
Can certain alkali minerals explain the slow reactivity of granitic aggregates in dams?

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ABSTRACT: Swelling processes due to alkali-silica reactions are a major limitation to durability of concrete dams and hydraulic structures. These reactions occur in high humidity environments between the aggregates and the alkaline cement interstitial fluids, resulting in the formation of expansive alkali-silica gels.

The speed, or even the occurrence, of these reactions is quite difficult to predict because it is not related simply to the mineralogical nature of the aggregates. A mineral can even prove to

be stable or unstable in different rocks and the relative reactivity of various minerals is also different from aggregate to aggregate. So, there is controversy about which are the factors (chemical composition, structural type, micro-deformation, ...) that effectively control the alkali reactivity observed in some aggregates.

Besides, there is no consensus about what kind of alkaline minerals are more likely to release alkalis to the interstitial cement solution, and also on the factors that accelerate that solubilisation.

This paper aims to contribute to the ongoing discussion of this topic, and so different granitic aggregates, with sound and altered factions, were subjected to alkaline solubility tests in order to measure the alkalis released and to identify the mineral phases that contribute to alkali media raise.

The results obtained confirm that granitic aggregates release alkalis in alkaline environment, being this release dependent on the degree of alteration of these aggregates. Natural altered aggregates have less capacity to release alkalis than the non-altered aggregates. In the tested granite samples we observe a higher release of potassium, which is attributed to the higher natural alteration of plagioclase in comparison to K-feldspars.

KEYWORDS: ASR, alkalis release, granites, alteration, quantitative evaluation

1. Introduction

Concrete swelling is one of the main degradation mechanisms that affects the hydro concrete structures nowadays. The alkali-silica reactions (ASR) are probably the ones that deserve more concern worldwide. These internal reactions involve an alkaline attack to the siliceous aggregates, being their development rate very dependent on water or humidity supply, which is permanently available in hydraulic structures. The reaction products formed, referred as alkali-silica gels, are able to adsorb water from the surrounding cement paste or from the environment, inducing enough expansive pressure to damage concrete that may compromise the operation and safety of these structures (Soares et al., 2015).

Several dams in Portugal show signs of deterioration due to ASR, but most of these dams started to exhibit signs of degradation only several decades after construction. This situation is not exclusive of Portugal, since other countries presents a similar situation (Curtis, 2000).

To develop ASR in a concrete structure the following prerequisites must be simultaneously fulfilled: presence of alkali reactive minerals in the aggregates, high content of alkalis in concrete and sufficient moisture supply (at least 80 %). Prevention of ASR is therefore intended to eliminate at least one of the three aforementioned requisites. However, in the case of concrete dams some of these conditions may be difficult or impracticable to implement (e.g. reduce the access of moisture or the availability of local non-reactive aggregates).


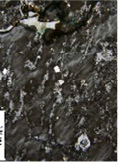
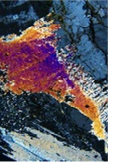
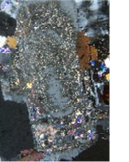
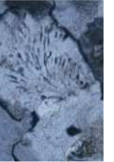
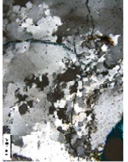
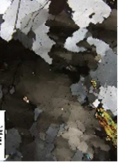
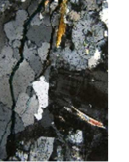
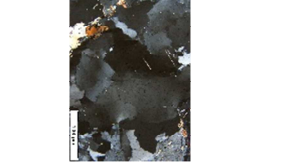
Controlling the alkalinity of the concrete is the preventive measure that is in general recommended to avoid or suppress ASR. Pozzolans or “supplementary cementitious materials” (SCMs), such as low-lime fly ash, silica fume or metakaolin, have demonstrated to be effective in this respect (Thomas, 2011). However, some of these SCMs can supply significant amounts of alkalis to the concrete pore solution therefore modifying the alkali control level of ASR.

Besides the alkalis present in the cementitious materials and cement, some aggregates are supposed to contribute to ASR by releasing alkalis from minerals such as alkali feldspars and mica, despite the fact that alkalis are in stable chemical bounds within the minerals. This subject has been studied by different authors (e.g. Bérubé et al., 2002; Constantiner and Diamond, 2003; Lu et al., 2006) and methods of analysis were suggested in order to determine the content of alkalis that can be released when the aggregates are reacting with strong alkaline solutions, such as sodium and potassium hydroxide (Bérubé and Fournier, 2004; Soares et al., 2015, 2016). Constantiner and Diamond (2003) examined mortars containing low-alkali cement and aggregates with alkaline feldspars and concluded that these minerals can contribute with alkalis and therefore participate in ASR. Granitic aggregates have also been identified as alkalis suppliers being this release dependent on the mineralogy and particle size of the aggregate (Soares et al., 2015).

Granites contain feldspars, quartz and mica as main minerals and are classified as slow reactive as structures with these aggregates can present manifestations of ASR decades after being built. Table 1 presents the features that can be identified by petrographic analysis and which are supposed to contribute to the potential alkali reactivity of these rocks.

The batches of granitic aggregates sold by quarries to concrete manufacturers usually contain rocks with variable degrees of alteration due to the heterogeneities of the rock masses. The objective of the present work is to determine the content of alkalis released by some known Portuguese granites and to identify the mineral phases that contribute to alkali media raise.

Table 1. *Characteristics observed under petrographic microscope of granitic rocks which may contribute to ASR.*

Type	Type of feldspar	Perthite	Presence of micas	Argillization	Myrmekite
Input	Type of alkalis release	Alkalis release	Alkalis release	Alkalis release	Alkalis and silica release
Photo					
Type	Microcrystalline quartz	Undulation extinction	Sub-granulation	Fracture	
Input	Silica release	Silica release	Silica release	Penetration of the interstitial fluids into the aggregate particle	
Photo					

2. Materials and Methods

2.1. Granitic aggregates and samples preparation

Four granitic aggregates identified as GR2, GR23, GR24 and GR29 were selected. For each of the samples selected, two different fractions were tested. One set of samples is composed of sound, not altered rock (N), the other set corresponds to altered granites (A), although with variable degree of alteration. The alteration is identified in these rocks by the dull appearance of the feldspars due to the replacement by clay minerals and by the chloritization of biotite.

These aggregates were previously tested by the accelerated RILEM AAR-4.1 concrete expansion test (RILEM AAR-4.1, 2016), which confirmed their potential reactivity. However, the expansion values obtained are different, namely GR23 and GR29 samples have expansion values of 0.03 % at 15 weeks, whilst GR2 and GR29 have expansions of 0.06 % at same age.

These granites were also characterized by chemical and petrographic analysis. The chemical analysis was performed on a representative sample of aggregate, crushed and grinded to pass a 106 μm sieve. For petrographic analysis, hand samples of different granitic aggregates were selected for production of 30 μm thickness thin-sections.

Finally, to evaluate the alkalis released by aggregates, the granitic samples were crushed and grinded to pass a 150 μm sieve.

2.2. Chemical analysis

The chemical analyses of main oxides were performed by $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ fusion at inductively coupled plasma (ICP).

2.3. Petrographic analysis

Petrographic characterization was performed by analysis of thin-sections under polarizing microscope, coupled with automatic point-counter. This method enables to quantify the relative volume of potentially reactive components to alkalis, as well as the mineral content which may provide the alkalis for the system (e.g. plagioclase, K-feldspars, muscovite and biotite).

The assessment of petrographic alkali reactivity was based on local experience with granitic aggregates, namely on the dimensions of the quartz crystals ($<100\ \mu\text{m}$ = microcrystalline quartz) and according to the classes established by RILEM AAR-1.1 (2016) and by the Portuguese specification LNEC E 461 (2007). Myrmekitic quartz was included in the microcrystalline quartz group and considered as a potentially reactive form of silica (Ramos et al., 2016).

2.4. Alkalis release

The method used to evaluate the alkali content released by the aggregates aims the extraction of Na^+ e K^+ ions in alkaline solutions simulating the interstitial pore solution of concrete (RILEM AAR-0, 2016). Therefore, an amount of representative aggregate sample (100 g) was immersed in a specific volume (400 mL) of alkaline solution at a ratio of 1:4 aggregate/solution. All sample materials were placed into hermetically sealed polyethylene bottles, and conditioned in a chamber at 38 °C and $\text{RH} > 95\%$ (test conditions of RILEM AAR-3). Twice a week, the test containers were gently rolled back for about 10 seconds, and in predefined time intervals (e.g.: 2, 7, 13 and 26 weeks) a sample was taken from the test solution (10 mL). After filtration and acidification, the determination of alkali released content (Na^+ and K^+) of the extraction solutions was performed by atomic absorption spectroscopy (AAS).

Two alkaline solutions were employed: NaOH 0.7M (for the evaluation of K supply) and KOH 0.7M (for the Na supply).

3. Results and Discussion

3.1. Chemical analysis

The results obtained for chemical bulk analysis (Table 2) show quite similar contents in SiO_2 and Al_2O_3 and low contents in Fe_2O_3 and CaO . Regarding the alkalis, all the samples are richer in K_2O than in Na_2O showing a ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ varying from 1.54 to 1.70.

Table 2. Chemical composition of the granites (%).

	GR2 (Ramos, 2013)	GR23	GR24	GR29
SiO_2	72.76	72.66	72.31	72.71
Al_2O_3	14.13	14.04	14.55	14.06
Fe_2O_3	1.58	2.13	1.65	1.95
MnO	0.03	0.03	0.02	0.04
MgO	0.48	0.48	0.38	0.29
CaO	0.57	0.85	0.64	0.74
Na_2O	2.81	3.00	2.99	3.26
K_2O	4.43	4.96	5.19	5.08
$\text{Na}_2\text{O}_{\text{eq.}}$	5.72	6.26	6.41	6.60
TiO_2	0.21	0.26	0.26	0.17
P_2O_5	0.33	0.3	0.44	0.23
LOI	1.63	1.05	1.21	0.55
Total	98.98	99.77	99.64	99.09

Considering the sodium equivalent content of the granites tested, with the individual values ranging from 5.72 % (GR2) to 6.60 % (GR29), it can be said that the potential for alkalis release should be higher in GR29, assuming that higher total alkalis content was related to a higher alkalis release.

3.2. Petrographic analysis

The aggregates analysed are mainly fine- to medium-grained two mica granites, composed of quartz, K-feldspar, plagioclase (essentially albite, An_{0-10} , and oligoclase, An_{10-30}), muscovite and biotite, with variable contents of chlorite and other accessory minerals.

Aggregate GR2 is a coarse-grained granite exhibiting hypidiomorphic porphyritic texture with quartz, K-feldspar and plagioclase as main components, biotite and muscovite is much lower content. The rock is intensely deformed with stretched crystals, ribbons, sub-graining and fractures. In GR2-A, K-feldspar, mainly microcline, usually shows signs of alteration. The plagioclase (oligoclase) is more

altered than K-feldspar and the argillization is stronger in the core of the crystals (Figure 1). Biotite lamellar plates are partially to totally replaced by chlorite and muscovite larger crystals are deformed, showing kink-folds and symplectic fringes. There are some crystals of small dimensions of muscovite between the crystals of the main components of the rock, as well as microcrystalline quartz. In the altered fraction these characteristics are more intense, and biotite is almost totally altered to chlorite.

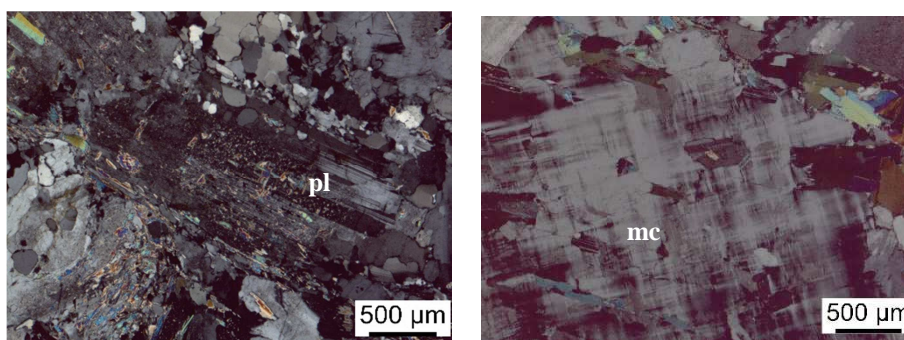


Figure 1. Aggregate GR2: deformation of the rock reflected in sub-graining of the quartz. Plagioclase (pl) is altered, mainly in the core of the zoned crystal and microcline (mc) does not show alteration (Crossed Polarized Light - CPL).

GR23 is fine- to medium-grained granite exhibiting hypidiomorphic porphyritic texture. K-feldspar is composed of microcline and orthoclase in megacrysts containing inclusions of plagioclase. These minerals show alteration, which is more intense in the cores of the plagioclase crystals in the altered fraction of the aggregate (GR23-A). The larger crystals of plagioclase are zoned, with albite in the outer rims and Ca-rich fractions in the cores which show sericitization and crystals of muscovite developed along the cleavage planes (Figure 2). In some crystals also calcite is formed due to the alteration. Myrmekites are quite common. Muscovite larger plates show symplectic fringes. Biotite is altered to chlorite mainly along the cleavage planes.

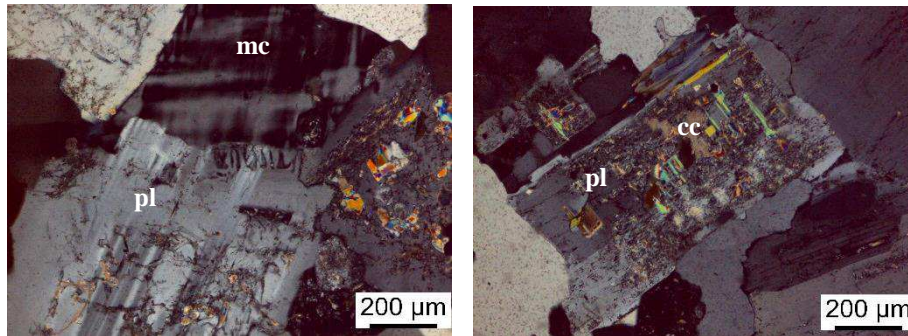


Figure 2. Aggregate GR23-A: crystals of microcline (mc) and plagioclase (pl). Plagioclase is altered to sericite and calcite (cc), mainly in the cores of the crystals (CPL).

GR24 is a fine to medium-grained granite in which plagioclase forms crystals of variable sizes. The more abundant have the size of the crystals of the matrix and correspond to albite, the smaller are mainly oligoclase and occur as inclusions in the K-feldspar crystals. Fraction GR24-A exhibits argillization of the feldspars, which is stronger in the core of the crystals of plagioclase. K-feldspar, mainly microcline and some orthoclase, both perthitic, is also altered although in a lower intensity than plagioclase. Muscovite often shows symplectic fringes, mainly in the larger tabular crystals, but it can also occur as clusters of small crystals disposed in radial layout. Biotite lamellae are partly altered to chlorite. The main characteristic related to deformation of this rock is the presence of strain corridors and a fracturing network often lined by fine-grained quartz (Figure 3). In GR24-A also microcrystalline muscovite is present lining the fractures.

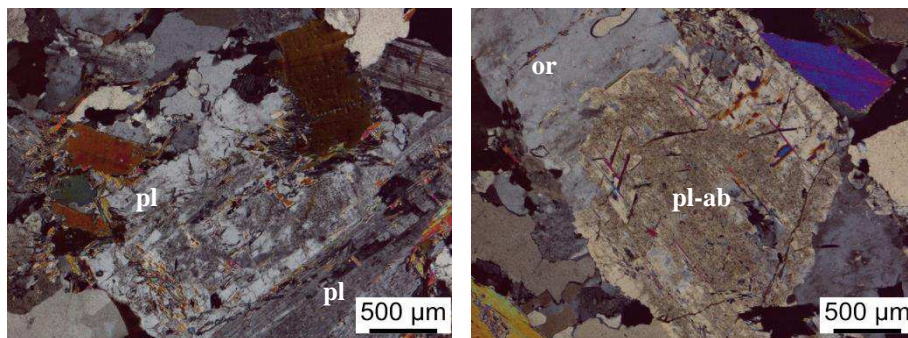


Figure 3. Aggregate GR24-A: crystal of zoned plagioclase (pl). Albitization of K-feldspar (orthoclase - or) crystal and alteration of albite (pl-ab) to clay minerals (CPL).

Aggregate GR29 is medium-grained granite. Perthitic orthoclase, which is the dominant K-feldspar, and microcline form the largest crystals in the rock and show some argillization, mainly in the altered fraction of the rock (GR29-A). There are two types of plagioclase, one occurring as small inclusions in the K-feldspar and mostly composed of oligoclase, and the largest crystals corresponding essentially to albite. These minerals show signs of seritization, which is more intense in the cores of the crystals, although it may affect, with less intensity, the whole crystals (Figure 4). In the altered fraction, crystals of muscovite occur along the cleavage planes of the plagioclase. Muscovite is the most common mica in the aggregate and has irregular boundaries. Biotite, less common, is frequently altered to chlorite.

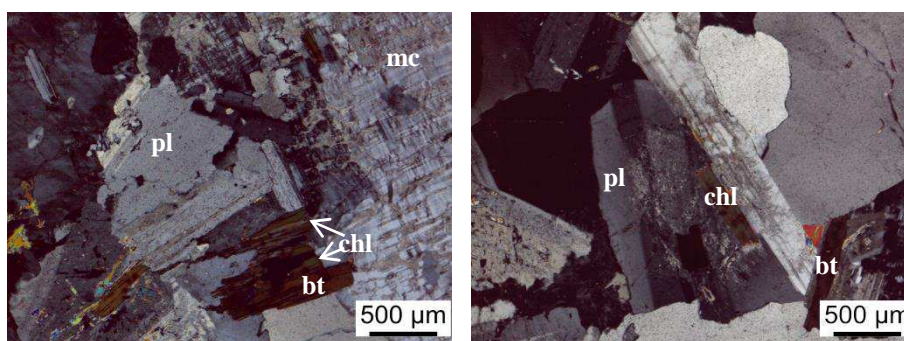


Figure 1. Aggregate GR29: perthitic microcline (mc) and plagioclase (pl) crystals. Biotite (bt) lamellae are partially replaced by chlorite (chl) (CPL).

Table 3 presents the mineral composition obtained by point-counting.

Table 3. Mineral composition of the granites obtained by point counting.

	GR2 (Ramos, 2013)	GR23	GR24	GR29
K-feldspar	26.3	29.9	31.4	32.9
Plagioclase	26.1	19.5	20.3	24.6
Quartz	34.2	34.4	33.7	32.7
Muscovite	9.7	7.5	10.0	4.0
Biotite + chlorite	3.1	8.1	4.1	5.7
Accessory minerals	0.6	0.6	0.6	0.3

Quartz is the main component of three of the samples (exception is GR29) and K-feldspar (26.3 to 32.9 %) is more abundant than plagioclase (19.5 to 26.1 %). The content of muscovite is higher than biotite + chlorite in GR2 and GR24 with a ratio of 3.1 and 2.4, respectively. Biotite + chlorite are slightly more abundant in GR23 and GR29.

3.3. Alkalis release

Figure 5 presents the results obtained for the Na₂O and K₂O contents released (mass %) during 26 weeks by the tested granites.

The analysis of these charts shows that for all the samples the altered fractions (A) release less alkalis than the non-altered fractions (N), although in the altered fractions there are more cracks and voids allowing the access of the pore fluids to the interior of the aggregate particles. In the altered fractions, feldspars have lost K⁺ and Na⁺ due to the alteration to clay minerals, which means that in these fractions there is lower alkalis content left to be leached during the tests. From these results, it can be concluded that the natural mechanisms of alteration have a stronger role in the releasable alkalis than the fact of the facilitated access of the fluids and the larger specific area available to the alkaline attack due to cracking.

It can also be verified that the content of K₂O released is higher than Na₂O in all the samples. This fact can be explained by the higher content in potassium in all the samples but, mainly, due to the cause above explained. In fact, the petrographic analysis allows to identify the alteration of the feldspars, which is in all the cases stronger for the plagioclase crystals than for the K-feldspars. Alteration in the cores of plagioclase crystals is visible even in the non-altered fractions. Therefore, there will be less Na available than K.

Also, the results of alkalis released show a good correlation with the K-feldspar content obtained by petrographic point counting. The granites GR24 and GR29 are the ones with higher Na₂O_{eq.} released (Figure 6), and the same that have the higher content in K-feldspar (Table 3).

Regarding the content in mica minerals obtained by petrographic analysis, it seems that the content on these minerals is not affecting much the results of alkalis released. For example GR23 has 7.5 % of muscovite, against 4.0 % for GR29, although the last one presented a higher release of alkalis.

Taking into consideration these facts, it can be said that the granites behaviour in the accelerated expansion tests should not be attributed only to the reactive silica constituents but also to the degree of alteration of the feldspars. The natural alteration that is present in some alkaline minerals of the granitic rocks, in this particular the plagioclase and the K-feldspars, can perhaps explain the slow reactivity of these rocks in hydro structures. Besides, when considering the degree of alkalis release it seems to depend on the alteration state of the rock, and can justify also the slow alkali-reactive behaviour of the granites.

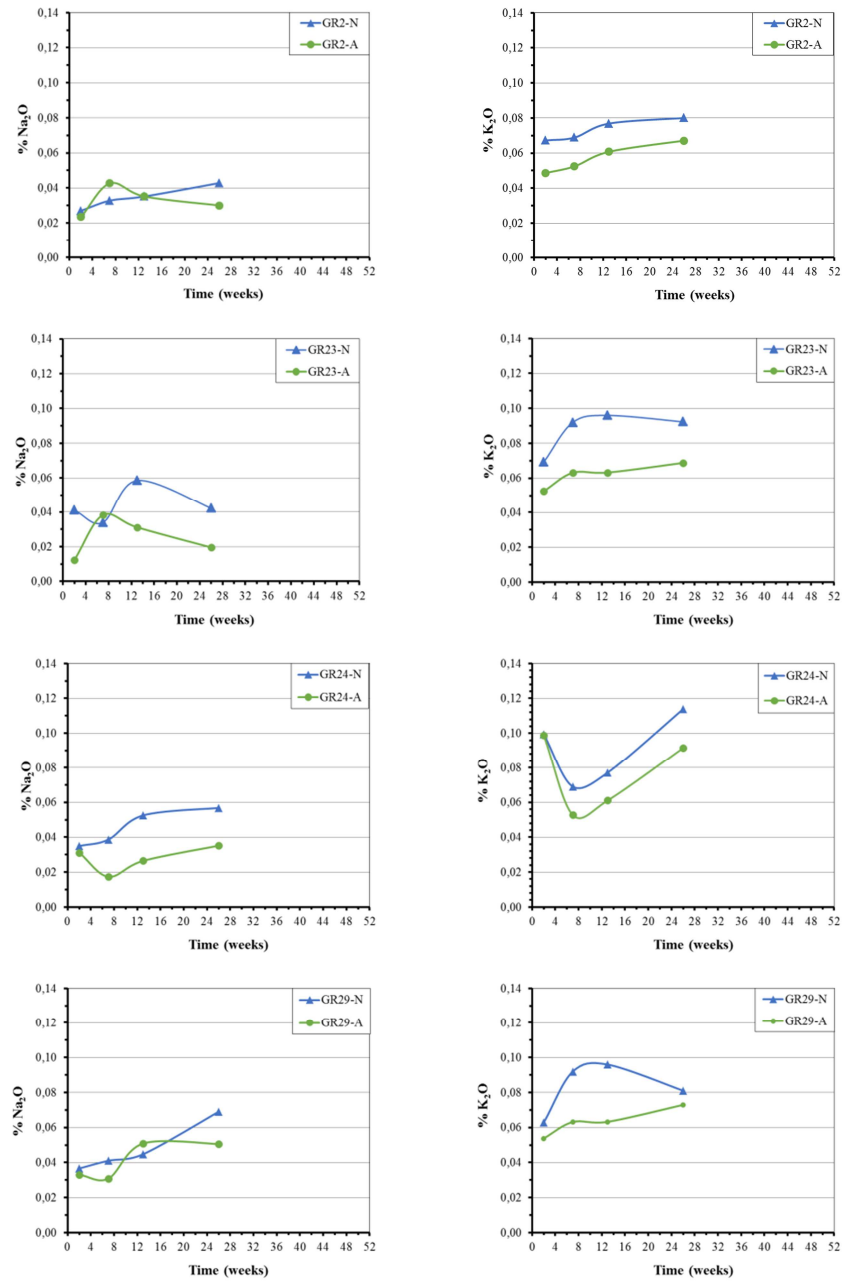


Figure 5. Na_2O and K_2O (%) contents released with time by granitic aggregates in alkaline solutions (Notation: N - not altered rock; A – altered rock).

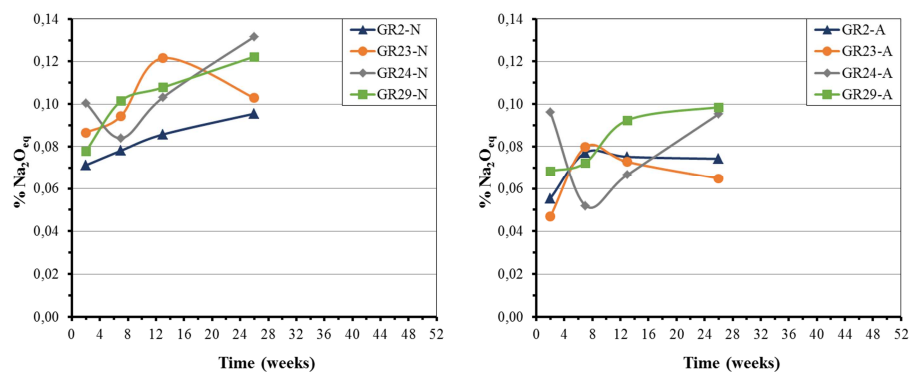


Figure 6. Na_2O_{eq} (%) content released with time by granitic aggregates in alkaline solutions (Notation: N - not altered rock; A - altered rock).

4. Conclusions

The work carried out is ongoing but confirms that granitic aggregates containing alkaline minerals in their composition are susceptible to release alkalis in alkaline environment. This release is dependent on the degree of alteration of these rocks. It has been found that natural altered aggregates, namely in terms of the dull appearance of the feldspars due to the replacement by clay minerals and by the chloritization of biotite, have less capacity to release alkalis than the non-altered aggregates. Also, for the four granites tested higher K extraction has been found, which is attributed to the higher natural alteration of plagioclase in comparison to K-feldspars.

Future studies should be conducted to confirm these findings in tests with different aggregates, and at longer extraction ages.

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