

Effect of rock mineralogy on mortar expansion

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Abstract. Alkali-silica reaction (ASR) is among one of the most important damaging mechanisms in concrete, depending primarily on aggregates which contain reactive minerals. However, expansion in concrete may not directly relate to the reactive minerals. This study aims to investigate the influence of ASR and the expansion of mortar bars depending on aggregate type containing various components such as quartz, clay minerals (montmorillonite and kaolinite) and micas (muscovite and biotite). In this study, the accelerated mortar bar tests (AMBT) were performed in two conditions (mortar bars in the same and sole NaOH solutions). Petrographic thin section studies, X-ray diffraction (XRD) analysis (Rietveld method), scanning electron microscopy (SEM) and chemical analyses were carried out. This study showed that quartzite bars led to increase in expansion values of mortar bars in diabase-1 and andesite when these were in the same NaOH solution. However, three samples (basalt, quartzite and claystone) were found having ASR expansion based on the AMBT when the special molds were used for each sample. SEM study revealed that samples which exhibit highest expansions according to AMBT had a generally rough surface and acicular microstructures in or around the micro-cracks. Basalt and quartzite showed more variable in major oxides than those of other samples based on the chemical analyses, SEM studies and AMBT. This study revealed that the highest expansions were observed to source not only from reactive aggregates but also from alteration products (silicification, chloritization, sericitization and argillisation), phyllosilicates (muscovite, biotite and vermiculite) and clays (montmorillonite and kaolinite).

Keywords: alkali silica reaction; mortar bar expansion and microstructure; rock mineralogy

1. Introduction

Concrete is one of the most commonly used materials in the world. It is a significant construction material utilized widely in buildings, roads, bridges and dams. However, the quality of concrete structures is affected by a lot of factors including raw material's quality, the ratio of coarse/fine aggregate, water/cement ratio, age of concrete and chemical reactions. Concrete structures are expected to be resistant to various environmental effects along with improved compressive strength. Alkali-silica reaction (ASR) is one of the most common reasons for the deterioration of concrete. ASR is a chemical reaction which takes place between alkali hydroxides existing in the pore solution within the concrete matrix and several reactive minerals such as quartz, chert, opal, tridymite and cristobalite available in aggregates (Diamond 1975, Malvar *et al.* 2002, Demir *et al.* 2018, Bakhytzhana 2019). Contrary to popular belief, there are different expressions in the literature for ASR. Gasparotto *et al.* (2011) studied petrographic investigation of paving deterioration related to the ASR. They stated that siliceous limestone, chert and flint available in the aggregate did not show any reactivity whereas ASR developed only from fine-grained silica-rich marls. Sujjavanich *et al.* (2017) examined potential alkali-silica reactivity of aggregate sources in Thailand and indicated that samples of same aggregate type had different reactivity

although had mineralogically similar compositions. Studies have demonstrated that ASR is a multistage process that occurs at the paste-aggregate interface (Ulm *et al.* 2000). Hydroxyl ions attack the silanol groups (Si-OH) and the siloxane bonds (Si-O-Si) in the first stage. The latter consists of the formation of expansion products. Internal pressure within the cement matrix occurs, triggering macroscopic expansion and subsequent degradation of this matrix, depending on the gel formation generated (Kupwade-Patil and Allouche 2013). ASR leads to the formation of a gel, which enlarges due to the humidity in concrete and alkali effect with sufficient amounts. This volume increase stems from the swelling in the concrete leading to tensile stress which then causes crack structures within the concrete (Ostertag and Monteiro 2007), leading to a decrease in the service life of concrete structures. However, while ASR occurs in concrete with a relative humidity ratio higher than 80%, it may not cause a serious threat to concrete that has remained relatively dry climate conditions during its service life (Demir and Arslan, 2013).

In the literature, non-reactive aggregates are used in order to decrease the ASR. Furthermore, the use of low-alkali cement and incorporation of supplementary cementing materials are proposed as a different way of ASR control (Lindgard and Sellevold 2013). Several validated test methods are preferred by the researchers such as petrographic method, accelerated mortar bar test, concrete prism test for determining the alkali reactivity of aggregates. Lindgard *et al.* (2013) mentioned that the findings from different test methods may vary widely since the test conditions (e.g., humidity, temperature, pre-curing

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and alkali content) can differ from one test method to another.

Rajabipour *et al.* (2010) studied the ASR of recycled glass aggregates in concrete materials and stated that larger size glass particles exhibited larger and more active micro-cracks which caused their high alkali-silica reactivity. Binal (2015) investigated the effect of aggregate size on ASR using the accelerated mortar bar test and found that reactive aggregates with 150–300 mm grain size indicated the highest expansion values. Sirivivatnanon and Mohammadi (2016) compared the new Australian test methods in the estimation of ASR for field concrete. They showed that accelerated test correspond with field performance with few exceptions while concrete prism tests were determined to be more reliable. Demir and Sevim (2017) studied the effect of sulfate on the hardened and fresh mortars including lithium additives to prevent ASR.

Ali *et al.* (2014) conducted important research for the usefulness of petrographic study to evaluate the rocks (granite, granodiorite, gneiss, mica schist, etc.) based on alkali-silica reactivity before using them in concrete structures. For this purpose, modal mineralogical composition of the rocks was determined by the authors and content of possible reactive minerals of rocks were evaluated according to national threshold limits of different countries, without performing any ASR experiments such as AMBT. They concluded that the presence of muscovite, biotite, chlorite and sericite in these rocks can make the aggregate susceptible to expansion by absorbing water.

In the literature, few studies were carried out on rock mineralogy concerning the ASR. Some of them investigated only one rock type such as basalts; some of them conducted petrographic investigation for identifying reactive silica and evaluated according to national threshold limits of different countries without performing any ASR experiments. Therefore, this study aims to determine the mineral constituents of different originated rock types which can be responsible for the expansion of mortar bars. Also, the effect of NaOH solution on mortar bars was firstly examined using same and different solutions. Accordingly, two types of mortar samples prior to AMBT and after exposed to the solution were also studied by using scanning electron microscopy (SEM) and chemical analyses.

2. Materials and method

2.1 Rock samples and cement

Nine different rock samples were collected from Rize (diabase), Trabzon (granodiorite and andesite), Ordu (basalt) and Samsun (limestone, claystone, quartzite and lapilli tuff) vicinities which are in the north of Turkey. In this study, to better understand the mortar expansion, it was made an effort to select rocks having clay, silica and alteration mineral composition. Some physical tests including unit weight, apparent porosity and water absorption per cent by weight were carried following ISRM (2007) suggested methods (Table 1). CEM I 42.5 R Portland cement (PC) was utilized in this study. Chemical composition of the Portland cement is given in Table 2.

Table 1 Some physical properties of rock samples

Rock name	Unit weight (kN/m ³)	Apparent porosity (%)	Water absorption (%)
Basalt	25.41±0.09	4.48±0.3	1.75±0.14
Diabase-1	27.76±0.05	4.64±0.13	1.67±0.05
Granodiorite	26.09±0.02	1.29±0.02	0.49±0.01
Diabase-2	27.86±0.18	2.33±0.08	0.82±0.05
Andesite	25.41±0.03	5.01±0.15	1.95±0.04
Quartzite	23.25±0.04	7.0±0.11	2.97±0.07
Limestone	26.19±0.02	0.74±0.16	0.28±0.06
Lapilli tuff	19.03±0.02	27.2±0.98	15.76±0.92
Clay stone	23.94±0.05	7.96±0.88	3.32±0.42

Table 2 Chemical composition of the Portland cement (PC)

Component (%)	PC	Component (%)	PC
SiO ₂	19.93	P ₂ O ₅	0.11
Al ₂ O ₃	5.12	MnO	0.07
Fe ₂ O ₃	3.12	Cr ₂ O ₃	0.04
CaO	62.72	SO ₃	2.95
MgO	2.59	Reactive SiO ₂	-
Na ₂ O	0.28	Free lime	2.30
K ₂ O	0.69	Loss on ignition	2.96
TiO ₂	0.26		

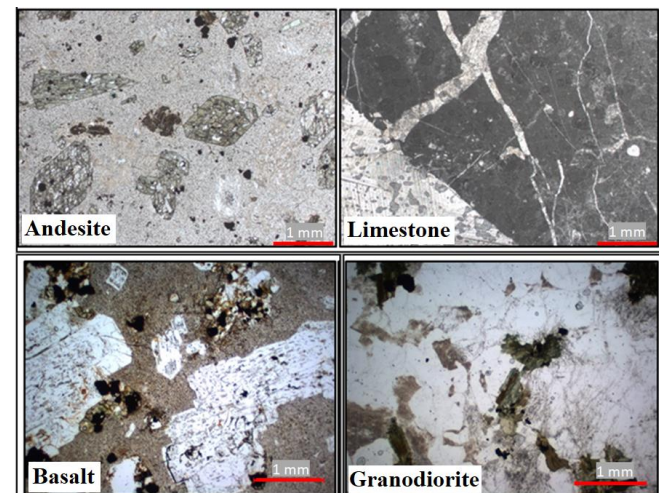


Fig. 1 Microscope images of representative andesite, limestone, basalt and granodiorite

Detailed characteristics of the cement can be found elsewhere (Cihangir *et al.* (2018)).

Petrographic studies, SEM examinations, XRD (Rietveld) and chemical analyses and accelerated mortar bar test (AMBT) were carried out on nine different rock aggregates from quarries and outcrops. Quantity of minerals (%) in rock samples including especially the type of clays were determined using XRD analysis (Rietveld method).

2.2 Petrographic examination and XRD studies for rock samples

The naming of rocks is generally based on the mineral

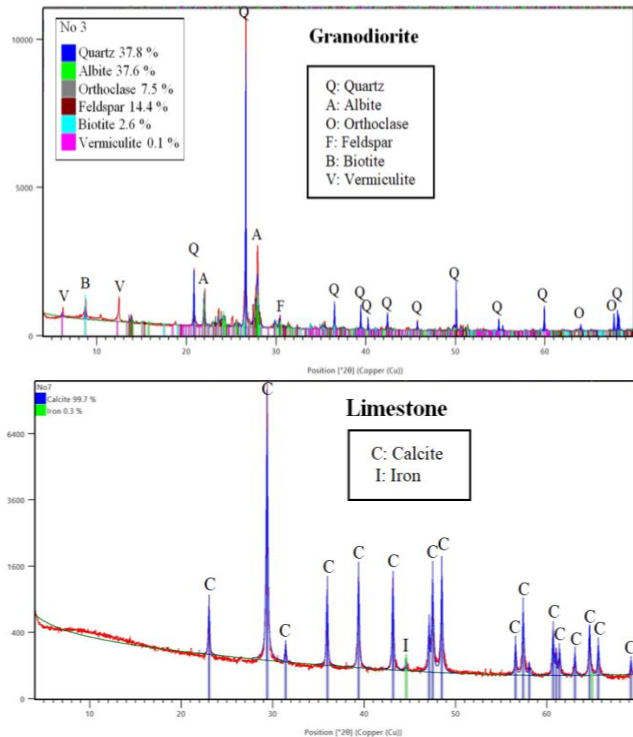


Fig. 2 Images of some representative samples from XRD (Rietveld) analyses

Table 3 Possible minerals enhanced expansive and alteration properties

Rocks	Possible minerals enhanced expansive	Alteration
Basalt	Quartz (9%)	Moderately silification, argillisation, serpentinization
Diabase-1	Vermiculite (Mica) (3.9 %)	-
Granodiorite	Quartz (37.8%), biotite (2.6%)	-
Diabase-2	Vermiculite (Mica) (2.8 %)	-
Andesite	Chlorite (14.9), quartz (12.1)	Moderately silification, epidotization, carbonation
Quartzite	Quartz (61.8), kaolinite (22.8)	Moderately silification, argillisation
Limestone	Iron (pyrite?) (0.3%)	Secondary carbonate
Lapilli tuff	Muscovite (45.8%), montmorillonite (0.7 %)	Volcanic glass shards, slightly argillisation
Claystone	Kaolinite (25.8), quartz/silica (33.4)	Moderately silification

type. Therefore, petrographic thin section studies are a very effective method of identifying the mineral types. In this study, nine representative rock samples were petrographically analyzed by trinocular research microscope. Furthermore, minerals and alteration constituents which would lead to expansive of mortar bars were examined by this method. Mineralogical analysis of some representative samples is given in Fig. 1.

The Rietveld method is a comprehensive mathematical minimization procedure, which uses intensity data from X-ray diffraction (XRD) to specify sample mineralogy. Rietveld analysis which is widely used (Rietveld 1969, O'Connor and Raven 1988, Oerter *et al.* 2007) was performed to determine the weight percentage of minerals



Fig. 3 All mortar bar in same NaOH bath (a, b), special NaOH bath for each sample, molding (d), measurement of bars (e)

Table 4 Expansion values (mm) of mortar bars for ASR

Sample name	2. day	5. day	11. day	14. day	21. day	28. day
Bottom (B)	B	T	B	T	B	T
Top (T)	B	T	B	T	B	T
Basalt	0.16	0.14	0.31	0.30	1.08	1.08
Diabase-1*	-	-	0.13	0.15	0.26	0.28
Diabase-1	0.17	0.16	0.20	0.19	0.23	0.20
Granodiorite	0.09	0.14	0.24	0.24	0.27	0.31
Diabase-2	0.17	0.14	0.17	0.15	0.21	0.20
Andesite*	0.42	0.42	0.74	0.81	0.98	1.06
Andesite	0.12	0.1	0.24	0.25	0.37	0.36
Quartzite*	0.09	0.09	0.18	0.15	0.24	0.23
Quartzite	0.26	0.23	0.34	0.33	0.53	0.58
Limestone	0.08	0.07	0.23	0.31	0.42	0.39
Lapilli tuff	0.08	0.07	0.18	0.19	0.32	0.3
Clay stone	0.11	0.11	0.54	0.54	0.59	0.58

*All mortar bars (nine items) were in same NaOH solution (30 L), for other group samples (three mortar bars) unique mold was used in different solution (2.5 L) for each sample, B: bottom of bar, T: top of bar

in a sample and to determine the type of clay minerals. In addition, the modal mineralogical composition which was obtained via XRD Rietveld method is listed in Table 3 with the result of petrographic studies. XRD analyses are given for some representative samples in Fig. 2.

2.3 Mortar bar preparation and test procedure

Accelerated mortar bar tests (AMBT) were performed to determine the effect of ASR of aggregates, according to ASTM (1999) suggested methods. AMBT contributes the curing conditions, accelerating the reaction, which provides the evaluation of the reactivity of the aggregates in a short time (16 days). The weight percentage of aggregates in mortar bar tests are varied from 150 μm (No:100, bottom) to 4.76 mm (No: 4, top). Prism specimens were produced

Table 5 Time dependent change in chemical composition of rocks and in mortar samples

Sample name	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	TiO ₂ %	P ₂ O ₅ %	MnO %	LOI
Basalt*	61.20	17.70	5.60	0.40	5.70	3.10	3.30	0.90	0.30	0.10	1.55
Basalt-1 [^]	45.23	13.55	4.97	0.82	18.40	2.21	2.94	0.53	0.22	0.10	10.90
Basalt-14 ^x	43.64	13.36	4.61	0.84	19.37	4.04	2.81	0.52	0.23	0.10	10.30
Diabase-1*	48.20	17.30	9.90	0.20	9.90	3.10	1.00	1.40	0.20	0.20	3.20
Diabase-1-1 [^]	36.27	12.33	8.25	5.33	21.87	2.32	1.07	0.73	0.15	0.14	11.30
Diabase-1-14 ^x	36.19	12.40	8.08	5.31	21.77	3.08	0.91	0.73	0.17	0.14	11.00
Granodiorite-1 [^]	54.57	10.17	2.62	1.00	17.89	2.59	1.56	0.24	0.08	0.06	9.10
Granodiorite-14 ^x	54.92	10.16	2.52	0.98	17.98	3.34	1.36	0.24	0.08	0.06	8.30
Diabase-2*	55.20	16.40	8.00	2.90	7.60	3.70	1.80	1.30	0.20	0.10	2.40
Diabase-2-1 [^]	42.01	12.72	6.16	2.82	20.64	2.71	1.73	0.66	0.19	0.11	10.00
Diabase-2-14 ^x	41.38	12.72	6.15	2.88	20.47	3.64	1.49	0.67	0.19	0.11	10.10
Quartzite-1 [^]	69.74	2.45	1.22	0.64	15.88	0.19	0.75	0.10	0.06	0.03	8.90
Quartzite-14 ^x	67.73	2.32	1.03	0.61	16.41	1.56	0.58	0.10	0.07	0.02	9.50
Lapilli tuff-1 [^]	46.75	11.61	2.80	1.07	20.11	2.22	1.71	0.41	0.16	0.04	13.00
Lapilli tuff-14 ^x	44.57	11.48	2.77	1.06	19.77	4.49	1.48	0.40	0.15	0.04	13.70

*Chemical composition of rock, [^]Chemical composition of mortars prior to AMBT tests, ^xChemical composition of mortars after exposure to NaOH solution

using molds of 25 x 25 x 285 mm³ (width x height x length) in dimension. Mortar mixture with a water to cement ratio 0.47 was prepared under the standard. A total of three mortar bars were prepared for each series. The mortar bar samples were demoulded after 24 h and initial lengths of the mortar bars were measured and the samples were subsequently cured for an additional 24 h in a 2.5-L water bath at 80±1°C. For 14 days following, the mortar bar samples which were subjected to NaOH (900 ml pure water 40 g NaOH) solution at 80° C (Table 4). To monitor the expansion due to ASR, subsequent length measurements were performed at 1, 2, 5, 11, and 14 days. Each series were subjected to separate NaOH solution. A digital comparator with the accuracy of 0.0025 mm was used for length measurements. Same processes were also carried out on three different rock mortar samples (diabase-1, andesite and quartzite) in the same solution (30 L water-NaOH solution at 80±1°C) to investigate the solution effect. A view from experimental studies for AMBT is depicted in Fig. 3.

2.4 SEM studies and chemical analyses for rock and mortar samples

Bulk samples which are obtained from mortar bars were prepared for microstructure analyses (SEM) (before AMBT tests, and at 7-14-28 days). SEM samples were coated with gold coating before SEM observation to enhance their stability and electron conductivity. SEM observation was performed prior to AMBT tests and at 14 days of exposure to the NaOH solution for the samples (basalt and quartzite) which exhibited high expansions. Additionally, to compare the surfaces, SEM studies were also carried out at 7 and 28 days of solution for two samples (granodiorite and

limestone) which show low expansion values. Chemical analyses (ICP-ES (major oxides, code LF302)) of the samples were performed in Acme Laboratory (Canada). Chemical analyses were performed only on three rock types while they were conducted six mortar samples prior to AMBT tests and at 14 days of NaOH solution. The chemical analyses results of the samples were given in Table 5.

3. Results and discussion

3.1 Mineralogical evaluation of rock samples

Mineralogical and semi-quantitative Rietveld X-ray diffraction analyses indicated that calcite and opaque minerals were present in the limestone sample. For example, iron was detected as an opaque mineral. Furthermore, kaolinite was found in quartzite and claystone, and montmorillonite was shown in lapilli tuff as clay minerals. Campbell (1986) reported that the matrix in the quartzite dominantly consist of sericite and kaolinite. Therefore, the rocks are virtually un-metamorphosed. In this study, it was shown that clay-bearing quartzite was studied when considering the mineralogical contents based on the petrographic and XRD analyses.

According to ASTM (1989), water absorption value of aggregate should be lower than 2.5%. From the point of water absorption, the aggregates are suitable for concrete, except quartzite, lapilli tuff and claystone. On the other hand, these three samples were specially selected to understand the clay mineral effect on the expansion of mortar bars. Korkanç and Tuğrul (2004) studied basalts having porosity values in the range of 2.4 – 10 % and mentioned that all studied basalts were suitable for concrete aggregate, considering the other tests. In this study, all porosity values (except lapilli tuff) have less than 10 % (Table 1).

3.2 Assessment of expansion considering rock mineralogy

In this study, AMBT was carried out for two different investigations. In the first, all mortar bars of diabase, andesite and quartzite samples were placed in the same NaOH solution to determine whether they were affected or not. Latter, each sample was put into a separate NaOH solution (Fig. 4a-c). According to Fig. 4, all mortar bars were affected when they were in the same solution. According to ASTM (1999), the percentage of expansion in length for 14 days should be under 0.10% for non-alkali reactive aggregates. Since the expansion value of quartzite (potentially reactive aggregate) changed between 0.10–0.20 (%), comparator readings (length measurements) of mortar bars were taken until 28 days. Average expansion of samples were higher than the suggested limit of 0.2% at 14–28 days exposure to same NaOH solution, which indicated that all three rock types (diabase-1, andesite and quartzite) were reactive aggregates. Diabase-1 and andesite were obtained to be about three times greater than those of their unique mold following 14-28 days for same NaOH.

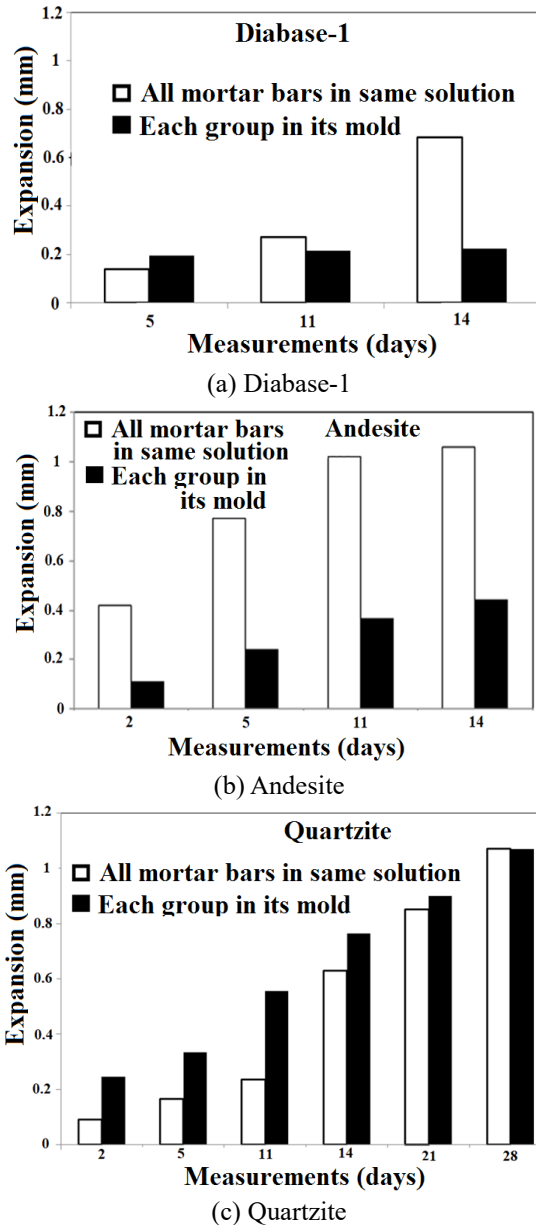


Fig. 4 The effect of solution on mortar bars (a, b, c)

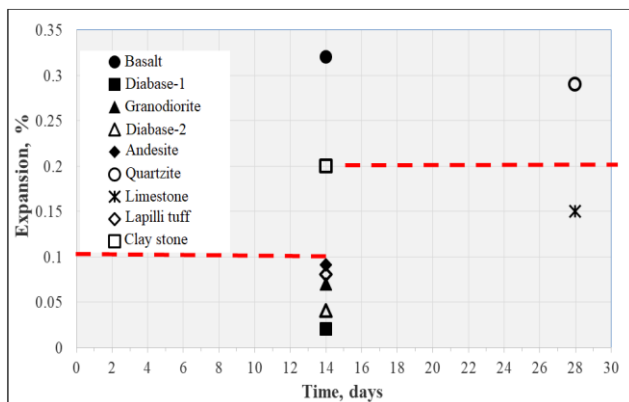
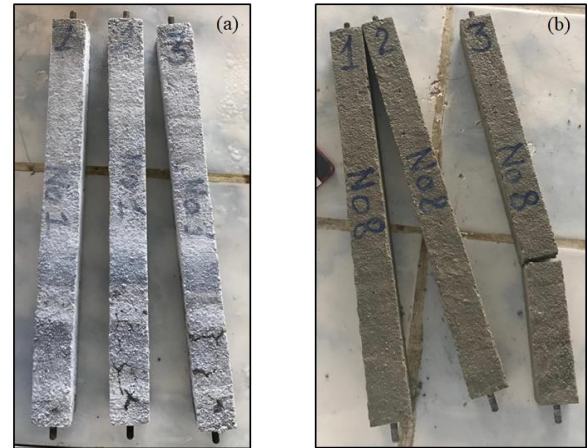


Fig. 5 Final expansion (%) values of the mortar bars

However, after 28 days of exposure, the quartzite exhibited the same average expansive values (1.07 mm)



(a) Cracks after test

(b) Breaking before test

Fig. 6 Cracks in basalt mortars after AMBT (a), weak lapilli tuff mortar samples prior to AMBT (b)

even if it was in the same NaOH solution with other mortar bars. It was estimated that diabase-1 and andesite were affected by reactive pore solution associated with quartzite.

Each series of the mortar bars made with nine different types of aggregates were also examined in this study for a separate NaOH solution. Three samples (basalt, quartzite and clay stone) were found to have ASR based on the AMBT (Fig. 5). On the macro-scale, the mortar bars of basalt aggregates exhibited a network of ASR cracking (Fig. 6a) following exposure to NaOH solution (14 days). Mortar bars made with basalt showed the highest expansion according to AMBT containing quartz as well as moderately silification, argillisation, serpentinization (Table 3). The expansion in per cent and cracking of these samples indicated alkali-silica reactivity due to the quartz content and alteration minerals. Katayama *et al.* (1989) mentioned that basalt can be potentially reactive if the silica content of the bulk composition exceeds 50%. According to chemical analyses (Table 5), basalt has more than 50% SiO₂ (61.2 %). Furthermore, the quartz content of basalt was found to be 9.0 % based on the Rietveld analysis. Korkanç and Tuğrul (2005) stated that the reactivity of basalts was controlled by the presence of alteration minerals, volcanic glass, and the SiO₂ content (>50%). Lukschova (2009) studied on mortar specimens and mentioned that quartz-rich aggregates showed a medium degree of ASR.

In the current study, the other sample which showed reactivity was claystone. This rock has a lot of quartz filled veins within it. Moreover, water can lead to volume expansion of the rock because of the swelling of clay minerals (Ercikdi *et al.* 2016). Furthermore, similar to the claystone, swelling soil is common engineering problems in the world (Angin and Ikizler 2018, Hamidi and Marandi 2018). In the current study, ASR risk according to the expansion of mortar bars in claystone aggregates could be attributed to its high content of clay (kaolinite) and quartz minerals. Quartzite is rich in silica indicating high risk for ASR. Additionally, the other reason for high expansion value could be attributed to the clay minerals. It is not surprising that claystone and quartzite exhibited high expansion when their constituents were examined through

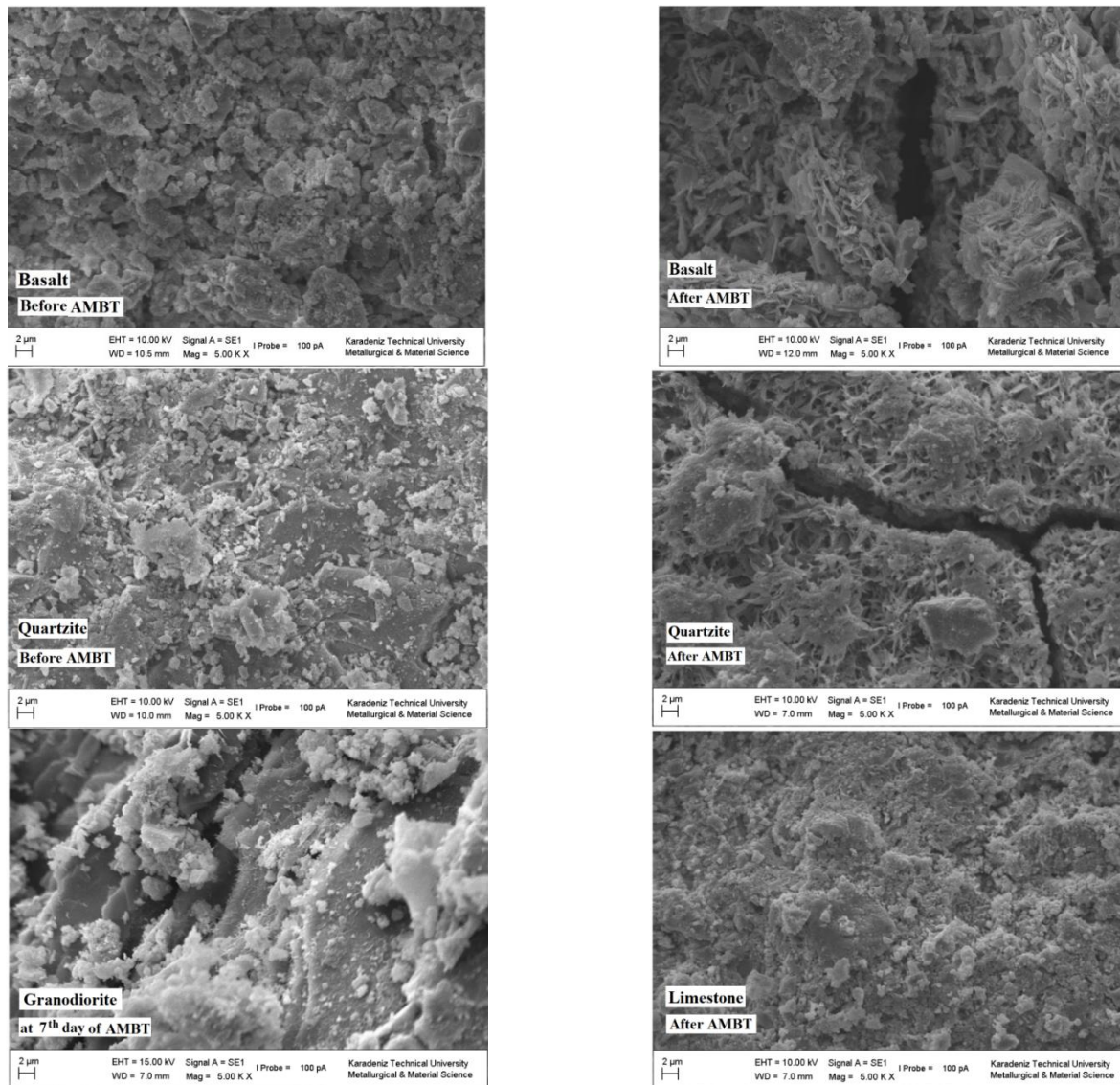


Fig. 7 SEM examination of the samples

detailed petrographic and XRD studies.

Marfil and Maiza (2001) mentioned that volcanic rocks, having volcanic glass, are not favourable from the point of alkali-silica reactivity. St. John (1988) also stated that volcanic glass present in rhyolite, dacite and andesite is the main reactive constituent of rocks. Similarly, the petrographic study of lapilli tuff indicated that volcanic glass fragments in addition to mica (muscovite) and clay mineral (montmorillonite) which causes swelling and volume increase were present within this rock. Therefore, ASR expansion of this rock was close to the threshold limit as in the andesite consisting of chlorite, quartz, silification, epidotization and carbonation. Lapilli tuff and andesite samples produced relatively higher expansion values for ASR when compared with other rock mortar samples. Since the amount of montmorillonite is not enough to cause expansion; lapilli tuff was considered to have low ASR risk. However, this rock is very weak with high porosity and may not suitable for use in concrete (Fig. 6b). For this reason, two additional sets of mortar bars were prepared for lapilli tuff and one sample was broken again. Mortar bars made

with andesite aggregate is generally considered as reactive due to its mineralogical composition (Katayama *et al.* 1989, Sirivivatnanon and Mohammadi 2016).

In the current study, the expansion value of andesite was very close to the limit value for reactivity according to ASTM (1999). This study showed that mortar bars which show high expansion may not directly result from ASR due to the reactive minerals since the expansion may stem from clays, micas and alteration minerals within the aggregates. Therefore, additional studies are recommended for more information about mortar bar expansion with XRD (Rietveld method). Diabase-1, 2 and granodiorite indicated the lowest expansion due to the scarcity of deleterious alteration mineral constituents. Also, although diabase-1 and diabase 2 don't contain any quartz mineral, they have silica content about 48-55%.

3.3 Microstructural analysis of mortar bars via SEM studies

Mortar bars were also examined via SEM studies to

Table 6 Differences in chemical composition of mortar bars before and after AMBT

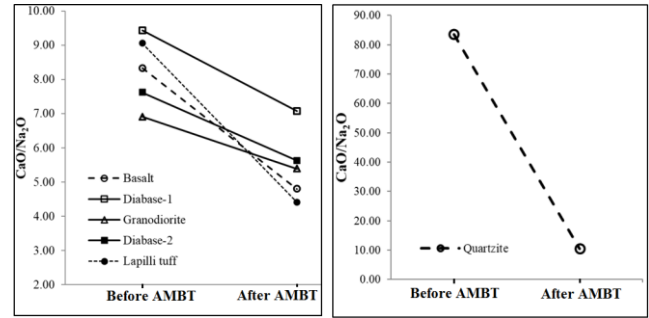
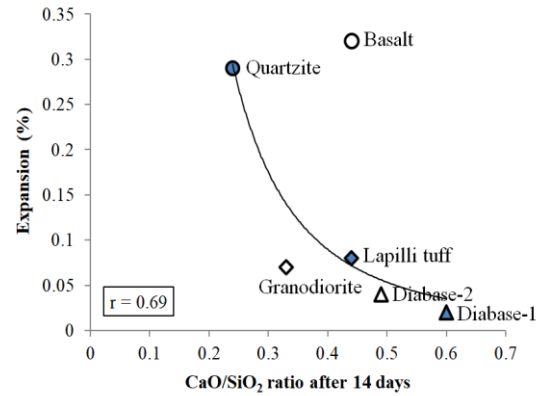
Mortar name	SiO ₂ %	Dif. %	Al ₂ O ₃ %	Dif. %	Fe ₂ O ₃ %	Dif. %	CaO %	Dif. %	Na ₂ O %	Dif. %	K ₂ O %	Dif. %
Basalt	-1.59	3.50	-0.19	1.40	-0.36	7.24	0.97	5.27	1.83	82.8	-	4.42
Diabase-1-1 [^]	-0.08	0.22	0.07	0.60	-0.17	2.06	-0.1	0.46	0.76	32.8	-	14.9
Granodiorite-1 [^]	0.35	0.64	-0.01	0.09	-0.10	3.82	0.09	0.5	0.75	28.9	-	12.8
Diabase-2-1 [^]	-0.63	1.50	0.0	0.0	-0.01	0.16	-	0.84	0.93	34.3	-	13.9
Quartzite-1 [^]	-2.01	2.97	-0.13	5.30	-0.19	15.6	0.53	3.34	1.37	721.1	-	22.7
Lapilli tuff-1 [^]	-2.18	4.70	-0.13	1.10	-0.03	1.07	-	1.69	2.27	102.3	-	13.5

evaluate micro-cracks due to the expansion and to compare relative surface properties before and after AMBT (Fig. 7). SEM observations didn't perform for claystone. However, granodiorite and limestone samples were examined at 7 days and 28 days, respectively. Demir and Arslan (2013) stated that ASR products mainly formed in voids, in aggregate cracks and between cement expansion gel and aggregate according to the SEM images.

According to SEM micrographs of 14 days taken from bar surfaces, the samples had a generally rough surface and acicular microstructures around the micro-cracks. No changes were observed before the AMBT tests on mortar bar samples. In granodiorite sample, micro-cracks and acicular microstructures have just begun to form at 7th days and considering that it wasn't enough for ASR. The limestone didn't show any acicular microstructures and micro-cracks although it was kept in NaOH solution for 28 days. The limestone was also determined to be non-reactive for ASR according to AMBT. SEM observations confirmed that the mortars made from basalt and quartzite aggregates could be affected by ASR. The SEM method provided detailed identification of both micro-crack and morphology of the ASR products between before and after AMBT tests.

3.4 Chemical analysis of mortar bar samples

Several parameters such as type of cement, composition of accelerating solution, temperature during test period, length of test period, type of sample (experimental mortar sample), w/c ratio and/or aggregate petrographic characteristics and hardening period affect the chemical composition and volume of alkali-silica gels (Wang and Gillott 1991, Kurtis *et al.* 1998, Peterson *et al.* 2006, Fernandes 2007). To investigate the changes in chemical composition of mortar bars, chemical analyses were carried out (before and after AMBT tests). The results of chemical analyses indicated that all samples were dominated by SiO₂. As shown in Table 5, 6, the SiO₂, Al₂O₃, Fe₂O₃ and K₂O contents were found to decrease while Na₂O contents were observed to increase due to the NaOH solution. No significant changes in some major oxides (TiO₂, P₂O₅, MnO and Cr₂O₃) contents were found. Differences which can be important in chemical composition of mortar bars are shown in Table 6. Differences between major oxides before and after AMBT tests are also calculated as percentage since they are present in various amounts in samples. For

Fig. 8 CaO/Na₂O versus timeFig. 9 Ca/SiO₂ versus expansion values

example, although variation in SiO₂ is more than Fe₂O₃, the variation percentage of Fe₂O₃ is higher than SiO₂. According to the chemical analyses results, basalt and quartzite which suffered from ASR were generally seen to more variable in chemical composition of major oxides than those of other samples.

The ratios of some major oxides related to the ASR were investigated by some authors. Prezi *et al.* (1997) reported that the reaction-product gels containing larger amounts of equivalent sodium oxide (Na₂O) and smaller CaO/Na₂O ratio caused larger expansions in the mortar bars. In the current study, the CaO/Na₂O ratio was plotted versus time (before and after AMBT tests) (Fig. 8).

As shown in Fig. 8, the CaO/Na₂O ratio showed a significant decrease in quartzite mortar bar samples and it was followed by basalt and lapilli tuff mortar bar samples. Phillips (2015) investigated the ASR mitigation using high volume fly ash and found that the CaO/SiO₂ had little effect on the amount of expansion. He obtained a moderate relation between expansion and CaO/SiO₂ ratio. The author mentioned that the amount of expansion (%) increased as the CaO/SiO₂ ratio increased for some fly ashes, and the expansion decreased for other fly ashes. In this study, the data shown in Fig. 9 follows a general trend of a decrease in expansion (%) as the CaO/SiO₂ content increases.

Grattan-Bellew and Beaudouin (1980) stated that phlogopite mica including about 10% K₂O; soluble K⁺ would contribute to the alkalinity of the concrete pore solution enhancing its possible expansivity when it is composed of alkali-rich aggregate. According to some authors, some mineral phases within the aggregate particles

such as volcanic glasses, unwashed marine sands, altered feldspars, micas, clay minerals and zeolites can also, with time, supply significant amounts of alkalis to the pore solution in concrete (Grattan-Bellew and Beaudouin 1980, Kawamura 1989). This could explain why many concrete structures are affected by ASR (Bérubé *et al.* 2002). Therefore, this study showed that some rock types including certain minerals, e.g. micas (muscovite, biotite and vermiculite), clay minerals (kaolinite and montmorillonite), and volcanic glass and some alterations (silification, chloritization, sericitization and argillisation, etc.) adversely contributed to mortar bar expansion via releasing significant quantities of alkalis, into the concrete pore water.

4. Conclusions

SEM studies revealed that samples which are reactive according to AMBT had generally rough surface and acicular microstructures in or around the micro-cracks. SiO_2 , Al_2O_3 , Fe_2O_3 and K_2O contents exhibited decrease while Na_2O contents increased due to the NaOH solution. Chemical analyses indicated that basalt and quartzite exhibited ASR expansion according to the AMBT. These rocks were seen to show more variation in chemical composition of major oxides than those of other samples. The ratio of $\text{CaO}/\text{Na}_2\text{O}$ showed a decrease with time (before and after AMBT tests) for all samples where the most decrease was found in quartzite, basalt and lapilli tuff samples. CaO/SiO_2 content increased while expansion (%) values decreased. Diabase-1 and andesite were affected by reactive solution associated with quartzite when these were in the same NaOH solution. This study therefore suggested that special mold should be used for each sample. Furthermore, rock mineralogy should be identified in terms of alteration phases since clay minerals (kaolinite and montmorillonite), micas (muscovite, biotite and vermiculite), volcanic glass and some alterations (silification, chloritization, sericitization and argillisation, etc.), caused expansion in mortar bars in addition to reactive minerals such as quartz.

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References

Ali, A., Sajid, M., Ali, L. and Usman, M. (2014), "Petrographic study of coarse aggregate to evaluate their susceptibility to Alkali Silica Reactivity in different rocks of District Shangla, Swat, Pakistan", *J. Himalayan Earth Sci.*, **47**(2), 125-139.

Angin, Z. and İkizler, S.B. (2018), Assessment of swelling pressure of stabilized Bentonite, *Geomech. Eng.*, **15**(6), 1219-

1225. <https://doi.org/10.12989/gae.2018.15.6.1219>.

ASTM C 1260 (1999), *Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar Bar Method)*, in *Annual Book of ASTM Standards*, ASTM Publication Office, Philadelphia, Pennsylvania, U.S.A., 650-653.

ASTM, (1989), *Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate*, ASTM C 127-88.

Bakhytzhan, A. (2019), "Investigation of the effect of aggregate properties on alkali silica reaction in concrete", Master Thesis, Karadeniz Technical University, Trabzon, Turkey (in Turkish).

Bérubé, M.A., Duchesne, J., Dorion, J.F. and Rivest, M. (2002), "Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali-silica reactivity", *Cem. Concrete Res.*, **32**, 1215-1227. [https://doi.org/10.1016/S0008-8846\(02\)00766-4](https://doi.org/10.1016/S0008-8846(02)00766-4).

Binal, A. (2015), "The pressimum ratio and aggregate size effects on alkali silica reaction", *Proc. Earth Planet. Sci.*, **15**, 725-731. <https://doi.org/10.1016/j.proeps.2015.08.103>.

Campbell, F.K. (1986), "Petrology and sedimentation of the Flambeau Quartzite, in Greenberg", *Geosci. Wisconsin*, **10**, 38-45.

Cihangir, F., Ercikdi, B., Kesimal, A., Ocak, Y. and Akyol, S. (2018), "Effect of sodium-silicate activated slag at different silicate modulus on the strength and microstructural properties of full and coarse sulphidic tailings paste backfill", *Constr. Build. Mater.*, **185** 555-566. <https://doi.org/10.1016/j.conbuildmat.2018.07.105>.

Demir, I. and Arslan, M. (2013), "The mechanical and microstructural properties of Li_2SO_4 , LiNO_3 , Li_2CO_3 and LiBr added mortars exposed to alkali-silica reaction", *Constr. Build. Mater.*, **42**, 64-77. <https://doi.org/10.1016/j.conbuildmat.2012.12.059>.

Demir, I. and Sevim, O. (2017), "Effect of sulfate on cement mortars containing Li_2SO_4 , LiNO_3 , Li_2CO_3 and LiBr", *Constr. Build. Mater.*, **156**, 46-55. <https://doi.org/10.1016/j.conbuildmat.2017.08.148>.

Demir, I., Sevim, O. and Kalkan, I. (2018), "Microstructural properties of lithium-added cement mortars subjected to alkali-silica reactions", *Sâdhanâ*, **43**, 112. <https://doi.org/10.1007/s12046-018-0901-3>.

Diamond, S. (1975), "A review of alkali-silica reaction and expansion mechanisms 1. Alkalies in cement and in concrete pore solutions", *Cem. Concrete Res.*, **5**(4), 329-346. [https://doi.org/10.1016/0008-8846\(75\)90089-7](https://doi.org/10.1016/0008-8846(75)90089-7).

Erçikdi, B., Karaman, K., Cihangir, F., Yilmaz, T., Aliyazicioğlu, S. and Kesimal, A. (2016), "Core size effect on the dry and saturated ultrasonic pulse velocity of limestone samples", *Ultrasonics*, **72**, 143-149. <https://doi.org/10.1016/j.ultras.2016.08.006>.

Gasparotto, G., Bargossi, G.M., Peddis, F. and Sammassimo, V. (2011), "A case study of alkali-silica reactions: petrographic investigation of paving deterioration", *Periodico di Mineralogia*, **80**(2), 309-316. <https://doi.org/10.2451/2011PM0022>.

Grattan-Bellew, P.E. and Beaudouin, J.J. (1980), "Effect of phlogopite mica on alkali-aggregate expansion in concrete", *Cem. Concrete Res.*, **10**, 789-797. [https://doi.org/10.1016/0008-8846\(80\)90007-1](https://doi.org/10.1016/0008-8846(80)90007-1).

Fernandes, I., Noronha, F. and Teles, M. (2007), "Examination of the concrete from an old Portuguese dam: Texture and composition of alkali-silica gel", *Mater. Char.*, **58**(11-12), 1160-1170. <https://doi.org/10.1016/j.matchar.2007.04.007>.

Hamidi, S. and Marandi, S.M. (2018), "Effect of clay mineral types on the strength and microstructure properties of soft clay soils stabilized by epoxy resin", *Geomech. Eng.*, **15**(2) 729-738. <https://doi.org/10.12989/gae.2018.15.2.729>.

ISRM (2007), *The Complete ISRM Suggested Methods for Rock*

- Characterization, Testing and Monitoring: 1974-2006*, Kozan Ofset, Ankara, Turkey.
- Katayama, T., St John, D.A. and Futagawa, T. (1989), "The petrographic comparison of rocks from Japan and New Zealand—Potential reactivity related to interstitial glass and silica minerals", in *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, Kyoto, Japan, July.
- Kawamura, M., Koike, M. and Nakano, K. (1989), "Release of alkalis from reactive andesitic aggregates and fly ashes into pore solution in mortars", *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, Kyoto, Japan, July.
- Korkanç, M. and Tugrul, A. (2004), "Evaluation of selected basalts from Niğde, Turkey, as source of concrete aggregate", *Eng. Geol.*, **75**, 291-307. <https://doi.org/10.1016/j.enggeo.2004.06.015>.
- Korkanç, M. and Tugrul, A. (2005), "Evaluation of selected basalts from the point of alkali-silica reactivity", *Cem. Concrete Res.*, **35**, 505-512. <https://doi.org/10.1016/j.cemconres.2004.06.013>.
- Kurtis, K.E., Monteiro, P.J.M., Brown, J.T. and Meyer-Ilse, W. (1998), "Imaging of ASR gel by soft X-ray microscopy", *Cem. Concrete Res.*, **28**(3), 411-421. [https://doi.org/10.1016/S0008-8846\(97\)00274-3](https://doi.org/10.1016/S0008-8846(97)00274-3).
- Kupwade-Patil, K.N. and Allouche, E. (2013), "Impact of alkali silica reaction on fly ash-based geopolymer concrete", *J. Mater. Civ. Eng.*, **25**(1), 131-139. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000579](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000579).
- Lindgard, J., Sellevold, E.J., Thomas, M.D.A., Pedersen, B., Justnes, H. and Ronning, T.F. (2013), "Alkali-silica reaction (ASR)—performance testing: Influence of specimen pre-treatment, exposure conditions and prism size on concrete porosity, moisture state and transport properties", *Cem. Concrete Res.*, **53**, 145-167. <https://doi.org/10.1016/j.cemconres.2013.05.020>.
- Lukschuva, S. (2009), "Alkali-silica reaction of aggregates in real concrete and mortar specimen", *Acta Res. Reports*, **18**, 79-86.
- Malvar, L.J., Cline, G.D., Burke, D.F., Rollings, R., Sherman, T.W. and Grene, J. (2002), "Alkali-silica reaction mitigation" state-of-the-art and recommendations", *ACI Mater. J.*, **99**(5), 480-489.
- Marfil, S.A. and Maiza, P.J. (2001), "Deteriorated pavements due to the alkali-silica reaction: A petrographic study of three cases in Argentina", *Cem. Concrete Res.*, **31**(7), 1017-1021. [https://doi.org/10.1016/S0008-8846\(01\)00508-7](https://doi.org/10.1016/S0008-8846(01)00508-7).
- O'Connor, B.H. and Raven, M.D. (1988), "Application of the Rietveld refinement procedure in assaying powdered mixtures", *Powder Diffract.*, **3**, 2-6. <https://doi.org/10.1017/S0885715600013026>.
- Oerter, E.J., Brimhall, Jr. G.H., Redmond, J. and Walker, B. (2007), "A method for quantitative pyrite abundance in mine rock piles by powder X-ray diffraction and Rietveld refinement", *Appl. Geochem.*, **22**, 2907-2925. <https://doi.org/10.1016/j.apgeochem.2007.08.002>.
- Ostertag, C.P., Yi, C. and Monteiro, P.J.M. (2007), "Effect of confinement on properties and characteristics of alkali-silica reaction gel", *ACI Mater. J.*, **104**(3), 276-282.
- Peterson, K., Gress, D., Van Dam, T. and Sutter, L. (2006), "Crystallized alkali-silica gel in concrete from the late 1890s", *Cem. Concrete Res.*, **36**(8), 1523-1532. <https://doi.org/10.1016/j.cemconres.2006.05.017>.
- Phillips, W.J. (2015), "Alkali silica reaction mitigation using high volume class C fly ash", Theses and Dissertations, University of Arkansas, Fayetteville, Arkansas, U.S.A.
- Prezi, M., Monteiro, P.J.M. and Sposito, G. (1997), "The alkali-silica reaction, part I: Use of the double-layer theory to explain the behavior of reaction-product gels", *ACI Mater. J.*, **94**(1), 10-16.
- Rajabipour, F.M.A.S.C.E., Maraghechi, H. and Fischer, G. (2010), "Investigating the alkali-silica reaction of recycled glass aggregates in concrete materials", *J. Mater. Civ. Eng.*, **22**(12), 1201-1208. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000126](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000126).
- Rietveld, H.M. (1969), "A profile refinement method for nuclear and magnetic structures", *J. Appl. Cryst.*, **2**, 65-71. <https://doi.org/10.1107/S0021889869006558>.
- Sirivivatnanon, V., Mohammadi, J. and South, W. (2016), "Reliability of new Australian test methods in predicting alkali silica reaction of field concrete", *Constr. Build. Mater.*, **126**, 868-874. <https://doi.org/10.1016/j.conbuildmat.2016.09.055>.
- St. John, D.A. (1988), "Alkali-aggregate reaction and synopsis of other data", *N. Z. Concr. Constr.*, **32**, 7-14.
- Sujjavanich, S., Won-In, K., Meesak, T., Wongkamjan, W. and Jensen, V. (2017), "Investigation of potential alkali-silica reactivity of aggregate sources in Thailand", *Int. J. Geomate*, **13**(35), 108-113. <http://dx.doi.org/10.21660/2017.35.6712>.
- Ulm, F.J., Coussy, O., Kefei, L. and Larive, C. (2000), "Thermo-chemomechanics of ASR expansion in concrete structures", *J. Eng. Mech.*, **126**(3), 233-242. [https://doi.org/10.1061/\(ASCE\)0733-9399\(2000\)126:3\(233\)](https://doi.org/10.1061/(ASCE)0733-9399(2000)126:3(233)).
- Wang, H. and Gillott, J.E. (1991), "Mechanism of alkali-silica reaction and the significance of calcium hydroxide", *Cem. Concrete Res.*, **21**(4), 647-654. [https://doi.org/10.1016/0008-8846\(91\)90115-X](https://doi.org/10.1016/0008-8846(91)90115-X).

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