

Alkali–silica reaction in volcanic rocks: a worldwide comparative approach

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ABSTRACT: The potential alkali–silica reactivity (ASR) of volcanic aggregates, especially basalts, remains a source of debate in the scientific community. When evaluating the potentially deleterious character of this type of aggregate, different laboratory testing methods may produce contradictory data; this is particularly evident when using the accelerated mortar bar test (AMBT). In order to better understand such discrepancies, this study applied several methods of characterizing potential aggregate alkali reactivity, including the accelerated mortar bar test (AMBT), petrographic characterization, and the concrete prism test (CPT). Moreover, this study assessed volcanic aggregate samples from sites around the world, including the Azores, Brazil, Canada, the Canary and Hawaiian Islands, Iceland, Japan, Mozambique, New Zealand, Norway, and Turkey. The results obtained contribute to accurately assessing the potential alkali reactivity of volcanic aggregates and enhance the understanding of their different behaviours.

KEYWORDS: Alkali–Silica reaction; Petrography; Accelerated expansion tests; Volcanic aggregates.

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RESUMEN: *Reacción álcali–sílice en rocas volcánicas: un enfoque comparativo mundial.* La reactividad potencial álcali–sílice (RAS) de los áridos volcánicos, especialmente basaltos, sigue siendo una fuente de debate en la comunidad científica. Se puede obtener información contradictoria dependiendo de los métodos de ensayo utilizados en el laboratorio para evaluar el carácter potencialmente perjudicial de tales áridos, especialmente en el caso del ensayo acelerado de barra de mortero. Para comprender mejor esta discrepancia, se realizaron una serie de ensayos: caracterización petrográfica, ensayo acelerado de barra de mortero y de prisma de hormigón. Además, se seleccionaron para este estudio varios áridos volcánicos de diferentes partes del mundo (i.e., Azores, Brasil, Canadá, Islas Canarias y Hawaianas, Islandia, Japón, Mozambique, Nueva Zelanda, Noruega, Turquía). Los resultados obtenidos contribuyen a evaluar la reactividad alcalina potencial de estos áridos y permiten comprender mejor los diferentes comportamientos de los distintos áridos volcánicos estudiados.

PALABRAS CLAVE: Reacción álcali–sílice; Petrografía; Ensayos de expansión acelerada; Áridos volcánicos.

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1. INTRODUCTION

Basaltic rocks are used as concrete aggregates in many countries owing to their local abundance and their propensity to improve concrete strength and quality (1). However, the role that basalts play in alkali-silica reactions (ASR) remains poorly understood. Researchers disagree as to whether basalts should be considered non-reactive (2, 3) or reactive (4-6). The potential alkali reactivity of basalts varies from one geological context to another and even between samples within the same geological area. According to Fernandes *et al.* (7), this might be due to the regional geological history of a rock and the presence of both reactive and innocuous varieties of the same type of rock stemming from subtle differences in their mineralogical composition and/or texture.

In the literature, the reactivity of basaltic rocks is usually associated with the presence of volcanic glass (8-14), devitrified volcanic glass (13), different types of reactive silica (e.g., chalcedony, opal, and microcrystalline and cryptocrystalline silica) (8-13), and swelling clay minerals that are alteration products of volcanic glass (10, 12). Some authors have described problems in concrete related to basalt use (6, 8-12, 15). Severe ASR problems were observed in Iceland during the 1970s (16) arising from the use of reactive aggregates with high rhyolitic content and altered basalts (7), the use of some unwashed sea-dredged material (16) together with high-alkali cements, and adverse environmental conditions (15, 17).

Petrographic characterization is considered the first essential step in assessing the potential alkali reactivity of concrete aggregates (18), as stated in the RILEM AAR-0 test standard (19). Petrographic analysis of aggregates allows classification in terms of reactivity based on the presence of potentially reactive mineralogical phases. An aggregate is categorized into one of three classes according to RILEM AAR- 1.1 (13): Class I (very unlikely to be alkali-reactive); Class II (alkali reactivity uncertain); and Class III (very likely to be alkali-reactive). Lindgård *et al.* (20) indicated that the petrographic method can produce results relatively quickly and is generally effective in identifying reactive materials. For fine-grained rocks, such as volcanic rocks, optical microscope analysis usually requires the use of complementary methods such as X-ray diffraction and scanning-electron microscopy to identify reactive components.

Final classification as either innocuous or potentially alkali-reactive depends on which laboratory expansion test is used to assess an aggregate. The most common such tests are the accelerated mortar bar test (AMBT-80°C) (ASTM C 1260 (21) or RILEM AAR-2 (22)), the concrete prism test (CPT-38°C) (ASTM C 1293 (23) or RILEM AAR-3 (24)), and the

accelerated concrete prism test (CPT-60°C) (RILEM AAR-4.1 (25)). Although the AMBT is useful as a rapid test, there is no consensus as to the validity of the results it furnishes, especially when compared to the results of petrography and those obtained from the CPT (26). Positive experiences using the AMBT have been reported in the EU "PARTNER" project (20) and in inter-laboratory trials conducted under the International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM). Gadea *et al.* (27) also reported positive results using the AMBT, and concluded that it is a simple and reliable way to determine the reactivity of an aggregate. However, Nixon and Fournier (28) noted that, for a wide range of aggregates, namely the slow/late-reactive aggregates as identified in (20), the 14-day AMBT can be erroneous and misleading compared to the more accurate and realistic one-year concrete prism test (CPT-38°C). In work by Ramos (29) and Ramos *et al.* (30), slow/late-reacting aggregates were tested using different methods including the AMBT extended to 28 days, the CPT-38°C, and the accelerated concrete prism test (CPT-60°C). The authors concluded that the AMBT gave false-negative results for the granite, basalt, and limestone samples tested and led to some aggregate classifications that disagreed with those arising from the petrographic method. Moreover, while the CPT-38°C and CPT-60°C tests are well-correlated, the AMBT shows poor correlation with both concrete prism tests. Therefore, care should be exercised in using the ASTM C 1260 (21) to assess the potential alkali-reactivity of slow/late-reacting aggregates.

Over recent decades, suggestions have been made for overcoming these discrepancies in aggregate classification, namely by extending the duration of the tests and/or applying more conservative (lower) reactivity thresholds, particularly for slow/late-reactive aggregates (31-35). More recently, Santos Silva *et al.* (36) recommended that basaltic aggregates be evaluated by applying the CPT with an extended test period of two years.

The aim of the present study is to examine the potential alkali-silica reactivity of basaltic rocks from locations around the world using petrographic characterization methods, the AMBT, and the CPT to determine which methods are best for classifying aggregates of this type.

2. MATERIALS AND METHODS

Volcanic aggregates from twelve countries were tested in this study. Most of the aggregates originated from quarrying operations and consisted of basaltic rocks. Aside from basalts in the strict sense of the term, including trachybasalts, basanites, trachyandesite, basaltic andesite, and trachyte, additional rocks were also assessed for comparative purposes. These

rocks included two andesites (from Japan and Turkey) and one rhyolite (from Mozambique). The aggregates were obtained from different regions and geological settings, and were represented by either a single sample (Brazil, Canada, Japan, Mozambique, Norway, and Turkey) or more than one sample (the Canary Islands (Spain), Iceland, New Zealand, the Azores Archipelago (Portugal), and the Hawaiian Archipelago (United States of America)). Table 1 shows the label assigned to each sample.

In addition to the quarried aggregates, basaltic sands from the Hawaiian Islands (HW7 sand) and from Iceland (ICL1 fine sand, ICL1 coarse sand, ICL3 sand, and ICL4 sand) were assessed by the AMBT and the CPT. These sands were mixed with non-reactive coarse (high-purity limestone) aggregates in order to evaluate their behaviour in the CPT.

A different set of methods was used to better understand the potential ASR of the volcanic rocks considered in this study. In accordance with RILEM AAR-0 (19), examination using a petrographic/polarizing microscope was the first method used to evaluate the potential alkali reactivity of the aggregates. The main objective of this petrographic study was to identify potentially reactive forms of silica in the samples studied. In volcanic aggregates, these forms include volcanic glass, tridymite, cristobalite, microcrystalline quartz, opal, chalcedony (13), and clay minerals (10, 14). Potentially reactive forms of silica may be present at the sub-microscopic level, especially in volcanic rocks. In order to examine certain areas of the samples in more detail and to complement the petrographic study, two other methods were used: (a) scanning-electron microscopy–energy-dispersive X-ray spectrometry (SEM/

EDS) and (b) electron probe microanalysis (EPMA). Bulk-rock chemical analyses were performed at Activation Laboratories Ltd. in Canada using the lithium metaborate/tetraborate fusion–inductively coupled plasma (ICP) method and the inductively coupled plasma–mass spectrometry (ICP/MS) method. Chemical classification was performed on all aggregates with the exception of ICL1, ICL2, and ICL4 because of their diverse materials (polymictic gravel). Together with the petrographic analysis, these analyses provide complementary information about the rock composition.

Petrographic studies were conducted on conventional thin sections using an Olympus CX31 polarizing microscope in order to identify the aggregate materials' mineralogical and textural characteristics and the potentially reactive forms of silica present (7, 18). A number of photomicrographs were captured using an Olympus SC100 camera. Notably, the point counting described in RILEM AAR-1.1 (13) was not performed owing to the (fine) size of the minerals present in the samples. As the very fine grains of extrusive rocks can present a challenge to mineral identification under the polarizing microscope, other techniques such as EPMA and SEM/EDS were used on carbon-coated, polished thin sections. Quantitative geochemical data were obtained by EPMA performed at Université Laval, Québec, Canada, where a CAMECA SX-100 electron microprobe was used for samples from Brazil, Canada, Spain, Hawaii, Iceland, Japan, Mozambique, Norway, and Turkey. Only certain samples from the Azores (SMG-SM1, TER-SM1, and TER-SM2) were analysed by SEM/EDS. Semiquantitative geochemical EDS analyses of phases in the SMG-SM1 and TER-SM2 samples were per-

TABLE 1. Each sample was given a unique label. The rock types indicated are based on the combined results of geochemical analysis and petrographic examination.

Country	Rock	Label	Country	Rock	Label	Country	Rock	Label
Brazil	Basalt	BRAZ		Basanite	SMA-SM1	Portugal (Azores)	Mugearite	F L O - SM2
Canada		CAN			SMA-SM2		Hawaiite	CRV
Iceland	Gravel	ICL1		Potassic chybasalt	SMG-SM1	Spain (Canary Is- lands)	Basanite	CANY1
		ICL2			SMG-SM2			CANY2
	Basalt	ICL3		Basalt	SMG-SM3	Turkey	Andesite	TK
	Gravel	ICL4		Trachyte	TER-SM1		Basalt	HW1
Japan	JAP	Basalt	TER-SM2	HW2				
Mozambique	Rhyolite	MOZ		Hawaiite	GRA-SM1	USA (Hawaii Islands)		HW3
New Zealand	Basanite	NZ1		Basalt	SJO-SM1		Mugearite	HW4
	Basalt	NZ2		Basalt	PIC-SM1			HW5
	Basalt	NZ3		Hawaiite	FAI-SM1		Basalt	HW6
Norway	Basalt	NOR		Benmoreite	FLO-SM1			HW7

formed in Japan by Kawasaki Geological Engineering. For the TER-SM1 sample, this was also done at the Materials Centre of the University of Porto in Portugal (Centro de Materiais da Universidade do Porto – CEMUP) using EDS (JEOL JSM-6301F SEM with a Noran Voyager EDS: 15 kV, 15-mm working distance, 60-s collection time, and 30% dead-time).

The potential alkali reactivity of the aggregates considered was further evaluated using the AMBT and the CPT. Different accelerated mortar bar test series were performed as part of this study: (a) 29 mixes at Université Laval, Québec, Canada, and (b) 13 mixes at the National Laboratory for Civil Engineering (Laboratório Nacional de Engenharia Civil, LNEC), Lisbon, Portugal, within the scope of the ReAVA and IMPROVE research projects. The mortar mixtures at Université Laval were prepared in accordance with the CSA A23.2-25A standard (37) and incorporated a general use (GU) Portland cement with an alkali content of 0.94% $\text{Na}_2\text{O}_{\text{equiv}}$, while tests performed at LNEC followed the ASTM 1260 standard (21) using cement type CEM I 42.5 R (38) with 0.86% $\text{Na}_2\text{O}_{\text{equiv}}$ and a water/cement (w/c) ratio of 0.47. In all cases, the bars were immersed in a 1N NaOH solution at 80°C and length-change measurements were taken at regular intervals for up to 28 days (37). The 29 mixes prepared in Canada included samples NOR, CAN, BRAZ, CRV, JAP, MOZ, NZ1, NZ2, NZ3, CANY1, CANY2, TK, HW1, HW2, HW3, HW4, HW5, HW6, HW7, HW7 sand, ICL1, ICL1 fine sand, ICL1 coarse sand, ICL2, ICL3, ICL3 sand, ICL4, ICL4 sand, and GBS (sand from Iceland). The control used was Spratt aggregate: a highly reactive siliceous limestone aggregate from Ontario, Canada. The mixes prepared in Portugal included aggregate samples from the different islands of the Azores Archipelago: SMA-SM1, SMA-SM2, SMG-SM1, SMG-SM2, SMG-SM3, TER-SM1, TER-SM2, GRA-SM1, SJO-SM1, PIC-SM1, FAI-SM1, FLO-SM1, FLO-SM2.

An additional CPT series was conducted for this study: (a) 30 mixes at Université Laval and (b) 13 mixes at the LNEC, within the scope of the ReAVA and IMPROVE research projects. For the CPT, an extra mix with coarse and fine aggregates from the same source (HW7-CA+FA) was prepared at Université Laval. The CPT series at Université Laval were conducted in accordance with the CSA A23.2-14A standard (39) (equivalent to ASTM C 1293 (23)) and incorporated a GU Portland cement with an alkali content of 0.94% $\text{Na}_2\text{O}_{\text{equiv}}$. A cement content of 420 kg/m^3 and a w/c ratio of 0.43–0.44 were used in all mixtures. The aggregate grading consisted of three equal-mass portions of 5–10 mm, 10–14 mm and 14–20 mm size fractions. NaOH was added to the mix water in order to raise the total alkali content in the mix to 1.25% (by cement mass); i.e., a total concrete alkali content of 5.25 kg/m^3 . The CPT performed at the LNEC followed RILEM AAR-3 (24). The concrete mixes were prepared with the

same cement used for the AMBT and with fine and coarse aggregates from the same origin (< 22.4 mm). A cement-to-aggregate ratio of 0.25 and a w/c ratio of 0.45 were used in the 13 mixes. A total cementitious material content of 440 kg/m^3 was used in those mixtures and NaOH was added to the mix water in order to raise the total alkali content in the mix to 1.25% (by cement mass); i.e., a total concrete alkali content of 5.50 kg/m^3 .

In all Université Laval and LNEC test series, the test prisms were stored at 38°C and R.H. > 95% and length-change measurements were taken regularly over the specified one-year test period.

3. RESULTS

3.1. Petrography and complementary techniques

Petrographic characterization in terms of basic composition indicated similarities between the samples. In general, relatively large, conspicuous crystals (phenocrysts) of olivine, pyroxene, and plagioclase were present in various proportions. The groundmass was mainly fine-grained with intergranular texture and was formed of the same mineral assemblage plus apatite and opaque minerals. The latter sometimes showed a skeletal form when present as phenocrysts. Olivine was absent from the groundmass in a few samples. Some samples contained chlorite, either together with zeolites (ICL1, ICL2) or alone (CAN and NOR - Figure 1a and b). Zeolites were present in samples SMA-SM1, CANY1 and ICL1. The presence of these two minerals was confirmed by EPMA. Additionally, quartz was recognised by the same analysis in samples ICL1, ICL2, and NOR. Microcrystalline quartz was detected by SEM/EDS in TER-SM1. Using EPMA, a silica material was identified in the BRAZ sample, and optical properties examined using a petrographic microscope suggested the presence of quartz between green celadonite minerals (Figure 1c). Clay minerals were also detected by EMPA in samples BRAZ, CAN, and ICL2. Petrographic microscope examination showed that volcanic glass was present in almost half of the samples (Figures 1d-g). For each sample, the presence of volcanic glass was also confirmed by EPMA; results are shown in Table 2. Depending on the sample, glass appeared to various extents, varied in colour, and ranged from a dark to a lighter, brownish appearance. Notably, the NZ1 sample contained some whitish fragments between the darker volcanic particles. Under the microscope, these whitish particles were revealed to be fine-grained chert with microcrystalline forms of silica and tectonite with deformation structures mainly composed of microcrystalline quartz.

From a macroscopic perspective, the natural

(rounded) gravel aggregates ICL1, ICL2, and ICL4 presented different textures and the frequent presence of shells. Under the microscope, differences were apparent between these gravel aggregates from Iceland and the other samples. The former included a mixture of rock fragments of different origins: mainly basalts, metabasalts (metamorphic derivatives of basaltic rocks), some rhyolites, and a few highly altered plutonic rocks (probably altered gabbro). The fragments of these mixtures showed textures similar to those of the other basaltic samples in this study with the same mineral assemblage. Volcanic glass and devitrified volcanic glass appeared scattered in the groundmass and featured a rusty colour, probably due to palagonite (Figures 1d and f). The fragments of metabasalts exhibited peculiar features: pore spaces were filled with zeolites with surrounding chlorite. There were also fragments of dacites in ICL4 with a very fine-grained groundmass containing phenocrysts of plagioclase. The rhyolite fragments present in gravels ICL1 and ICL2 featured a fine-grained groundmass with quartz and feldspar as the dominant minerals.

The two investigated andesites (Figure 1h) were

very similar. Both were porphyritic with plagioclase phenocrysts, pyroxene, and some olivine. The groundmass of TK was composed of volcanic glass and plagioclase. Volcanic glass appeared to be absent in the JAP sample, though it did contain an unidentified silica form (possibly tridymite). The rhyolite (MOZ) was aphyric (Figure 1i) and contained microcrystalline silica. The groundmass appeared to be banded with lighter and darker areas. According to the EPMA analysis, both areas consisted of volcanic glass.

EDS analyses were performed on three samples from the Azores (SMA-SM1, SMG-SM2, and TER-SM1). For volcanic glass, the EDS results showed SiO₂ content of 58% and 55% for SMG-SM1 and TER-SM2, respectively. The interstitial silica detected in the TER-SM1 sample was confirmed as microcrystalline quartz (40).

Table 2 summarizes EPMA results for presumed volcanic glass in samples where this material was identified initially by petrography. These identifications were positive except in the BRAZ sample, where high SiO₂ content revealed by EPMA indicated

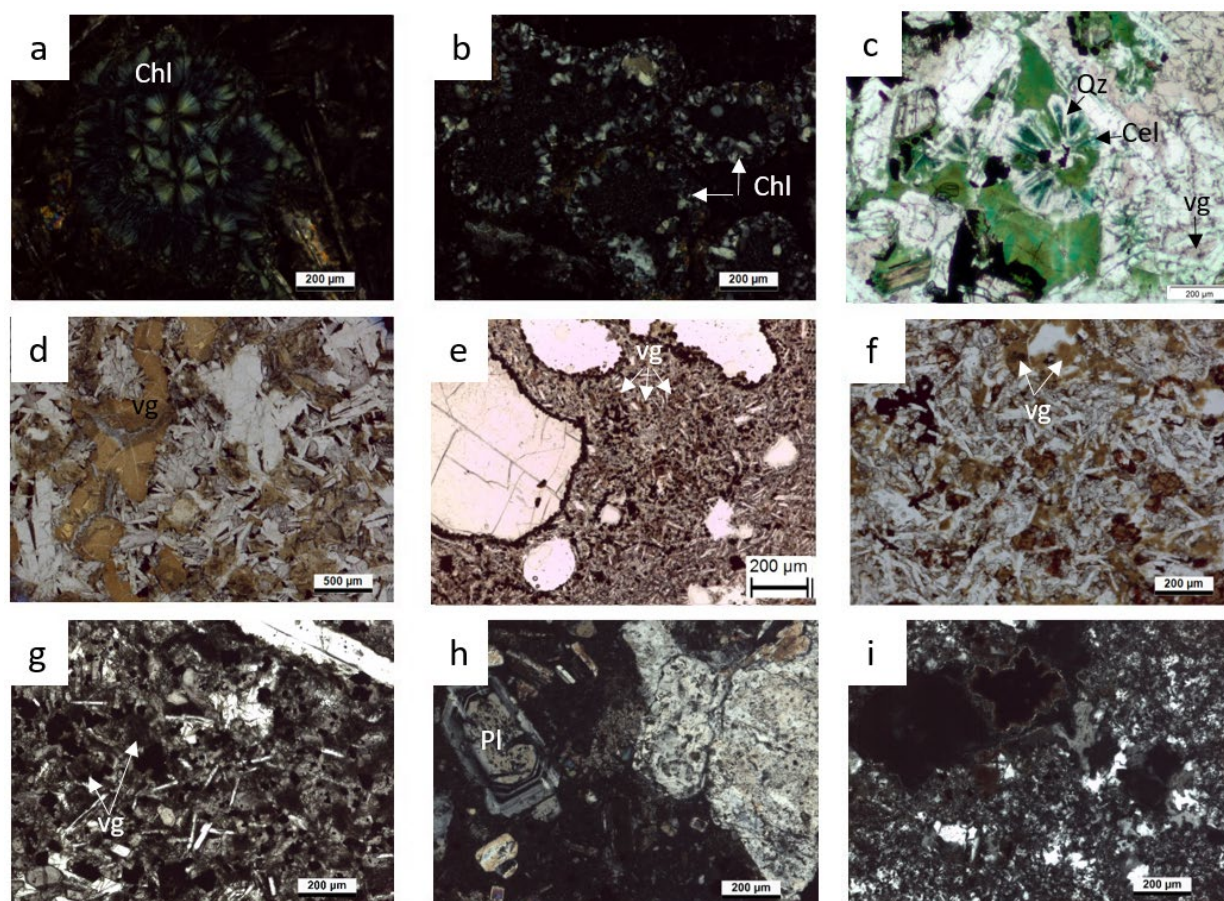


FIGURE 1. Photomicrographs of selected samples under plane-polarized light (PPL) and crossed-polarized light (XPL): (a) chlorite in basalt, XPL (CAN); (b) chlorite in basalt, XPL (NOR); (c) volcanic glass and quartz between green celadonite in basalt, PPL (BRAZ); (d) altered volcanic glass (rust colour), PPL (ICL2); (e) volcanic glass in basalt, PPL (HW1); (f) volcanic glass, PPL (ICL1); (g) volcanic glass in basalt, PPL (NZ1); (h) porphyritic texture with phenocrysts of plagioclase in andesite, XPL (JAP); (i) aphyric texture in rhyolite, XPL (MOZ). Labels: Chl = chlorite; vg = volcanic glass; Pl = plagioclase; Cel = celadonite; Qz = quartz.

TABLE 2. EPMA data for volcanic glass (except for BRAZ (*), where quartz was also identified) as first identified under a petrographic microscope.

Samples	BRAZ		CAN	ICL1	ICL2	ICL3	ICL4	MOZ	HW1	HW5	HW6
SiO ₂ %	53.89	97.68*	54.13	73.35	43.05	49.47	52.10	71.64	79.12	62.77	77.37
TiO ₂ %	0.02	0.00	0.13	0.10	0.04	1.93	1.47	0.10	0.66	0.33	0.83
Al ₂ O ₃ %	2.56	0.55	10.45	15.02	8.25	14.45	2.00	15.32	12.55	22.14	12.10
MgO %	6.23	0.00	4.08	0.05	16.38	7.11	13.26	0.01	0.04	0.04	0.05
CaO %	0.00	0.08	0.26	0.50	1.42	11.74	19.06	0.27	2.98	4.47	1.80
MnO %	0.02	0.00	0.08	0.05	0.09	0.19	0.39	0.00	0.01	0.02	0.00
FeO %	20.09	0.29	18.08	0.81	20.62	13.23	13.77	0.29	0.62	0.99	1.73
Na ₂ O %	0.02	0.19	0.12	6.26	0.32	0.84	0.34	1.69	3.77	7.31	4.44
K ₂ O %	9.01	0.08	8.36	3.96	0.58	0.17	0.02	7.98	0.23	2.45	0.81
Total %	92.20	98.86	95.72	100.11	90.76	99.27	102.42	97.32	99.97	100.52	99.31

quartz instead. Several analyses were performed for each section within each sample. One set of EPMA data is provided per geological setting with the exception of the BRAZ sample, where a second column shows the analysis of quartz. Note that no petrographic characterization was performed on the sands or in the control aggregates (Spratt aggregate and GBS sand) since this study focused on coarse aggregates.

3.2. Expansion tests

The 14- and 28-day AMBT expansion results for the aggregates investigated in this study are presented in Figure 2. The Canadian standard CSA A23.2-27A (41) states that an expansion of >0.15% after 14 days indicates a potentially reactive aggregate. ASTM Standard Guide C1778 (42) considers that 14-day mortar bar expansions of <0.10% represent innocuous aggregates, in most cases. Aggregates that generate mortar bar expansions of >0.10% are considered potentially deleterious; the CPT is then recommended to confirm reactivity. In ASTM C 1260 (21), it is stated that an expansion of >0.20% after 14 days indicates potentially deleterious behaviour while expansions of <0.10% generally suggest innocuous behaviour. Expansions between 0.10% and 0.20% correspond to aggregates that fall into either category based on field performance: some innocuous while others deleterious.

The AMBT results at the end of the 14-day period showed that samples BRAZ, ICL1 fine sand, ICL4, ICL4 sand, JAP, MOZ, NZ3, TK, HW1, HW3, HW5, HW6, HW7, and HW7 sand were potentially reactive since their expansion values ranged from 0.22 to 0.98%. Samples ICL3 and TER-SM1 presented values corresponding to aggregates that can be either innocuous or potentially reactive. The rest of the samples showed expansion values <0.10% and were therefore considered non-reactive, including SMA-

SM1, SMA-SM2, SMG-SM1, SMG-SM2, SMG-SM3, TER-SM2, GRA-SM1, SJO-SM1, PIC-SM1, FAI-SM1, FLO-SM1, FLO-SM2, CRV, CAN, ICL2, NZ1, NZ2, CANY1, CANY2, HW2, and HW4. The results of the AMBT for the majority of the Azores samples are presented in Medeiros *et al.* (40).

The one-year concrete prism expansion results for the various aggregates investigated in this study are illustrated in Figure 3. The Canadian standard CSA A23.2-27A (32) and ASTM Standard Guide C1778 (42) state that an aggregate inducing an expansion of <0.040% (cited as 0.04% for the ASTM standard) is considered non-reactive and may be used in concrete without any further testing for ASR. On the other hand, both standards consider that a one-year concrete prism expansion greater than or equal to this critical value indicates a reactive aggregate and that preventive measures are required if the aggregate is to be used in concrete construction. On the basis of trials conducted on aggregate combinations of known field performance from various parts of the world, RILEM AAR-3 (24) recommends that test results (usually measured after 12 months) of <0.05% be considered as likely indicating non-expansive materials. The CPT showed that two samples from Iceland (ICL1, which contained both coarse and fine aggregate, and ICL4), ICL4 sand, JAP, TK, and HW7 sand were considered reactive at the end of the one-year period, with expansion values ranging from 0.13 to 0.34%. The rest of the samples were considered non-reactive according to the CPT. The results of the CPT for the Azores samples are presented in Medeiros *et al.* (40).

4. DISCUSSION

The petrographic study showed that almost half of the samples contained volcanic glass. Other forms of potentially reactive material were also identified,

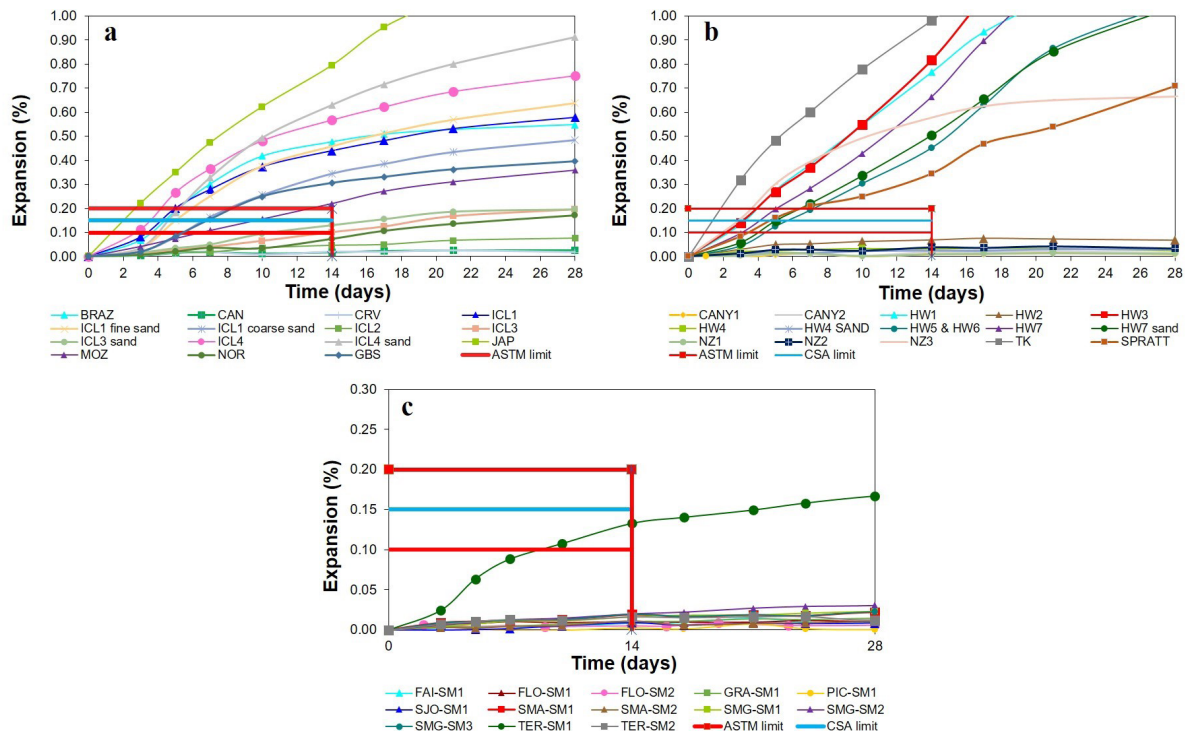


FIGURE 2. AMBT expansion results: (a) BRAZ, CAN, NOR, CRV, ICL1, ICL1 fine sand, ICL1 coarse sand, ICL2, ICL3, ICL3 sand, ICL4, ICL4 sand, JAP, MOZ, NOR, and GBS; (b) CANY1, CANY2, HW1, HW2, HW3, HW4, HW4 sand, HW5 & HW6, HW7, HW7 sand, NZ1, NZ2, NZ3, TK, and Spratt; (c) FAI-SM1, FLO-SM1, FLO-SM2, GRA-SM1, PIC-SM1, SJO-SM1, SMA-SM1, SMA-SM2, SMG-SM1, SMG-SM2, SMG-SM3, TER-SM1, and TER-SM2.

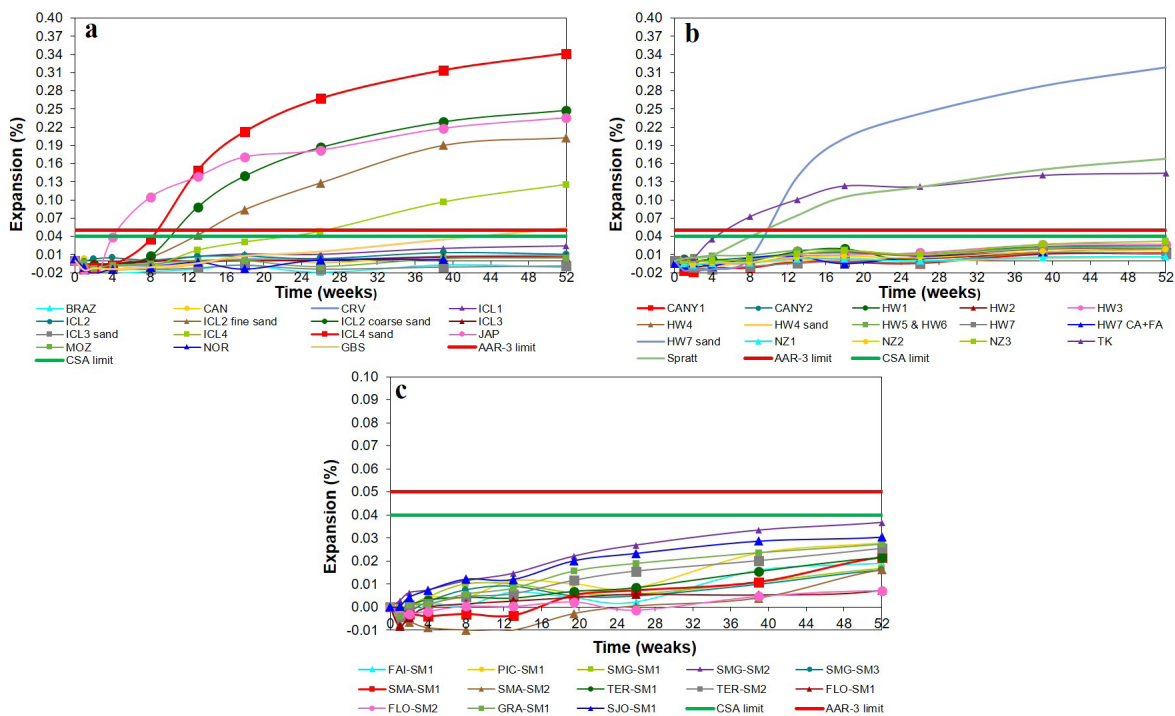


FIGURE 3. CPT expansion results: (a) BRAZ, CAN, CRV, ICL1, ICL1 fine sand, ICL1 coarse sand, ICL2 fine sand, ICL2 coarse sand, ICL3, ICL3 sand, ICL4, ICL4 sand, JAP, MOZ, NOR, and GBS; (b) CANY1, CANY2, HW1, HW2, HW3, HW4, HW4 sand, HW5 & HW6, HW7, HW7 CA+FA, NZ1, NZ2, NZ3, TK, and Spratt; (c) FAI-SM1, PIC-SM1, SMG-SM1, SMG-SM2, SMG-SM3, SMA-SM1, SMA-SM2, TER-SM1, TER-SM2, FLO-SM1, FLO-SM2, GRA-SM1, and SJO-SM1.

such as devitrified volcanic glass in ICL1, ICL2, and BRAZ, and micro- to cryptocrystalline silica in TER-SM1 and in ICL4. Furthermore, the presence of tridymite and cristobalite was observed in ICL2 and ICL3, and tridymite was also observed in JAP. In addition, clay minerals were recognized in two samples: BRAZ and ICL2.

Volcanic glass is an amorphous material that results from rapidly cooling magma; its usual composition ranges from 40 to 77 wt% SiO₂. The volcanic glass analysed by EPMA for the different aggregates showed a range of SiO₂ content from 43.05 to 79.16% SiO₂. According to Katayama *et al.* (12), volcanic glass is highly reactive when its SiO₂ content is >65% (rhyolitic glass); however, andesitic glass (57–63 wt% SiO₂, (43)) can be considered less reactive or even non-reactive. The same authors have mentioned that even basalts and andesites can include rhyolitic glass despite being, respectively, basic and intermediate rocks. The presence of reactive volcanic glass with an SiO₂ content of >50% has also been reported by Korkanç and Tugrul (1) in some basalts from Turkey. Furthermore, RILEM AAR-1.1 (13) describes volcanic glass as a potentially alkali-reactive constituent of different rock types usually occurring as rhyolitic glass or hydrated rhyolitic glass. Additionally, devitrified volcanic glass is considered potentially alkali-reactive (13, 44). According to some authors, swelling clay minerals are also deleterious (10, 12), as they result from the alteration of volcanic glass (12). In general, from the point of view of petrography, samples that contain deleterious constituents are regarded as potentially reactive. Some of the samples, especially those from Iceland (ICL1) and the Hawaiian Islands (HW1, HW5, and HW6), contained volcanic glass with high SiO₂ content in basaltic aggregates (63–79%). This merits further investigation; these high values might be due to the presence of some form of silica in the groundmass (45).

Regarding the AMBT, Korkanç and Tugrul (14) studied basalts from Turkey in which the presence of volcanic glass with acidic–intermediate character showed expansions of >0.10%. Wigum *et al.* (9) studied several Icelandic basaltic aggregates and showed that most of them were considered deleterious at the end of 14 days of expansion. According to Marfil *et al.* (10), if a basalt contains clay minerals that are expansive, then they may increase the expansion observed in the AMBT. The same authors have reported that the presence of volcanic glass and clay minerals are associated with the expansion measured in the mortar bars. Madsen *et al.* (6) have put forth the same opinion. On one hand, there is generally a direct relationship between the results of the AMBT and the content of volcanic glass plus clay minerals. On the other hand, Menéndez *et al.* (46) reported that a Spanish basalt containing quartz with straight extinction (but in low proportion) did

not show any reactivity according to the AMBT. In the present study, the classifications of most samples considered between potentially reactive to reactive according to the AMBT were supported by petrographic analysis results. However, there were some exceptions: CAN, ICL2, NZ3, NOR, and TER-SM2. Only a few samples were considered reactive according to all the presented assessment methods. These samples included JAP and TK, which were used as controls, as well as Spratt aggregate and GBS, for which the reactivity was already known. The basaltic samples that were classified as reactive according to all methods were: ICL1 coarse and fine sand, ICL4, ICL4 sand, and HW7 sand.

Notably, the mixture HW7 CA+FA (coarse aggregate plus fine aggregate from the same source) was found to be non-reactive according to the CPT, while the HW7 sand was reactive according to the same test (including a very high one-year expansion of 0.32%). This result merits further analysis. An interesting result contrary to expectations was that the MOZ rhyolite sample was considered non-reactive according to the CPT. According to Wigum (47), high amounts of reactive sand in Iceland may be responsible instead of the gravels (coarse fraction) for the high degree of expansion observed in the CPT. However, experience from an outdoor field exposure site shows the opposite trend for the same materials (47). In the present study, alkali reactivity occurred in the sand fractions rather than in the coarse aggregate fractions in Icelandic and Hawaiian samples. Different field exposure sites have been established in the US and in Europe. One of these sites (since 2011) is located at the University of Hawaii at Manoa, Hawaii, with 30 concrete blocks cast mainly using local basaltic aggregates in various mixtures. Only one of these basaltic aggregates showed signs of ASR expansion and cracking in the field study: a basalt not used for concrete manufacture (48).

Figure 4 plots the results of the 14-day AMBT along with the one-year CPT expansion results; yel-

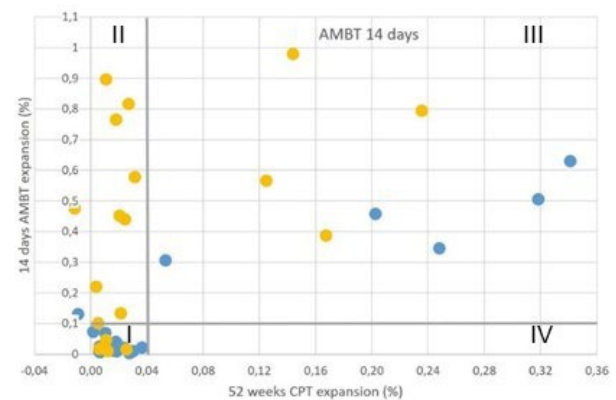


FIGURE 4. In the figure, the quadrants I to IV are not identified, as it was in previous versions of the figure. Also, the vertical line corresponding to the 0.10% expansion limit in the AMBT and the 0.04% expansion limit in the CPT should be identified as such.

TABLE 3. Results of all methods used for all samples. Grey highlight indicates samples classified as reactive according to both laboratory expansion tests. Orange highlight indicates samples containing volcanic glass or reactive forms of silica that are classified as potentially reactive by petrographic examination. A star (*) indicates that no petrographic examination was done.

Samples	Country	Chemical Classification	Potentially reactive forms of silica identified by petrographic characterization	AMBT expansion, %		CPT expansion, % (1 year)
				14 days	28 days	
BRAZ	Brazil	Basalt	Volcanic glass, devitrified volcanic glass, clay minerals	0.48	0.55	-0.01
CAN	Canada	Basalt	Volcanic glass	0.02	0.03	0.01
Spratt		Limestone	*	0.39	0.71	0.17
ICL1	Iceland	Gravel (basalts, metabasalts, rhyolite)	Volcanic glass, devitrified volcanic glass, tridymite and cristobalite	0.44	0.58	0.02
ICL1 fine sand		Sand	*	0.46	0.64	0.20
ICL1 coarse sand		Sand	*	0.34	0.48	0.25
ICL2		Gravel (basalts, metabasalts rhyolites)	Volcanic glass, devitrified volcanic glass, clay minerals, tridymite and cristobalite	0.05	0.08	0.01
ICL3		Basalt	Volcanic glass	0.10	0.20	0.01
ICL3 sand		Basalt	*	0.13	0.20	-0.01
ICL4		Gravel (basalts, dacite, gabbro?)	Volcanic glass, devitrified volcanic glass, microcrystalline silica	0.57	0.75	0.13
ICL4 sand		Sand	*	0.63	0.92	0.34
GBS sand		Basalt	*	0.30	0.40	0.05
JAP		Japan	Andesite	Tridymite	0.79	1.30
MOZ	Mozambique	Rhyolite	Volcanic glass and microcrystalline silica	0.22	0.36	0.00
NZ1	New Zealand	Basanite	Volcanic glass	0.009	0.01	0.01
NZ2		Basalt	-	0.04	0.03	0.02
NZ3		Basalt	Volcanic glass	0.58	0.67	0.03
NOR	Norway	Basalt	-	0.07	0.17	0.00
SMA-SM1	Portugal (Azores Islands)	Basanite	-	0.02	0.02	0.02
SMA-SM2		Basanite	-	0.01	0.01	0.02
SMG-SM1		Potassic trachybasalt	-	0.02	0.02	0.02
SMA-SM2		Potassic trachybasalt	-	0.02	0.03	0.04
SMG-SM3		Basalt	-	0.02	0.02	0.02
TER-SM1		Trachyte	Volcanic glass Micro- to cryptocrystalline silica	0.13	0.17	0.02
TER-SM2		Basalt	Volcanic glass	0.02	0.01	0.03
GRA-SM1		Hawaiite	-	0.01	0.01	0.03
SJO-SM1		Basalt	-	0.01	0.01	0.03
PIC-SM1		Basalt	-	0.00	0.00	0.03
FAI-SM1	Hawaiite	-	0.01	0.01	0.02	
FLO-SM1	Benmoreite	-	0.01	0.01	0.01	
FLO-SM2	Mugearite	-	0.01	0.01	0.01	
CRV	Hawaiite	-	0.02	0.02	0.01	
CANY1	Spain (Canary Islands)	Basanite	-	0.01	0.01	0.01
CANY2		Basanite	-	0.02	0.01	0.02
TK	Turkey	Andesite	Volcanic glass	0.98	1.62	0.14
HW1	USA (Hawaiian Islands)	Basalt	Volcanic glass	0.77	1.13	0.02
HW2		Basalt	-	0.07	0.07	0.01
HW3		Basalt	Volcanic glass	0.82	1.58	0.03

TABLE 3 (cont.). Results of all methods used for all samples. Grey highlight indicates samples classified as reactive according to both laboratory expansion tests. Orange highlight indicates samples containing volcanic glass or reactive forms of silica that are classified as potentially reactive by petrographic examination. A star (*) indicates that no petrographic examination was done.

Samples	Country	Chemical Classification	Potentially reactive forms of silica identified by petrographic characterization	AMBT expansion, %		CPT expansion, % (1 year)
				14 days	28 days	
HW4	USA (Hawaiian Islands)	Mugearite	-	0.03	0.02	0.02
HW5		Basalt	Volcanic glass	0.45	1.05	0.02
HW6		Basalt	Volcanic glass	0.02	0.02	0.02
HW7		Basalt	Volcanic glass	0.90	1.25	0.01
HW7 sand		Basalt	*	0.50	1.04	0.32
HW7 CA+-FA		Basalt	Volcanic glass	-	-	0.01

low dots represent aggregates containing volcanic glass. Four zones are labelled in the figure as I, II, III, and IV. Most of the samples fell into zone I, classified as innocuous according to both tests. Samples categorized within zone II showed excessive expansion in the AMBT but were not considered reactive according to the limits established for the CPT. The samples in zone III were classified as potentially reactive according to both the AMBT and the CPT. Significantly, none of the aggregates fell into zone IV, in which CPT and AMBT results would suggest, respectively, potentially reactive and innocuous. These results show that the mortar bar test is more sensitive to the presence of volcanic aggregates than the CPT, causing a number of samples to fall into zone II (i.e. “false-positive”). The latter are less problematic than “false negative” results, which would be located in zone IV. Overall, in their evaluation of the potential alkali reactivity of aggregates, the CPT and AMBT were in agreement for 78% of the cases evaluated in this study (i.e., results that fell into zones I or III).

Table 3 summarizes the results obtained for all samples and methods applied in this study.

5. CONCLUSIONS

The main objective of this study was to assess the potential alkali–silica reactivity of a wide range of basaltic aggregates from distinct parts of the world using different test methods. The main conclusions from the above investigations are as follows:

- Petrographic characterization identified volcanic glass as the main constituent responsible for potential alkali–silica reactivity in almost half of the samples. Other deleterious species were also identified, such as clay minerals, micro- to cryptocrystalline silica, tridymite, and cristobalite;

- EPMA showed high SiO₂ content in volcanic glass present in the basaltic aggregates from Iceland (ICL1) and the Hawaiian Islands (HW1, HW5 and HW6);
- According to the AMBT, twelve samples were considered potentially reactive according to measurements taken at the end of the 14-day testing period: one from Brazil (BRAZ), five samples from Iceland (ICL1, ICL4, ICL1 sand, and ICL4 coarse and fine sands), one from Japan (JAP), one from Mozambique (MOZ), one from New Zealand (NZ3), one from Turkey (TK), and six from the Hawaiian Islands (HW1, HW3, HW5, HW6, and HW7, including HW7 sand). However, most of the samples were classified as non-reactive by this method;
- CPT results showed that the majority of the samples were non-reactive, with the exception of four samples from Iceland (ICL1, both aggregate and fine aggregate, and ICL4, both coarse and fine sand), Japan (JAP), Turkey (TK), and one from the Hawaiian Islands (HW7 sand);
- The samples from Japan and Turkey were considered reactive according to all methods, as expected. This was due to their intermediate character. However, the sample from Mozambique was considered non-reactive in spite of being a rhyolite with volcanic glass;
- Basaltic samples considered reactive according to all methods were: ICL1, coarse and fine sand, and ICL4, both aggregate and sand, both samples from Iceland, and HW7 sand from the Hawaiian Islands;
- Most of the tested sands seem to be responsible for reactivity as observed in the CPT;
- There was clear evidence that the AMBT overestimated the reactivity of many basalts, which probably indicates that this method is

too conservative to evaluate reactivity in basalts.

According to the literature on this subject, the presence of volcanic glass and silica minerals is known to influence the potential alkali reactivity of volcanic rocks. In this work, the intermediate to acidic character of volcanic glass and the presence of silica minerals identified in petrographic studies seemed to dictate the potential reactivity of the aggregates studied.

However, the results obtained show that much work remains to be done in order to clarify the potential alkali reactivity of basaltic rocks. Future work will extend the duration of the CPT, and a gel pat test will be performed for further clarification. Furthermore, examining samples from real concrete structures or outdoor exposure sites could help to understand the reactivity of various types of basalt.

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vision: I. Fernandes, B. Fournier, J.C. Nunes, A. Santos-Silva. Writing, original draft: S. Medeiros. Writing, review & editing: I. Fernandes, B. Fournier, J.C. Nunes, A. Santos-Silva, V. Ramos, D. Soares.

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