

RILEM TC 258-AAA Round Robin Test: Alkali release from aggregates and petrographic analysis. Critical review of the test method AAR-8

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ABSTRACT: To create an international recommendation concerning the release of alkalis, test method AAR-8 was developed within the scope of RILEM TC 258-AAA activities. The first round robin test was performed using five aggregate types, and further investigation was conducted as RRT2, leading to the final version of the AAR-8 recommendation. Five aggregates with different mineralogies and origins were immersed in specific volumes of NaOH or KOH solutions with excess calcium hydroxide maintained 38 °C and 60 °C respectively. Samples of the immersion test solution were removed at intervals of 2, 6, 13, 26, and 52 weeks by pipetting and chemically analyzed for NaOH or KOH test solutions. The amount of alkali released was expressed in grams of Na₂O, K₂O, and Na₂O_e per kilogram of the respective aggregate. The results obtained are presented. Based on the data, several changes to the original version of the test method are proposed.

KEYWORDS: Alkali-release; Aggregates; Alkali-aggregate reaction; Chemical composition; Methodology.

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RESUMEN: RILEM TC 258-AAA Round Robin Test: Lixiviación de álcalis de los áridos y análisis petrográfico. Revisión crítica del método de ensayo AAR-8. Con el fin de crear una recomendación internacional sobre la lixiviación de álcalis de los áridos, se desarrolló el método de ensayo AAR-8 en el ámbito de las actividades de RILEM TC 258-AAA. El primer Round Robin Test (RRT1) de AAR-8 se realizó utilizando cinco tipos áridos y se llevó a cabo una investigación adicional como RRT2 que condujo a la versión final de la recomendación AAR-8 publicado recientemente. Se sumergieron cinco áridos con diferente mineralogía y origen (fonolita, cataclasita, granodiorita, granito y una arena dragada de mar) en volúmenes específicos de soluciones de NaOH o KOH con exceso de hidróxido de calcio mantenido a 38 °C y 60 °C. A las 2, 6, 13, 26 y 52 semanas, se extrajeron muestras de la solución de prueba de inmersión mediante pipeteo y se analizaron químicamente para determinar el potasio (solución de prueba de NaOH) o sodio (solución de prueba de KOH). La cantidad de álcalis lixiviados se expresó en gramos de Na₂O, K₂O y Na₂O_e por kilogramo de áridos. En este artículo, se presentan los resultados obtenidos de los álcalis lixiviables por los áridos probados se presentan en los cinco laboratorios participantes. A partir de los datos obtenidos, se proponen varios cambios en la versión original del método de prueba para mejorarlo.

PALABRAS CLAVE: Lixiviación de álcalis; Áridos; Reacción árido-álcali; Composición química; Metodología.

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1. INTRODUCTION

The investigation developed for decades, regarding the mechanisms of alkali-aggregate reactions, indicates that some aggregates or mineral phases used in concrete can leach significant quantities of alkali to the interstitial solution over time (1, 2). To reduce the risk of alkali-silica reaction (ASR) developing in the concrete, the total alkali content of the concrete should be controlled for concrete exposed to wet environments. Therefore, it is necessary to control the alkali content of all components of the concrete, including the additives and water, but especially to limit the alkali content of the cement, and/or to use specific amounts of supplementary cementing materials (3).

Most rocks commonly used as aggregates contain minerals with Na and/or K. Plagioclase, K-feldspar, and K/Na-feldspar exist in a large number of aggregates, but feldspathoids, mica, clay minerals, zeolites, amphibole, volcanic glass, and unwashed marine sands contain alkalis. Aggregates containing these minerals have been investigated owing to the suspicion that they might increase the alkali content of the concrete (4-8).

The first laboratory test to evaluate alkali release by aggregates was proposed by Van Aardt and Visser (9), who studied the behavior of feldspars and clay minerals in the presence of calcium hydroxide solutions. The authors observed that the reaction in an aqueous suspension at 39 °C allowed the precipitation of tetracalcium aluminate hydrates, free alkalis, alkali silicates, and hydrogarnets, depending on the type of feldspar. It was also observed that the reaction of calcium hydroxide with sericite, shale, and some igneous rocks, originated from the hydrogarnets, hydrated calcium silicates, and free alkalis when the materials are boiled at 95 °C (9, 10).

Several studies have been conducted regarding the release of alkalis from various minerals over time when exposed to a high-pH environment, such as concrete. The rate and amount of alkali released also depends on the temperature, local porosity, and permeability of the cement paste. Additionally, the alkali release is affected by the diverse properties of the aggregates, such as the particle size, lithological composition, mineral grain size, mineral modal content, total alkali content, and bonding of mineral constituents. Furthermore, the degree of alteration, spatial microstructure, fabric or texture, as well as the internal porosity and permeability of the aggregate particles must be considered (11-13). Release of the respective ions depends on the crystallographic structure of the minerals and the bonding strength between the ions within their structure.

The main principle behind the tests suggested in the recent decades refers to the immersion of the aggregate sample in saturated lime solutions, with or without excess solid lime, or in alkaline solutions

(NaOH, KOH) to evaluate the alkali contribution to the concrete from the respective aggregate. However, as of yet no agreement has been reached regarding the amount of alkali released and the procedure for estimating them.

The objective of RILEM TC 219-ACS ‘Alkali-aggregate reactions in concrete structures’ (2007–2014) was to establish and validate a number of general international ASR performance-based testing concepts. To maintain relevance to the field structures when testing samples in the laboratory, it is crucial that the basic conditions do not change to an extent where the correlation of performance ranking under the two different conditions is not maintained. As Lindgård *et al.* confirmed (14), several parameters may influence the results obtained in an accelerated performance test compared to the field behavior of concrete structures. These parameters are the type of aggregate, type of binder, mix design, and conditions during pre-storage and ASR exposure. Furthermore, the degree of alkali leaching depends strongly on the storage conditions and mineralogy (2, 3, 9, 10, 14-18), and the pre-storage conditions might further influence the rate and extent of alkali leaching significantly. Considering this comparison, Lindgård *et al.* (14) found that specimen size clearly has a large impact on expansion, and this effect can be largely ascribed to the leaching of alkalis from smaller specimens. In their study, they also found that the impact of alkali leaching was lower for larger concrete prisms, although it was still significant. However, they concluded that none of the currently available or commonly used test methods met all criteria for an ideal performance test (14).

According to Jozwiak-Niedzwiedzka *et al.* (19), the classification of aggregates by petrographic methods in terms of the likelihood of alkali-aggregate reactions focuses mainly on the identification of rocks and forms of silica that are known to be reactive, that is, chert, novaculite (form of chert) volcanic glass, cristobalite, tridymite, and opal. Thin sections can also be analyzed for the size of quartz crystals to clearly determine the ASR susceptibility of the aggregate. Different deleterious materials are sought depending on the rock type, namely, microcrystalline quartz in granite, volcanic glass in volcanic rock, cryptocrystalline quartz in carbonate rock, and deformed particles of quartz, especially strained quartz, in the case of metamorphic rocks (19).

RILEM AAR-8 is a test method intended to assess the potential amount of alkalis released by aggregates using an alkali solution saturated with calcium hydroxide. A draft of the RILEM AAR-8 was prepared in 2013 in the scope of TC 219-ACS, and a round robin test (RRT1) was carried out using five aggregate samples and five laboratories. The potential amounts of sodium and potassium ions released by aggregates were then measured by the

immersion of the aggregate particles, whose sizes were further reduced by grinding them to a sand size fraction (0.125 to 4.00 mm), in NaOH (K release) and KOH (Na release) solutions at elevated temperatures. The solutions should be in contact with excess (solid) calcium hydroxide, as this is the situation with concrete in practice and can potentially increase alkali leaching through ion exchange with Ca^{2+} (8, 11, 20-23).

However, the conclusions of RRT1 pointed out that there was a wide variability between laboratories, and stricter information regarding the procedure needed to be included. The research was further carried out within the scope of RILEM TC 258-AAA, Avoiding Alkali Aggregate Reactions in Concrete – Performance Based Concept (2014-2020). The performance of the test by five laboratories showed more coherent results, and an improved revised draft of the test (2018) was used in the second RRT (RRT2), for which five samples were then selected.

In the present work, the original version of the method is presented, as well as the limitations observed are discussed, explaining the need for a revised methodology. Five aggregates were tested and analyzed under an optical microscope and scanning electron microscope to identify the minerals that compose each of the samples. In addition, chemical analysis of the bulk rock was carried out to compare with the results obtained in the RRT-1 of AAR-8 laboratory tests. It should be highlighted that the outcome of AAR-8 is indicative of the potential maximum amount of alkalis that can be released by the aggregates. It should be noted that there is still no verification of the actual alkali release under field conditions; therefore, the method cannot be used at this stage to limit the total alkali content in concrete. The verification of the method requires the assessment of concrete structures in which these aggregates have been used and knowledge of the alkali content in the original concrete is conclusive.

2. MATERIALS AND METHODS

2.1. Aggregate samples

Table 1 lists the five aggregates used in this test, indicating lithology and provenance. Some of these aggregates are known to be reactive in the field structures. These correspond to four samples of crystalline rocks of igneous and metamorphic origin and one sample of polymictic sand containing a large variety of igneous volcanic lithologies. Samples weighing 500 g were sieved to obtain the granulometric distributions presented in Table 2. The aggregates were then analyzed in five research institutes: Université Laval in Canada, SINTEF in Norway, IETcc-CSIC in Spain, LNEC in Portugal,

and RSESpA in Italy. The last laboratory (Italy) analyzed only three of the aggregates tested: cataclasite, granodiorite, and granite.

TABLE 1. Designation and provenance of the samples and information of the laboratories that performed the tests.

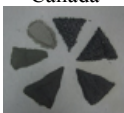

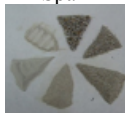
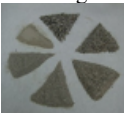

Type of aggregate	Phonolite	Cataclasite	Granodiorite
Supplying laboratory	Université Laval	SINTEF	IETcc-CSIC
Country	Canada 	Norway 	Spain 
Aspect			
Laboratory participated in RRT1	Yes	Yes	Yes
Type of aggregate	Granite	Sea dredged, basalt	-
Supplying laboratory	LNEC	MANNVIT	-
Country	Portugal 	Island 	
Aspect			
Laboratory participated in RRT1	Yes	No	

TABLE 2. Grain size distribution used in the RILEM AAR-8 tests.

Grain size distribution	Percentage of mass
4 mm – 2 mm	10 %
2 mm – 1 mm	20 %
1 mm – 500 μm	20 %
500 μm – 250 μm	25 %
250 μm – 125 μm	15 %
<125 μm	10 %

2.2. Characterization of aggregates

2.2.1. Porosimetry

To determine the porosity of the studied aggregates, the mercury intrusion porosimetry technique

was applied to samples of dimensions $1 \times 1 \times 1 \text{ cm}^3$ using Autopore IV equipment, model 9505.

2.2.2. Chemical composition

In the present study, the chemical composition of the aggregates was determined by X-ray fluorescence (XRF) using a Bruker S8 Tiger wavelength dispersion X-ray spectrometer.

The percentage of CO_2 was determined by the calcination loss test described in the standard UNE-EN 196-2 (24), using a NETZSCH Model ST409 device, registering the weight and enthalpy variation between $20 \text{ }^\circ\text{C}$ and $1000 \text{ }^\circ\text{C}$. The alkali composition (Na_2O and K_2O) and minor compounds were determined using the induced coupled plasma technique (ICP) with a Varian model 725-ES.

2.2.3. Mineralogy, petrography and SEM/EDS

Regarding the mineralogical composition of the aggregates, to characterize the crystalline phases present in the aggregates, both the majority and minority crystalline compounds were determined by X-ray diffraction (XRD). The samples were then ground and sieved until a grain size smaller than $80 \text{ }\mu\text{m}$ was obtained. The powder samples were further analyzed using a D8 ADVANCE Theta-Theta equipment diffractometer with a 2.2 kW copper anode.

Particles of fraction 4.00–2.00 were selected for petrographic characterization. Rock and sand particles were inserted into a mold filled with resin. After hardening, a 10 mm-thick slice was cut, glued to a glass slide, and then ground and polished to obtain polished thin sections of $30 \text{ }\mu\text{m}$ in thickness. No coverslips were applied.

The thin sections were analyzed under an optical microscope (Leica DM750P), and photomicrographs were obtained using a Leica ICC50 HD camera. The lens magnifications were $4\times$, $10\times$ and $40\times$, and the observations included plane-polarized light (PPL) and cross-polarized light (XPL). Fine-grained rocks were also studied using an electron probe micro-analyzer (EPMA) model JEOL JXA-8200 with microanalysis by energy dispersive spectroscopy (EDS) to obtain spectra and element maps.

2.3. Alkali extraction method (AAR-8, 2015)

The alkali extraction test of the aggregates was performed based on the methodology proposed by Université Laval (Quebec, Canada). The test consisted of submitting a representative sample of $500 \pm 1 \text{ g}$ of crushed and graded aggregates, with the grain size distribution described in the RILEM TC 219-ACS procedure (2, 6, 18, 20, 23, 25), in different alkaline solutions for 52 weeks. The aggregates were immersed in specific volumes of 0.7 M NaOH and

KOH solutions with excess calcium hydroxide maintained at $38 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ (Table 3), using a solution:aggregate ratio of 4:1 L/kg. The sealed storage containers were resistant to the alkali solutions at high temperatures.

TABLE 3. Designations and test conditions.

Conditions	Solution	Temperature
1 (Na-38)	NaOH 0.7M + $\text{Ca}(\text{OH})_2$ sat	$38 \text{ }^\circ\text{C}$
2 (Na-60)		$60 \text{ }^\circ\text{C}$
3 (K-38)	KOH 0.7M + $\text{Ca}(\text{OH})_2$ sat	$38 \text{ }^\circ\text{C}$
4 (K-60)		$60 \text{ }^\circ\text{C}$

The test containers were agitated for approximately 10 s twice a week. At 2, 6, 13, 26, and 52 weeks of age, the samples were removed from the oven, where they were stored in contact with the extraction solution, and the samples were left in an idle position at ambient temperature for 24 h. Subsequently, 10 mL of the solution was extracted and filtered, and the alkalis were determined using analytical methods (atomic absorption spectroscopy, atomic emission spectroscopy, or inductively coupled plasma): potassium (NaOH test solution) or sodium (KOH test solution). This procedure was also performed on a blank sample (extracting solutions), which was tested under the same conditions as the aggregate samples. The blank solutions not only served to quantify the alkalis extracted, i.e., the difference between the sodium and potassium concentrations measured in the blank and test samples, but they also had the function of being the solutions that serve to replenish the volume extracted and thus keeping the solid:liquid values constant. The amount of alkali released was expressed in mg of Na_2O , K_2O , and Na_2O_e per kilogram of aggregates and in %.

3. RESULTS AND DISCUSSION

In this section, the results of the physical properties, chemical and mineralogical composition, and petrographic analyses are presented for each sample, as well as the results of the AAR-8 tests performed.

3.1. Porosimetry

The results obtained for the bulk density and porosity are listed in Table 4. The porosity values reveal that sea-dredged sand and phonolite are the most porous. In the case of sea-dredged sand, this can be attributed to the presence of vesicular basalt grains, whereas for phonolite, the values of these index properties can be related to the alteration of the

rock. The higher porosity can contribute to a greater contact surface with the chemical solutions used in the tests, and eventually lead to a greater release of alkalis. However, Ferraz et al. (26) concluded that alkali release is lower for altered rock than for healthy/sound rock; therefore, the relationship between porosity and test results must consider other factors, such as chemical and mineralogical composition as well as the texture of the rock.

TABLE 4. Bulk density and porosity of the aggregate samples.

Type of aggregates	Bulk density (g/cm ³)	Total porosity (%)
Phonolite	2.4	3.8
Cataclasite	2.7	2.2
Granodiorite	2.5	3.3
Granite	2.6	1.4
Sea dredged, mainly basalt	2.7	5.6

3.2. Chemical composition

The bulk chemical compositions of the samples presented in Table 5 indicate that they are alkali-bearing aggregates. The alkali content of the phonolite is much higher than in the other lithologies, corresponding to double the content in the granodiorite, which exhibits the second highest value.

3.3. Mineralogy, petrography, and SEM/EDS

X-ray diffraction (XRD) and petrographic analysis showed that phonolite is composed of nepheline, Na-feldspar, K-feldspar, and other minor silicate minerals; cataclasite contains Na-feldspar, K-feldspar, and quartz; while granodiorite and granite contain Na-feldspar, K-feldspar, quartz, traces of mica (illite), and muscovite. On the other hand, polymictic sea-dredged sand contains particles of variable lithology, dominantly corresponding to basalt. It is mainly composed of Na-feldspar and Ca-feldspar

(plagioclase) and contains pyroxenes, such as diopside and augite, which specifically belong to the clinopyroxene group.

In Figure 1, the dominant texture and the main minerals that compose the rocks are observed. The sample that exhibited the strongest signs of alteration was granodiorite, with dull large K-feldspars and sericite formed on plagioclase crystals (Figure 1c). The rock also showed strain features in both quartz and feldspar crystals. The crystals in the granite sample were finer and the rock was slightly altered, with the smallest generation of plagioclase crystals showing argillization. The sea-dredged sand contains variable lithologies, mainly in terms of grain size and content of volcanic glass (Figure 1e and 1f). Palagonite is abundant in some sand grains. Phonolite and cataclasite are fine-grained, while the latter exhibits intense deformation. Phonolite contains abundant nepheline, which is a feldspathic mineral. Finally, the type of feldspar composing the rock is difficult to distinguish in cataclasite on this scale. As the aggregates were very fine-grained, samples of phonolite, cataclasite, and sea-dredged sand were studied using SEM/EDS to identify some of the minerals. Figure 2 presents an example of the SEM/EDS analyses performed, highlighting the importance of this method in the identification of alkali-bearing minerals.

3.4. Alkali extraction by AAR-8 procedure, problems during the test

3.4.1. Na₂O_e at 26 and 52 weeks

The average percentages of Na₂O, K₂O, and Na₂O_e (in mass %) released from each aggregate were calculated from the results obtained by all the five participating laboratories. The results are expressed as a function of time for both exposure temperatures, 38 °C and 60 °C. Table 6 shows the variation in the release of Na₂O_e with respect to the temperatures, comparing the results for 60° and 38 °C for each sample, and the time of testing, comparing the results after 52 weeks with those obtained at 26 weeks.

TABLE 5. Chemical composition of the aggregate samples (wt %).

Samples	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₂ O ₃	CO ₂	CaO	MnO	Cr ₂ O ₃	ZrO ₂	P ₂ O ₅	TiO ₂	MgO	Na ₂ O _e
Phonolite	55.66	19.30	12.30	5.42	2.68	2.72	0.84	0.33	0.02	0.12	0.00	0.31	0.00	15.87
Cataclasite	64.77	15.40	4.26	1.78	4.52	1.64	4.72	0.07	0.09	0.02	0.10	0.50	2.04	5.43
Granodiorite	72.77	13.99	4.06	4.59	1.67	0.95	0.70	0.02	0.20	0.01	0.38	0.15	0.24	7.08
Granite	71.82	14.00	3.40	5.08	2.42	1.22	0.58	0.03	0.20	0.01	0.35	0.31	0.50	6.74
Sea dredged, basalt	45.09	12.10	2.46	0.42	14.01	3.21	11.66	0.19	0.07	0.01	0.21	2.21	8.17	2.74

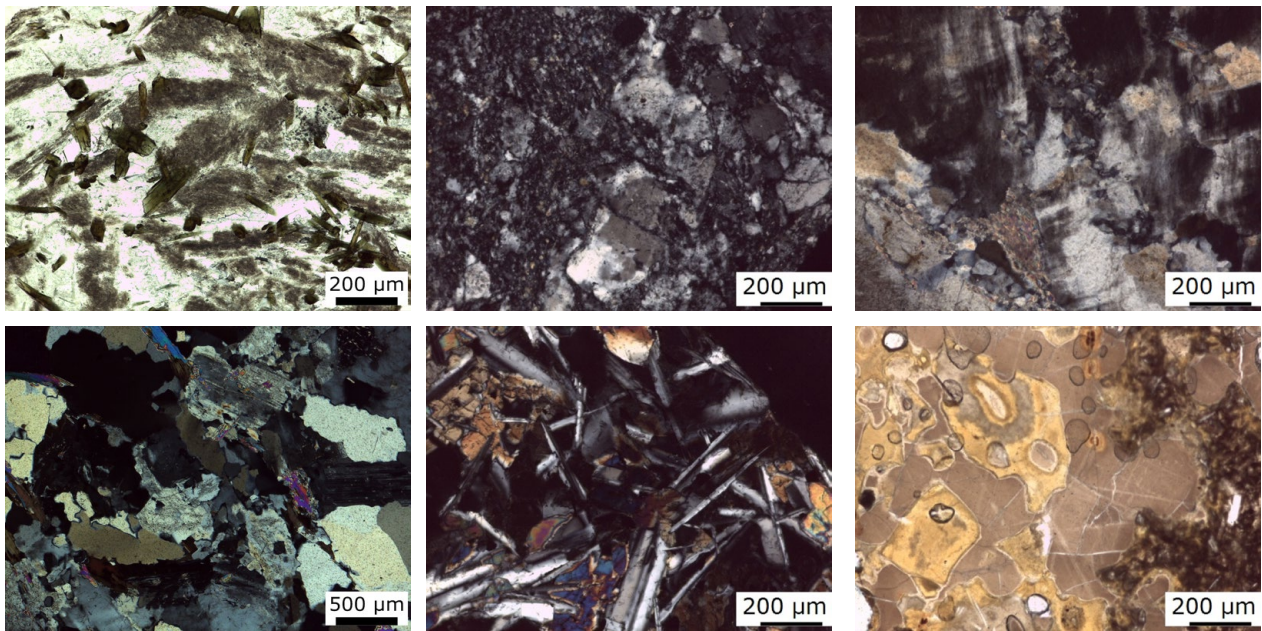


FIGURE 1. Optical photomicrographs (under plane polarized light N// and crossed polarized light NX) of samples tested: (a) phonolite, (b) cataclasite, (c) granodiorite, (d) granite, (e) and (f) particles of basalt in the sea-dredged sand.

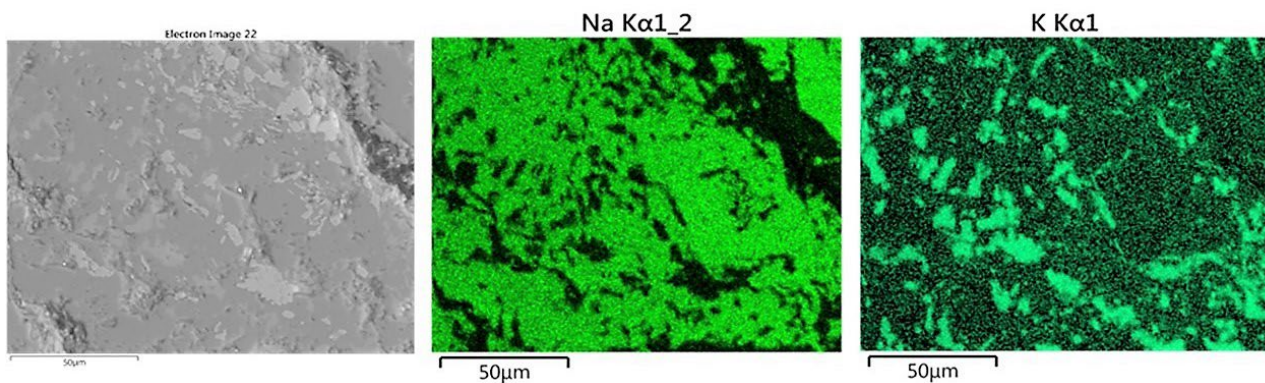


FIGURE 2. SEM image of the cataclasite and X-ray element maps of Na and K, showing the abundance of the minerals containing alkalis (albite and K-feldspar).

TABLE 6. Na_2O_e concentration (mass %) measured at 26 and 52 weeks of testing.

Aggregate	Temperature	Na_2O_e (26 weeks)	Increase from 38 to 60 °C (%) at 26 weeks	Na_2O_e (52 weeks)	Increase from 38 to 60 °C (%) at 52 weeks	Increase from 26 to 52 weeks (%)
Phonolite	38 °C	0.39	43.6	0.57	29.8	46.2
	60 °C	0.56		0.74		32.1
Cataclasite	38 °C	0.11	0.0	0.17	-11.8	54.5
	60 °C	0.11		0.15		36.4
Granodiorite	38 °C	0.07	42.9	0.11	0.0	57.1
	60 °C	0.10		0.11		10.0
Granite	38 °C	0.04	150.0	0.07	57.1	75.0
	60 °C	0.10		0.11		10.0
Sea dredged, basalts	38 °C	0.41	12.2	0.46	21.7	12.2
	60 °C	0.46		0.56		21.7

3.4.2. Na_2O , K_2O and Na_2O_e at 38 °C and 60 °C

Figure 3 exhibits the curves showing the evolution of alkali release. The rates of alkali release always tended to decrease with time, but after 52 weeks of testing, the results still did not reach a plateau, and the aggregates continued to release alkalis.

For the majority of the samples, there was a high release of Na^+ than K^+ , except for granodiorite and granite. Figure 3 also shows that phonolite and sea-dredged sand are the two aggregates that released the highest amounts of alkalis, whereas granodiorite and granite released the least, with values that reach a maximum of 0.11% Na_2O_e at one year. Finally,

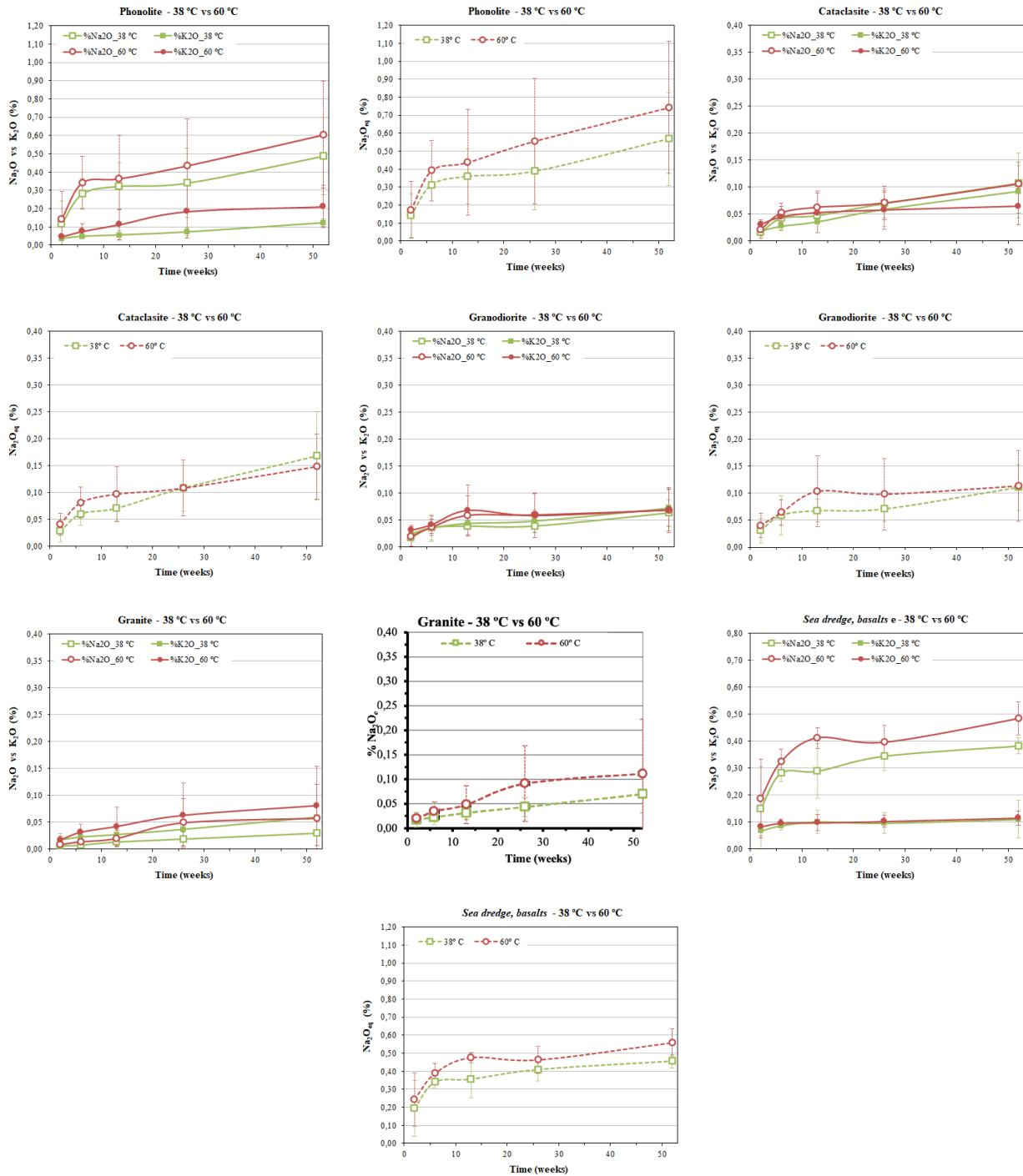


FIGURE 3. Curves obtained from the average of results of all laboratories test of alkalis released in 52 weeks at 38 °C and 60 °C for each aggregate.

cataclasite released slightly more alkali than the last two lithologies, but the values still remained low.

This Figure 3, shows that all the aggregates studied release alkalis in the solution. For most of the aggregates tested, storage at 60 °C allowed the release of a larger quantity of alkalis than at 38 °C, except for the cataclasite at 38 °C (26 weeks) and the granodiorite at 60 °C (52 weeks). Cataclasite showed anomalous behavior at 60 °C, for which the release was slightly higher at 38 °C than at 60 °C. The temperature did not seem to be an important factor for this aggregate. However, the granite sample is the one that showed the lowest values of alkali release, mainly at 26 weeks. The effect of temperature was the most severe, with an increase of 150% from 38 °C to 60 °C at 26 weeks and of 57.1% after 52 weeks.

According to Menéndez *et al.* (6), the potential contribution of alkalis is released from the granodiorite-generated products of the alkali-silica reaction in the concrete of a dam. The analysis of the granodiorite from the quarry used for the manufacture of the dam concrete with different extraction solutions showed that solutions (Ca(OH)₂, sat.) and (0.1M NaOH + 0.6M KOH + Ca(OH)₂, Sat.) were the most efficient; however, the alkali potential extraction could have been overestimated. In fact, the proposed rock samples were tested under conditions that did not strictly reproduce the field concrete conditions. Additionally, the particles tested are smaller than those applied in the manufacture of concrete with a larger specific surface area, which can in turn lead to higher reactivity.

The order of alkali release was as follows: phonolite > dredged sand (mainly basalt) > cataclasite > granodiorite > granite.

3.4.3. Limitations of the method

The results of the RRT1 pointed out some limitations of the method and showed some aspects that might be owing to the dispersion of the values obtained. An explanation for the variable results was needed to improve the method. It was verified that the method was not exactly the same in all five laboratories. In Table 7, the amount of excess calcium hydroxide (Ca(OH)₂) used in the alkaline solutions to obtain hydrated lime saturated solutions is presented, along with the different acidification procedures applied at the laboratories involved.

Furthermore, there was induration of the solids over time. Agglomeration of the particles could be due to the presence of 10% of the sample mass smaller than 125 µm. Although the samples were stirred twice a week, the energy applied to break up the agglomerations may vary among laboratories. Moreover, the fact that the sample was of solid (0.5 kg) and alkaline solution (2 L) contributed to the compaction of the particles owing to the difficulty of homogenization.

TABLE 7. Procedures for Ca(OH)₂ addition and for acidification procedures applied at the five laboratories.

Participant	Added Ca(OH) ₂ (g/L)	Acidification
Université Laval (Canada)	0.5	0.5 mL HNO ₃ /10 ml alkaline solution
SINTEF (Norway)	2	20 drops HNO ₃ /10 ml alkaline solution
IETcc-CSIC (Spain)	2	3 drops HNO ₃ /10 ml alkaline solution
LNEC (Portugal)	12	Dilution 1:20 of alkaline solution in HNO ₃ 1 %
R.S.E.S.p.a (Italy)	20	Concentrated nitric acid. until pH<2

By analyzing the results obtained during RRT1, it was clear that the method would need to be improved to obtain a test that safeguards repeatability and reproducibility.

4. CONCLUSIONS

Five samples of aggregate were characterized from the physical, chemical, and mineralogical points of view, including petrographic analysis and the performance of a new suggested method, AAR-8, to extract alkalis using an alkali solution saturated with calcium hydroxide. The test performed at five independent laboratories demonstrated that the release of Na₂O_s increased with time; however, the curves did not level out after 52 weeks of exposure, even though the rate of release significantly decreased over time. There was also a slight increase in alkali release with increasing temperature.

It is concluded that the mineral composition of the samples, as well as the size of the crystals, the existence of cracks, and the texture of the rocks, influence the exposure to the solution used in the tests. On the other hand, the sample that releases a higher amount of alkalis (phonolite) also presents a much higher alkali content in bulk rock analysis compared to other samples; however, the much higher content in the alkalis of phonolite is not proportional to the substantially higher release in alkalis. This result demonstrates that the release of alkalis depends on other factors, such as the stability of the mineral or glass in which the alkalis are bound, and the texture of the rock. The sea-dredged sand, although presenting a low content of alkalis in the bulk rock analysis, has a relatively high release of Na₂O, which suggests that the alkalis contained within the volcanic glass are much more easily released than those contained in crystalline minerals. In addition, some seawater may have remained after washing, contributing to

the release observed in the tests. Finally, the investigation showed that the potential for alkali release is more closely related to the mineralogy of the sample than to the alkali content determined by bulk rock chemical analysis, which demonstrates the importance of properly identifying the components of the aggregates that have significant release potential, such as feldspatoids and volcanic glass.

From the results obtained in this testing campaign, several changes are proposed to be made to the test in order to improve the method:

- As performed in the laboratories involved in the present study, the standard to be developed must state that the containers must be resistant to high temperatures in contact with alkaline solutions and shall be of a single use to avoid breakages.
- The coarse fractions of the aggregates should be washed to remove finer particles and later dried at 105 °C before the test to avoid overestimation of the alkali release.
- To avoid aggregate agglomeration and alkali precipitation, the quantity of aggregate sample must be reduced to 100 g, the liquid: solid ratio must be maintained at 4:1, and the container is to be shaken twice a week for 30 s and rolled 20 times at a longitude of 80 cm.
- The solution must be stabilized using 0.25 ml of HNO₃ concentrated (65%) for each 10 ml of alkaline solution.
- The extraction solutions must be added with 2 g/L Ca(OH)₂ to obtain a saturated calcium hydroxide solution with excess solid Ca(OH)₂, and to avoid interference, the withdrawn solution shall not be replenished.
- For the filtration process of the solution containing the extracted alkali, a micropore filter with a size of 0.2 µm should be used to reduce the errors related to the method, instead of using a vacuum pump.
- The sampling time should be fixed at 0, 2, 6, 13, and 26 weeks instead of 52 weeks. In addition, the test temperature must be set to 38 °C due to no significant differences in the results obtained at 60 °C, in keeping with the energy saved.
- Finally, to validate the analytical results, specimens mimicking concrete mixes for field structures should be prepared and tested in the laboratory or, preferably, in field exposure sites, measuring the increase in alkali content in the concrete fluids over time.

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REFERENCES

1. Berube, M.A.; Duchesne, J.; Dorion, J.F.; Rivest, M. (2002) Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by ASR. *Cem. Concr. Res.* 32 [8], 1215-1227. [https://doi.org/10.1016/S0008-8846\(02\)00766-4](https://doi.org/10.1016/S0008-8846(02)00766-4).
2. Santos Silva, A.; Fernandes, I.; Ferraz, A.R.E.; Soares, D. (2017) Can certain alkali minerals explain the slow reactivity of granitic aggregates in dams?. in *Swelling Concrete in Dams and Hydraulic Structures – DSC 2017*. Edited by Alain Sellier, Étienne Grimal, Stéphane Multon, Eric Bourdarot. ISTE, pp. 93-105.
3. Stark, D.; Sydney, D. (1993) Eliminating or minimizing alkali-silica reactivity. National Research Council. Washington. U.S.A. Report SHRP-C-343. Retrieved from <https://onlinepubs.trb.org/Onlinepubs/shrp/shrp-c-343.pdf>.
4. Grattan-Bellew, P.E.; Beaudoin, J.J. (1980) Effect of phlogopite mica on alkali-aggregate expansion in concrete. *Cem. Concr. Res.* 10, 789–797.
5. Gillot, J.E.; Rogers, C.A. (1994) Alkali-aggregate reaction and internal release of alkalis. *Mag. Concr. Res.* 46, 99-112.
6. Menéndez, E.; Prendes, N.; Márquez, C.; Aldea, B. (2012) Evaluation of granitic aggregate behaviour in relation with the alkaline extraction and compositional change in their phases. 14th ICAAR, Austin, EEUU, Ma 2012. Paper 052011
7. Menéndez, E.; Ruiz, S.; García-Rovés, R. (2016) Alkali release from aggregates; contribution to ASR. *Const. Mat.* 169 [4], 206-214. <https://doi.org/10.1680/jcoma.15.00072>.
8. Bérubé, M.A.; Duchesne, J.; Dorion, J.F.; Rivest, M. (2002) Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete surfaces affected by alkali-silica reactivity. *Cem. Concr. Res.* 32, 1215-1227. [https://doi.org/10.1016/S0008-8846\(02\)00766-4](https://doi.org/10.1016/S0008-8846(02)00766-4).

9. Van Aardt, J.H.P.; Visser, S. (1977) Calcium hydroxide attack on feldspars and clays: Possible relevance to Cement-aggregate reactions. *Cem. Concr. Res.* 7, 643-648. [https://doi.org/10.1016/0008-8846\(77\)90046-1](https://doi.org/10.1016/0008-8846(77)90046-1).
10. Van Aardt, J.H.P.; Visser, S. (1977) Formation of hydrogarnets: Calcium hydroxide attack on clays and feldspars. *Cem. Concr. Res.* 7, 39-44. [https://doi.org/10.1016/0008-8846\(77\)90006-0](https://doi.org/10.1016/0008-8846(77)90006-0).
11. Bérubé, M.A.; Fournier, B. (2004) Alkalies releasable by aggregates in concrete: significance and test methods. In: Tang, M. and Deng, M. (editors): Proceedings of the 12th International Congress on Alkali-Aggregate Reactions in Concrete, Beijing, China, pp. 17-30.
12. Lu, D.; Zhou, X.; Xu, Z.; Lan, X.; Tang, M.; Fournier, B. (2006) Evaluation of laboratory test method for determining the potential alkali contribution from aggregate and the ASR safety of the Three-Gorges dam concrete. *Cem. Concr. Res.* 36, 1157-1165. <https://doi.org/10.1016/j.cemconres.2006.01.004>.
13. Drolet, C.; Duchesne, J.; Fournier, B. (2017) Validation of the alkali contribution by aggregates to the concrete pore solution. *Cem. Concr. Res.* 98, 10-23. <https://doi.org/10.1016/j.cemconres.2017.04.001>.
14. Lindgård, J.; Andiç-Çakır, Ö.; Fernandes, I.; Rønning, T.F.; Thomas, M.D.A. (2012) Alkali-silica reactions (ASR): Literature review on parameters influencing laboratory performance testing. *Cem. Concr. Res.* 42, 223-243. <https://doi.org/10.1016/j.cemconres.2011.10.004>.
15. Constantiner, D.; Diamond, S. (2003) Alkali release from feldspars into pore solutions. *Cem. Concr. Res.* 33, 549-554. [https://doi.org/10.1016/S0008-8846\(02\)01001-3](https://doi.org/10.1016/S0008-8846(02)01001-3).
16. Yujiang, W.; Guiyu, Y.; Ming, D.; Mingshu, T.; Duyou, L. (2008) The use of thermodynamic analysis in assessing alkali contribution by alkaline minerals in concrete. *Cem. Concr. Res.* 30, 353-359. <https://doi.org/10.1016/j.cemconcomp.2007.03.003>.
17. Yujiang, W.; Min, D.; Mingshu, T. (2008) Alkali release from aggregate and the effect on AAR expansion. *Mater. Struct.* 41, 159. <https://doi.org/10.1617/s11527-007-9227-z>.
18. Soares, D.; Santos Silva, A.; Mirão, J.; Ramos, V.; Fernandes, I.; Menéndez, E. (2015) Assessment of alkalis released by aggregates. Contribution to the alkalinity increase and AAR development in concrete. Second International Dam World Conference. Lisbon. LNEC. pp. 10.
19. Jozwiak-Niedzwiedzka, D.; Gibas, K.; Glinicki, M.A. (2017) Petrographic identification of reactive minerals in domestic aggregates and their classification according to RILEM and ASTM recommendations, Roads and Bridges – Drogi i Mosty 16, Warsaw, Poland, pp. 223-239.
20. LCPC (1993) Essai de granulat – Détermination des alcalins solubles dans l'eau de chaux. Méthode d'essai n° 37, LCPC, Paris, France. pp. 13.
21. Berube, M.A.; Duchesne, J.; Rivest, M. (1996) Alkali contribution by aggregates to concrete. 10th ICAAR. Melbourne. Australia. pp. 899-906.
22. Berube, M.A.; Fournier, B. (2002-b) Alkalies releasable by aggregates in concrete: significance and methods. Reference Report RILEM/TC-ARP/02/12 distributed at the 2002 meeting. Reykjavik. Iceland. pp. 15.
23. Menéndez, E. (2013) Extraction of alkalis from aggregates. Workshop RILEM/TC-ACS-219. Lisbon. Portugal. Unpublished oral presentation.
24. EN 196-2:2014 Method of testing cement-Part 2: Chemical analysis of cement. CEN, Brussels. pp. 78.
25. Menéndez, E.; Fournier, B.; Santos Silva, A.; Justnes, H. (2015) AAR-8: Determination of alkalis releasable by aggregates in concrete. Draft recommendation RILEM TC 219-ACS. July 2015.
26. Ferraz, A.R.; Fernandes, I.; Soares, D.; Santos Silva, A.; Quinta-Ferreira, M. (2017) Assessment of the alteration of granitic rocks and its influence on alkalis release. WMESS conference. IOP Conference Series: Earth and Environmental Science 95 (2017) 022001. <https://doi.org/10.1088/1755-1315/95/2/022001>.