Investigations of the new gate tower from Corvins’ Castle

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Abstract. The archaeometric study of some samples from New gate Tower from Corvins’ Castle are analyzed in this paper in order to identify the raw materials nature and weathering / deterioration processes of these artifacts. Modern analytical techniques, as XRD, FTIR, Raman, SEM-EDS, colorimetry, porosimetry, thermal analysis are used to evaluate the structure and chemical composition (quartz, mica, dolomite, feldspar and plagioclase as albite and microcline minerals). Some minerals similar with apatites have been evidenced being responsible for the consolidated resistance structure inside of the towers.

1. Introduction

The Corvins’ Castle, also known as the Hunyadi Castle, is a Gothic-Renaissance castle in Hunedoara, with a long and tumultuous history. It was given to John Hunyadi’s father in 1409 by Sigismund, King of Hungary, and began the rebuilding in 1446 when John Hunyadi was elected regent governor of the Kingdom of Hungary, wishing to transform the former building built by Charles I of Hungary [1].

Based on a fourteenth century stone fortress, in the first half of the 15th century, John Hunyadi transformed the military building into a gothic style building. After John Hunyadi die in 1456, the castle work stopped until 1458 when numerous Renaissance elements were added in the building architecture. In 1480, work was completely stopped, and even so, the castle was recognized as being one of the biggest and most impressive buildings in Eastern Europe. During the 17th century, two new towers were constructed for military purposes. The White Tower and the Artillery Tower and an external yard was added, for administration and storage. Now, the castle is a large and imposing structure with tall towers, bastions, an inner courtyard, diversely colored roofs, and myriads of windows and balconies adorned with stone carvings, Figure 1.
Figure 1. The Corvins’ Castle (personal photo).

Figure 2. The new gate tower from Corvins’ Castle (personal photo).

For an enhanced fortification the castle has a double wall, flanked by both rectangular and circular eight towers, built for military purposes. The defense towers of the medieval fortress have transformed it into a settlement almost impossible to conquer. The actual entrances to the castle were made by bridges, supported by stone pillars, the last sections of the bridges being mobile. Incorporating a fourteenth century stone fortress, the castle is the result of two stages of construction, in the time of John of Hunedoara (the first half of the 15th century), which transformed the military building into a state-of-the-art gothic style, the late phase, having as a model the most evolved patterns of military and civilian architecture of the moment. The overall appearance is due to the restoration works from the 19th century to the 20th century.

The new gate tower was built in sec. XIV, was extended between 1440-1453 (under John of Hunedoara) and transformed between 1618-1620. From place to place there are also stones shaped in the style used for the construction of the Dacian fortresses, Figure 2. It is a massive construction with a high ground floor, complete with three levels of defense, with openings for firearms. According to historians, among the original Gothic elements in the tower's composition, there is a bellows placed on four consoles and a massive balcony.

From previous reports, predominates the plaster, dolomite of small size, large blocks of dolomite lime, summary shaped, bound with mortar, porous mortar with residues of dolomite, ground black soil containing prehistoric material, where have been dug the foundations. Given the historical importance of this monument and the lack of studies archaeometric and details needed to continue the restoration procedures, a complex archaeometric study is required to be made, which relate to the materials used in these towers, their degradation and techniques to build this monument [2-4].

During the last decades, multiple interdisciplinary research with analytical techniques have been published in the cultural heritage field. New and modern techniques have been adopted for the study of objects, including non-invasive ones: Ultraviolet-Visible Spectrophotometry (UV-vis), recognized as a fingerprint for the material, which allows identification of the material’s composition, finding the constituents present in a material having unknown chemical composition, understanding the degradation and the stability of materials, Fourier-Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy as common techniques used for the study of organic components of cultural heritage materials, X-Ray Fluorescence (XRF), as an ideal method for analyzing low concentrations of specific elements and helps in the provenance studies, determining major and minor elements and a selected number of trace elements of the investigated sample, and identifying of the provenance of
their manufacture materials, X-ray diffraction (XRD), as the most popular technique for determining mineral phases of ancient ceramics, Gas Chromatography coupled with Mass spectrometry (GC-MS) and ion chromatography for the study of organic components in artworks, for the identification of dyes and binders and even the degradation processes such as black crust formation due to environmental pollution.

Except all these techniques, microscopy techniques are intensively used, too, as follows: optical microscopy (OM), Scanning electron microscopy (SEM), atomic force microscopy (AFM) for characterization of the internal morphology and topology, for the pore structure.

The aim of this paper is an archaeometry study of some samples from the New Gate Tower, Figure 2, which is now the main gateway to the Corvins’ Castle, on the formerly mobile bridge, raised by a lever system, the nature of raw materials for collecting information about the natural resources and the manufacturing production and weathering / deterioration processes of these artefacts.

Sensitive analytical techniques, as Fourier-Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy, X-Ray Fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), Scanning electron microscopy (SEM-EDS), petrographic analysis, Induced Coupled plasma with mass spectrometry (ICP-MS), colorimetry and ion-chromatography are used and the results are discussed, too.

2. Experimental part

2.1. Materials
The samples received from archaeologists contain only stone samples, which are at different stages of degradation, as shown in Figure 3.

![Figure 3. The aspect of the samples taken from the site (the significance in the text).](image)

The succession of the excavated samples is the following: (a) the new ground floor, made of dolomite river boulders of large size, bound with mortar containing small pebbles, (b) yellowish level, compact, made of granular dolomite, (c) brown level, with large dolomite, (d) old floor level, made up of river boulders and dolomite fragments, laid directly on a loamy black soil, (e) brownish white level, containing medium-sized dolomite, mortar granules and a massive stone block, shaped with large amounts of mortar, (f) light brown level, composed of river gravel, (g) brown-yellow-grey level, composed of medium and large dolomite, with few mortar granules, without binder, but with traces of charcoal, (h) black level, compact, containing pre-historic material.

2.2. Methods
Fourier transformed infrared spectroscopy (ATR-FTIR) has been recorded with a Vertex 80 spectrometer (Bruker Optik GMBH, Germania) in the range of 4000–400 cm⁻¹, equipped with DRIFT accessory.
Raman spectra have been recorded with a portable dual wavelength Raman (Rigaku, USA) analysers equipped with a standard diode-pumped, air-cooled Nd:YAG laser source with power of 252 mW (785 nm and 1064 nm), with high sensitivity and a resolution of 4 cm\(^{-1}\). Data have been processed with the software Opus 7.0 (Bruker Optics GmbH).

The diffraction data (XRD) have been recorded with a X-ray diffractometer Rigaku Ultima IV, the main parameters being: vertical goniometer 0 / 0 (285mm radius) in geometry G / 9; X-ray tube - Cu anode (2 kW); detector - NaI; Bragg-Brentano with high-resolution geometry; Software: PDXL 2.2. (processing), ICDD-PDF4 + 2016 (database).

The wavelength dispersed X – Ray Fluorescence Spectrometry (WDXRF) was performed in order to provide qualitative and quantitative elementary composition and to complete the chemical analysis. (elements ranging from 8O to 92U). The system is equipped with 3 analyser crystals (with automated exchange): LiF (200) for Heavy Elements (Ti-U), PET and RX 25 pt light elements (O-Mg and Al-Sc) with power of 200W (50kV tens, 4mA int). Detection limit: 1ppm - 10ppb; Accuracy <0.1-0.5%.

The petrographic analysis was conducted on an Olympus BH-2 petrographic microscope, using only 4× and 10× magnifications.

Induced Coupled plasma with mass spectrometry (ICP-MS) has been used for providing high-performance elementary analysis. ICP-MS includes PFA nebulizer, quartz spray, cyclonic, quartz torch, demountable, shieldless, quartz injector, 2.5mm. The samples are processed with a TOP WAVE digestor, which assure a digestion under pressure with microwave.

For the optical microscopy a Primo Star ZEISS optical microscope (magnification between 4X and 100X) was used in order to investigate the samples in transmitted light and a software that allowed real-time data acquisition. The images have been collected with a digital video camera (Axiocam 105) that processed in 2D in 3D format for a better viewing.

The Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) has been recorded with a SU-70 (Hitachi, Japan) microscope, for surface morphology and elemental composition, respectively.

For chromatic parameters a CM-2600d spectrophotometer (KONICA MINOLTA) (Japan) has been used, with a D65 light source and 10° for an observer angle. The parameters L*, a*, and b* and ΔE*, have been calculated by using the equations from JIS 2008 [5]. L* (lightness of a color) varies from the darkest black (L* = 0) to the brightest white (L* =100); a* (greenness/redness) varies from a* < 0 for green to a* > 0 for red; b* (blue/yellow) varies from negative values of b* for blue, and positive values of b* for yellow.

The ion chromatography has been achieved by using an anion column Ion Pac AS14A Dionex with 8 mM Na2CO3/ 1 mM NaHCO3 and 1ml/min flux, equipped with a ASRS-ULTRA Dionex suppressor. The analyses were carried out on powdered sample in water solution. An amount of 3 g air-dried soil was combined with 30 mL de-ionized water and allowed to stand in an ultrasonic bath for 30 min, after which filtration was performed using 0.45-μm filters. Anion levels were quantified using ion chromatography with a Dionex ICS-1000 and calibrated standards. The salt uptake during the crystallization test was measured by electrical conductivity measurements using a AMEL 160 multi-range laboratory conductometer equipped with a conductivity probe, on powdered samples in water solution (100 mg sample/100 ml distilled water). All anion levels are reported as mg/kg dry-weight of original soil.

3. Results and discussion

Located in the Southern Carpathians area, Hunedoara region is a very complex geological area, with sediment-volcanic units, sedimentary formations (limestone, sandstone, magmatite (basalt), andesite, and many others) [6].

From macroscopic point of view, the stone samples are brownish - yellow coloured, with grey grain aspects, and with visible weathering and significantly alterations and microcracks. Their colour varies from different shades of yellow grey to creamy and whitish-reddish because of deposits of
ferruginous minerals. The degree of compaction is variable, influenced by both the contact with atmospheric factors and the strength of the rock’s saturation.

The stones from this area have a medium texture, without defined grains and with microcline and plagioclase crystals. The mineralogical composition (quartz crystals with varied sizes, K-feldspar (larger sizes), plagioclase and biotite). Stretched and recrystallized crystals were observed surrounding the plagioclase and microcline minerals.

The petrographic analysis reveals feldspar, quartz and garnet are common minerals. In these samples microcracks and some alterations could be related to weathering effects. Also, they are large, lenticular eye-shaped mineral grains or mineral aggregates visible in some foliated metamorphic rocks, Figure 4.

Figure 4. Photomicrograph of the pre-historic mortar: Qtz=quartz, Bio=biotite, Cc=calcite, K-spar=K-feldspar, and Plag=plagioclase.

The presence of apatite in the deeper layers at the base of the tower could be an explanation for the durability of the old floor (pre-historic material). Apatite derivatives are recognized as good stabilizer and antimicrobial agents [30]. Except the above-mentioned minerals, mica, zircon and titanite could be identified by the XRD analysis, but in very low concentration, such result being in agreement with those expected to Gneiss stones mentioned by the literature. From compositional point of view, clay as raw material could contain magnesium, calcium, manganese, limestone granules, sulphates, aluminum hydrate especially in the production of bricks, and different organic substances with various effects on the timing of the bricks [7].

Table 1. Mineralogical composition (wt. %) of the samples studied by X-ray diffraction.

| Sample No. | C | Q | Gy | Ha | Ar | Do | Pl | Cl | M | Go | Ap |
|------------|---|---|----|----|----|----|----|----|---|----|----|
| 1          | x | x | x  | x  | x  | x  | -  | x  | x | -  | -  |
| 2          | x | x | x  | x  | -  | x  | -  | -  | - | -  | -  |
| 3          | x | x | x  | x  | -  | -  | -  | -  | - | -  | -  |
| 4          | x | x | -  | x  | -  | x  | -  | -  | - | x  | x  |
| 5          | x | x | -  | x  | -  | -  | -  | -  | - | -  | -  |
| 6          | x | x | x  | -  | x  | -  | -  | -  | - | x  | -  |
| 7          | x | x | -  | x  | -  | -  | -  | -  | - | x  | -  |
| 8          | x | x | -  | x  | -  | -  | -  | -  | x | -  | x  |
| 9          | x | x | x  | x  | x  | -  | -  | x  | - | -  | x  |

C: Calcite, Q: Quartz, Gy: Gypsum, Ha: Halite, Ar: Aragonite, Do: Dolomite, Pl: Plagioclase, Cl: Clay minerals, M: Micas, Go: Goethite, Ap: Apatite.
In the same context, the XRF analysis on this stone shows values approximately 7% magnesium (Mg), 60% silicon (Si) and 16% aluminium (Al), with traces of other elements (Figure 5), well correlated with ICP-MS data (Table 2), in good agreement with literature [8].

![Figure 5. WDXRF diagram for the pre-historic mortar.](image)

Table 2 shows the results of these ions determined by ICP-MS analysis. As it was mentioned earlier, P is identified again, as an evidence for apatite derivative generated in the depths of the earth at depths higher than 4 m.

| Sample | Na  | Al  | Si  | K   | Ca  | Fe  | Mg  | S   | P   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|        | 0.42| 3.56| 17  | 0.27| 28  | 2.4 | 0.92| 0.15| 0.85|

*Ti, Cr, Cu, Mn < detection limit

Also, has been observed that the height of the tower is decreasing from sample 1 to 9, and the conclusion is the following: smaller the height, higher the concentration in halide, gypsum and apatite. A sign in this matter is the presence of P, detectable by ICP and EDS. All the other minerals could be identified aleatory without any correlation with the tower height. The main elements identified in the samples have been determined by EDS technique (Table 3).

The composition of the investigated mortars, achieved by SEM-EDS indicated the presence of finely divided quartz (sand) (0.02–0.04 mm), dolomite and kaolinite (Al₂[Si₂O₅]([OH]₄)), feldspar (KAlSi₃O₈) and other compounds that contain sodium (Na), potassium (K), or calcium (Ca), Table 3.

Usuallly, physical, chemical, mechanical and biological weathering contribute to the alteration of the stone structural properties. The atmospheric conditions and air pollutants led to a complex stone ageing process.

In the presence of salts as sodium sulphate, black crusts, efflorescence and staining could be identified as one of the most destructive agents in porous stones. Also, the formation of gypsum crystals and halite inside the porous building stones induces the stone destruction due to the internal stresses, when the available space in the pores is limited [9].
Table 3. EDS analysis with elements identification.

| 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  |
|----|----|----|----|----|----|----|----|----|
| Na | 0.15 | 0.1 | 0.24 | 0.17 | 0.34 | 0.22 | 0.05 | 0.18 | 0.12 |
| Mg | 10.77 | 7.61 | 17.15 | 2.76 | 3.5 | 3.86 | 3.97 | 0.67 | 2.02 |
| Al | 1.05 | 0.43 | 0.97 | 1.87 | 2.91 | 0.67 | 0.2 | 1.81 | 0.81 |
| Si | 0.19 | 2.1 | 14.27 | 3.76 | 6.44 | 18.26 | 0.46 | 8.26 | 1.77 |
| P  | 0.11 | 0.21 | 0.12 | 0.97 | 1.41 | 1.59 | 0.48 | 0.21 | 0.99 |
| S  | 0.14 | 0.07 | 0.14 | 0.11 | 0.74 | 0.12 | 0.02 | 0.27 | 0.13 |
| K  | 0.14 | 0.07 | 0.14 | 0.11 | 0.74 | 0.12 | 0.02 | 0.27 | 0.13 |
| Ca | 12.63 | 27.68 | 4.56 | 25.72 | 15.66 | 13.19 | 27.06 | 20.47 | 25.49 |
| Ti | 0.07 | 0.14 | 0.15 | 0.25 | 0.17 | 0.61 | 0.06 | 0.09 | 0.12 |
| Cr | 0.06 | 0.52 | 0.36 | 1.41 | 1.59 | 0.48 | 0.21 | 0.99 | 0.99 |

Table 4. The anions concentration of the investigated soil.

| F  | Cl | NO | NO$_3^-$ | PO$_4^{3-}$ | SO$_4^{2-}$ |
|----|----|----|---------|------------|-----------|
| 0.0610 | 1.286 | 0.019 | 1.579 | 0.72 | 3.118 |

The qualitatively and quantitatively identification of different anions has been achieved by ion-chromatography, Table 4. The white stains found in some samples indicated apparently an alterability caused by NaCl, also identified by ion-chromatography technique.

Figure 6. FTIR spectra of the investigated soils samples from the New Gate Tower at different height.

Figure 7. Raman spectra of the materials sampled from New gate Tower.
From FTIR spectra, could be detected the following composition: quartz, detected in all the samples: 1088-1092 cm\(^{-1}\) through the bands belonging to the Si-O (stretching mode, symmetrical stretching and bending modes) from 796 and 777-783 cm\(^{-1}\) and 692-694 cm\(^{-1}\); Muscovite (1026-1036, 1007 and 530 cm\(^{-1}\)); Feldspars (752-758, 646 and 465-471 cm\(^{-1}\)); Pyroxenes (519 cm\(^{-1}\)); Silicate, phosphate or sulfate bands could overlap each other in the region (900–1000 cm\(^{-1}\)); Apatites (through bands of PO\(_4\)\(^{3-}\) group from 560 and 600 cm\(^{-1}\); from 1000–1100 cm\(^{-1}\) and 630 cm\(^{-1}\); CO\(_3\)\(^{2-}\) from 1460 and 1530 cm\(^{-1}\)[10].

Also, RAMAN spectra, Figure 7, add a real value to these data, putting into evidence the present materials, pointing out that due to the geo-morphological and structural compositions of this area, a phosphate compound is formed here as a strong consolidant material, similar with hydroxyapatite. Also, some information regarding the glassy phase and the pore structure could be obtained by microscopical techniques as OM (Figure 8) and SEM-EDS (Figure 9) [11].

![Figure 8. SEM images for the investigated samples.](image)

For all the experiments the samples have the following significance: (a): mortar sample, brown-gray color, with large fragments of dolomite without a binder and with traces of charcoal (a) (0.2-0.6m); (b) Mortar with bricks (1.1-1.45m); (c) mortar sample, gray color, with traces of charcoal (1.5-1.75m); (d) grey level with a lot of charcoal (1.53 – 1.55 m); (e) sandy yellow under the mortar lens, composed of medium and large dolomite, with a few mortar-free granules, containing fragments of building materials (tiles, olans, mortar) (2.4-2.6m); (f) ash level, whitish, granular mortar, containing medium- sized dolomite, mortar granules (3.1m); (g) mortar layer, a mixture of mortar and small dolomite (3.10-3.56m); (h) grey level, soily with a lot of coal, composed of river gravel (3.7-4.1m); (i) under the mortar level, pre-historic material (>4.1m).
Large rounded white lump with an open and porous structure visible in the SEM images, are visible in the obtained images, Figure 9. SEM images of apatite crystals grown shows several spherical clusters and few crystals of 0.1mm (i).

![Figure 9. OM of different samples from New Gate Tower.](image)

Gypsum is clear visible in the images, as an advanced state of damage. Hydroxyapatite that was identified in the pre-historic material shows a disordered structure and a highly agglomerated mosaic of particles of different sizes and morphologies. The agglomeration of the particles is probably due to the ripening process.

In the color space, $L^*$ (lightness), $a^*$ and $b^*$ are the main chromatic parameters. The sample (a) is yellow grey ($L^*=57.51$, $a^*=8.17$; $b^*=25.82$). For the other samples $L^*$ which represents the lightness of a color, maintain a similar value ~50, $a^*$ which indicates greenness/redness of a color, have a higher value, and denotes red, while $b^*$ which axis expresses blue/yellow opponent colors, keep a similar value around 25, specific for yellow. The samples (b)-(h) show changed chromatic parameters, either due to firing or time weathering. For the sample (i) which is dark brownish-black with high amounts of dark red putties, the color parameters are: $L^*=53.55$; $a^*=17.33$; $b^*=27.47$. The sample (i) contains hydroxyapatite responsible to its stability, recognized by other literature sources [12].

4. Conclusions
In this paper an archaeometry study of some samples from the New Gate Tower, which is now the main gateway to the Corvins’Castle, has been analyzed for identifying the raw materials, natural resources, the manufacturing, the weathering / deterioration processes of these artefacts. Specialized analytical techniques, as Fourier-Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy, X-Ray Fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), Scanning electron microscopy (SEM-EDS), petrographic analysis, Induced Coupled plasma with mass spectrometry (ICP-MS), colorimetry and ion-chromatography are used and the results are discussed, too. The
mineralogical composition is based on quartz, K-feldspar, plagioclase, biotite, muscovite, garnet, have been identified. Gypsum is clear visible in the images, as an advanced state of damage. Hydroxyapatite that was identified in the pre-historic material shows a disordered structure and a highly agglomerated mosaic of particles of different sizes and morphologies and is responsible for the stability and durability of these layers.

5. References

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