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Potentially Reactive Forms of Silica in Volcanic Rocks Using Different Analytical Approaches

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Abstract. Several concrete structures show signs of deterioration resulting from internal chemical reactions, such as the alkali-silica reaction (ASR). It is well known that these swelling reactions occur in the presence of moisture, between some silica mineral phases present in the aggregates and the alkalis of the concrete, leading to the degradation of concrete structures and consequently compromising their safety. In most of the cases, rehabilitation, demolition or even rebuilding of such structures is needed and the effective costs can be very high. Volcanic rocks are commonly used as aggregates in concrete, and they are sometimes the only option due to the unavailability of other rock types. These rocks may contain different forms of silica that are deleterious to concrete, such as opal, chalcedony, cristobalite, tridymite and micro- to cryptocrystalline quartz, as well as Si-rich volcanic glass. Volcanic rocks are typically very fine-grained and their constituting minerals are usually not distinguished under optical microscopy, thus leading to using complementary methods. The objective of this research is to find the more adequate analytical methods to identify silica phases that might be present in volcanic aggregates and cause ASR. The complementary methods used include X-Ray Diffraction (XRD), mineral acid digestion and Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM/EDS), as well as Electron Probe Micro-Analysis (EPMA).

1. Introduction

Concrete is the most commonly used construction material worldwide, allowing the edification of several structures from residential buildings to bridges and dams. Despite its great resistance and durability, concrete is not immune to deterioration, causing the reduction or even loss of concrete properties with time and putting the structures at risk. A common cause that leads to concrete's degradation is the alkali-aggregate reaction (AAR) that occurs inside the concrete, causing cracking due to the formation of internal expansive products. The present work focus on the alkali-silica reactions (ASR), a type of alkali-aggregate reaction, in which the potentially reactive forms of silica, present in the aggregates, react with the alkalis present in the cement paste forming an alkali-silica or alkali-silicate gel, which expand in the presence of moisture. The best way to prevent these reactions is by selecting



non-alkali reactive aggregates to be used in concrete, allowing a longer lifetime of the structures. For the assessment of aggregates regarding ASR, RILEM AAR-0 [1] recommends that the petrographic study is the first step of a cascade of laboratory tests aiming at classifying the aggregates in one of the following classes: class I, very unlikely to be reactive; class II, reactivity uncertain; class III, very likely to be alkali-reactive (e.g. aggregates containing opal).

The aggregates used in concrete can be of different natures. Volcanic rocks are a valid option in certain places such as in volcanic islands, due to the inexistence of other rocks and the low aggregates' economic value, which makes the import of these materials non-rentable. The volcanic rocks contain, in many cases, silica phases that might be alkali-reactive namely volcanic glass, which makes it necessary to study the reactivity of the rocks and the identification of the silica forms present, before the use for concrete manufacture.

Therefore, this study aims at the identification of potentially alkali-reactive forms of silica in volcanic rocks to be used in the concrete production, with different alkali-reactivity levels and from different locations around the world in order to relate the silica phases present in the rocks with their potential reactivity. The petrographic method complemented by scanning electron microscopy with energy dispersive x-ray spectrometry (SEM/EDS), electron probe micro-analysis, X-ray diffraction (XRD) and phosphoric acid digestion were carried out aiming to verify the usefulness of each method. The results obtained are presented and discussed.

2. Materials and methods

Twelve samples of volcanic rocks have been selected from different areas worldwide. For the majority of the samples, the reactivity is already known. The samples' selection was based on their potential reactivity in order to compare the results obtained by petrographic examination and complementary tests with the performance in laboratory expansion tests. A rhyolite containing abundant cryptocrystalline quartz and tridymite was used as reference.

The methodology applied to perform the mineralogical characterization of the samples started with the petrographic analysis of each sample under optical microscope. This analysis was mainly focused on the identification of the forms of silica, which could trigger the ASR [1]. In addition, other minerals that are considered to cause damage to concrete, namely clay minerals of the smectite group, were identified [2]. SEM/EDS was used for the qualitative chemical analysis of some mineral phases. Electron Probe Micro-Analysis (EPMA) was performed to obtain the quantitative chemical composition of volcanic glass. The equipment used is JEOL JXA 8200, coupled with EDS Oxford INCA X-act. The operating conditions of the X-ray tube were current intensity of 1 nA, accelerating voltage of 15 kV, and 5 μ m diameter of the electron beam. The acquisition peak count time was of 20 seconds.

Volcanic rocks are characterized by the very fine grain size of their components, which are usually difficult to identify under optical microscope. Therefore, for the identification of the minerals present in the rocks, the samples were pulverized and analysed using XRD Panalytical X'PERT PRO equipment, equipped with X'Celerator detector. The analyses were made from 5° to 70° of the 2 θ angle, with spacing of 0.033° and 75 seconds of scan step time. The generator settings for the Cu anode tube are 35 mA and 40 kV. For the identification of the minerals the High Score Plus software was used with PDF-2 database.

As in these types of rocks some forms of silica may occur in concentrations below the XRD detection limits, the phosphoric acid method initially created by Talvite [3] was applied. This chemical attack is applied to < 75 μ m grinded samples submitted to 25 ml of phosphoric acid (H₃PO₄) at a temperature of 250 °C for 12 minutes. After boiling for 3 minutes the Erlenmeyer bottle was stirred for 3 minutes in successive steps to avoid overheating. After cooling to room temperature, 125 ml of hot water was added, plus 10 ml of fluoroboric acid (HBF₄) and 10 ml of filter paper pulp, followed by 25 ml of water. The residue was then washed with hot hydrochloric acid (HCl) 1:10 and abundant water. The filter paper was put in the oven at 1000 °C \pm 50 °C for 30 min. This process aimed at inducing the dissolution of the minerals in the rock, with the exception of the free silica phases which are preserved in the residue. The

residue produced during this test was analysed using XRD, allowing the detection of concentrated silica minerals present, which could be compared with the previous XRD analysis of the whole rock.

3. Results and discussions

The designations and origin of the samples, as well as the results obtained from the previous laboratory expansion tests, are summarized in Table 1. The results of the bulk rock XRD analyses are also presented.

Table 1. Designation, potential reactivity and composition of the samples obtained by XRD of bulk rock (plg-plagioclase, px-pyroxene, ol-olivine, fds-feldspar, qtz-quartz, trd-tridymite, n.a.-information not available).

| Designation | Location | Lithology | Reactivity | XRD analysis |
|-------------|-------------------------------|---------------|--------------------------|---------------|
| MFU | Madeira, Portugal | Basalt | Non-reactive [4] | Plg+px+ol |
| MMA | Madeira, Portugal | Basalt | Non-reactive [4] | Plg+px+ol |
| VFX | Vila Franca de Xira, Portugal | Basalt | Non-reactive [4] | Plg+px+clay |
| TF-AZ | Azores, Portugal | Volcanic Tuff | n. a. | Fds+px+clay |
| T15 | Turkey | Andesite | Reactive [5,6] | Plg+px |
| HW4 | Hawaii, USA | Basalt | n. a. | Plg+px |
| HW5 | Hawaii, USA | Basalt | n. a. | Plg+px+pyrite |
| HW6 | Hawaii, USA | Basalt | n. a. | Plg+px |
| ISL-TOL | Iceland | Basalt | Potentially reactive [7] | Plg+px+ol |
| ISL-RA | Iceland | Basaltic Sand | Non-reactive [7] | Plg+px |
| ISL-HV | Iceland | Basaltic Sand | Highly reactive [7] | Plg+px+ol |
| RLM | Mozambique | Rhyolite | Reactive | Qtz+trd+fds |

3.1. Petrographic Analysis

The samples from Madeira Island (MFU and MMA) are holocrystalline basalts composed mostly of a matrix of plagioclase, pyroxene (augite) and opaque minerals, the majority of them corresponding to magnetite. In MFU sample, olivine phenocrysts are present and show intense alteration to iddingsite and serpentine. Iron oxides are more abundant in some sectors of the rock; some areas are constituted by a groundmass of plagioclase and volcanic glass, and contain quite altered large augite and plagioclase phenocrysts. The volcanic glass varies in composition and tonality from dark to light brown, with variable degree of alteration to clay minerals. Sample MMA has a lot less olivine, but its alteration is more intense, with clay minerals surrounding the primary crystals and also abundant in the matrix.

VFX sample is a porphyritic basalt with a matrix of plagioclase, pyroxene and magnetite. Phenocrysts are composed of olivine and pyroxene. It contains extremely altered sectors, in which the augite phenocrysts are deeply altered and replaced by smectite. This alteration zone is dominated by zeolites, and a mixture of serpentine and chlorite. There are some crystals that might correspond to silica phases, but this cannot be confirmed at the scale of the petrographic microscope.

The Azores' tuff is a complex sample that contains various types of clasts preserved in the thin sections. Most of them are of trachytic nature with a well-marked flow orientation, composed mainly of plagioclase and pyroxene. There are many pomitic clasts containing dark brown volcanic glass. The potentially reactive components are quartz and tridymite, besides the dark volcanic glass and some small amounts of a light-brown volcanic glass.

The Turkish (T15) andesite shows porphyritic texture and contains a matrix of volcanic glass and plagioclase laths with some pyroxene. There are abundant phenocrysts of plagioclase and pyroxene, and also magnetite in fine/medium-grained crystals. The light-brown volcanic glass also occurs as abundant inclusions in the plagioclase phenocrysts. Serpentine associated with microcrystalline quartz and a few crystals of chalcedony occur as alteration products of olivine (Figure 1). The occurrence of chalcedony was confirmed by EDS qualitative analysis.

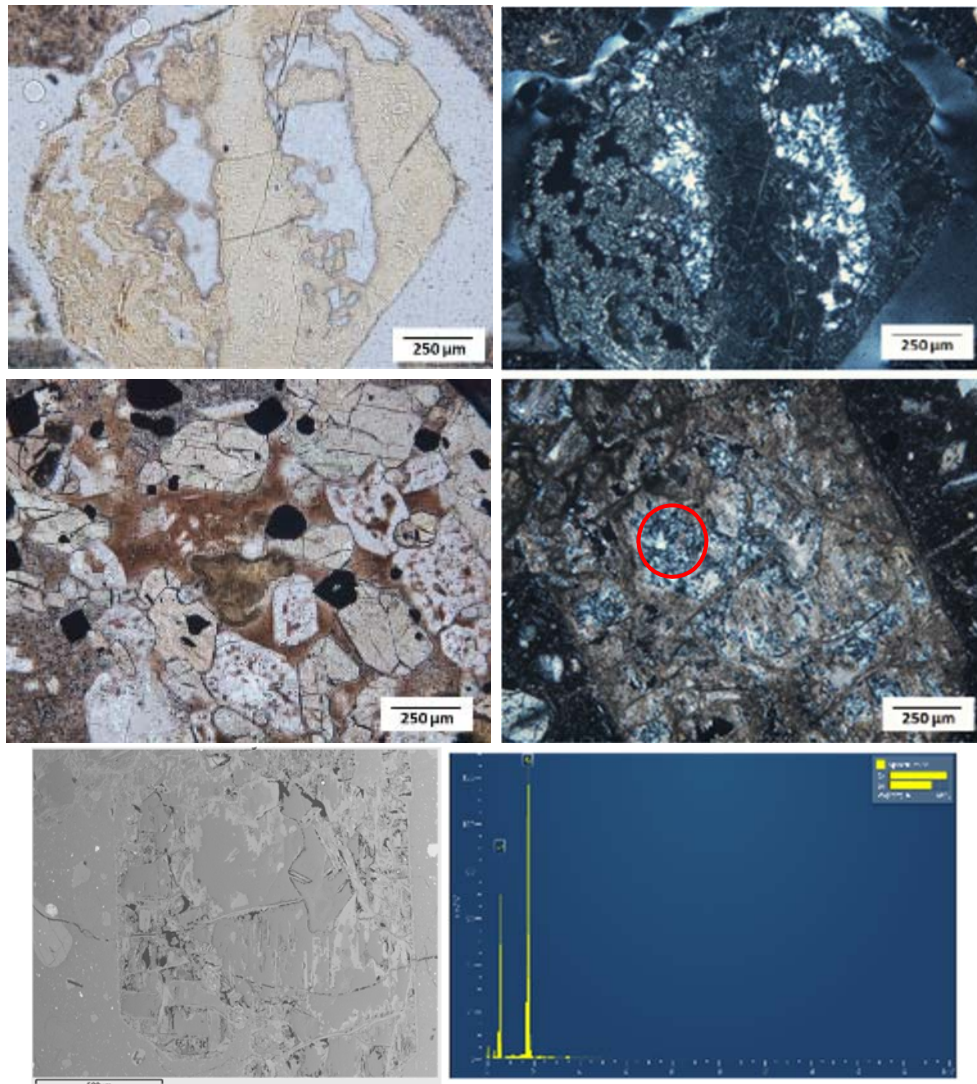


Figure 1. Photomicrographs showing potentially reactive forms of silica in sample T15 such as volcanic glass and feather-like chalcedony, carbonate and serpentine replacing a phenocryst of olivine (left, plane polarized light; right, crossed polarized light). Below, backscattered electron image at SEM and the EDS spectrum in the red circle zone confirming the silica presence.

Both HW4 and HW5 samples from Hawaii have aphanitic texture and are composed mostly of plagioclase and some iron oxides. There are also some crystals of olivine in both samples and pyroxene with some smectite in the sample HW4. Microcrystalline quartz associated with serpentine in HW4 and some biotites in HW5 were detected. The matrix in HW6 sample is composed of plagioclase, pyroxene and magnetite, and the rock has some phenocrysts of pyroxene, plagioclase and olivine. HW6 is similar to HW4, with plagioclase as the dominant component.

The sample ISL-RA contains lithoclasts of a rock formed by pyroxene and plagioclase, with a small amount of olivine. It also includes volcanic glass partially altered to palagonite. The basaltic sand from Iceland (ISL-HV) shows wide variety in its composition, and a lot of potentially reactive phases have been identified, namely cryptocrystalline quartz, volcanic glass and chalcedony. Volcanic glass is abundant and in some of the rock fragments that constitute the sand particles, it is devitrified (Figure 2). The ISL-TOL sample contains plagioclase, pyroxene, olivine and magnetite, and no harmful components to the concrete were identified.

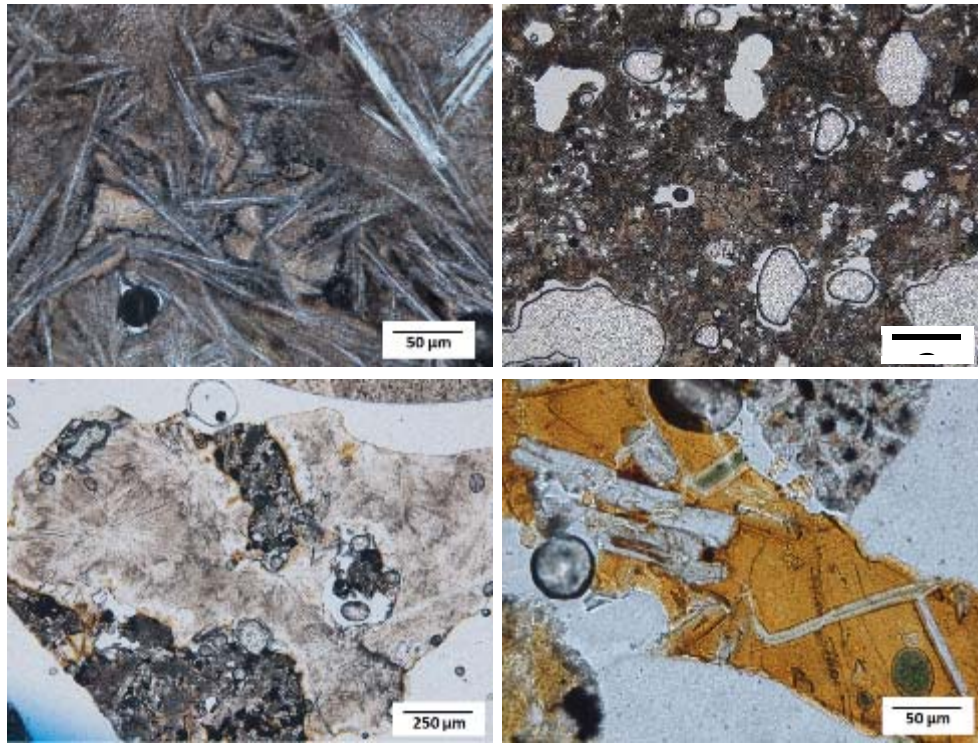


Figure 2. Photomicrographs showing different aspects of the Icelandic sands: volcanic glass is abundant in all these particles and is usually devitrified and/or replaced by clay minerals (plane polarized light).

The RLM sample is classified as rhyolite with aphanitic texture. It contains intergrowths of quartz and feldspars, which are difficult to distinguish due to the extremely small size of the crystals of the rock. In this rock, tridymite was identified in high proportions. Figure 3 shows the main aspects of the rock. To distinguish the microcrystalline quartz from the feldspar, elemental maps obtained by SEM/EDS were used.

3.2. X-Ray Diffraction and Phosphoric Acid Method

The analyses by XRD confirmed the minerals that are most abundant within the samples and allowed to identify some components not detected by the petrographic examination, which occurred in two of the samples.

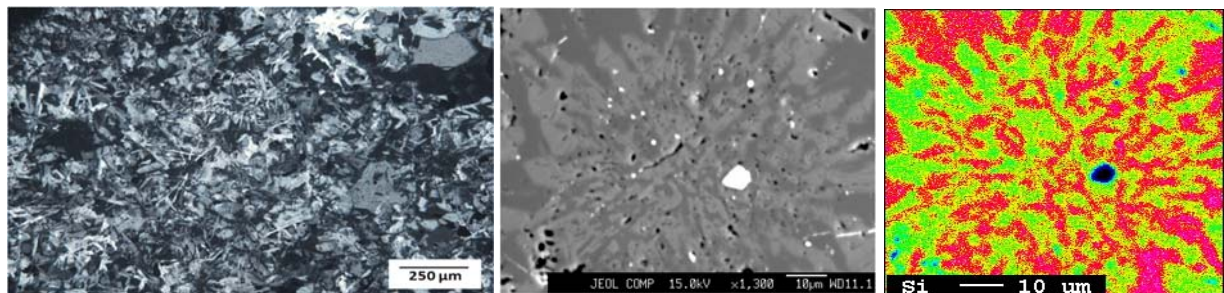


Figure 3. RLM with tridymite in thin tabular plates and cryptocrystalline quartz and feldspar intergrowths. Photomicrograph obtained under optical microscope (XPL), image obtained by SEM and Si elemental X-ray map (Si in red).

The dissolution of the samples used in the phosphoric acid method allowed to identify phases of silica occurring in very low content and that were not observed under microscope (Table 2). Quartz has been detected in all the samples, with exception of the sample ISL-RA, while tridymite was identified in two of the samples: RLM, confirming the petrographic results, and HW6. Five of the samples contain cristobalite (T15, HW4, ISL-TOL, ISL-RA, ISL-HV). In HW4 sample, besides cristobalite, also opal and some amorphous matter were identified, which may correspond to the partially non-crystalline structure of opal, or to volcanic glass.

Table 2. Results of XRD of the phosphoric acid residue (n.a. - information not available as the tests are still being performed). The products identified in the phosphoric acid residue of each sample are rated as abundant, moderate, low and traces.

| Sample | Quartz | Tridymite | Cristobalite | Amorphous phases | BPO ₄ |
|---------|----------|-----------|--------------|------------------------------|------------------|
| MMA | Traces | n.a. | n.a. | n.a. | Abundant |
| MFU | Traces | n.a. | n.a. | n.a. | Abundant |
| VFX | Traces | n.a. | n.a. | n.a. | Abundant |
| VFX2 | n.a. | n.a. | n.a. | n.a. | Abundant |
| TF-AZ | Abundant | n.a. | n.a. | n.a. | Traces |
| T15 | Abundant | n.a. | Low | Abundant (volcanic glass) | Present |
| HW4 | Traces | n.a. | Low | Present (opal) | Abundant |
| HW5 | Traces | n.a. | n.a. | n.a. | Abundant |
| HW6 | Low | Traces | n.a. | n.a. | Abundant |
| ISL-RA | n.a. | n.a. | Traces | n.a. | Abundant |
| ISL-HV | Abundant | n.a. | Traces | n.a. | Present |
| ISL-TOL | Traces | n.a. | Traces | n.a. | Abundant |
| RLM | Abundant | Present | n.a. | n.a. | Traces |

In the samples RLM, HW5 and HW6, the dissolution of the silicates was not totally successful, and low quantities of plagioclase remained in the residue. In all the samples, a compound that was formed during the chemical test (BPO₄), due to the use of phosphoric and fluoroboric acids, was identified. The diffractograms of the phosphoric acid residue corresponding to the samples HW4 and RLM can be found in Figure 4.

3.3. Quantitative Chemical Analysis of Volcanic Glass

Volcanic glass was analysed by EPMA in three of the samples, MFU, T15 and ISL-HV, in order to determine the content of SiO₂. The results of the average content of silica present in the volcanic glass phases of each sample are (approximately) MFU – 47.5%; T15 – 70%; ISL-HV – 45%. Therefore, only the sample T15 is classified as potentially reactive to alkalis based on the volcanic glass composition. The use of these complementary methods allowed the classification of the aggregates as summarized in Table 3.

Table 3. Classification of the samples according with RILEM AAR-1.1 [1].

| Class I | Class II | Class III |
|---------|----------|-----------|
| MFU | VFX | T15 |
| MMA | TF-AZ | ISL-HV |
| HW5 | HW4 | RLM |
| HW6 | ISL-RA | |
| ISL-TOL | | |

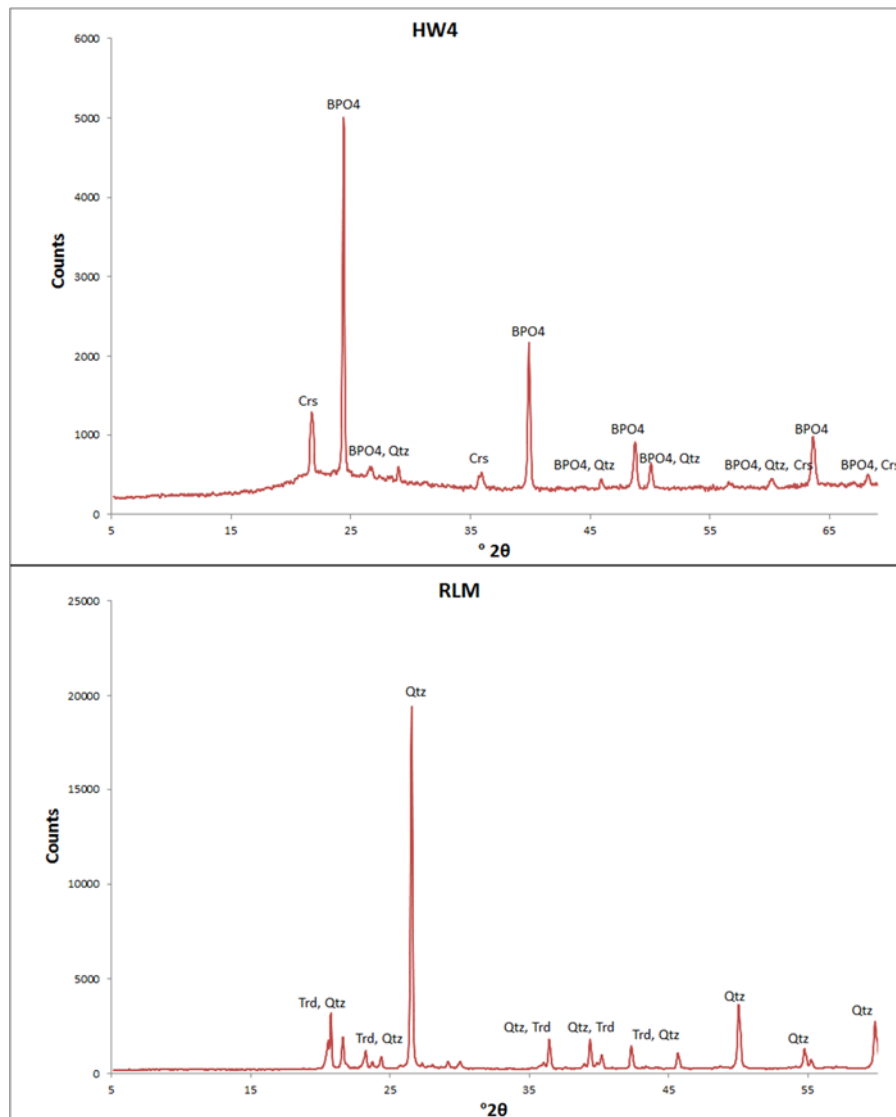


Figure 4. Diffractograms of the samples HW4 and RLM: residue of the phosphoric acid test. Besides silica phases, also BPO₄ was formed from the chemical products used (Crs – cristobalite, Opl – opal, Qtz – quartz, BPO₄ – boron orthophosphate, Trd - tridymite)

4. Conclusions

The petrographic analysis of the samples has been of extreme importance in order to describe the mineralogy of the samples and to allow the identification of some silica phases, but it is required to use other scales (SEM/EDS and EPMA) to confirm some of the minerals observed and to determine the silica content of the volcanic glass.

The study developed showed that the methods applied produce good results in the identification of silica forms in volcanic rocks. It has been also concluded that the silica phases related with the sample's higher reactivity are opal, volcanic glass (when the silica content is above 65%) and chalcedony.

The silica phases identified by XRD analysis are in low proportion and correspond to those that can usually be observed in the petrographic analysis. However, the XRD method applied to the residue obtained from the phosphoric acid chemical test allowed the identification of forms of silica such as cristobalite in the all samples from Iceland, T15 and HW4, and possibly opal in sample HW4. The

dissolution with phosphoric acid was not totally successful in the samples RLM, HW5 and HW6, where very low contents of plagioclase were still found in the residue.

Based on these tests performed, the samples considered non-reactive are the ones from Madeira and Azores Archipelagos, a sample from the Portuguese Mainland (VFX) and one sample from Iceland (ISL-RA). In these samples, no deleterious silica phases were detected. A limited sector of the thin section of MFU sample shows volcanic glass in the matrix, but the EPMA analysis indicates that it has low silica content. Some volcanic glass and traces of cristobalite were detected in the sample ISL-RA. The sample TF-AZ contains scarce tridymite crystals and also volcanic glass. The sample RLM, which was used as reference, has a high content in tridymite, and therefore it can be assumed that will have a reactive behaviour in the concrete.

T15 is a reactive rock, mostly due to the high content of Si-rich volcanic glass, with 70% of SiO₂. The sample ISL-TOL is potentially reactive, apparently due to some traces of cristobalite within the rock, and some rhyolitic volcanic glass [7]. The high reactivity of the ISL-HV sample is due to the presence of chalcedony, observed by microscopy and identified by XRD after the phosphoric acid method. The volcanic glass in this sample has shown to be most likely non-reactive, due to the low content of SiO₂. From the Hawaiian samples, only HW4 contains silica phases, namely opal, a highly reactive form of silica.

The petrographic examination of the aggregates is quite effective in the detection of deleterious silica forms that might be alkali reactive, providing immediate information about the potential performance in concrete, e.g. the Mozambique sample (RLM), which contains tridymite, the Turkish sample (T15), with Si-rich volcanic glass, and one Icelandic sample (ISL-HV), with different forms of silica.

However, complementary methods are required, such as the EPMA, extremely useful to analyse the composition of volcanic glass, e.g. in T15. The phosphoric acid method showed to be crucial for volcanic rocks, as it revealed reactive silica phases that were not observed under microscope, due to the very fine granularity of this type of rocks and to the very low content of these components in the rocks. It has been especially useful in the sample HW4, allowing to identify opal. As shown, the non-reactive rocks do not contain alkali reactive forms of silica, or just traces of cristobalite, volcanic glass in the sample ISL-RA and tridymite in the sample HW6. The most reactive samples are the ones containing tridymite, as RLM, volcanic glass with high silica content, such as T15, and ISL-HV which contains other forms of silica. The presence of opal in the sample HW4 also allows the classification of the aggregate as potentially reactive to alkalis.

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