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Dedicated to Professor Liviu Literat, at his 80th anniversary

MINERALOGY OF DEGRADATION PROCESSES AFFECTING THE MORTAR FROM BURU DAM (ARIEŞULUI VALLEY, CLUJ COUNTY)

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ABSTRACT. The objective under study is represented by the dam construction work across Arieş River on the area of Buru locality (Cluj County). The mortar used in dam construction is affected by carbonation, sulphates attack and alkali-silica reactions. Carbonation is materialized by calcite precipitation in matrix mortar, visible as efflorescences on surface and along the fissures within the mortar. Sulphate attack results in ettringite II genesis, located in the pores of the mortar. The alkali-silica reactions lead to the formation of silica gels deposited on the internal walls of the pores where they progressively crystallize and turn into cryptocrystalline silica. There are various causes for alteration processes, from atmospheric factors to the microenvironment resulted from the high polluants concentration into the Arieş River water.

Keywords: *mortar, carbonation, sulphate attack, alkali – silica reactions*

INTRODUCTION

The degradation processes affecting mortars represent the major factor determining their durability. These are controlled by both the exploitation condition for the works consisting of building materials and hydraulic binders, and the structural-textural and compositional properties of the mortar.

Concrete is a complex composite material used in various construction works, thus exposed to a wide range of destructive factors. The complexity of concrete types increased in time, due to increasing social requirements. The concrete applications and the exposure conditions represent great challenges for concrete durability. Thus it is important to be forseen the defects that may occur during the exploitation and that possibly can damage the concrete structure.

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Atmospheric factors such as rain – some of them acid, wind, drying-wetting or frost-thaw cycles affect the external surface of concrete in a large extent. Dissolution and gradual leaching of concrete under the action of slightly acid rains, or physical degradation due to drying-wetting cycles are easily predictable. The surface of concrete saturated in water is vulnerable to frost-thaw cycles which can trigger other destructive mechanisms [1].

The most frequent process brought about the atmospheric factors is concrete carbonation, this leading to a decrease of the concrete pH value from 13 to 8; and so initiates the steel reinforcement corrosion [2]. In concrete, the formation of carbonates is caused by the reaction between the product of cement hydration, $Ca(OH)_2$, and aggressive atmospheric or water dissolved CO_2. of The first phase of the process is calcite; it precipitates in the pores of the concrete, leading to its compaction and thus to an increase of its mechanical resistance. However, aggressive waters with variable contents of CO_2 can also infiltrate inside the concrete and dissolve the $Ca(OH)_2$. The higher rate of dissolution process considerably increases the pores water pressure, and consequently the concrete wall can be crossed by water. CO_2 reacts with $Ca(OH)_2$ forming a new calcite generation.

The following chemical reactions are responsible for these processes:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

Another cause for concrete degradation is the SO_4^{2-} bearing water. This ion reacts with $Ca(OH)_2$ from concrete, resulting a wide range of sulphate minerals. Gypsum ($CaSO_4 \cdot 2H_2O$) is the most widespread mineral identified in the strengthened concrete pores; its crystallization accompanied by a volume increase further intensify the internal tensions that possibly result in the concrete destruction. Another potential phase the ettringite ($Ca_6Al_2O_6(SO_4)_3 \cdot 31H_2O$) that forms according to the reaction:

$$Ca_3Al_2O_6\ 6\ H_2O + 3\ Ca^{2+} + 3\ SO_4^{2-} + 25\ H_2O = Ca_6Al_2O_6(SO_4)_3\ 31H_2O$$

The solid state reaction is accompanied by large volume variations that finally can damage the concrete or mortar. The intensity of the sulphate attack depends on SO_4^{2-} concentration in the water, as well as the presence of other cations and anions in the solution. The presence of primary ettringite resulted from the reaction of the calcium hydroaluminates from the cement matrix with the gypsum added for controlling the concrete strengthening and that of the secondary ettringite formed by water-related sulphate attack has been already evidenced [3].

Concrete composition

Concrete is a composite material consisting of cement matrix and natural or synthetic aggregates, the latter contributing up to 70 % to its mass, and having various grain sizes according to the concrete type and usage. Cement stone is obtained by hydration of mineralogical components of cement via an exothermal reaction leading to the formation of calcium hydrosilicates, hydroaluminates or hydroferrites that confer the final strength to the products [4]. The reactions are not a linear combination of hydration processes affecting individual components; for example, during the hydration of Ca_3SiO_5 and Ca_2 SiO_4 an amount of $Ca(OH)_2$ is released, which is not formed in the hydration of $Ca_3Al_2O_3$ and respectively Ca_4 $Al_2Fe_2O_{10}$. The aggregates are particles of various sizes of sand, fragments of natural rocks, synthetic materials, or waste materials, the most usual types being represented by natural rocks. The type of aggregate and its grain size depend on the composition and type of concrete.

The composition of a regular Portland cement stone is assumed to consist of 70 % C-S-H (calcium hydrosilicates) gels, 20 % portlandite, $Ca(OH)_2$, 3 % calcium hydroaluminates and sulpho-hydroaluminates and 3 % non-hydrated material [5]. Calcium hydrosilicates with high CaO content release a higher amount of $Ca(OH)_2$ as compared to those with low content of CaO, or to other hydrocomponents in the system [6]. Portlandite, $Ca(OH)_2$, from the cement matrix is concentrated at the interface with the aggregate particles giving birth to an aureole, or at the border of the pores resulted after the release of porosity water [7]. In contact with infiltration waters, $Ca(OH)_2$ gradually passes into solution until reaching its solubility limit, moment when the dissolution process ends. The solutions saturated in calcium hydroxide react with atmospheric, or the dissolved CO_2 with the bicarbonate ion from the infiltration waters leading to the formation of $CaCO_3$ and the decrease of the solution's pH; these processes finally result in the concrete degradation.

The aim of this study was to try to identify of degradation processes that altering the mortar used in the Buru dam (Cluj County), and the alteration minerals. The dam was made of concrete and finished by mortar (Figure 1). The dam mortar degradation si visible mainly due to the white efflorescences developed along irregular fissures cutting the mortar. The fissures affect the whole thickness of the mortar; they form a network imprinting a mosaic-like aspect enhanced by the presence, along their trajectory, of striking whitish carbonate deposits contrasting with the dark-grey colour of the mortar. Destruction processes show various intensities, from poorly-fissured areas to the detachment of irregular mortar fragments from the surface of the mortar layer. Samples were collected from intensely-fissured areas bearing white carbonate crusts. Sampling concerned the whole thickness of the mortar layer.

Figure 1. Fissures with carbonate deposits at the base of Buru dam (Cluj County).

RESULTS AND DISCUSSION

Petrographical features of the mortar. The Buru dam consists of concrete finished with mortar. The mortar layer up to 1 cm thickness consists of aggregate (65 %) and matrix (35 %). Structurally (Figure 2), the mortar is porphyroclastic (clasts -Terminology used in the petrography of natural rocks where *clast* means a fragment with variable composition and/or shape. *Porphiritic* refers to size-related features, suggesting inechigranular patterns, *i.e.* large sizes of the clasts as compared to the grains of the matrix of aggregate - of various compositions bound in a fine, crystallized matrix) and shows a porous texture. The primary pores are filled by secondary minerals resulted from degradation processes.

The aggregate consists of fragments of minerals and rocks. The mineral fragments are up to 1.0 mm in size and they are represented by quartz, microcline, plagioclase feldspar, muscovite, biotite, chlorite, green hornblende, garnet, vesuvianite etc. The lithic fragments consist of quartzites, micaschists, sericitic schists, gneisses, sandstones with carbonate cement, limestones. As a rule, the rock fragments are rounded but also angular in some cases; they show variable sizes, up to 1.5 – 3 mm. The mineralogic and petrographic characteristics of the aggregate suggest its source in the alluvia of the Arieş Valley. Granular fragments of non-hydrated clinker have been identified in the mortar, consisting of alite, belite and brownmillerite (Figure 3).

The matrix is finely-crystallized and microscopically it shows variable colouring. The carbonated areas are dominantly colourless, while the non-carbonated ones show brownish hues due to the co-existing iron hydroxides.

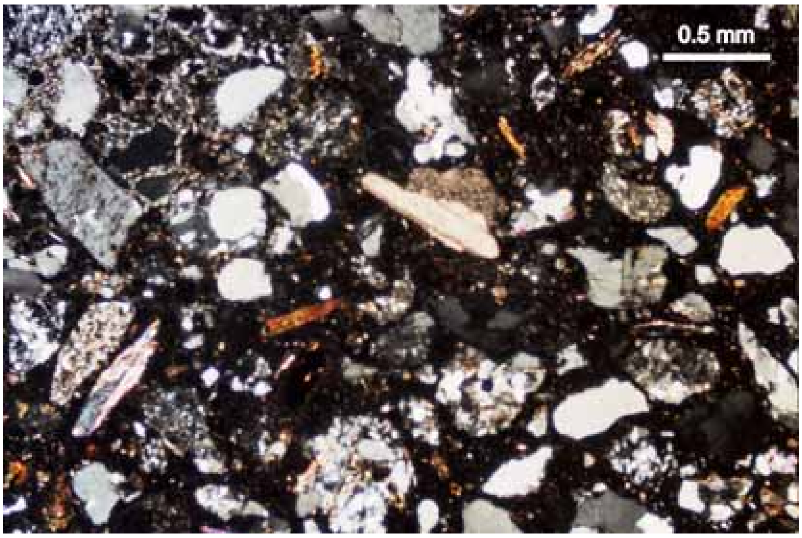

Figure 2. Porphyroclastic features of the mortar in the Buru dam. The matrix is finely-crystallized and impregnated with iron hydroxides (N+).

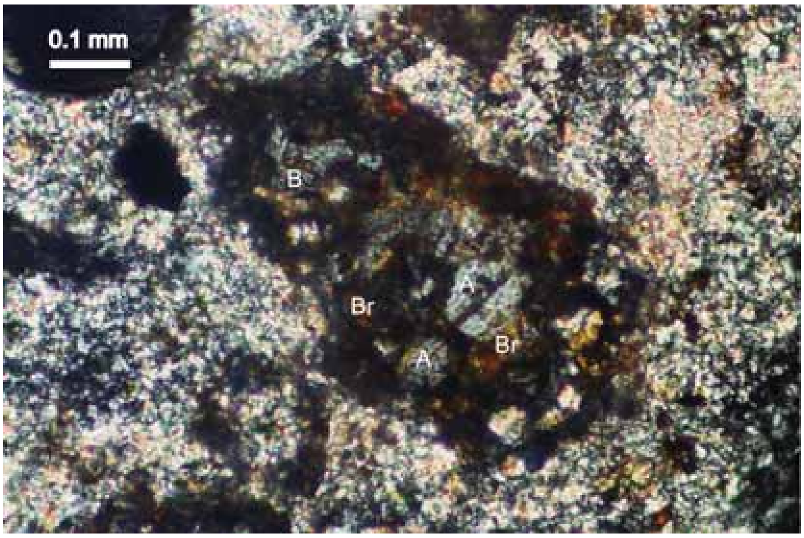

Figure 3. Non-hydrated clinker fragment in the matrix of the mortar (N+):
A – alite, B – belite, Br – brownmillerite

Mineralogical features of the degradation processes. Mineralogic and petrographic studies on the mortar of Buru dam have evidenced several degradation processes. Genetically, two types could be separated:

- Mechanical processes caused by frost-thaw phenomena. They are illustrated by the occurrence of fissures in the mortar mass, as well as at the concrete/mortar interface;
- Chemical–mineralogical processes: carbonation, sulphate attack and formation of silica gels following the alkalies – silica reactions (ASR). These processes are favoured by the mechanical ones and they consist in specific reactions between the hydration components of the mortar matrix and the various ions dissolved by the infiltration waters percolating through the pores and fissures within the mortar. They result in neoformation minerals specific to each degradation process. The spatial relationships among the new formed minerals and the primary components of the mortar, as well as those among new formed minerals typical to each degradation process allowed the chronological reconstruction of the alteration processes pathway.

Carbonation represents spatially, the most widespread degradation process. It was identified both macroscopically and microscopically and it consists in the impregnation of the mortar matrix and primary pores with granular calcite aggregates, as well as in the occurrence of crustiform white efflorescences along the fissures and in their proximity. It has to be noticed that carbonation occurs at the mortar/air, as well as to the mortar/concrete interfaces. The investigated samples pointed to a clear zonation of the carbonation process. Two distinctive areas could be identified in thin sections, under the microscope (Figure 4):

- Zone I – developed at the surface of the mortar, consisting of crustiform efflorescences built-up of successive layers of calcite with porous-spongy features. This particular texture of the crustiform calcite does not allow a good conservation of the material when thin sections are prepared transversal to the mortar layer. The stratified deposition of the secondary calcite is also obvious along the internal walls of the fissures within the mortar (Figure 5). X-ray diffractograms on samples from the white crusts have evidenced the presence of calcite and quartz, identified based on their specific d/n (Å) values (Figure 6). The source for quartz was, most probably, the sand used when the mortar was prepared.
- Zone II – occurs at the external margin of the mortar layer. It is up to 3 mm thick and it is characterized by the presence of finely granular calcite massively impregnating the mortar matrix. Calcite from zone II has been also identified in the pores of the mortar, where it fills the central area (Figure 8).

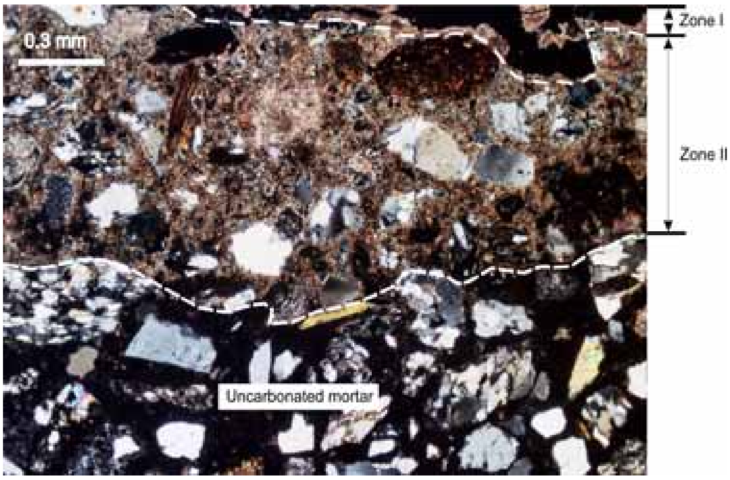

Figure 4. Zonation of the carbonation process (N+).

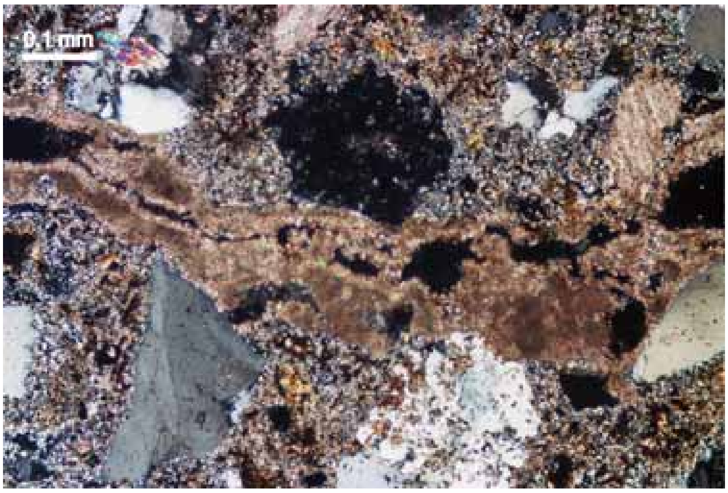

Figure 5. Stratified deposits of calcite along the walls of the fissures in the mortar, and as impregnations in the matrix (N+).

The formation of the secondary carbonates is attributed, mainly to the reaction between $Ca(OH)_2$ and the atmospheric CO_2.

A previous paper [8] has evidenced the presence of large concentration in anions: HCO_3^- (162 mg/l), SO_4^{2-} (~ 64 mg/l), and cations: Ca^{2+} (~ 49 mg/l), Mg^{2+} (7.1 mg/l), Na^+ (7.3 mg/l), in Arieş water (pH=7.4); these ions are responsible for the degradation process. The Arieş River pollution is caused by both mining activities in the area, as well as by the dissolution of some host rocks (carbonate rocks, andesitic rocks etc) in the neighbourhood.

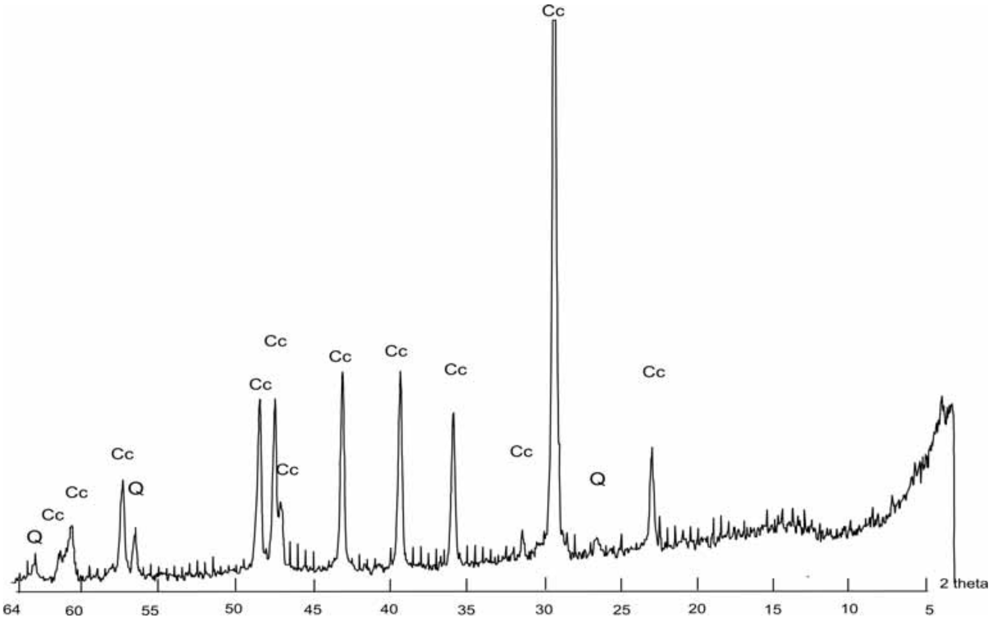

Figure 6. X-ray pattern of the carbonate crust developed along the fissures in the mortar (Cc – calcite, Q – quartz)

The sulphate attack has been evidenced during the microscopic study. Ettringite II results from this process; it is deposited in the primary pores of the mortar, where it is associated with calcite and secondary silica. Ettringite occurs as acicular crystals with random or sometimes radial orientation (Figure 7). Under polarized light it is characterized by parallel extinction, low birefringence and positive relief. Most probably, secondary ettringite forms as a product of the reaction between the calcium hydroaluminates from the cement matrix and SO_4^{2-} and Ca^{2+} present in the river water. The non-hydrated cement grains from the matrix, also gradually hydratea lead to the formation of calcium hydrosilicates and hydroaluminates, with the release of $Ca(OH)_2$. Thus, the sulphatation of hydrates represents a continuous process that follows alkali-silica reactions, as pointed out by the succession of layers in the primary pores of the mortar, images by optical microscopy.

Alkali-silica reactions (ASR) are poorly-represented in the studied samples; they have been identified only by optical microscopy, and resulted in the formation of cryptocrystalline silica deposited on the mortar pores.

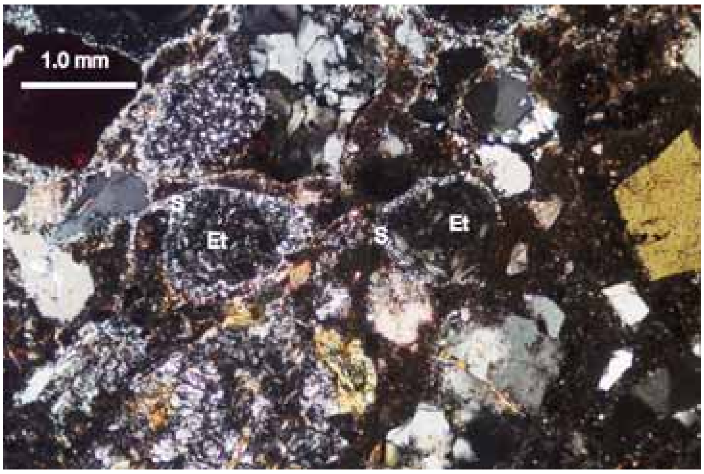

Figure 7. Acicular-fibrous crystals of ettringite (Et) in the primary pores of the matrix (N+). Cryptocrystalline silica covers the internal wall of the pores (S).

Cryptocrystalline silica represents the first product of the alteration process; under polarized light it shows low birefringence and relief (Figure 7). It forms by crystallization of silica gels present in mortar due to the interaction between alkalies from cement and the various species of active silica of the aggregate. The resulted gels have migrated from the mortar matrix towards the pores and fissures where they have gradually crystallized.

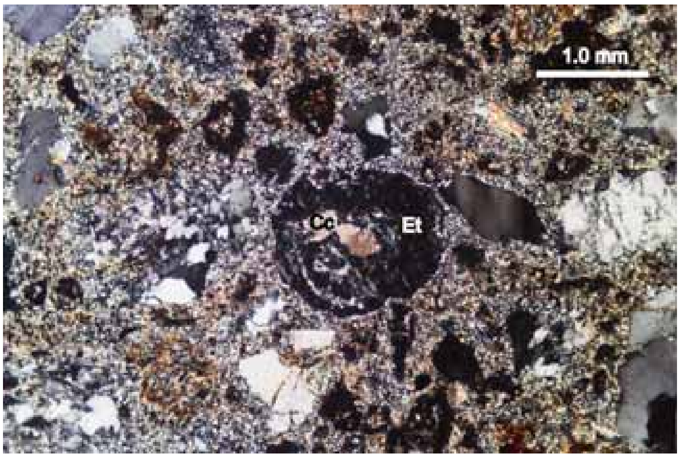

Figure 8. Pore in the mortar matrix filled by ettringite (Et) and calcite (Cc) in the central area (N+).

The spatial relationships between the alteration phases precipitated in the primary pores of the concrete have allowed the recognition of the temporal stages. Thus, the presence of the cryptocrystalline secondary silica (Figure 7) on the walls of the primary pores, points that it is the first product of alteration processes. It was followed by the ettringite II, which frequently fills completely the pores. Sometimes, the calcite resulted by carbonation appear as the latter filling of the central part of the pores (Figure 8). This succession indicated that carbonation followed the alkali-silica reactions and the sulphate attack.

CONCLUSIONS

The fissures produced within the concrete structure and the finishing mortar mainly resulted via frost-thaw cycles; additional to the primary porosity, they represented the access pathways for infiltration fluids. These fluids contain various ions from the Arieş River and the precipitation waters, as well as from the matrix of the mortar. Both CO_2 from the atmosphere and dissolved in the water, and SO_4^{2-}, Na^+ and Ca^{2+} ions contributed to the debut and progress of degradation processes (carbonation, sulphate attack, and alkali-silica reactions). The presence of SO_4^{2-} and Ca^{2+} in the mortar leads to the formation of ettringite II.

The original deposition of silica gels inside the pores suggests that the first reaction taking place in the concrete was between the silica in the aggregates and the alkalies from the matrix and from the infiltration waters. The silica gels are partly crystallized and they build-up the first (most internal) layer lining the pores. The high amounts of SO_4^{2-} and Ca^{2+} from the river waters as well as the retarded hydration of cement some compounds have facilitated the formation of secondary ettringite that represents the second layer within the pores.

The high concentration of $HCO3^-$ points to relatively lower amounts of aggressive CO_2, thus to its delayed reaction with $Ca(OH)_2$ resulting in the formation of $CaCO_3$ (calcite) consisting the last product precipitated within the pores.

The intense carbonation at the surface and in the fissures of the mortar suggest a strong diffusion of $Ca(OH)_2$ through the fissures and its reaction with atmospheric CO_2 during drying-wetting cycles.

The following time succession for the formation of secondary products could be documented: cryptocrystalline silica resulted by crystallization of silica gels is deposited along the internal walls of the voids, as a result of the first degradation process (alkali-silica reactions). This is followed by sulphate attack with the formation of ettringite II; the youngest stage was represented by carbonation. This precipitation succession is particular for the specific *in situ* microenvironmental conditions. In the case of the dam from Buru, the pollution degree of waters from Arieş River plays a dominant role in the succession of formation of secondary minerals. This pattern may differ in case of subaerial exposure, when the interaction with infiltration fluids containing dissolved ions is an intermittent process [3].

EXPERIMENTAL SECTION

Analytical methods. Several investigation methods were used complementary in the view of establishing the structural, textural and mineralogical characteristics of the mortar, as well as of the secondary minerals resulted by degradation processes. Macroscopic observations concerned the dam under study, which were used for selective sampling (mortar and material from the white efflorescences) in the view of laboratory study. These samples were cut into thin sections (25-30 microns) used for microscopic investigations. The study of the thin sections evidenced spatial relationships between the products of the various degradation processes, thus allowing a chronology of the deposition of neoformed (secondary) minerals to be established. These studies were carried out by optical microscopy under polarized light (Nikon Eclipse E 2000 microscope), under crossed (N+) or parallel (1N) nicols. The identification of secondary mineral species was additionally based on the results of X-ray diffraction investigation performed by using Dron 3 diffractometer with Cu anticathode in the 5 – 64^o 2θ interval.

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