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Mineralogical Assessment Regarding the Sustainability of Mortars Exposed to Sodium Sulfate Attack

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Abstract

The paper presents the mineralogical analysis in XRD and thin sections of three types of mortars, before and after immersion in a salty solution of sodium sulphate decahydrate (Na2SO4•10H2O). The proposal of the study it was to identify the chemical transformation of minerals, and the degree of mortars decay after 15 cycles of immersion in salty solution. These studies highlights the role of mineralogical analysis in conservation of building materials in order to avoid their deterioration when are exposed in aggressive environment.

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Keywords: XRD analysis; thin section; salt attack; minerals.

1. Introduction

Crystalisation of soluble salts in the pores of building materials with low density, can affect their sustainability and durability during constructions' lifecycle [1-8]. The scientific researcher's shows [9-12] that the chlorides effect can be less disruptive and produce lower disintegration of materials in respect to that reported in case of sulphates.

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The sulfate attack can be observed in numerous buildings (especially made of masonry works), directly as efflorescence on materials surfaces (rendering or masonry units), sub-efflorescence under the finishing (rendering) or as crypto efflorescence inside the pores of component materials (mortars and masonry units) [3-7].

At material level, chemical reactions can take place due to hydration product (calcium hydroxide, portlandite and alumina) which in the presence of water reacts with sodium and magnesium sulfate to form calcium sulfate (gypsum), delaying ettringite and thenardite [12-16].

The mineralogical content and chemical compound highlights the minerals transformation [15, 16], and their interaction with salt crystals.

The objectives of the study, it was to develop a new mortar recipe with improved physico-mechanical characteristics to resist to salt attack and to be used as an alternative to classical materials. In order to determine the sulfate attack on building materials have been realized 3 type of mortars recipe: sample 1 – mortar based on natural pozzolanic materials as substitute of cement in 50%, samples 2 and 3 - mortars based on natural pozzolanic materials as substitute of cement in 50%, with additives like plasticizer respectively air-entraining.

2. Materials and Methods

The study was performed on cubic samples of mortars, with dimension of 4x4x4cm. The test consisted in total immersion of samples for 2hours in a saturated solution of Na_2SO_4, 14% decahydrate (14g $Na_2SO_4 \cdot 10H_2O$ to 86g of deionized water). After immersion the samples were dried to constant weight in a ventilated oven at a temperature of 105ºC.

All samples were analyzed from mineralogical and petrographical point of view. The mineralogical content, the transformations and alteration processes were examined under transmitted light microscope in thin sections prepared according to STAS 6200/3-81 [17].

The X –ray diffraction (XRD) were recorded on BRUKER D8 Advance X-ray diffractometer, working at 45kV and 45mA. The $Cu_{K\alpha}$ radiation, Ni filtered was collimated with Soller slits. A germanium monochromator was used. The data of the X-ray diffraction patterns were collected in a step-scanning mode with steps of $\Delta 2\theta = 0.01°$. Pure alumina powder (standard sample) was used to correct the data for instrumental broadening.

3. Results and discussion

A partial disintegration of the samples at the corners was observed since the 5th wet-drying cycle. On the surface and in the pores began a progressive accumulation of salts from one cycle to another, consequently resulting an increases of mass for dry samples.

The X-ray diffraction patterns performed on samples are presented in figures 1-3.

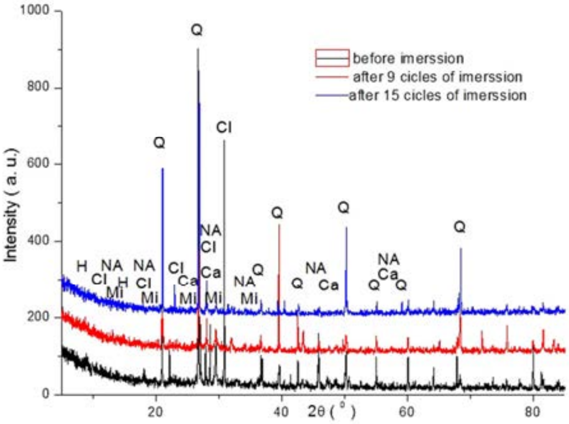


Fig. 1. The XRD pattern of sample 1

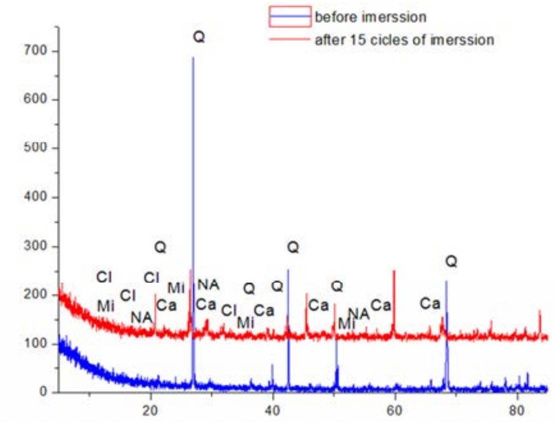


Fig. 2. The XRD pattern of sample 2

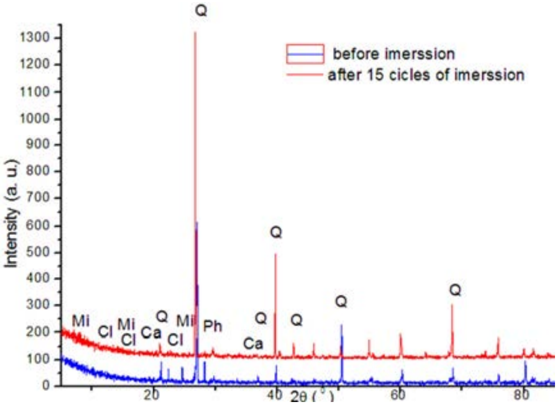


Fig. 3. The XRD pattern of sample 3

Table 1. XRD analysis of mortars samples

Mineral content (%)*	sample 1		sample 2		sample 3	
	before	after	before	after	before	after
Quartz (Q)	+++++	+++	++++	+++	++++	+++++
Calcite (Ca)	+++	+	++	+	+	+
Clinoptilolite (Cl)	+	+++	+++	+	+	-
Heulandite (Ca)	++	+++	++++	+++	+++	+
Heulandite (K)	+	-	+++	++	+++	+
Kaolinite (KA)	+	-	++	+	++	+
Phillipsite (Ph)	++	+++	+++	++	++++	-
Chlorite (Ch)	++	+++	++++	+++	++++	+
Biotite	+++	++++	+++	+++	+++	++
Natrolite (NA)	-	+++	-	+++	-	++
Laumontite (la)	-	+	-	++	-	+
Mirabilite (Mi)	-	+++	-	++	-	+
Thenardite (th)	-	+	-	+	-	+

- +++++ high content; +++ and ++++ medium content; ++ and + low content

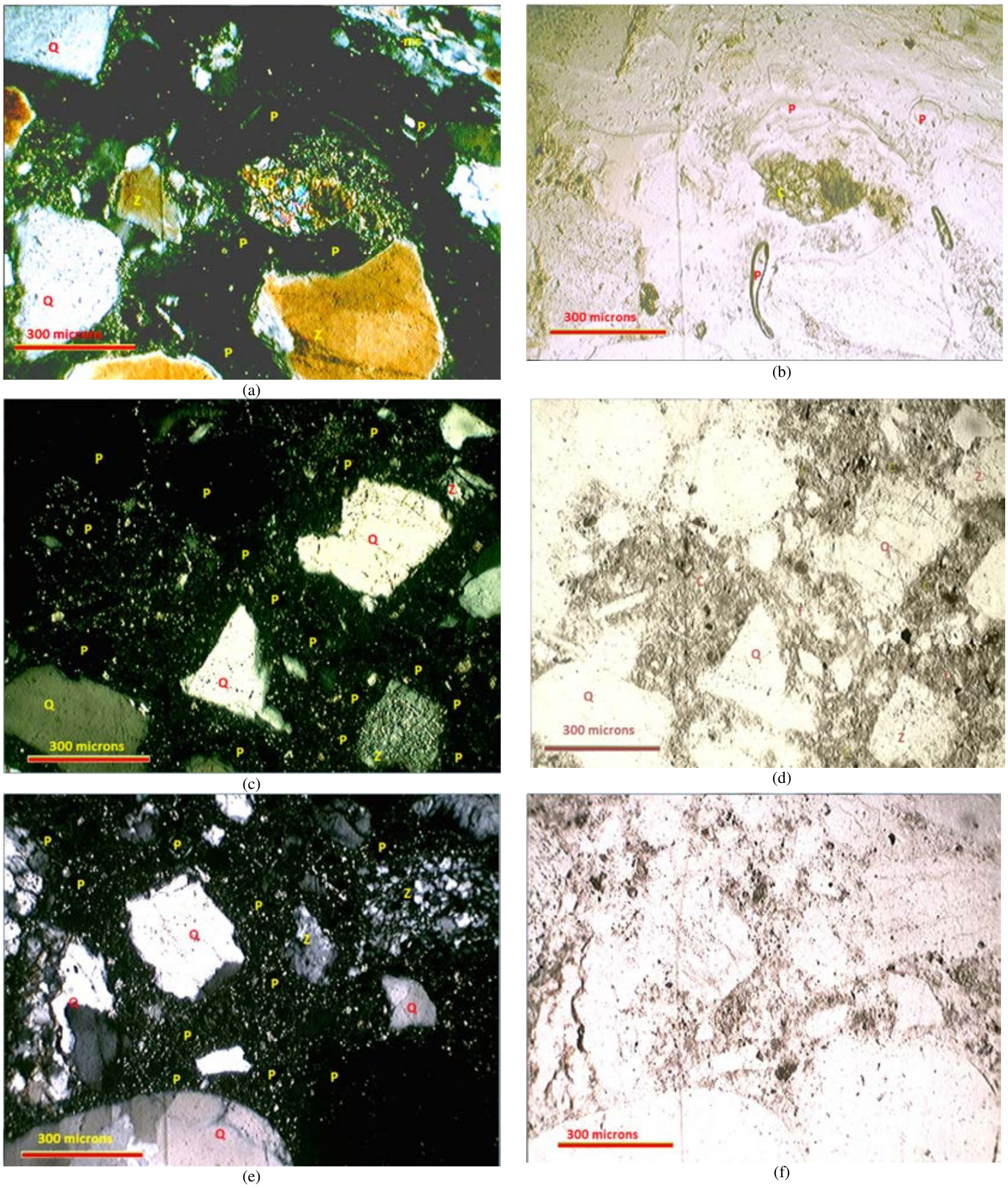
According to XRD analysis, the minerals with calcium content were affected by salt attack (probably due to zeolites ion exchange with the salty solution), and transformed into new zeolites (natrolite and laumontite).

The quantity of mirabilite and thenardite are higher in case of samples 1 and 2 in comparison of sample 3. The differences between the last two samples can be explained due to supersaturation ratios, which are higher in case of microporous than macroporous materials, phenomenon observed as well by the other researches [18].

The mineralogical analysis in thin sections shows that the samples have the following structure:

- sample 1: quartz, zeolites (clinoptilolite or heulandite), portlandite; the pores dimensions are about 200-250 microns and have different geometrical forms (Fig. 4 a,b);
- sample 2: quartz, zeolites, fine ettringite crystals, large zone with small crystals of carbonate and zone with non-hydrated cement. The pores have the dimensions of about 50-100microns (Fig. 4c-d) of circular shapes filled with zeolites, amorphous grains of cement or ettringite crystals.
- sample 3: quartz, zeolites, zeolitized feldspar, lithoclaste of quartzite. The cement matrix is amorphous with crystalline portlandite, ettringite and zeolites crystals. The pores are of different dimensions, as can be seen in Fig.4e-f.

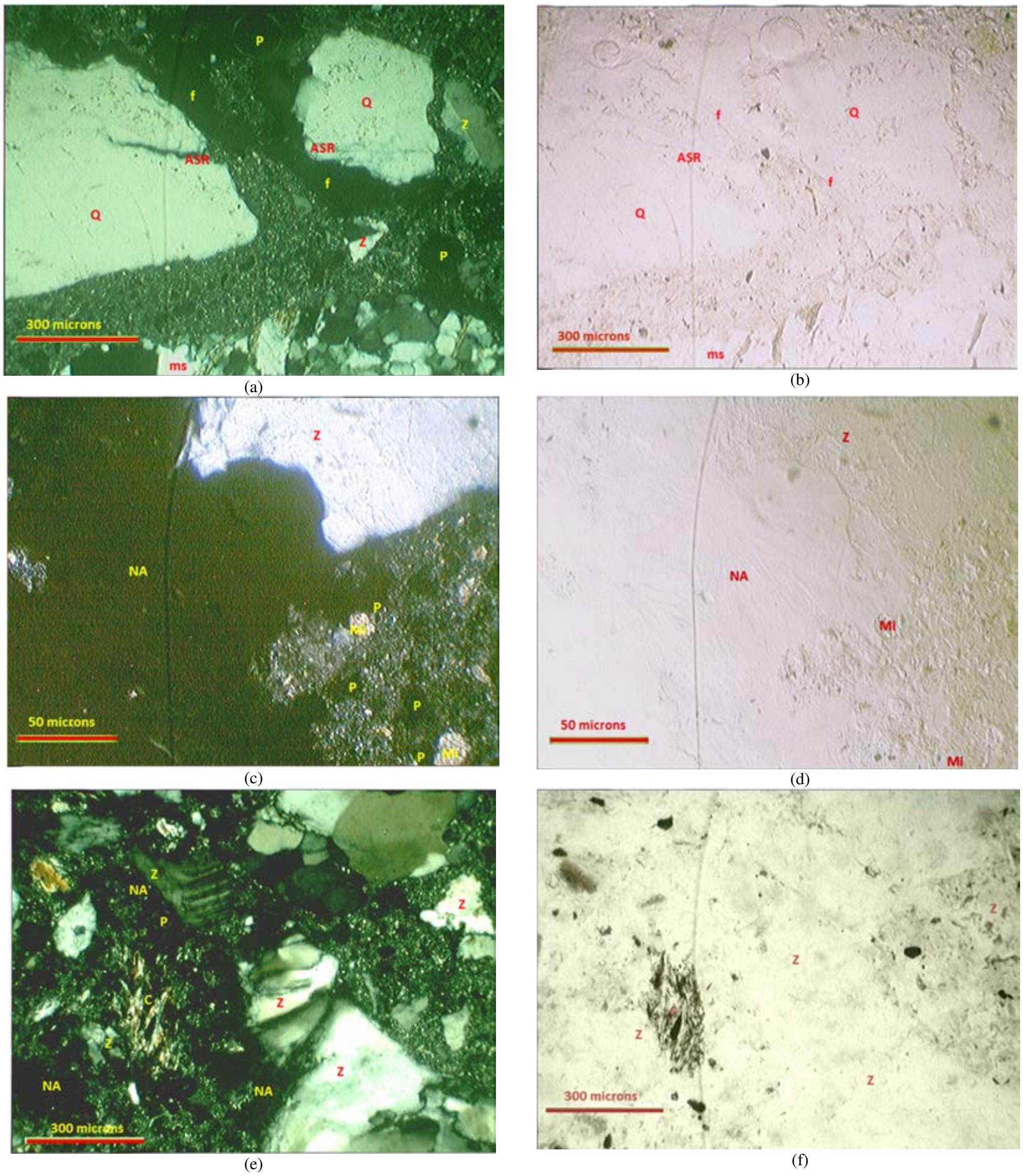
The pores shape are different from one sample to another one: in sample 1 they are interconnected and irregular while in samples 2 and 3 they are more or less isolated and rounded.



(a) (b) (c) (d) (e) (f)

Fig. 4. Thin section of sample 1 (a) N+; (b) NII; sample 2 (c) N+; (d) NII; sample 3 (e) N+; (f) NII:
Q- quartz, Z-zeolites, ms - micaschist, c- cement, P-pores

After immersion in $Na_2SO_4 \cdot 10H_2O$ the samples had a good behaviour, except the sample 1 who was more disintegrated than samples 2 and 3. These facts are influenced by interconnected and wider pores having as consequences more intense chemical reactions (due to ion exchange, formation of new minerals and alkali solution reaction on the surface of quartz). Finally mineralogical content is: quartz, garnet, amphibole, biotite,clasts of micaschist, gneiss, limestone and quartzite (Fig. 5). The matrix consist of cryptocrystalline hydrated cement minerals, portlandite, fine neddles of ettringite, zeolitized feldspar, fissures and pores filled by zeolites (possible natrolite, laumontite and philipsite). The samples contain thenardite and mirabilite in small quantities as it can be observed in XRD as well. The presence in the matrix and pores of the anhydrous crystals of minerals influence the fissuration degree because they have different molar volume: thenardite (Na_2SO_4) - 53 cm^3/mol whereas the mirabilite ($Na_2SO_4 \cdot 10H_2O$) has 220cm^3/mol [10,11].



(a) (b)

(c) (d)

(e) (f)

Fig. 5. Thin section of sample 1 after immersion in salt (a,c,e) N+; (b,d,f) NII:
Q- quartz, Z-zeolites, ms - micaschist, P-pores, NA- natrolite, C- non hydrated cement area, Mi- mirabillite, ASR- Alkali silica reaction, f-fissure

4. Conclusions

The analysis made on samples revealed that their degradability is associated with increase in volume due to hydration and crystallization of salt and chemical reaction between salt and existing minerals in the mortars component. The crystallization of mirabilite from thenardite inside pores, determine the appearance of high tension inside the pores and decay of the sample 1. Through the correlation of XRD and thin sections data it can be noticed a decreased content of calcite, heulandite, clinoptilolite, phillipsite and chlorite, due to dissolution, ion exchange and chemical transformation with the appearance of new minerals (laumontite, natrolite, mirabilite,thenardite).

As it was expected the samples of mortars with additives due to lower w/b ratio, cement porosity and water absorption have a higher resistance to salt attack (see Figs. 2-3 and Table 1) and may be used as rendering for basement wall especially in case of existing buildings as an alternative to classical mortars. In this way, the effect of sub-efflorescence may be reduced at a lower cost.

References

[1] Agyekum K, Ayarkwa J, Koranteng C. Holistic Diagnosis of Rising Damp and Salt Attack in Two Residential Buildings in Kumasi, Ghana. Hindawi Publishing Corporation Journal of Construction Engineering 2014; http://dx.doi.org/10.1155/2014/398627

[2] Balc R, Campian C, Mathe A. The behaviour of quay of Calais Harbour by finite elements. Acta Napocensis 2000; 43:75-88.

[3] Cobirzan N, Balog AA. Analysis of rendering mortars decay due to salt attack, Journal of applied engineering sciences 2013; 3(16): 21-26.

[4] El-Gohary Mohammed. Chemical deterioration of egyptian limestone affected by saline water. International Journal of Conservation Science 2011; 2:17-28

[5] Vacchiano CD. Renovation of ancient buildings in the historic centre of Salerno: decay analysis and materials compatibility. Università Degli Studi di Salerno- Italy 2006; PhD thessis:10-130

[6] Popa A, Ilies NM, Farcas VS, Muresan OC. Geotechnical problems on Transylvanian historical buildings consolidation. Proceedings of the XVI ECSMGE Geotechnical Engineering for Infrastructure and Development; VI: 3547-3552

[7] Ilieş NM, Popa A. Geotechnical problems on historical buildings from Transylvania. Geotechnical Engineering for the Preservation of Monuments and Historic Sites 2013; CRC Press Taylor & Francis Group;431-436

[8] Steiger M, Asmussen S. Crystallization of sodium sulfate phases in porous materials: The phase diagram Na2SO4–H2O and the generation of stress; Geochimica et Cosmochimica Acta; 72 (2008):4291–4306.

[9] Kryza R, Prell M, Czechowski F, Domaradzka M. Acidic weathering of carbonate building stones: experimental assessment (preliminary results). Studia Universitatis Babeş-Bolyai- Geologia 2009; 54 (1): 33 - 36.

[10] Rijniers LA. Salt crystallization in porous materials: an NMR study. Technische Universiteit Eindhoven 2004; PhD thessis

[11] Frossel F. Uscarea zidariilor si asanarea subsolurilor (Masonry Drying and Cellar Rehabilitation). Editura Tehnica 2005.

[12] Anantharaman S. Sulfate and Alkali Silica Resistance of Class C & F Fly Ash Replaced Blended Cements. Arizona State University 2008; Master Thesis.

[13] Molnar LM, Manea DL, Har N. The study of the hydration process of cement by optical microscopy and x-ray diffraction. International Journal of Modern Manufacturing Technologies 2011; 2:717-720

[14] Molnar LM, Manea DL, Aciu C, Jumate E. Innovative Plastering Mortars Based on Recycled Waste Glass. Elsevier 2015; Procedia Technology; 19: 299-306

[15] Cobirzan N, Balog AA, Aciu C, Iluţiu -Varvara DA. Sustainable uses of zeolitic tuff as building material.Elsevier 2014; Procedia Technology; 12: 542 – 547.

[16] Balog AA, Cobirzan N, Aciu C, Iluţiu - Varvara DA. Valorification of volcanic tuff in constructions and materials manufacturing industry. Elsevier 2014; Procedia Technology; 12: 323 – 328.

[17] STAS 6200/3-81. Piatra naturala pentru constructii. Luarea probelor confectionarea sectiunilor subtiri si a epuvetelor (Natural stones for building. Sampling, preparation of thin sections and test pieces).

[18] Rodriguez-Navarro C, Doehne E, Sebastian E. How does sodium sulfate crystallize? Implications for the decay and testing of building material. Cement and Concrete Research 2000; 30 :1527-1534.