ALKALI-SILICA REACTION - A CASE STUDY IN THE AZORES ARCHIPELAGO THROUGHT THE ReAVA PROJECT

SARA MEDEIROS
Research Fellow
University of Azores
Ponta Delgada-Portugal

ISABEL FERNANDES
Assistant Professor
University of Lisbon
Lisboa-Portugal

JOÃO CARLOS NUNES
Assistant Professor
University of Azores
Ponta Delgada-Portugal

ANTÓNIO SANTOS SILVA
Research Officer
National Laboratory for Civil Engineering
Lisbon-Portugal

DORA SOARES
Research Fellow
National Laboratory for Civil Engineering
Lisbon-Portugal

ABSTRACT

Concrete is one of the most widely used construction material in the world. However concrete structures can deteriorate during their lifetime due to material limitations, design and construction practices and severe exposure conditions. One of the causes of concrete deterioration is related to alkali-silica reactions (ASR) which are chemical reactions that occur between alkaline (Na^+ and K^+) and hydroxyl (OH^-) ions in the cement paste and certain forms of silica in some aggregates. This deterioration phenomenon causes expansion and cracking that consequently reduces the life service of concrete structures. Basalts and other volcanic rocks have been found to be the cause of premature concrete structures deterioration in concrete in several countries, such as Japan, Iceland and Turkey, due to the occurrence of ASR.

The characterization of the reactivity of volcanic aggregates in Azores has been implemented through the research project ReAVA (Characterization of Potential Reactivity of the Volcanic Aggregates from the Azores Archipelago: Implications on the Durability of Concrete Structures). Aggregates were selected and collected from a total of 13 places in 8 Islands. Corvo Island was the only exception due to the lack of local production. The program involved: (1) the petrographic characterization of the aggregates, (2) assessment of their performance in expansion tests and (3) site inspection of some existing large concrete structures in the Azores.

The results of the lab tests show that one of the aggregates is potentially reactive. Also one of the concrete structures studied in this project evidenced some degradation, showing features that are very similar to ASR.

This paper presents the results obtained on the characterization and performance of volcanic aggregates from Azores regarding the potential reactivity to alkalis using different methods and the concrete ASR diagnosis in a concrete structure.

KEYWORDS: Azores islands, volcanic aggregates, petrography, ASR, concrete

1. INTRODUCTION

Alkali silica reaction (ASR) affects many concrete structures worldwide. This reaction can cause the swelling of concrete due to the presence of an expansive alkali-silica gel and create a network of cracking. Although the cracking is not a distinctive characteristic of ASR it affects also this kind of concrete deterioration.
The progressive damage inflicted by ASR on concrete can affect the stability of a structure, especially when cracks propagate further more than previously induced by ASR and are subject to strong earthquakes. This could cause a possible structural failure [1] in the worst case scenario.
The reactivity of some volcanic rocks used for concrete purposes has been documented by several authors [2,3,4,5,6,7]. The cause of the reactivity in volcanic rocks is related to volcanic glass, opal, tridymite, cristobalite, chalcedony, microcrystalline and cryptocrystalline quartz [8] and minerals of alteration (e.g. clay minerals) [7]. In Portugal, there is only a case study performed by the National Laboratory for Civil Engineering (LNEC) on the airport concrete pavement of Santa Maria Island in Azores archipelago [9].
The research project ReAVA (Characterization of Potential Reactivity of the Volcanic Aggregates from the Azores Archipelago: Implications on the Durability of Concrete Structures) started in 2012 and has been developed at Azores University with the joint cooperation of the University of Porto, LNEC and the Regional Laboratory for Civil Engineering of Azores (LREC). The ReAVA program included mainly a petrographic characterization of the aggregates, the evaluation of their performance in expansion tests, concrete sampling of some concrete structures and its petrography analysis.
This paper presents the main results of the evaluation of volcanic aggregates by petrographic examination and expansion laboratory tests and the concrete petrography of one structure.

2. MATERIALS AND METHODS

2.1. Aggregates

Thirteen aggregates from eight Islands were selected and characterized by petrographic analysis and mortar and concrete expansion tests.
The majority of the aggregates were sampled directly in the quarries. Most of the quarries are located on lava flows of basaltic composition with the exception of one quarry that is of trachytic composition. One of the quarries is part of a submarine eruptive centre with an impressive volcanic neck 150 m high, submarine lava flows and intercalated levels of reddish hyaloclastites [10]. The exploitation areas that are not considered quarries consist of an excavation and some stockpiles of a crushing plant. The crushing plant belongs to the town hall of Lajes das Flores and the crushed aggregates taken from a river nearby.
The oldest aggregates belong to two quarries from Santa Maria Island, both of Pliocene age [11] being the rest younger than that age.
A code was given to the rocks for the islands of Santa Maria (SMA-SM1 and SMA-SM2), São Miguel (SMG-SM1, SMG-SM2 and SMG-SM3), Terceira (TER-SM1 and TER-SM2), Graciosa (GRA-SM1), São Jorge (SJO-SM1), Pico (PIC-SM1), Faial (FAI-SM1) and Flores (FLO-SM1 and FLO-SM2).

2.2. Concrete

Four concrete cores (D=100 mm) were sampled from an airport concrete pavement. The drilling was done in the areas showing more cracking. One of the sampling was

done on a longer longitudinal crack with more than 20 mm wide (Figure 1). Some of the cores showed a white deposit surrounding the coarse aggregate particles.
The cores were tagged with different codes (SMA1, SMA2, SMA3 and SMA4) and sealed on plastic bags to be transported for lab and tested.
In the lab the concrete cores were cut in slices with the objective to prepare polished thin sections. The thin sections produced were selected from different depths along the cores [12].

2.3. Methods for assessment and analysis

The petrographic examination of the rocks thin sections was performed under a polarizing microscope Olympus CX31 with an Olympus SC100 camera to determine mineral composition, textural features and to identify potentially reactive forms of silica.
A polarizing microscope Nikon Eclipse E 400 POL, with automatic camera AXION cam MRC was used for the concrete thin sections analysis, namely aiming the identification of ASR reaction products, volcanic glass and the extend and configuration of the microcracks.
The petrographic examination was complemented using a scanning electron microscope (SEM) FEI QUANTA 400 FEG ESEM/EDAX PAGASUS X4M equipped with an energy dispersive spectrometer (EDS) to determine the chemical composition in the rocks and in the reaction products on the concrete samples.
Geochemical analysis of the rock samples was also performed at Activation Laboratories, in Canada. The major oxides were determined by fusion-inductively coupled plasma (FUS-ICP: Thermo Jarrell - Ash ENVIRO II ICP). In order to classify the rocks from the chemical point of view, the values of the major oxides (SiO_2 and K_2O+Na_2O) were plotted in a TAS (Total Alkali Silica) diagram.
The expansion tests included: (1) accelerated mortar-bar test according with ASTM C 1260 [13] (14/28 days), (2) concrete prism test [14] (1/2 year) and accelerated concrete prism test [15] (15/20 weeks). The mortar mixes were made using a Portland cement type CEM I 42.5 R with 0.89% of Na_2Oe_{quiv}. with graded aggregates (0.15-4.75 mm), cement/aggregate (0.44) and water/cement ratio (0.47). For concrete mixes, the same cement type as above was used with graded aggregates (<22.4 mm), cement/aggregate (0.25) and water/cement ratio (0.45).

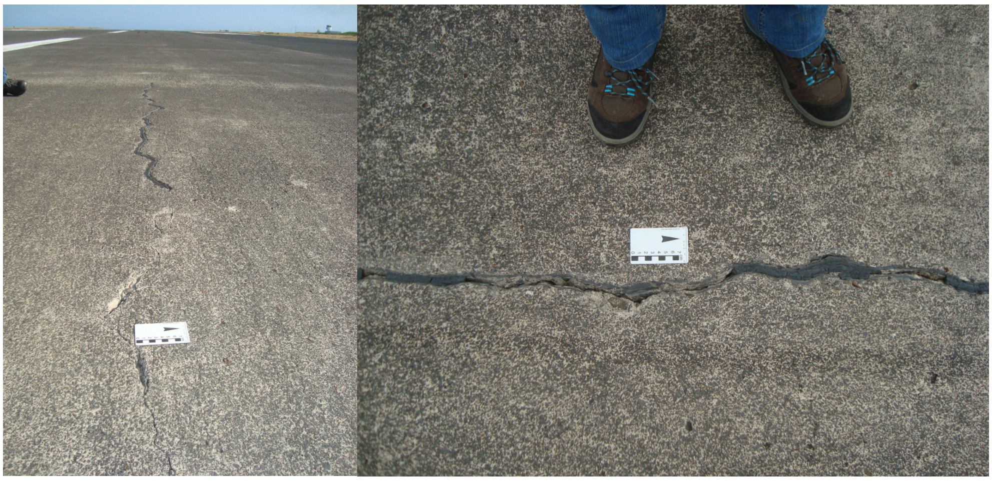

Fig. 1 – Image of the longest longitudinal crack pattern in the airport concrete pavement: (a) view N-S (left) and (b) a close-up of the crack (right).

3. RESULTS

The petrographic analysis of the rocks showed that the majority of the samples contain olivine, pyroxene, plagioclase and opaque minerals as phenocrysts with some variations for each sample. Those phenocrysts are set in an intergranular groundmass formed by the same mineral composition with different mineral proportion. All of them have porphyritic texture although some are aphyric with minute amount of phenocrysts, like the samples from Graciosa, Faial and Flores Islands.
The petrography examination of the rock samples from Santa Maria Island (SMA-SM1 and SMA-SM2) show that the olivines are partly altered to iddingsite in both samples. The SMA-SM1 sample contains zeolites, which composition was confirmed by SEM/EDS analysis. These are present in several areas of the thin sections occurring in the groundmass or filling the voids of the rock. In the same sample several amounts of carbonates were found filling the gaps of the rock. The SMA-SM2 sample has interstitial plagioclase with incorporated crystals of pyroxene and less amount of olive forming an ophitic texture.
The TER-SM1 sample is formed by large crystals mainly of sanidine and small crystals of sanidine, nepheline, biotite and opaque minerals. The trachytic groundmass consists of feldspars (plagioclase, anorthoclase), pyroxenes (aegirine, augite), amphibole (aenigmatite), apatite and opaque minerals (mainly magnetite).
The rock samples from Flores Island (FLO-SM1 and FLO-SM2) exhibit microporphyritic texture. In both samples the larger crystals are mostly plagioclase and the matrix is formed by biotite, opaque minerals, clinopyroxene, alkali feldspar and plagioclase. The presence of carbonates was observed in FLO-SM1 sample in the matrix or filling the cracks inside the plagioclase. In some cases the carbonates seem to be replacing the feldspars.
The presence of volcanic glass was identified only in three rock samples: SMG-SM1 (Figure 2), TER-SM1 and TER-SM2. The presence of interstitial pure silica as microcrystalline quartz was confirmed by SEM/EDS in the sample of TER-SM1 [16] as well as a sporadic interstitial brown glass. The same authors [16] also confirmed that the other samples have a SiO_2 composition of 58 % for SMG-SM1 and 55 % for TER-SM2.

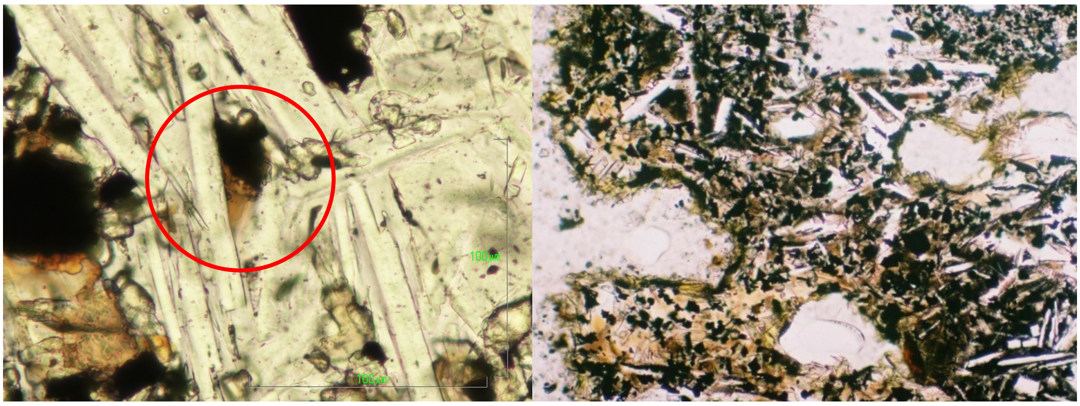

Fig. 2 – Aggregate petrography: interstitial volcanic glass in SMG-SM1 sample.

The geochemical analysis classified, according to Le Maitre et al. [17], most of the samples as basalts (SMG-SM3, SMG-SM2, TER-SM2, SJO-SM1 and PIC-SM1) or trachybasalts (SMG-SM1, SMG-SM2, GRA-SM1 and FAI-SM1). There are two basanites (SMASM1 and SMA-SM2), one trachyte (TER-SM1), one trachyandesite (FLO-SM1) and one basaltic trachyandesite (FLO-SM2). The loss on ignition (LOI) shows values higher than 1 % (SMA-SM1 = 2.15; SMA-SM2 = 3.25; TER-SM1 = 1.13; FLO-SM1 = 3.16) which means that the rocks have some degree of alteration, especially the basaltic rocks. This alteration is also confirmed by petrography.

The mortar-bar expansion tests (Figure 3) showed, after 14 days of testing, that only one aggregate (TER-SM1) is considered potentially reactive [13]. All the aggregates tested on the accelerated concrete prism test [14] did not show any deleterious reactivity at the end of 15 weeks of testing. The same aggregates submitted to the concrete prism test [14] did not show deleterious reactivity at the end of 1 year of testing. However, at the end of 2 years of testing the expansion curves of SMG-SM2, TER-SM2, GRA-SM1, SJO-SM1 and PIC-SM1 crossed the boundary limit of 0.05%.
The petrography examination made to concrete of the pavement showed that it contains crushed aggregates of basaltic nature. The sand fraction contains mainly grains of iddingsitized olivine, pyroxene and plagioclase minerals.
Volcanic glass was identified on the aggregate particles. Under plane-polarized light, the glass presents colors that range from beige to light-brown (Figure 4) or dark-brown [12] and is always isotropic under crossed polarized light.

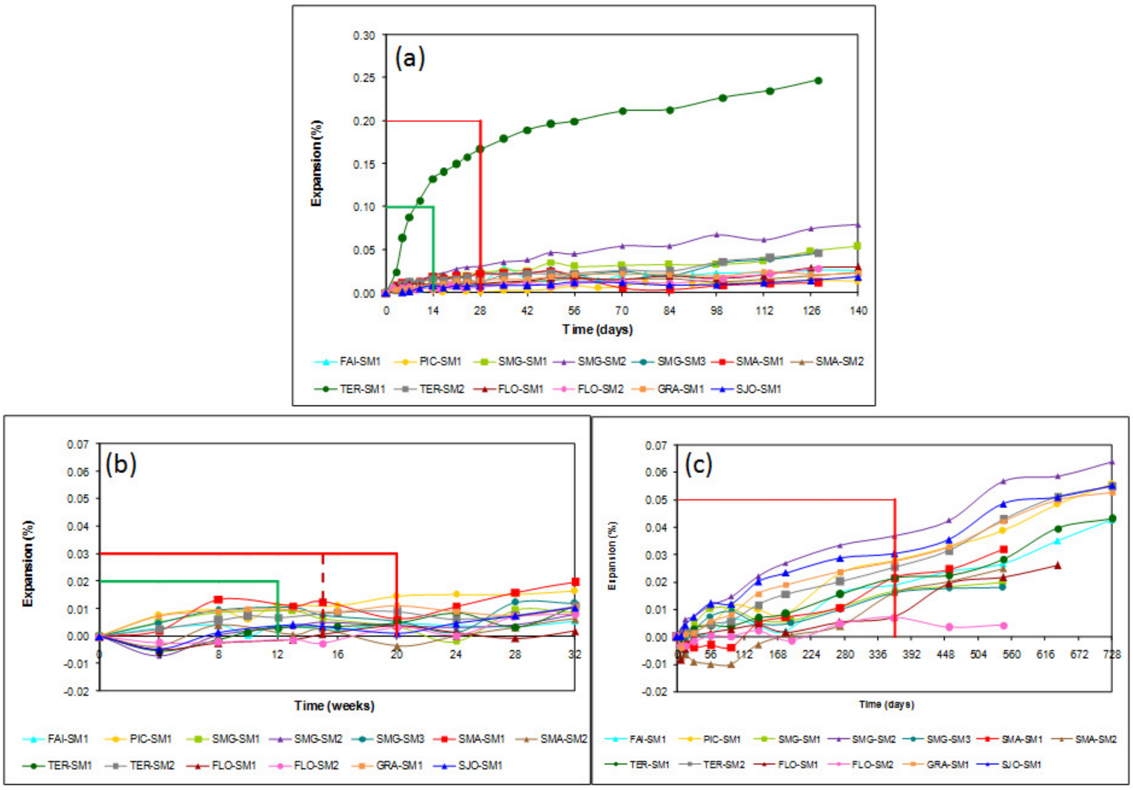

Fig. 3 – Expansion test results of the samples studied: a) ASTM C 1260; b) RILEM AAR-4.1; c) RILEM AAR-3.

The cement paste exhibits crack patterns known as map-cracking that are very similar to the retraction cracks on clay soils. Minerals of fibrous habit (Figure 4) were found in the interfaces between the cement paste and the aggregate particles and filling the voids of the rock. Clay minerals were also identified as alteration of the aggregate particles.
SEM/EDS analysis was performed on the cement paste, the volcanic glass and on the fibrous minerals. This examination showed that: (1) the cement paste has a composition of mainly Si with lower contents of Al, Ca, Na and residual Mg; (2) volcanic glass is mainly composed of Si and Al, with low Ca contents and very low K, Na, Fe and Mg contents and [12]; (3) the fibrous mineral in the interface contained mainly Si, Al, Ca and low Mg, Na, Fe and K [18].
Volcanic glass was also analysed by microprobe which showed that the silica composition varies between 31.59 % and 40.06 % [12].

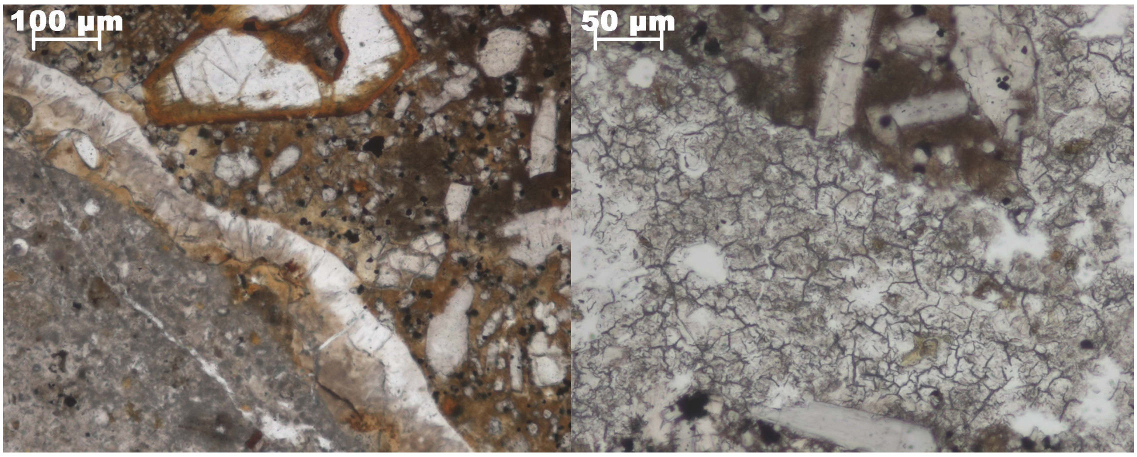

Fig. 4 – Concrete petrography: yellow to brown volcanic glass in the aggregate particle and fibrous mineral in the interface with the cement paste (left); map-cracking aspect of the cement paste (right).

4. DISCUSSION

Volcanic rocks are considered potentially reactive when they contain microcrystalline quartz, volcanic glass of rhyolitic or dacitic composition, quartz polymorphs [19], minerals of alteration and SiO_2 content of the bulk rock >50% [7].
The results obtained show that three rock samples (SMG-SM1, TER-SM1 and TER-SM2) contain volcanic glass. One of them is a trachyte (TER-SM1) which has a sporadic interstitial brown glass, the silica content is higher than 50 % and microcrystalline quartz was identified by SEM/EDS analysis. The presence of silica minerals (e.g. microcrystalline quartz) in a rock should be taken into consideration when there is excess of silica in the composition of the rock and especially if the interstitial volcanic glass is not dominant [5].
The other two samples (SMG-SM1 and TER-SM2) showed a volcanic glass of andesitic composition (58 % for SMG-SM1 and 55 % for TER-SM2) that is bellow the content of 65 % of SiO_2 to be considered potentially reactive. According to Katayama [20] volcanic glasses with SiO_2>65 % (dacitic and rhyolitic glasses) are considered potentially reactive whereas basaltic glass is innocuous.
The geochemical analysis showed that some of the samples (SMA-SM1, SMA-SM2 and FLO-SM1), especially basaltic rocks, present some degree of alteration (LOI > 1 %) which was also confirmed by petrography analysis.
The results of the expansion tests showed that only one aggregate (TER-SM1) is considered potentially reactive in the accelerated mortar-bar test [13] which is also confirmed by petrography and chemical analysis. The accelerated concrete prism test [15] did not identify any of the aggregates as potentially reactive. The concrete prism test [14] showed that at the end of 2 years of testing the expansion curves of SMG-SM2, TER-SM2, GRA-SM1, SJO-SM1 and PIC-SM1 crossed the boundary limit of 0.05 %. The RILEM recommendations establish that an aggregate is considered reactive when the expansion curve crosses the limit of 0.05 % after 1 year of testing. However this kind of aggregates may exhibit late expansive reactions which probably might need more time of testing to develop the reaction. For the samples which curve crossed the limit established by the RILEM recommendations it should be taken into consideration the final use given to the aggregates, especially for concrete structures with high structural demanding such as dams or bridges. Concrete structures with deterioration caused by ASR are more susceptible to seismic events. According to Pan et al., [1] the seismic stability of a concrete structure like a dam is significantly reduced due to the ASR-induced deterioration of concrete compared with a non-affected dam.

The microscopic characterization results of the concrete cores showed that the composition of the cement paste of the pavement is different from the typical composition of a Portland cement which has higher content of Ca than found in these analyses. The fibrous minerals which are similar to a zeolitic composition contain mainly Si, Al and Ca. The presence of Ca and Al in these minerals and the lower content of the same elements in the cement paste could suggest a reaction between the cement paste and the aggregate. According to Fernandes et al. [12] the composition obtained of the fibrous minerals shows different characteristics when compared to alkali-silica gel. The study performed by LNEC revealed that the deterioration of the concrete was due to a complex process which involved expansive reactions associated with montmorillonite (e.g. clay minerals) and zeolites [9]. Also Batic et al. [21] obtained similar results in basaltic rocks from Argentina. Volcanic glass also tends to alter to zeolites, clay and silica minerals [22]. The presence of clay minerals is also stated by some authors (eg. Korkanç & Tugrul, [7]) as being one of the conditions for basalts to show reactivity. The volcanic glass analysed by microprobe showed a silica composition below 65 % which indicates that the volcanic glass is not potentially reactive.

5. CONCLUSIONS

From the study of volcanic aggregates of the Azores and on a concrete sample of an airport pavement the following conclusions can be drawn:

- The petrography identified the presence of volcanic glass in three aggregate samples, however their chemical composition shows less than 65 % of silica which does not make them potentially reactive. The trachyte sample contains microcrystalline quartz as confirmed by SEM/EDS analysis. The geochemical analysis shows a silica content higher than 50 % which can contain silica minerals considered reactive as stated by some authors. The accelerated mortar-bar test performed on this aggregate showed that it is potentially reactive after 14 days of testing.
- The TAS diagram showed that the majority of the rocks analysed are basalts and trachybasalts. There is only a Si-rich rock - trachyte, two rocks of intermediate composition, a basaltic trachyandesite and a trachyandesite, and two basanites. The values of LOI showed that the samples of SMA-SM1, SMA-SM2 and FLO-SM1 are moderately altered which was also confirmed by the petrography examination.
- The concrete prism test (RILEM AAR-3) performed using the aggregate samples showed that after 2 years of testing some expansion curves crossed the limit boundary of 0.05 %. These results could indicate a slowly deleterious reactivity and should be further confirmed in order to understand the long-term behaviour of these aggregates.
- The petrographic examination of samples of a deteriorated concrete pavement reveals the presence of volcanic glass, zeolitic fibrous minerals and clay minerals in the aggregate particles. The volcanic glass is considered non-reactive due to the low silica content obtained by the microprobe analysis. However, the presence of a fibrous mineral of zeolitic composition seems to be related with a reaction between the cement paste and the particle aggregates.

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