STUDII ASUPRA GRADULUI DE ALTERARE, CONSERVARE ŞI AL COMPATIBILITĂŢII MATERIALELOR DE CONSTRUCŢII FOLOSITE LA RENOVAREA ZIDULUI DE FORTIFICAŢII AL BISERICII REFORMATE DIN DEJ, MONUMENT ISTORIC (JUD CLUJ)

WEATHERING, CONSERVATION STATE AND COMPATIBILITY STUDIES ON THE CONSTRUCTION MATERIALS USED FOR RENOVATION OF THE HISTORICAL DEJ REFORMED CHURCH FORTIFYING WALLS

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The paper presents an interdisciplinary study based on: site inspections, petrographical and mineralogical research (staining methods, transmission polarizing microscopy, XRD analyses) and water absorption tests performed on samples extracted from replaced masonry units (tiles, blocks), weathered and non-weathered Portland cement mortars and tuff tiles from fortifying walls of a monumental tuff-made construction. The main outlined weathering processes were: intensive cracking (drying shrinkage; alkaline-aggregate-reaction, carbonation and salt crystallization, frost attack) and leaching associated with secondary carbonation and sulphate (intrinsic and extrinsic) attack induced expansive phenomena. The chemical and physical incompatibility between tuff, brick and cement based mortar beside the high level of stagnant humidity along the zeolites- bearing tuff blocks surfaces appears to be the first cause of decay and deleterious effects.

Lucrarea reprezintă un studiu cu caracter inter-disciplinar asupra zidurilor de fortificaţie din tuf vulcanic ale unui monument istoric, bazându-se pe: observaţii in situ, cercetări petrografice şi mineralogice (metoda colorării diferenţiate, microscopie în lumină polarizată prin transmisie, analize DRX) şi testări de absorbție a apei asupra unor probe extrase din elemente de construcţie înlocuite (plăci şi blocuri), mortare pe bază de ciment Portland alterate şi nealterate, plăci de tufuri vulcanice. Principalele procese de alterare evidenţiate au fost: fisurare intensă (fisuri de uscare, reacţii alcalii-aggregate, carbonatare, cristalizare săruri, îngheţ-dezgheţ şi levigări asociate carbonatării secundare şi fenomene expansive induse de atacul sulfaţilor (având cauze interne şi externe). Studiul a evidenţiat faptul că în procesele de alterare şi degradare rolul principal îl are nivelul ridicat al umidității stagnante în lungul suprafețelor blocurilor de tuf cu conținut ridicat de zeolit alături de lipsa de compatibilitate chimică, fizică între tufurile vulcanice, cărămizi şi mortarul pe bază de ciment.

Keywords: *historical building, volcanic tuffs, petrographic microscopy, sulphate-attack, staining methods, compatibility.*

1. Introduction

Until the end of eighteenth century and beginning of nineteenth century the most used mortars had air- hardening lime binder and since then were used hydraulic lime-based binder (due to simultaneous burning of limestone and clay) in building construction. From around 1845 (owing to I.C. Johnson countings and experiments) the Portland cement became the most important binder in building material, which had higher compressive strength, lower porosity, higher durability than previously used ones. But using the Portland cement based mortars in restoration of historical buildings appeared to be at least recommended solution, driving to the acceleration of damages in buildings, due to the internal stresses created by contact between Portland cement based restoration materials (with high resistance, low porosity, low water absorption capacity, low freeze -thaw effects) and old mortars (with specific mortar structure and acceptable performance during the centuries, high capillary porosity, water absorption capacity and freeze-thaw effects), but also due to the internal sulphate attack released by SO_4^{2-} content of Portland cement. The cause was the physico-mechanical and chemical incompatibility between the old and renovation mortars. New standards for evaluating mortars for repair of historic buildings were discussed, for example, by Groot, 2010, Tanner et al, 2011 [1, 2]. The characterization of old mortars and those for repair historical buildings was the topic of many scientific papers. Studies on the physico-mechanical properties of old mortars (porosity of lime mortars, which can drive to the decay of building stones and affect the conservation

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state) were performed by Malinowski (1981), Wisser et al, 1988, Duffy et al, 1993, Groot,et al, 1999, Mosquera et al,2002, Degryse et al, 2002. [3- 8].

Alvarez-Galindo, J.I. 2003 [9] outlined that for the good quality of restoration works in cultural heritage it is obligatory existence of compatibility between old and rehabilitation mortars. The compatibility refers not only to the physico-mechanical but also to the chemical features. Bicer-Sismir et al, 2009 [10] and Callebaut et al, 2001 [11] made researches on natural hydraulic lime-based mortars, using petrographic analysis, SEM- EDX, XRD. A special blood lime-based mortars for repair the historical buildings were experienced by Shiqiang et al, 2015 [12] obtaining improved durability properties.

In the last decades the other important compatibility type was recognized in mortars and concretes, between the aggregates and binder, such as alkali-silica-reaction (ASR). Guthrie and Carey, 2015 [13] outlined that pozzolans, used as mortar's aggregates not generate ASR in opposite to other aggregates containing only amorphous silica. This statement could be of the major importance in restauration of historical buildings composed by volcanic tuff blocks, because these rocks are well-known as pozzolans. Researches for creation and characterization of a new type of restoration mortars were experienced by Griffin, 2004 [14] and Slavid et al, 2013 [15]. The later authors created a lime- metakaolin grout, using pozzolanic admixture, dehydroxylated clay, which could be a base for conservation materials. Compatibility studies on lime-based repair mortars for hystoric monuments to improve the durability was also performed by Stefanidou, 2013 [16], who added nano-SiO_2 to mortars. The obtained nano-modified lime-pozzolana binder had dense structure with reduced large pores. Balog et al, 2014 [17], and Cobirzan et al, (2015) [18], also showed the importance beside the physico-mechanical features the petrographic properties compatibility ones between the renovation building stone and the historical building masonry. Arizzi, 2012 [19], in her Ph.D. thesis focused on physical, chemical, mineralogical and petrographical characterization of mortars, components and studied also durability of the mortars. To improve durability of lime-mortars (calcitic lime + calcareous aggregate), used different admixtures such as $Ba(OH)_2$, for resistance towards freeze and thaw cycles, added synthetic/natural flexible fibres to improve compactness and deformability. The author also evidenced that compatibility problems between the mortar and building stone can arise when "use cement as additive in lime-based mortar, because it impair the longevity of the masonry that encloses it". Based on previously presented researches, in our study we focused on the volcanic tuff used for construction of residential and monumental buildings in areas with large deposits of tuff. Around the northern and southern-southeastern border of Transylvanian Basin outcrops an important Badenian stratigraphic level and marker horizon in gas and salt exploration (Szakács et al, 2012, Krézsek and Bally, 2006, Mârza et al, 1991, Ciupagea et al, 1970 [20- 23]) the "Dej tuff complex", (known also under various names such as: Hădăreni tuff, Dej tuff, Tiocu tuff, Slănic tuff, Persani tuff etc) consisting of: "volcanoclastic sandstones and conglomerates, medium to fine- grained tuffs and alternating thin layers of tuffs, tuffites and tufaceous marl…" (Szakács, 2003) [24]. Dej is one of the Romanian towns located in Transylvania in which there are many buildings made of tuff blocks. Due to long time activity of the Dej cellulose factory (4km distance from the town centre), a high quantity of greenhouse gases have been emitted into the atmosphere and air pollution with SO_2, CO_2, H_2S and acid rain have been the consequence. The acidic rain could caused external sulphate attack on tuff-made buildings. The anthropogenic pollution along with other natural phenomena (temperature, rainfall and humidity conditions of transitional continental temperate climate type, groundwater, Badenian salt- containing geological background, surface weathering, settlement etc.) leads to the degradation of a high number of tuff outcrops and buildings, one of them being the historical Reformed Church from Dej (Cluj County, Romania).

The Reformed Church (*Fig.1*) was built in the early fifteenth century, and since 1902 has been considered a historical monument (Kádár et al, 1902) [25]. From an architectural point of view, the monument was built in the Transylvanian Gothic style, with carved stone elements. The church was traditionally surrounded by fortifying walls. Few wall inscriptions and other written documents (Kádár et al, 1902, Entz, 1942) [25, 26] indicate restauration data, such as: 1588 or after 1591 burning (during the reign of Báthory Zsigmond (1581–1602)). In 1612, under Báthory Gábor's governance (1608–1613) the fortifying wall was enlarged and later, under the governance of King Rákoczy György (1630–1648) was restored many times between 1634 and 1642.

At the end of 1880s, the fortifying walls of the church were demolished and rebuilt their present form using the plans of Ferenczi Endre and Debreczeni Balázs. The last restauration works from 2013 mainly consisted of replacing carved stone in the south, south-eastern and eastern fortifying walls and church building with tuff tiles and blocks from Tiocu quarry (close to Dej) and mortars composed of cement, lime and aggregates (river sand). The northern wall and the ornamentation of the south-western wall are still in the previous state of alteration and exfoliation.

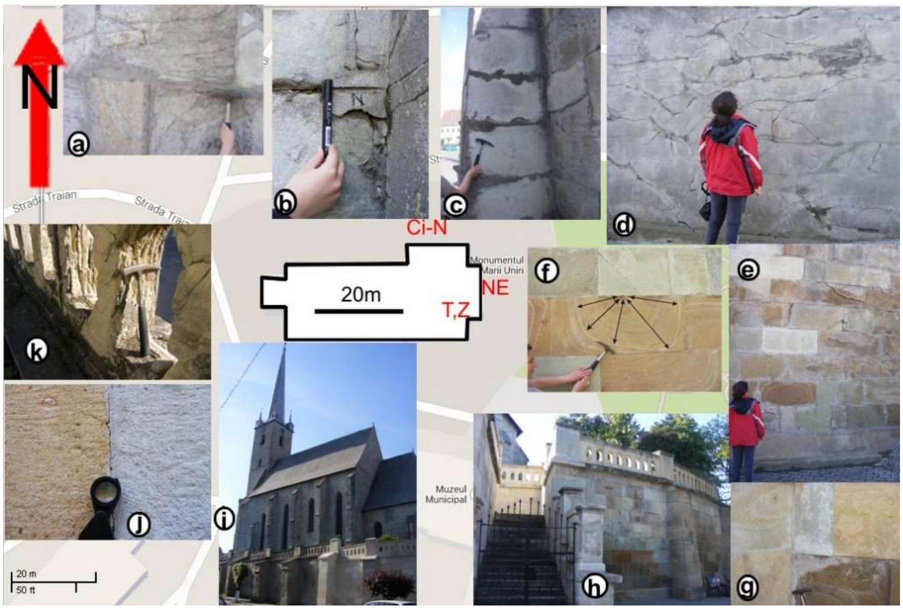


Fig. 1 - The church plan and investigated elements: north part of the wall (a- d); east (e- g) south-est (h, j), south (i) and south-west (k); the CiN, NE, T, Z sample locations. ./ *Planul bisericii şi elementele investigate: partea N a zidului (a- d); partea E (e- g); partea SE (h, j); partea S (i) şi SV (k); figurează locaţiile probelor CiN, NE, T, Z*

The topic of paper was an archaeometric study investigating the causes of building material decay and its conservation/degradation state. These investigations can help the future historical restoration works in area with big volcanic tuff resources and to find the best fitting compatible (from all points of view) building stones and mortars.

2. Results and discussion

Our research was based on site inspections and investigations made on mortar and tuff block samples (samples G, NE, CiN from *Table 1*,) removed from construction during the last restauration process and new materials (tuff tiles– sample 3a, 3b and mortars– sample T, Z) used for the last renovation. All the collected samples were analyzed petrographically and mineralogically, in thin sections under a Jenapol transmission polarizing microscope, in plane polarized light (N//) and cross polarized light (N+). The data were completed by XRD analyses. The mineral phase identifications made by X-ray diffraction were performed with a Bruker D8 Advance diffractometer with Bragg-Brentano geometry, CoK$\alpha 1$ with λ = 1.78897, Fe filter and a one-dimensional detector, using corundum (NIST SRM1976a) as an internal standard. The data were collected on a 2θ = 5 - 64° interval, at a 0.02°, with the measuring step of 0.2 seconds. The identification of the mineral phases was performed with the Match 2.1 software, using the PDF-2 (2012) database. To outline the sulphate attack minerals staining methods (Friedman method, 1959, [27] adjusted by Ingham 2013 [28] for dolomite and gypsum identification) were also applied. Other studies implied water absorption determination, according to STAS 2414- 91 and STAS 6200/12- 73 [29, 30]) on previously (NE sample- mortar and tuff) and last used (3a, 3b samples of tuff tiles) building materials samples, saturated in water at 21ºC, then dried in oven at 105ºC until constant mass. The applied formulas for water absorbtion was:

$a = [(m_s - m_d)/m_d].100$,

where a= water absorbtion, m_s= water- saturated sample mass, m_d= dried sample mass. Measurement units: %.

2.1. Field inspections

The visual investigation on site revealed different states of conservation of the building walls: weathered old tuff blocks having stratification planes normal to the exposed surface (*Fig. 1a*); biological attack (fungi, lichens, moss) overexposed to high stagnant humidity zones, (*Fig. 1b*); blocks and mortars (used for repointing and rendering) on which observed different stagnant humidity (*Figs. 1c, d*); different sort types of tuff tiles and blocks, having different positions of stratification plane in exposed surfaces; diffusion controlled concentric

Table 1

Sample locations and descriptions/ *Localizarea probelor şi descrierea lor.*

Samples	Location	Descriptions
CiN	N of wall	-Felt piece of previously used mortar, weathered.
N	N of wall	-Alteration crust with salt efflorescences which was scraped along the inner side of the CiN sample
NE	E of wall	-Felt piece, due to weathering, consisting of mortar + tuff parts.
T	SE of wall	-Last restauration mortar: small conical moulded pieces with 2cm radius (for mortar color testing ?)
Z	SE of wall	-Appears to be the same as T, but is a felt piece from wall..
G	SE of wall	-Alteration crust (calcite- dominated) on old tuff block
3a		Tiocu tuff tile, grey colored
3b		Tiocu tuff tile, yellowish colored

weathering zones (yellow, yellowish-brown) along the vertical stratification plane (arrows show the diffusion directions) (*Figs. 1e- i*); shrinkage fissures along bed joints between two sorts of tuff tiles (*Fig. 1j*); exfoliation of carved stone on the western side (*Fig. 1k*).

2.2 Sulphate attack evidence - staining method

Applying a specific staining solution on inner, outer-surface and transversal section of rendered layer, the gypsum is stained purple, dolomite- very pale purple, but calcite and quartz is not colored. (*Figs. 2a- d*). This staining method of Friedman, 1959 [27] for dolomite discrimination was adjusted by Ingham (2013) [28] for dolomite and also gypsum identification. The result should be: "gypsum stains purple, anhydrite and calcite remain unstained, while dolomite stains very pale purple." [28] In our case, it appears that gypsum is enriched both in the outer and the inner part of the rendering layer. The causes of such gypsum enrichment are both intrinsic (the chemical composition of cement binder and extrinsic (environment pollution and moisture).

2.3. Petrography and mineralogy by transmission polarizing microscopy

The Dej tuff's (sample 3a and 3b) components are: crystalloclasts (60 % rock volume) of maximum 500 micrometer size (quartz, feldspar, biotite and finely dispersed iron-bearing opaque minerals), lithoclasts (gneiss, carbonatic sandstone, bioclasts) and a porous glassy groundmass (40% of the rock's volume) with chloritised, sericitised, zeolitised, and carbonated volcanic glass, hyaloclasts. (The nature and characterization of zeolites from other locations of Dej tuff complex level were made e. g. by Bedelean et al, 2010; Mocanu et al, 2008) [31, 32]; stability and genesis possibility (exogenetic weathering, at low temperatures) of secondary zeolites was also outlined by Bogdanov et al, 2009 [33] experiments). The rock pores obviously have channel-like shapes, containing secondary carbonate infillings and/or iron hydroxides. The studied two tuff samples have different colors and degrees of weathering: sample 3a, grey colored and sample 3b, yellowish colored, the later is due to more advanced alteration of rock's mafic iron-containing minerals, such as biotite and opaque minerals.

Sample G represents a weathered layer on replaced tuff block, which consist of an external mainly hard calcitic cover with iron hydroxide films (*Fig. 3a*). Under it, there is a palagonitic volcanic glass matrix (60 % of the rock's volume) with shards and phenocrysts of quartz, chloritised biotite, amphibole and carbonated zeolitised plagioclase. The weathered, exposed side of tuff contains many elongated voids running normal and subparallel with its surface. The voids are outlined by calcite grains and a thin film of $Fe(OH)_3$.

The microscopically studied **NE sample** is a little piece of exfoliated mortar or grout which fell due to moisture and weathering. The mortar is cement-dominated and appears as a cryptocrystalline carbonated mass with hydrated and partially hydrated relic cement grains (belite, ferrite). In the external part, it is intensively leached, having microporous structure with secondary carbonate deposits containing gypsum filled voids.

Fig. 2 - Evidence of the gypsum by the staining method, before and after coloring the CiN sample (a, b inner surface; c, d transversal section) */ Evidenţierea ghipsului prin colorare diferenţiată a probei CiN, înainte şi după colorare (a, b suprafaţa interioară; c, d secţiunea transversală).*

The mortar’s fine aggregates, mainly feldspars, were partially or totally pseudomorphosed (replaced) by gypsum crystals and ”popcorn calcite” (Sibbick and Crammond, 2003 [34]) deposition.

In *Figure 3b* of **NE mortar** there is a porous secondary CO_3 crust (upper right corner) on the cement based mortar surface. In the mortar can also observe bleeding fissures and leaching effects. In an elongate void there appears to be ettringite filling (needles with dark grey birefringence). In the same NE mortar sample from *Figure 3c* can observe plagioclase clast and “popcorn calcite” deposition, the later due to cement + unhydrated lime based mortar decay. The *Figure 3d* of NE sample illustrates weathered mortar surface with high porosity, shrinkage fissures, bleeding fissures (channels) network with carbonate, promoted by AAR. The voids (circular pores, V- shaped extensional fissures) linked between by bleeding fissures running parallel with the surface and are lined by gypsum and secondary carbonate. The map fissures, meeting in triple points (dry shrinkage, French, 1991 [35]) are filled also by secondary minerals (e.g. calcite, gypsum or secondary ettringite) .

The **CiN sample** is a Portland cement based old rendering collected from the N part of the fortifying wall. The petrographic observations (*Fig. 4a)* showed that in mortar, the cement: aggregate ratio is of about 1:2. The carbonated cement binder is highly porous and partially leached in elements. The mortar matrix is mainly amorphous up to cryptocrystalline in the inner part of the render. The

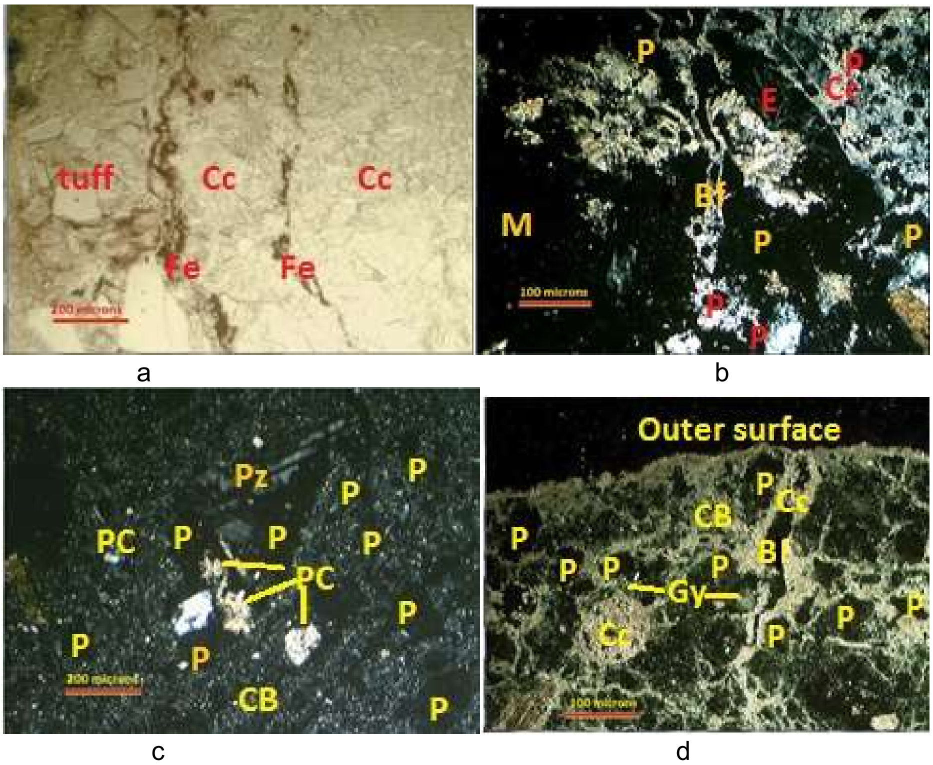


Fig. 3 - Microphotos of G, NE sample thin sections: a) G sample: boundary between tuff (left side) and weathering iron hydroxide + carbonate crust (right side). Scale bar 200 micrometers (N//), (Cc = calcite, Fe = iron hydroxides). b) NE sample of mortar: porous secondary carbonate crust (upper right corner) on the cement based mortar surface. There are bleeding fissures and leaching effects. In an elongate void there appears to be ettringite filling. Scale bar 100 micrometers (N+) (Cc= calcite crust, P= pores, Bf= bleeding channel, fissure, E= ettringite needles). c) NE sample of mortar: plagioclase clast and “popcorn calcite” deposition. Scale bar 200 micrometers (N+), (Pz= weathered plagioclase clast, P= pore, PC= popcorn calcite, CB = carbonated cement binder). d) NE sample of mortar: weathered cement + lime based mortar surface: high porosity, shrinkage fissures, V- shaped extensional fissures, bleeding fissures network with carbonate, promoted by AAR. The voids lined by gypsum and secondary carbonate. Scale bar 100 micrometers (N+). (P=pores, CB= porous carbonated cement binder)./ *Microfotografii de secţiuni subţiri pe probele G, NE: a) Proba G: limita dintre tuful vulcanic (partea stângă) şi crusta de alterare cu hidroxizi de fier + carbonat (partea dreaptă). Bara de scară 200 micrometri (N//). (Cc = calcit, Fe= hidroxizi de fier). b) Proba mortar NE: crustă de carbonat secundar, microporoasă (colţul drept sus) pe suprafaţa mortarului pe bază de ciment. Se observă fisuri şi efecte de levigare. Într-un por alungit pare să fie umplutură de ettringit. Scara de bară 100 micrometri (N+). (Cc= crustă calcit, P= micropori, Bf= canal de levigare, E= ace de ettringit). c) Proba mortar NE: Clast de plagioclaz din mortar şi depuneri de calcit tip popcorn. Scara de bară 200 micrometri (N+). (Pz= clast de plagioclaz alterat, P= por, PC= calcit tip popcorn, CB= liant de ciment carbonatat). d) Proba mortar NE: suprafaţă alterată de mortar pe bază de ciment + var: porozitate ridicată, fisuri contracţionale de uscare, fisuri extensionale sub formă de ”V”, reţea fisuri de levigare cu umplutură carbonatică, iniţiată de AAR. Golurile sunt tapetate cu ghips şi carbonat secundar. Bara de scară 100 micrometri. (N+). (P= por, CB= liant de ciment carbonatat, poros).*

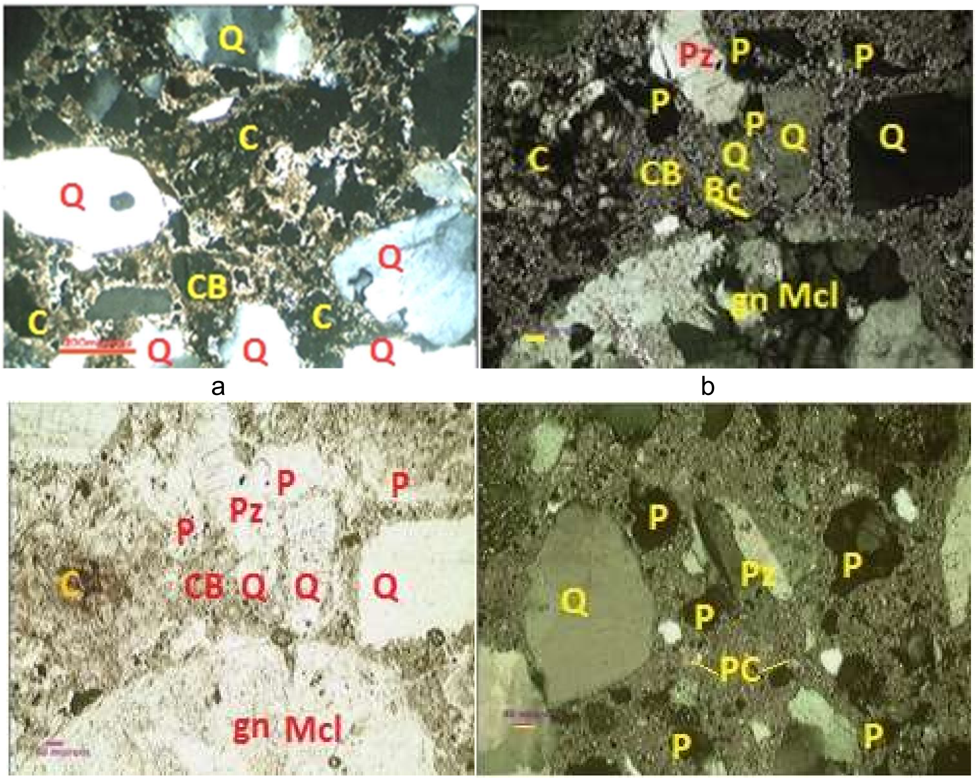
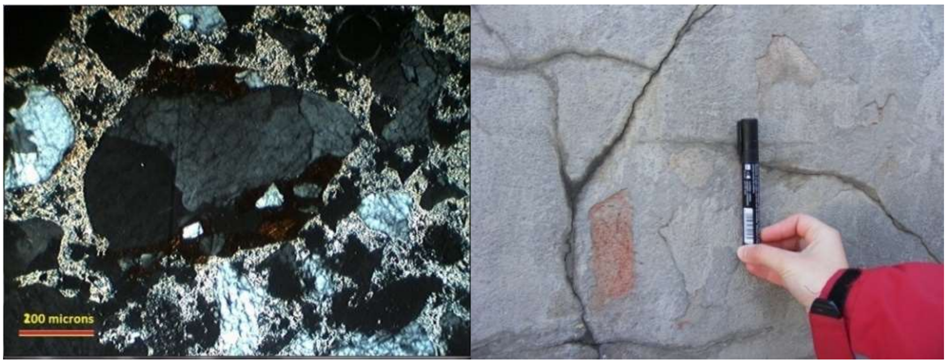


Fig. 4 - Microphotos of old (CiN) and newer (T, Z) mortar samples: a) CiN sample: relic Portland cement grain (alite C_3A, belite C_2S, opaque ferrite) with carbonated corona in the mortar's binder. Scale bar 200 micrometers. (N//) (C= insufficiently hydrated relic cement grain, CB= hydrated cement binder, Q = quartz grain). b) T sample: poorly sorted (graded) sand in mortar. Microcline gneiss lithoclasts and quartz grain having a good reaction (adherent) corona with the cement binder. On the left side is an insufficiently hydrated relic cement grain containing C_3S, C_2S with twin lamellae, isotropic C_3A and opaque ferrite. Scale bar 40 micrometers. (N+) (gn Mcl = lithoclast of microcline gneiss, Pz= plagioclase, Q= quartz, C= relic cement grain, Bc = bleeding channel linking pores, CB = carbonated cement binder). c) Same as b), but N//. Scale bar 40 micrometers. d) Z sample: zeolitised twinned plagioclase (Pz) and quartz clasts are in a carbonated cement + hydraulic lime (evidenced by "popcorn calcite") binder matrix. The pores are sometimes linked between by bleeding channels (bottom right corner). Scale bar 40 micrometers. (N+) / *Microfotografii pe probe de mortar vechi (CiN) şi mai nou (T, Z): a) Proba CiN: granul de ciment relict (C_3A izometric, C_2S cu lamele de maclă, C_3S izometric având birefringenţă gri), având o coroană carbonatică subţire, Bara de scară= 200 micrometri. (N+). (C= granul de ciment relict:, CB= liant de ciment hidratat, Q= granul de cuarţ). b) Proba T: nisip slab sortat (sortare gradată) în mortar: litoclast de grais microclinic şi granul de cuarţ, având coroană de reacţie bine dezvoltată (aderentă) la contactul cu liantul de ciment. În partea stângă a imaginii este un granul relict de ciment insuficient hidratat, conţinând C_3S, C_2S cu lamele de maclă, C_3A izotrop şi ferrit opac. Bara de scară 40 micrometri. (N+). (gn Mcl= litoclast de gnais microclinic, Pz= plagioclaz, Q= cuarţ, C= granul ciment relict, Bc= fisuri de levigare interconectând micropori, CB= liant de ciment carbonatat). c) Similar cu b) dar N//. Bara de scară 40 micrometri. d) Proba Z: Claste de cuarţ şi plagioclaz (Pz) maclat, zeolitizat, dispuşi în matricea liantului compus din ciment carbonatat + var (ultimul subliniat de "calcit tip popcorn"). Porii uneori sunt interconectaţi prin fisuri de levigare (colţul dreapta jos). Bara de scară 40 micrometri. (N+).*

voids are frequently filled with secondary minerals ($Fe(OH)_3$, sulphates and carbonates). The aggregates are angular, sub-angular and present fissured and sub-rounded mainly feldspar, quartz, garnet grains, and lithoclasts of andesite, quartzite and gneiss. Along grain boundaries there are many pores, linked between by leaching fissures and an ASR induced microscopic pore network. Can also observe many relic Portland cement grains in the mortar's binder probably due to using incorrect water: cement ratio. The insufficiently hydrated relic cement grains contain: opaque ferrite C_4AF needles, short prismatic alite C_3S, light colored lamellae of belite C_2S. Relic cement grains were covered by a thin carbonated corona.

Samples T and ***Z*** *(Figs 4b-d),* both represent newer restauration mortars with a binder: aggregate ratio around 1:3. It is based on: Portland cement, hydraulic lime and fine aggregates of natural sand. The sand component contains mixed rounded (mainly 1-2mm size) and sub-angular grain forms (pyroxene, amphibole, garnet, quartz, perthitic feldspar, zeolitised plagioclase, opaque minerals, biotite, calcite and lithoclasts of andesite, microcline- gneiss and quartzite) with graded granulometry, i.e. poorly sorted sand which ensures a very good adherence between mortar components and low permeability, based on Ingham, 2013 [28] observations. In the fine grained carbonated binder was also observed: partially hydrated cement grains (belite, alite and intergranular phases such as ferrite and aluminates) of 100 micrometers, entrapped irregular pores of 30-40 micrometers, circular entrained voids of around 50 micrometers, probably owing to using an additive (providing more space for freezing water). The render have porosity of 10-20 % of thin section area, but porosity may also due to inadequate



a b

Fig. 5 - a) Microphoto of old CiN mortar (dark rims of ASR gels, in the left part, N+). The scale bar is 200 micrometers. b) Macroscopic map fissures on the same wall as sample CiN . The red colored brick appears under weathered render. Here may also observe that the brick was covered, at least twice, by Portland cement based render./ *a) Microfotografia mortarului vechi CiN (conture izotrope de geluri tip ASR, partea stângă). Bara scării este de 200 micrometri. Imagine N+. b) Fisurare tip hartă la scară macroscopică, pe acelaşi perete ca proba CiN. O cărămidă roşie apare de sub tencuiala alterată.Se pot de asemenea observa şi două straturi de tencuială pe bază de ciment Portland acoperind cărămida.*

compaction. The pores appear to be linked by bleeding channels. The mortar binder consists of carbonated cement and hydraulic lime, the latter evidenced by ”popcorn calcite”. On the left side of *Fig 5c* there is an insufficiently hydrated relic cement grain containing: C_3S, C_2S with twin lamellae, isotropic C_3A and opaque C_4AF. The frequency of relic cement grains are also due to unproper binder recipe, i.e. incorrect water: cement ratio and the water insufficiency could have been intensified by zeolites hydration.

An ASR (a type of alkali-aggregate-reaction –AAR- Stanton, 1940 [36]) deleterious phenomenon can be observed in the sample CiN microphoto (*Fig. 5a*). Highly fissured quartz grain experienced ASR. Resulting silica gels are cryptocrystalline (dot-like spots with white birefringence in *Fig. 5a*), were deposited along its fissures and around grain radiating micrometric fissures in the carbonated matrix. In *Figure 5b* is outlined the intrinsic ASR combined with frost attack and leaching and the map-fissures resulted on macroscopic scale. The alkali sources are cement minerals and bricks’metakaolinite. In the picture may also observe that the brick was covered by two successive thin layers of Portland cement based render, of which humidity could reactivate the dissolution- deposition cycles.

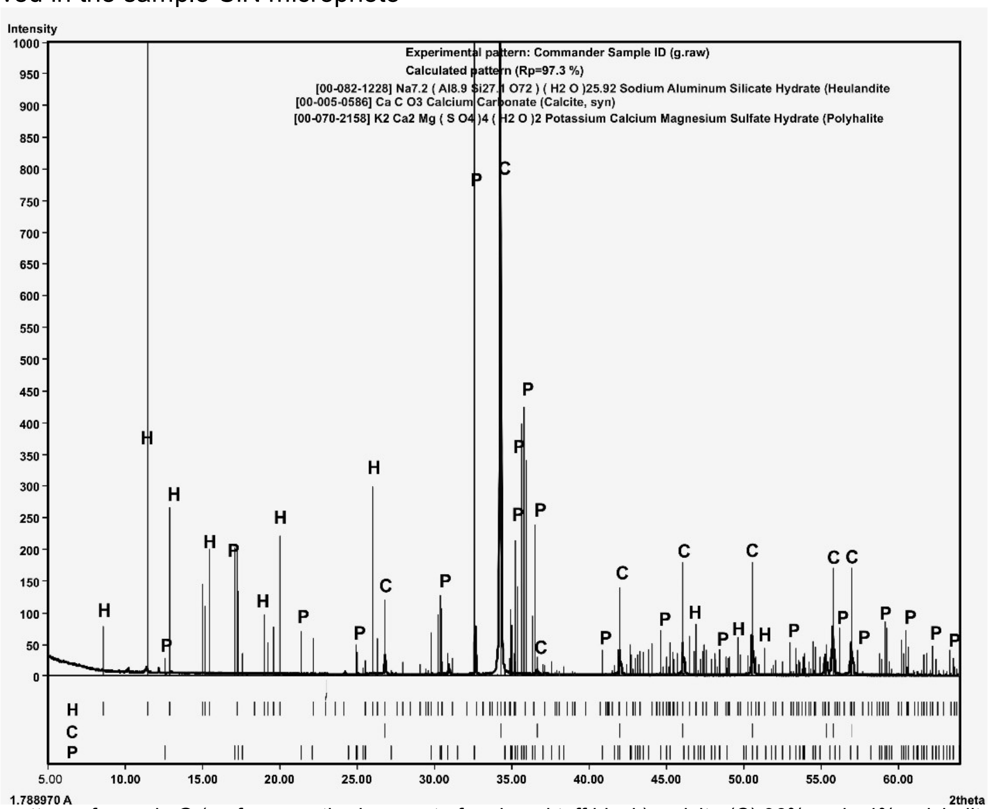


Fig. 6 -The XRD pattern of sample G (surface weathering crust of replaced tuff block): calcite (C) 96% and <4% polyhalite (P) and heulandite (H)./ *Difractograma probei G (crustă de alterare): calcit (C) 96%, iar polihalit (P) şi heulandite (H) sub 4%.*

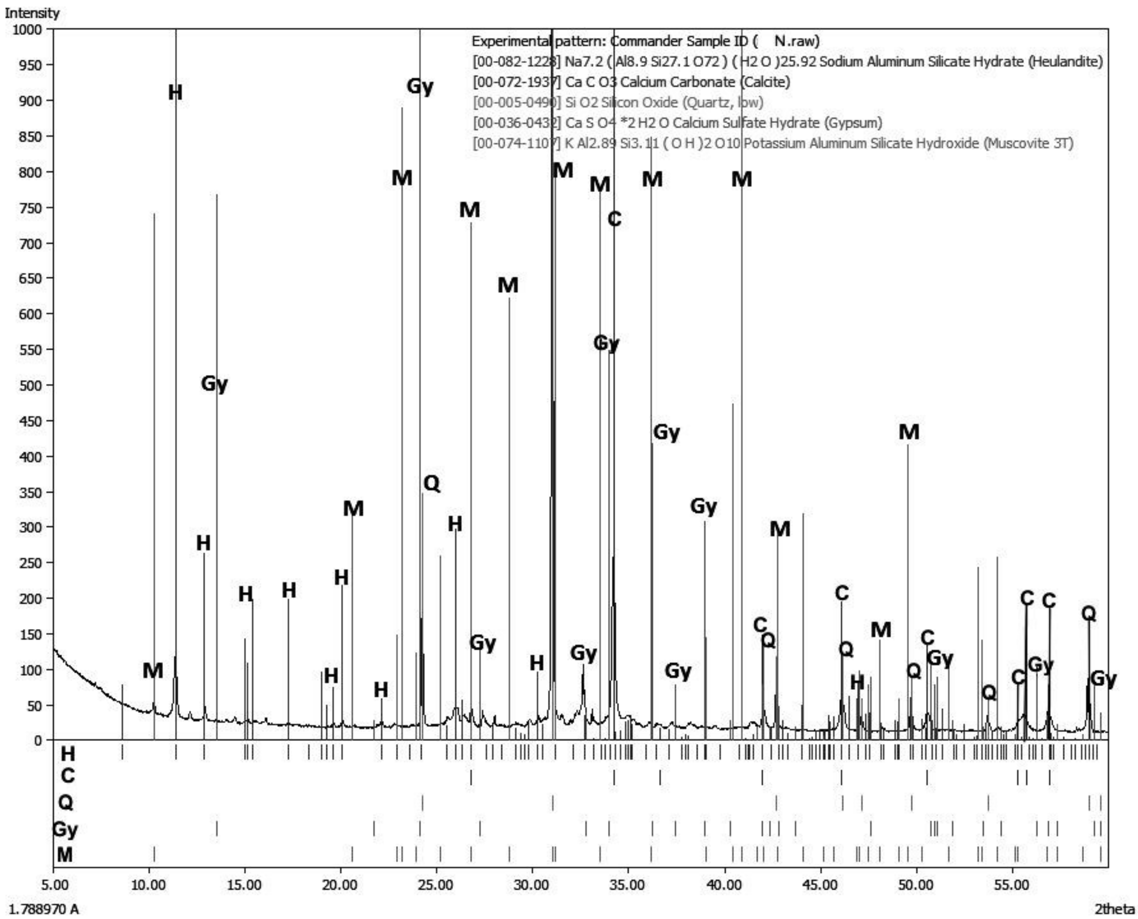


Fig. 7 - The XRD pattern of sample N (render's weathering crust from the northern wall). Composition: heulandite (H) 2.9%, calcite (C) 10.6%, quartz (Q) 9.6%, gypsum (Gy) 20.3%, muscovite (M) 56.6%. / *Difractograma probei N (crustă de alterare pe tencuială din zidul N). Compoziţia: heulandit (H) 2,9%, calcit (C) 10,6%, cuarţ (Q) 9,6%, ghips(Gy) 20,3%, muscovit (M) 56,6%.*

2.4 Mineralogy of weathering crust by XRD

The XRD pattern of sample G (*Fig. 6*) demonstrated the presence of calcite (96 %) in the weathering crust of replaced tuff blocks and a potentially high probability of polyhalite beside secondary heulandite. Other secondary minerals could not been identified by this method due to very low quantity and the metastable or instable feature of such secondary minerals, depending on the sample's moisture.

Sample N is an alteration crust with salt efflorescence which was scraped along the inner side of the CiN sample. The XRD analysis of resulted dust (*Fig. 7*) was able to show that besides the muscovite (crystal blades used whether as an ornamental component or as admixture in render recipe for improving the deformability), there are few secondary minerals such as calcite, heulandite and gypsum (the later also evidenced on the same CiN sample by staining methods (*Fig. 2*).

2.5 Water absorption tests

The water absorption measurements of samples were made in order to verify the compatibility between component materials from masonry works (tuff block and mortar). Unfortunately, water absorption of newer mortar could not determined due to very small size of available sample. The water absorption tests on replaced tuff and mortar samples demonstrated for the NE tuff sample: 8.269 % and for used mortar: 1.521 % at exterior and 6.405 % for the inner part of same mortar layer. The humidity stagnation at the boundary between the two materials increased leaching-deposition effects and the consequence was a higher porosity of inner parts with salts infillings. Sample 3a (grey tuff sort) has water absorption of 1.04 %, but sample 3b (yellowish brown, weathered tuff sort) – 4.84 %, both sample originating from Tiocu quarry (close to Dej). The differences in water absorption capacity between two neighboring tuff tile in a masonry means that the tuff with higher absorbency extracts more water during mortar hardening and insufficiently hydrated mortar side creates shrinkage fissures along bed joints. These fissures will enlarge due to moisture-induced leaching, diffusion, dissolution and salt crystallization expansion forces, freeze-and-thaw, all resulting in a high state of degradation of the construction. The old render sample CiN from the N wall has lower humidity (1.37 %) and lower porosity than the neighboring weathered old tuff blocks of the wall. It is also a physical incompatibility between component materials, because the porosity differences creates a stagnant humidity and salt mobilization- deposition phenomena along the slower breathing material boundary which intensifies their decay.

3. Conclusions

The identified decay processes in fortifying walls have been caused by external (natural environment, climate and anthropic pollution) and internal factors (due to building stone mineralogy: volcanic glass, reactive silica content, zeolites content; petrography: the lower weathering resistance along stratification plane of tuffs and applied mortar mix compositions). The physical and chemical incompatibility of Portland cement-based mortar and volcanic tuff blocks or bricks beside the volcanic tuff blocks in the fortifying walls recently represents the most important decay factor and in the end all accumulated leaching and expansion effects are connecting to this feature. Different types of cracking could be detected: physical: drying shrinkage, salt crystallization; chemical: ASR, cement carbonation, leaching associated with secondary carbonation and sulphate attack induced expansive phenomena; thermal cracking: frost attack. The used materials compatibility and moisture are the cause of many deleterious phenomena, such as frost attack, salt crystallization, sulphate attack and AAR which all promote expansive processes. Intrinsic and extrinsic sulphate attack could be detected owing exclusively to the anthropogenic effect: acidic rain (Dej Cellulose Factory- air pollutant gases emissions), Portland cement SO_4^{2-}content and sulphate minerals expansive crystallizations. The humidity induced degradation (exfoliation) appeared to intensify where the tuff tiles were put in the masonry with stratification planes in vertical position. The weathered, carbonated, zeolitised tuff blocks and bricks assembly containing salts and active silica and alumina was covered, at least twice, by a wet Portland cement based render which reactivated the salts dissolution-deposition cycle. The high impermeability of the hardened render maintained for a long time the salt mobilization under the render layers and increased secondary porosity along the boundary between the tuff and render.

The progressing decay processes could be minimizing if the following suggestions taking into consideration:

- all the tuff tiles in vertical position should be replaced with tiles cut perpendicular to the stratification in order to prevent rain water penetration;
- the use of bricks between tuff blocks should be avoided, due to geochemical incompatibility and alkali salt attack risk in walls;
- for repointing of bed layer blocks, one should use mortar having mixture compositions compatible with tuff and existing mortar (e.g. tras or hydraulic lime as binder and natural uncrushed riversand to avoid ASR) and possibly some admixtures either for biologic disinfect or freeze- thaw effect reduction or to improve mortar workability;
- the petrographic feature (stone sort) of the tiles should be the same for all elements (the same porosity, permeability, petrography, mineralogy);
- the water/binder ratio of mortar should be measured, taking also into consideration for the stone's water-absorption capacity;
- all cement based render and brick elements should be removed and replaced by unweathered grey colored tuff blocks from the same quarry (Tiocu). For fixing the tuff blocks, the same mortar receipt as previously presented should be used;
- occasionally, a compatible thin protection rendering on the tuff blocks could be applied.

Based on archaeometric study results, the causes of masonry decay are very complex and require a multidisciplinary approach from a petrographic, mineralogical, geochemical, physico-mechanical compatibility point of view.

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