CHARACTERIZATION OF ASR PRODUCTS IN A 40-YEAR-OLD HIGHWAY. PROVINCE OF CÓRDOBA, ARGENTINA

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Abstract

The majority of crushed aggregates utilized in Argentina come from the Sierras Pampeanas of Córdoba, (Province of Córdoba). Many of the exploited lithologies are quartz-rich and have undergone deformation processes affecting their texture and producing internal microstructures. Previous studies have shown that those characteristics make rocks potentially alkali reactive. In order to compare those results with performance of aggregates in concrete structures, an important highway that links Córdoba and Villa Carlos Paz cities was studied. Preliminary results showed that this deterioration could be interpreted as a normal aging of concrete, accelerated by humidity problems and ASR development.

In this work, further studies on reaction products were carried out through a stereomicroscope, a polarized light microscope, powder XRD and SEM-EDS analyses. Calcium silicates with variable contents of sodium and potassium, associated with ettringite, were identified in fissures, mortar, in the mortar-aggregate interface and filling air voids.

Keywords: alkali-silica reaction, reaction products, petrography, XRD, SEM-EDS

1 INTRODUCTION

1.1 General

The concrete pavement of the National Route No 20 (Córdoba - Carlos Paz Highway), in the Province of Córdoba, Argentina, (Figure 1) shows generalized damage. In previous studies, deterioration processes were attributed to alkali-silica reaction (ASR) development [1,2]. A calcium silicate with minor quantities of aluminum and potassium in the mortar and filling cavities was identified and defined as a "zeolite-like" material [clinoptilolite: $(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}.12H_2O$]. Crystallizing over this material, ettringite with acicular morphology and growing to the interior of the cavities was also observed. Recently [3], other silicates with variable contents of calcium, sodium, potassium and sulfur were recognized through SEM-EDS observations. A white material filling an air void was studied by XRD analyses revealing the presence of tobermorite ($Ca_5Si_6(O, OH)_{18}.5H_2O$) associated with ettringite.

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Important evidence to determine ASR in a concrete structure is the determination of reaction products in cracks, filling cavities, in the aggregates and/or in mortar-aggregate interface. These products have been studied in numerous structures and laboratory specimens after accelerated tests, showing morphological and compositional variability [4-7]. In general, the main elements detected through EDS analyses were Si, Ca, Na, K, and minor quantities of Al, Fe, Mg and S.

Although the ASR product has historically been defined as an "alkali-silica gel", different silicates with amorphous or poorly crystalline to very crystalline structures can be recognized. SEM-EDS and petrographic studies, in combination with mineral species identification through XRD analyses, have contributed to their characterization and to understanding which factors influence their compositional and morphological variations.

The objective of this work is to proceed further in the characterization of reaction products from National Route No 20 pavement through stereomicroscopy, polarization microscopy, powder XRD (X-ray Diffraction) and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy).

1.2 The highway

This study was carried out in a highway which links Córdoba city (capital of the Province of Córdoba, Argentina) with Villa Carlos Paz city, an important touristic place of the country (the traffic in 2010 was about 12.600.000 vehicles). The concrete pavement has a two-way and a dual carriageway built around 1970 and approximately 25 km in length. The aggregates are mainly composed by biotitic gneisses, migmatites and subordinate amounts of amphibolites, marbles and granitic to tonalitic rocks, affected by deformation processes of variable intensity. Both the aggregates and the cement used in concrete structure are of local origin.

The highway is of a typical design with embankments made of rocks and land of variable height, and land clearing with rock cuts. It consists of a granular base with brittle material (0-20 mm) seven-percent cemented, 8.10 m wide and 0.12 m thick; the mixture was made in a fixed concrete plant and placed with mechanical distribution in a single pass.

Each carriageway is 0.20 m thick and 7.50 m wide with slabs 9.95 m long between transversal joints. Internal boundaries between carriageways are separated by 22 m. Slabs have a steel mesh placed halfway through their thickness to control cracking, with dowel bars in transverse joints and tie bars in longitudinal joints. The design is completed with road shoulders paved with an asphalt mixture. The internal and external road shoulders are 0.50 m and 2.50 m wide, respectively.

In order to improve serviceability conditions in some sectors of the highway (due to problems associated with loss of pneumatic-pavement adherence), texturing practices and asphaltic coatings were performed in the year 2000.

2 MATERIALS AND METHODS

2.1 Ocular inspection and sampling

First, an ocular inspection of the structure to detect signs and extension of deterioration was made according to IRAM 1874-2 guidelines [8]. Then, samples from replaced slabs (especially those showing signs of ASR) were collected using a hand hammer.

2.2 Methods for assessment and analysis

Macro observations

Macro observations of samples were performed using a stereomicroscope Olympus SZ11-CTV trinocular with magnification between x18 and x110. Materials filling fissures, air voids, in the mortar-aggregate interface and in the mortar, were separated with a needle for XRD analyses. Additionally, fragments with reaction products were separated for SEM-EDS analyses.

Polarization microscopy

Textural observations on thin sections of concrete samples were made trough a polarized light microscope Leica DM EP trinocular with magnification between x25 and x500. The mortar, aggregate and mortar-aggregate interface were studied in order to identify and characterize fissures and reaction products. Textural and microstructural concrete aggregate characteristics were also studied, and relations with the reaction products were analyzed.

X-ray powder diffraction (XRD)

Materials separated under the stereomicroscope were characterized by X-ray powder diffraction (XRD) using a Rigaku D-Max III-C diffractometer, with Cu (Kα) radiation of wavelength λ=1.54059 Å and graphite monochromator, at 35 kV and 15 mA. Diffractograms were recorded from 3-60 °2θ, in 0.04 °2θ increments with 1 s counting time per increment.

Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS)

Small concrete fragments separated under the stereomicroscope were studied in a JEOL 35 CF scanning electron microscope (SEM) with energy dispersive spectroscope (EDS) for qualitative chemical analyses of microareas. Samples were sputtered with a thin carbon layer.

3 RESULTS

3.1 Ocular Inspection

Concrete structure can be divided in two sectors. One repaired with asphalt covering due to macrotexture problems and other still exposed to traffic.

The first sector is generally in good condition, however some areas show intense map cracking and reflective cracking at joints.

The second sector shows more deterioration. Concrete slabs show transverse joint faulting, broken areas next to transverse and longitudinal joints, longitudinal and transverse cracking, broken corners, intense cracking in transverse joints (in dowel bars), map cracking and areas with polished aggregates due to loss of the superficial mortar. Different works were made in these sectors involving partial or total replacement of slabs (Figure 2a) and localized areas repaired with asphalt mixtures.

In severely cracked areas such as the middle zone of slabs and next to transverse joints, white materials filling cracks 2 to 3 mm thick are seen (Figure 2b). In other sectors of the highway, the slabs present color variations, with a whitish central zone and boundaries with a yellowish color of lustrous shine.

3.2 Macro observations

At this scale, deterioration problems are not so evident. However, collected concrete samples show some microcracks affecting mortar and mortar-aggregate interface.

Secondary materials are also detected, filling air voids, on the surface of coarse aggregates, at the mortar-aggregate interface and filling microcracks.

Those materials are variable in habit and color but in general two varieties are identified, massive (white, opaque or transparent to translucent) and well-defined long prismatic crystals (white), radially or randomly arranged.

In Figure 3a an aggregate totally covered by a massive and white material can be seen. It turns shiny at the boundary of the aggregate and translucent and brown at the mortar-aggregate interface. Finally, a massive, white and cracked material covers the surface of the surrounding mortar. In Figure 3b a white and crystalline material of needle habit can be seen.

3.3 Polarization microscopy on thin sections

Concrete aggregates are mainly composed of biotitic gneisses with minor quantities of migmatites, amphibolites, granitic intrusives and marbles. The first group shows marked sin-metamorphic foliation and evidence of posterior deformation. The content of quartz is above 50% and presents a lot of microstructures associated with brittle deformation (small particles due to cataclasis) and brittle-ductile deformation (undulating extinction, deformation bands and subgrains, Figure 4a). The grain size ranges from a few millimeters to some dozen micrometers.

The mortar shows intense microcracking. A fibrous material crystallized perpendicular to fissure walls can be seen and it becomes bigger in air voids crystallizing radially to the interior of the cavities (Figure 4b).

Some materials in the cavities show fissures like "mud cracks" possibly due to dehydration and contraction processes. Air voids are partially or totally filled with ettringite (Figures 4c and 4d).

Carbonation of mortar is localized in cracked zones, in the mortar-aggregate interface and in cavity boundaries.

3.4 XRD

The massive and white material of low hardness and cracked, which covers air voids and the mortar, was identified as calcite (C) (Figure 5a). Another massive and white material of low hardness filling air voids was identified as a mixture of vaterite (V) ($CaCO_3$), calcite and a calcium silicate hydrate (S) with reflections coincident with tobermorite mineral (Figure 5b). The white material of low hardness but more compact in the mortar-aggregate interface was identified as a mixture of calcite and ettringite (E) (Figure 5c). In this sample, there are some reflections coincident with a calcium aluminum silicate hydrate (A) with zeolitic structure (gismondine). In the diagram there is only one reflection that is not superimposed with the other phases. The translucent and shiny material was identified as vaterite (Figure 5d).

Another massive and white material (but harder) in the mortar-aggregate interface was separated. It was identified as a cryptocrystalline variety of silica with reflections assignable to tridymite mineral; however, more material is needed to confirm its presence.

Due to the limited amount of separated material, only major reflections were matched. The quartz identified comes from the aggregates.

3.5 SEM-EDS

A laminar material that is detached from the concrete surface and forms tubes is observed (Figure 7a). It is composed of Si, O, Ca, Na and K. Due to its low percentage in the sample, XRD determination was not possible.

Filling cavities and on the mortar surface, prismatic crystals of needle habit were observed. They are composed of S, Al, Ca and O (Figure 6b). This material was identified as ettringite through XRD analysis.

A massive and cracked material at the mortar-aggregate interface and in the mortar was observed (Figures 6c and 6d). Over this material some prismatic crystals forming radiated groups were also identified. This prismatic material is composed of S, Al, Ca, O and Si (the latter possibly being a contribution from the massive material in the background). The massive product consists of Si, Ca, O, Al and C. All these materials were identified though XRD as a mixture of ettringite, calcite and a calcium aluminum silicate hydrate that possibly corresponds to a phase with zeolitic structure (Figure 5c).

4 DISCUSSION

Concrete deterioration in the Córdoba-Villa Carlos Paz Highway is related to different processes. Rupture of concrete was probably due to construction problems and even defects at the project stage, such as defective curing. The ingress of water through fissures to the interior of the concrete could trigger ASR development as has occurred in other pavements in Argentina (e.g. Route No 127) [9].

A climatic factor seems to have played an important role in this sector of the structure. The high humidity and increasing permeability of concrete slabs due to cracking, broken slabs, joints with deficient maintenance and other factors, increase deterioration processes. This high humidity condition alternating with dry periods has possibly contributed to the mobilization of ions through the concrete pore solution, enabling ion-aggregate and ion-mortar interactions to form reaction products in cavities and fissures [3].

Ettringite was detected in air voids, fissures, on the mortar surface, and over ASR products. Its formation is related to normal aging of concrete and is classified as secondary ettringite formation according to Scrivener and Skalny [10]. The amount of ettringite probably increased due to the aforementioned humidity problems and ASR.

All these processes have also contributed to calcium carbonate generation in the mortar due to carbonation processes triggered by the increase of concrete permeability.

Although there are no records about alkali content of the cement utilized, its dosage and aggregate composition, petrographic studies in concrete samples provided valuable information. The aggregates have a high content of metamorphic rocks (mainly gneisses and migmatites) and present different intracrystalline microstructures associated with quartz deformation (such as undulating extinction, deformation bands and subgrains). Previous studies in quartz-bearing rocks from this region [11] have shown that those characteristics make rocks potentially alkali reactive, therefore these aggregates probably have provided the silica for generating different silicates that have been identified in the mortar-aggregate interface, in fissures and filling air voids.

These phases show compositional (Si, Ca, Na, K, Al, S) and morphological variations (e.g. massive, laminar, elongated prisms of needle habit), which agrees with the literature [e.g. 12 and references therein].

However, these variations appeared to respond to an evolution path where reaction products evolve from a silica gel with variable contents in Na and K, which migrates within concrete, taking up calcium from the cement paste and leaching alkalis and approaching the compositions of CSH gel, similar to that formed by the hydration of the cement silicates alite and belite [13].

The asphalt deterioration observed in some repaired sectors of the structure is due to the deterioration progress of the underlying concrete slabs, evidenced by map cracking and reflective cracking at joints.

5 CONCLUSIONS

The concrete pavement of the Córdoba - Carlos Paz Highway shows important deterioration. Cracking and broken concrete slabs are mainly due to humidity problems in the structure. ASR products, ettringite and carbonate (calcite, vaterite) development are probably a consequence of the initial deterioration that increased internal humidity in concrete.

Concrete slabs show intense cracking associated with ASR products. Silicates formed show variable contents in calcium, sodium, potassium and aluminum, and are located in fissures, air voids and in the mortar-aggregate interface.

Secondary ettringite formation in fissures and filling air voids is not related to a sulfate attack process but to a normal aging of concrete accelerated by the deterioration of concrete slabs due to humidity problems and ASR development.

Metamorphic quartz-bearing aggregates that present internal deformation microstructures played an important role producing slow/late expansions once initial deterioration began and continue affecting concrete slabs nowadays.

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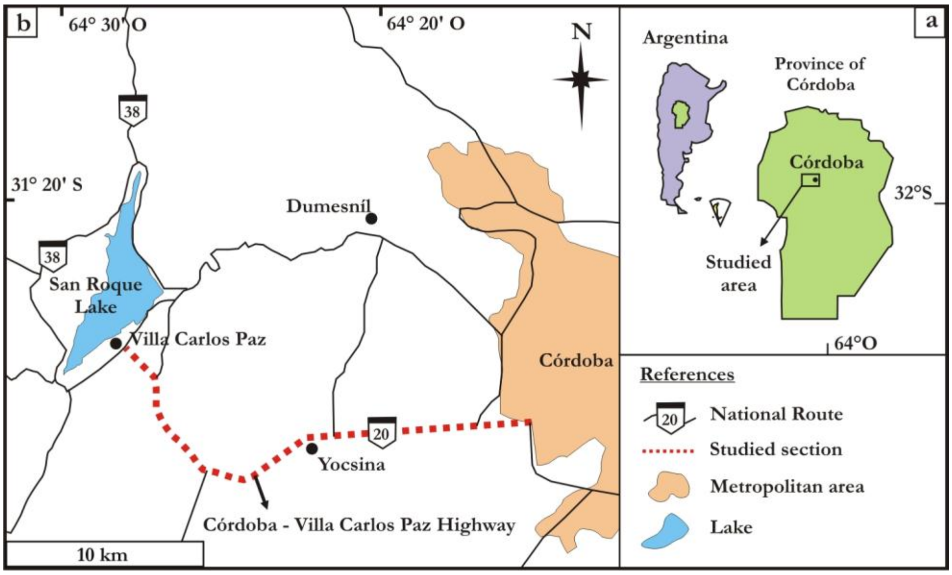

FIGURE 1: a) Location of the studied area in the Province of Córdoba. b) Location of the section studied (red dotted line).

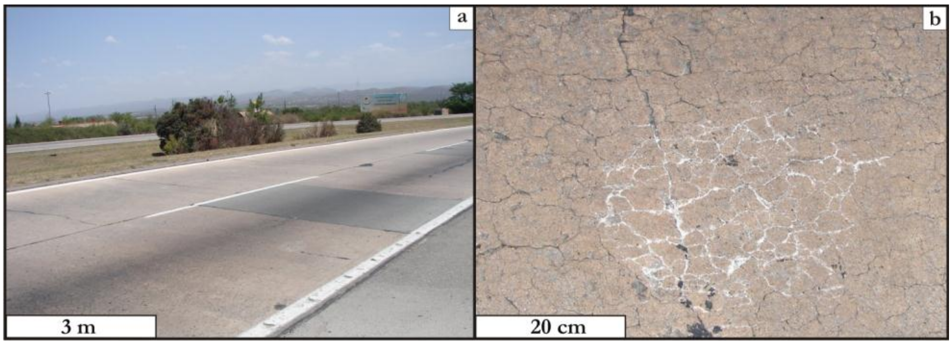

FIGURE 2: Photographs of the structure. a) Sector of the highway without asphalt cover with partial slab replacement. b) Map cracking with white material filling fissures.

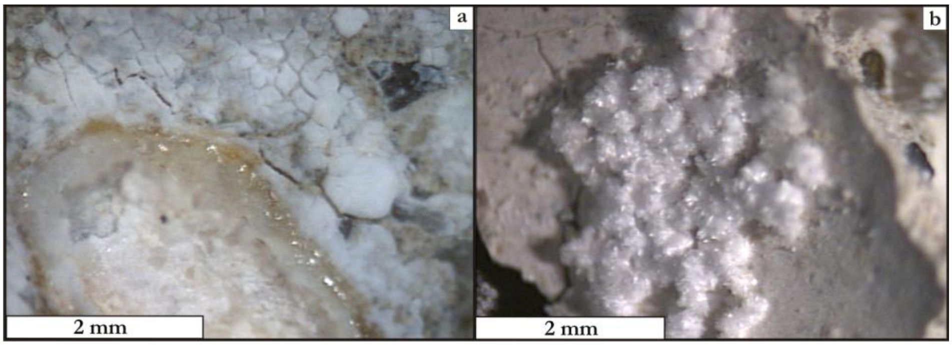

FIGURE 3: Photographs of concrete samples under the stereomicroscope. a) Aggregate covered and surrounded by reaction products. b) Air void partially filled with a white and crystalline material forming groups of radial crystals of needle habit.

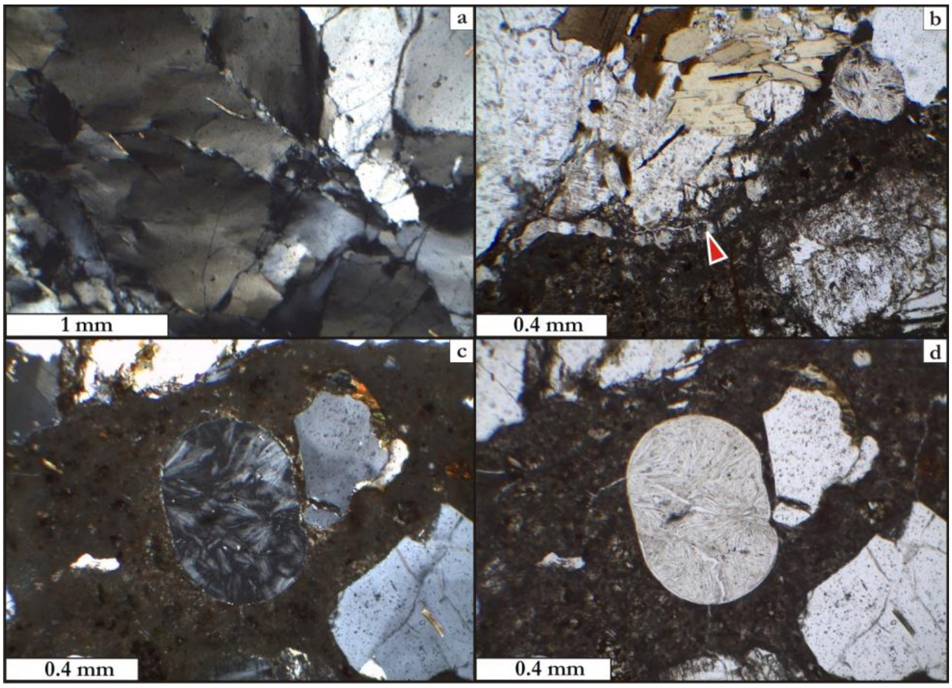

FIGURE 4: Photomicrographs. a) Gneissic aggregate showing quartz crystals with undulating extinction, deformation bands and incipient subgraining. Crossed nichols. b) Microfissure in the mortar-aggregate interface (red arrow) filled with a fibrous material. At the end of the fissure the material crystallizes in an air void of larger size. Parallel nichols. c) Air void filled with ettringite. Crossed nichols. d) The same picture with parallel nichols.

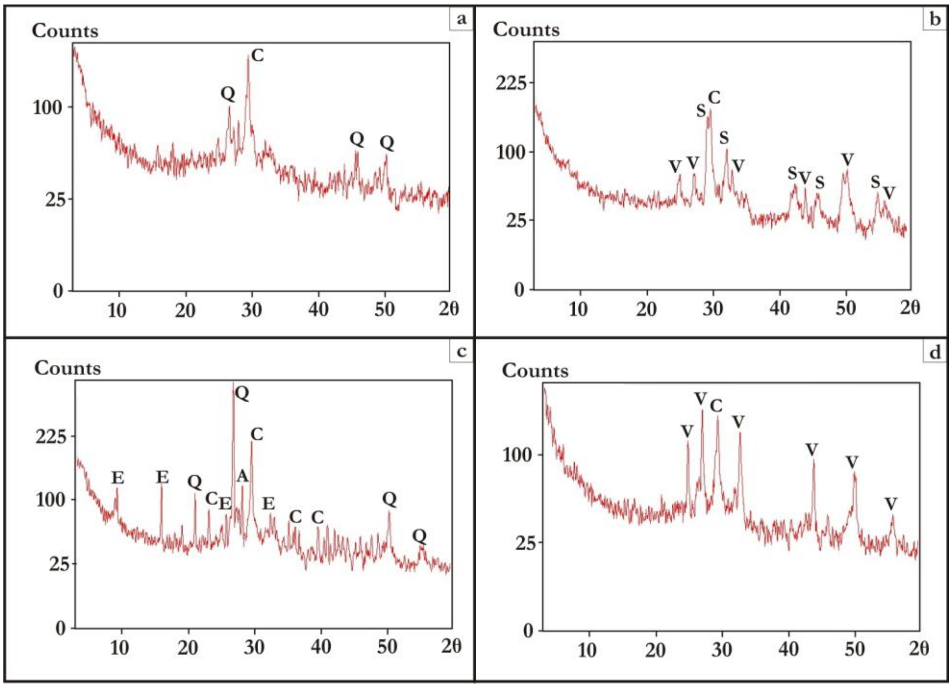

FIGURE 5: XRD diffractograms. a) Material that covers air voids and mortar. b) Material filling air voids. c) Material in the mortar-aggregate interface. d) Translucent and shiny material in the mortar-aggregate interface. Calcite (C), quartz (Q), vaterite (V), calcium silicate hydrate (S), ettringite (E), calcium aluminum silicate hydrate (A).

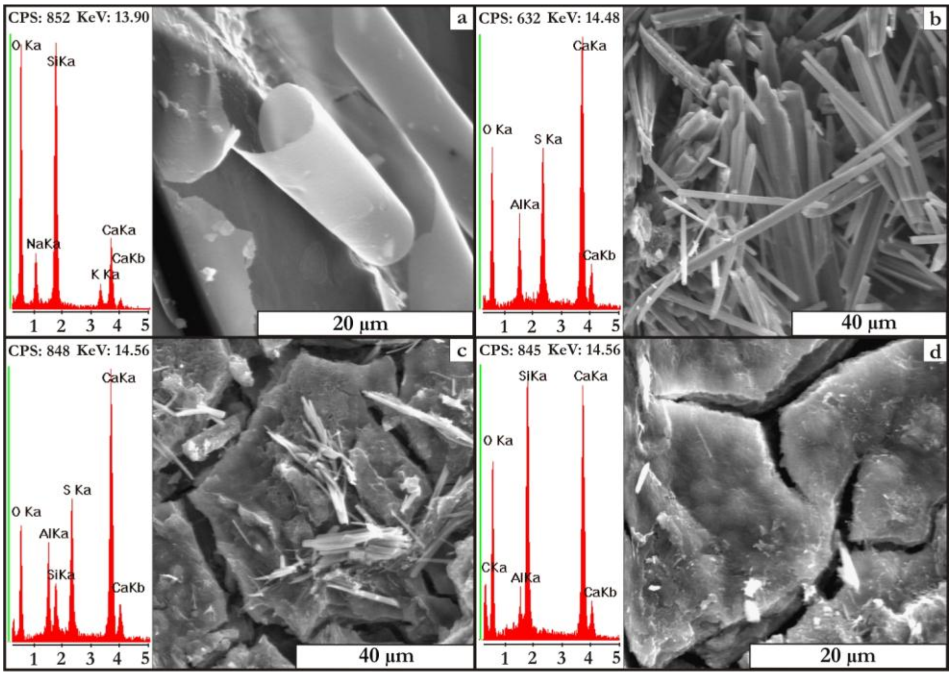

FIGURE 6: SEM-EDS determinations. a) Laminar material that is detached from mortar forming tubes. b) Prismatic crystals of ettringite in air void. c and d) Massive and cracked material on the mortar surface. Radiated groups of prismatic crystals over the massive and cracked material are also observed (c).