Volcanic Aggregates from Azores and Madeira Archipelagos (Portugal): An Overview Regarding the Alkali Silica Reactions

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Abstract. Alkali-silica reaction (ASR) is a type of deterioration that has been causing serious expansion, cracking and durability/operational issues in concrete structures worldwide. The presence of sufficient moisture, high alkali content in the cement paste and reactive forms of silica in the aggregates are the required conditions for this reaction to occur. Reactive aggregates of volcanic nature have been reported in different countries such as Japan, Iceland and Turkey, among others. The presence of silica minerals and SiO2-rich volcanic glass is regarded as the main cause for the reactivity of volcanic rocks. In Portugal, volcanic aggregates are mainly present in Azores and Madeira Archipelagos and, for several years, there was no information regarding the potential alkali-reactivity of these rocks. Since the beginning of this decade some data was obtained by the work of Medeiros (2011) and Ramos (2013) and by the national research projects ReAVA, (Characterization of potential reactivity of the volcanic aggregates from the Azores Archipelago: implications on the durability of concrete structures) and IMPROVE (Improvement of performance of aggregates in the inhibition of alkali-aggregate reactions in concrete), respectively. In order to investigate the potential alkali-reactivity of aggregates from both archipelagos, a total of sixteen aggregates were examined under the optical microscope and, some of them, also under the Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy. A set of geochemical analyses and laboratory expansion tests were also performed on those volcanic aggregates. The main results showed that the presence of volcanic glass is rare in both archipelagos and that the samples of Madeira Archipelago contain clay minerals (mainly from scoria/tuff formations inter-layered with the lava flows), which can play a role in concrete expansion. The results of the laboratory tests showed that one of the samples performed as potentially reactive in the accelerated mortar-bar test (ASTM C 1260) and that the majority of the Azores samples started to show some expansion just after one year of testing in the concrete prism test (CPT) at 38°C.
1. Introduction
Volcanic rocks are amongst the most common rock types worldwide. The reactive character of these rocks has been reported in countries such as Japan, Iceland, USA and Turkey, among others. The presence of silica minerals and SiO₂-rich volcanic glass are the main causes for the reactivity of this kind of rocks.

Azores and Madeira Archipelagos are formed mainly by volcanic rocks that are exploited to produce aggregates for Civil Construction and Public Works. The majority of the aggregates is of basic composition and comprises especially basalts and trachybasalts. In Azores Archipelago, there is only one quarry of trachyte composition that is used for concrete purposes.

In Portugal, the deterioration of concrete by alkali-silica reaction (ASR) was first identified in the decade of 1980's in a dam [1]. Since that time, several structures were recognized to be affected by ASR but only one is related with the use of volcanic aggregates – a concrete airport pavement in Azores Archipelago [2]. The presence of ASR in the archipelagos was not well known until the beginning of this decade. The work done by Medeiros [3] and Ramos [4] and the research projects of ReAVA (Characterization of potential reactivity of the volcanic aggregates from the Azores Archipelago: implications on the durability of concrete structures) and IMPROVE (Improvement of performance of aggregates in the inhibition of alkali-aggregate reactions in concrete) gave a better clarification about the potential alkali reactivity of the Portuguese volcanic aggregates. In the scope of both projects, this paper presents the results of the petrographic examination, the geochemical analysis and the laboratory expansion tests of the investigated aggregates.

2. Materials and methods
A total of sixteen aggregates were selected, thirteen of them are from Azores Archipelago and three came from Madeira Archipelago. The assessment of the potential reactivity was performed by petrographic examination (optical microscopy, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)), geochemical analysis and accelerated mortar and concrete prism expansion tests. The thin sections and the geochemical analysis were prepared from hand-picked rocks representative of the rock facies present in the different quarries.

The Azorean aggregates were studied under an Olympus CX31 polarizing microscope and the aggregates from Madeira Archipelago were examined under a Nikon Eclipse E 400 POL microscope. SEM-EDS were also used to identify reactive forms of silica whenever the use of the polarizing microscope was not sufficient. Samples were carbon-coated and examined by SEM-EDS (Quanta 400 FEG ESEM/EDAX Genesis X4M, 15 kV and 10.0 mm working distance) at the Materials Centre of the University of Porto (CEMUP).

The geochemical analysis of the aggregates was performed at the Activation Laboratories (Actlabs), in Canada, by fusion-inductively coupled plasma (FUS-ICP: Thermo Jarrell - Ash ENVIRO II ICP). The results were plotted in a Total Alkali Silica (TAS) diagram to obtain the chemical classification of the rocks.

The accelerated mortar bar (AMBT) and the concrete prism tests (CPT) were carried out at National Laboratory for Civil Engineering (LNEC). Both mortar and concrete mixes were made with cement type CEM I 42.5 R and 0.89% of Na₂O<sub>eq</sub>. In mortar mixes, water/cement ratio of 0.47 and graded aggregates of 0.15-4.75 mm were used. The bars were immersed in 1N NaOH solution at 80°C and measurements were taken for 14 days, but in case of doubt, the measurements were extended until 28 days [5]. In concrete mixes, fine and coarse aggregates ranging from 0-4 mm to 4-22.4 mm, cement/aggregate ratio of 0.25 and water/cement ratio of 0.45 were used. The concrete prisms were stored at 60°C or 38°C with humidity higher than 95% for 36 weeks (RILEM AAR 4.1 test [6]) and 2 years (RILEM AAR-3.1 test [7]), respectively.
3. Results
The results of the geochemical analyses, petrography and accelerated expansion tests for each studied aggregate are presented in Table 1.

Table 1. Results of the different test-methods used to assess the reactivity to alkalis of the aggregates

| Aggregate | TAS classification | Petrographic classification | AMBT 80°C | CPT 38°C | CPT 60°C (1 yr) | CPT 38°C (> 0.04 @2yr) |
|-----------|--------------------|-----------------------------|-----------|----------|----------------|------------------------|
| SMA-SM1   | Basanite           | NR                          | NR        | NR       | NR             | √                      |
| SMA-SM2   | Basanite           | NR                          | NR        | NR       | NR             | √                      |
| SMG-SM1   | Trachybasalt      | PR                          | NR        | NR       | NR             | √                      |
| SMG-SM2   | Trachybasalt/Basalt | NR                          | NR        | NR       | NR             | √                      |
| SMG-SM3   | Basalt             | NR                          | NR        | NR       | NR             | √                      |
| TER-SM1   | Trachyte           | PR                          | NR        | NR       | NR             | √                      |
| TER-SM2   | Basalt             | PR                          | NR        | NR       | NR             | √                      |
| GRA-SM1   | Trachybasalt      | NR                          | NR        | NR       | NR             | √                      |
| SJO-SM1   | Basalt             | NR                          | NR        | NR       | NR             | √                      |
| PIC-SM1   | Basalt             | NR                          | NR        | NR       | NR             | √                      |
| FAL-SM1   | Trachybasalt      | NR                          | NR        | NR       | NR             | √                      |
| FLO-SM1   | Trachyandesite    | NR                          | NR        | NR       | NR             | √                      |
| FLO-SM2   | Basaltic trachyandesite | NR                          | NR        | NR       | NR             | √                      |
| BS6       | Trachybasalt; Basalt; Basanite | PR                          | NR        | NR       | NR             | √                      |
| BS7       | Basanite           | PR                          | NR        | NR       | NR             | √                      |
| BS8       | Basalt             | NR                          | NR        | NR       | NR             | √                      |

NR = non-reactive; PR = potentially reactive; yr = years

3.1. Geochemical analysis
The geochemical classification showed that the majority of the aggregates analysed from Azores and Madeira Archipelagos are of basic nature. According to the TAS diagram, the aggregates are classified mainly as basalts and trachybasalts and they belong to the alkali series. There is only one rock of acid composition in the Azores, which is a trachyte (TER-SM1 sample).

3.2. Petrography
The petrographic analysis showed that the samples are generally formed by the same mineralogy, with variable amounts of olivine, clinopyroxene, plagioclase, opaque minerals and sometimes apatite and biotite and, less frequently, amphibole. The phenocrysts and microphenocrysts mainly consist of olivine, clinopyroxene and plagioclase with different variations depending on the sample. The groundmass is formed by the same minerals with opaque minerals and apatite. Olivines, clinopyroxenes and plagioclases with euhedral to subhedral forms frequently exhibit disequilibrium features (reaction rims and embayments) and also glomeroporphyritic and sieve textures. The trachyte sample from Azores presents a different mineralogy, with large crystals mainly of sanidine and with smaller crystals of nepheline, biotite and opaque minerals. The groundmass consists of feldspars (plagioclase, anorthoclase), pyroxenes (aegirine, augite), amphibole (aenigmatite), apatite and opaque minerals [8]. In the Azorean rocks, the presence of volcanic glass is rare and it was only identified in three samples: SMG-SM1, TER-SM1 and TER-SM2. The first rock sample (SMG-SM1) is a vesicular rock where the volcanic glass occurs scattered in the groundmass with a brownish to yellow colour (Figure 1a). The EDS analysis of this glass shows a composition of 58% of SiO₂ [9]. The same sample also shows a xenocryst of quartz surrounded by clinopyroxenes (Figure1b).
Figure 1. Photomicrographs showing: (a) volcanic glass (brownish to yellow colour and (b) a xenocryst of quartz both in the sample of SMG-SM1 from Azores Archipelago

The second rock sample (TER-SM1) has sporadic brown glass in the intergranular groundmass and interstitial silica as microcrystalline quartz confirmed by SEM/EDS. The last sample (TER-SM2) has inclusions of volcanic glass within the plagioclase with a composition of 55% to 58% of SiO₂ by SEM/EDS [9] (Figure 2).

Figure 2. Photomicrographs of TER-SM1 sample showing: above, volcanic glass inclusions; below, SEM image with silica in trachyte, present as microcrystalline interstitial quartz and EDS spectrum
Concerning Madeira Archipelago, only sample BS6 showed reddish and colourless glass-like materials present in the groundmass and in inclusions in olivine phenocrysts, respectively. However, though formerly volcanic glass, these materials are now products of its alteration, i.e., clay minerals. SEM/EDS analysis showed that the majority of the samples from this archipelago contain clay minerals that belong predominantly to the smectite group (Figure 3) [10].

![Figure 3. Photomicrographs of BS6 sample showing: (a) Yellowish-brown smectite filling a vesicle and (b) vesicle lined by clay minerals from Madeira Archipelago](image)

3.3. Accelerated expansion tests
The AMBT showed that the trachyte sample is considered potentially reactive with expansion values higher than 0.10% at 14 days. The rest of the aggregates are considered non-reactive with expansions lower than 0.10%, the limit value between non-reactive and potentially reactive aggregates [5].

The CPT at 60°C showed that all the aggregates are considered non-reactive according to all the different limits suggested in LNEC E 461 [11], RILEM AAR-0 [12] and Lindgård et al. [13].

In the CPT at 38°C, all the aggregates are considered non-reactive after 1 year of testing and with expansion limits lower than 0.05% according to LNEC E 461 [11]; RILEM AAR-3 [7]. However, the expansion shows rising trends for most of the aggregates after 1 year of test and at the end of 2 years of testing, some of the aggregates cross the boundary limit between non-reactive and reactive [7]. Further testing should be done to understand the behaviour of these aggregates.

4. Discussion
The petrographic analysis showed that the presence of volcanic glass is rare in the rocks of both archipelagos. Silica minerals are present only in the rock of acid composition (a trachyte), as interstitial microcrystalline quartz, and as a xenocryst of quartz in a basic rock, both of Azores Archipelago. The composition of the volcanic glass in two of the samples is about 58% of SiO₂, which cannot be considered potentially reactive. According to Katayama [14], volcanic glasses with SiO₂>65% (rhyolitic glass) are considered potentially reactive even when present in basalts or andesites, while basalitic and andesitic glass are classified as innocuous. However, Katayama [15] mentions that a basalt studied by other researchers was considered reactive with a composition of 20% of andesitic volcanic glass. Clay minerals are present in two of the three samples studied in Madeira Archipelago and, according to Ramos [4], they were the result from the alteration of volcanic glass to clay of the smectite group. Marfil and co-workers [16] concluded that clay minerals are one of the main minerals that play an important
role in the reactivity of basaltic rocks. The geochemical analysis also showed, that the lithology is silica undersaturated and belong to the alkaline series, where the presence of volcanic glass is rare.

The results of the expansion tests indicate that all the rocks are non-reactive with the exception of the trachyte sample, which was classified as potentially reactive in the AMBT test. The CPT tests at 38°C show that some of the samples seem to have some reactivity after 2 years of testing; however, they are considered non-reactive after 1 year of testing according to the recommendations in RILEM AAR-3 [5]. One of the issues concerning this test is related with the time period given to the testing. This test should be extended until 2 years for basaltic aggregates to understand the behaviour of this type of rocks. Also further petrographic work is in progress on the test prims that completed their expansion testing (2 years) in order to identify potential signs of alkali-reactivity.

5. Conclusions
The majority of the samples are considered non-reactive according to all the methods used. Nonetheless, some of the samples can be considered potentially reactive based in the petrographic examination. This is the case of three samples from Azores Archipelago (SMG-SM1, TER-SM1 and TER-SM2) and two samples from Madeira Archipelago (BS6 and BS7). This potentially reactivity is regarded due to the presence of volcanic glass (in spite of the SiO₂ composition of volcanic glass being lower than 65%), silica minerals and clay minerals.

Further investigation is needed in order to completely understand the role of these minerals in ASR and to justify the expansion values reached by some aggregates in CPT at 38°C after 2 years of testing. These results suggest that the present expansion tests might have to be adjusted in temperature of exposure, threshold or duration in order to be adequate for the characterization these slow reactive types of rocks.

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