.D.	N.D.	0.34	0.33	N.D.	0.15
Iron	1.24	1.23	1.68	1.67	1.27	1.28
Potassium	0.57	0.58	0.64	0.63	0.26	0.25
Magnesium	0.37	0.36	1.08	1.09	0.54	0.52
Sodium	0.48	0.47	0.90	0.91	0.45	0.46
Sulphur	10.95	10.93	0.13	0.12	1.04	1.04
Chlorine	N.D.	N.D.	0.89	0.88	0.18	0.19
Phosphorus	0.33	0.32	0.54	0.53	0.16	0.18
Oxygen	51.84	51.83	56.46	56.47	56.51	56.52
TOTAL	**91.83**	**91.72**	**98.18**	**98.17**	**94.06**	**94.21**

(N.D. = Not Determinate)

The results found with the Stereo Microscope (Figure 6) are given comparatively, before (a) and after laser cleaning (b) and respectively after cellulose poultice cleaning (c).



a) b) c)

Fig. 6 Cross section in the sample taken, before (a), after laser cleaning (b) and after cellulose poultice cleaning (c)

An insignificant reduction of the film of black crust at the sample surface is found after laser cleaning (Figure 6b) and, oppositely, a considerable diminishing of the crust after cellulose poultice application (Figure 6c); the comparison is made in both cases with the size of the film before laser and cellulose poultice cleaning respectively (Figure 6a).

Therefore, the cellulose poultice is efficient as a physical method of extracting and removing chemical elements and particles at the surface of the limestone used to erect St. Michael's Church in Cluj-Napoca, Romania.

IV. CONCLUSIONS

The laser chemical method used to remove black crust elements found on the surface of the building materials used for St. Michael's Church in Cluj-Napoca, Romania, has an insignificant effect.

The ammonium hydrogen carbonate soaked cellulose poultice method has a significant effect during the black crust removing procedure applied in St. Michael's Church in Cluj-Napoca, Romania.

The cellulose poultice method is favoured to the laser-based method for the extraction of the chemical elements and particles at the surface of the limestone in St. Michael's Church in Cluj-Napoca, Romania.

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