

EVALUATION OF GRANITIC AGGREGATES BEHAVIOR IN RELATION WITH THE ALKALINE EXTRACTION AND COMPOSITIONAL CHANGE IN THEIR PHASES

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Abstract

Granites can release alkalis and influence ASR, especially in structures in permanent contact with water, as dams. Alkali release from aggregates can be tested using high pH solutions. Usually, these solutions use a single ion (calcium) or two ions (calcium and potassium or sodium). Although, pore solution are composed by ion´s mix (calcium, potassium and sodium).

In the present work change in alkali phases and alkali release of granitic long time exposed to six extraction solutions has been analyzed in comparison with the same aggregates from a dam affected by ASR in some areas. Granite has been extracted from the quarry used to manufacture the concrete dam. Microstructural and compositional analyses of the aggregates have made using BSE-EDX. Alkali release from alkaline feldspars has been detected, mainly in Na-feldspars, but no significant variation in Al/Si ratio is produced in feldspars, showing no alteration in siliceous phases of alkaline feldspar.

Keywords: alkali release, granite, alkaline feldspars, compositional changes, extraction solutions

1 INTRODUCTION

The ASR development in concrete is associated mainly with the alkalis provided by the cement. Although, other components may provide alkalis to the concrete. Some works raised the release of alkalis from feldspar exposed to $\text{Ca}(\text{OH})_2$ solutions at 95°C with reaction of K-feldspar to form hydrogarnet [1]. And, also that weathered material and sodium and calcium feldspars were less resistant to alkali attack than fresh feldspar. Kawabata et al. indicate that alkali release from aggregate in Japan promote risks of ASR [2]. Also, several authors indicate that alkaline feldspars can supply significant amount of alkalis when are exposed to alkaline solutions [3]-[8]. Others works indicate that micas can release alkalis and promote the ASR [9],[6],[8]. Although, some works found only indirect evidences that alkali released increase ASR in field concretes [6],[10],[8].

Some works found evidences of ASR in concretes, due to the migration of alkalis from feldspars, with dawsonite y nepheline-bearing aggregates [11],[12]. Also, other work shown that Na-feldspar and K-feldspars in alaskite aggregate could enhance the AAR expansion and concluded that feldspar-bearing aggregates can induce an increase of expansion in concrete, especially when low alkali cement are using, due to incorporation of alkalis to pore solution [8]. Other observed that K-feldspar contributing to form ASR products [13].

However, other authors are critical in relation with the role of alkalis migration from aggregates. Some suggest the need to consider alkali release from aggregates efficiency in comparison with alkalis released form cement. Since, alkalis released by the cement are produced in conditions of high presence of CaO avoid that Na^+ and K^+ are fixed [14],[8]. Also, suggests that in case of K-feldspars potassium is release, but Al_2O_3 y SiO_2 remains. These acid oxides need combined with CaO or K_2O and Na_2O to form products with high pH [14].

The release of alkali from aggregates contributes to increase in OH^- ions and pH in the pore solution, causing its variation. However, greatest contribution of alkalis to the pore solution is due to the contribution of cement, while this contribution depends on the type of cement used [13],[15]. Dachensen y Berubé [16]

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indicate that the incorporation of alkalis to the hydration products are about 0.43% with a OPC, while in cements with 40% of fly ashes the percentage of alkalis incorporated to hydration products is significant higher, between 1,35% and 1,41%. In general, the analysis of potential extraction of alkalis from aggregates is done with alkaline solutions with a single ion ($\text{Ca}(\text{OH})_2$ saturated) or mixtures of two alkaline ions (NaOH and $\text{Ca}(\text{OH})_2$ sat. or KOH and $\text{Ca}(\text{OH})_2$ sat.). It is difficult to produce the decomposition of feldspars in solutions of KOH , NaOH y $\text{Ca}(\text{OH})_2$ saturated [8],[7]. In these cases the increase of alkali in solution or in the porous phase is due to ion exchange of Na and K with Ca. Also, some of the alkalis extracted are added to the reaction products, although the type of products formed depends on the composition of the solution and the amount of Ca [17]. According the experimentation of [8], Na-feldspars of the alaskite are stables in alkaline solutions of KOH 0,5N and $\text{Ca}(\text{OH})_2$ sat. While, K-feldspars in the same solutions causing the decrease of Al/Si ratio and generate the formation of reaction products. However, pore solution in concrete is a mixture of alkali ions that produce the high pH. Several authors propose different solutions with high pH and alkaline mixture of ions to simulate the phase composition of concrete pore [18]-[20]. It is found that these solutions consist of various ions are more suitable to evaluate the behavior of aggregates, since they look more to the concrete pore solution. And, they are equally effective for evaluating alkalis release from aggregates [17].

This work analyzes the behavior of a granitic aggregate tested with six alkaline solutions, with different mixtures of alkalis and high pH [17]. Potential alkali extraction and modification of the composition of alkaline feldspars from the aggregate is analyzed. These granite aggregates have been extracted from the quarry used for the manufacture of concrete from a dam that shown alteration by ASR. The dam is 55 years old. This dam has been diagnosed ASR damage concentrated in one of the higher margins, while other areas shown no incidence of the reaction or very little reaction. Therefore, is important to analyze the potential influence of migration of alkalis from the aggregates in relation with the heterogeneity of ASR damage in the dam [21]-[23]. Samples of aggregates extracted in different areas of the quarry are studied. And, we evaluate the behavior of the aggregates tested in alkaline extraction solutions compared with granite aggregate in the concrete areas of the dam with and without ASR.

2 MATERIALS AND METHODS

2.1 Granitic rock from quarry

Four cores 6 meters deep were extracted from the quarry so that the material obtained would be representative of it. Granitic samples to be tested were selected in function of their chemical composition, determined by X-ray Fluorescence (XRF), and their mineralogy, determined by petrographyc analysis by thing section. Three granitic samples were selected to be tested with different alkaline extraction solutions. The denomination of the granitic aggregate samples are:

- *S1-C3*: Aggregate from probe 1. Deep from the quarry surface 6 meters. Without apparent alteration.
- *S2-C3*: Aggregate from probe 2. Deep 2 meters. Slight weathering and diaclasation.
- *S2-C3*: Aggregate from probe 2. Deep from the quarry surface 6 meters. Without apparent alteration.

The granitic rock can be considering as potential reactive, according ASTM C227 and ASTM C1260 standards [24],[25], with slow reactivity. The expansion with ASTM C227 test is 0.01% at 90 days and 0.17% at 180 days of test, and 0.10% at 14 days and 0.21% at 28 days according ASTM C1260 test

X-ray fluorescence (XRF)

Representative samples of aggregates have been taken to analyze the chemical composition by X-ray Fluorescence using an equipment S8 Tiger Bruker. LOI was determined gravimetrically by weighing before and after ignition at 1 000 °C and Na_2O , K_2O , MgO , CaO , MnO , Al_2O_3 , Fe_2O_3 , TiO_2 , SiO_2 , P_2O_5 , SO_3 , Rb_2O , Cr_2O_3 and MnO were analyzed by XRF. The chemical composition of each aggregate sample is shown in Table 1. Chemical composition is quite similar between the different aggregate samples. But, we can remark the presence of 0.23% of sulphur in sample S1C3. On the other hand, the average of alkalis that are between 4.33 and 4.53% in K_2O and 2.91 and 2.55% in Na_2O .

Petrography

The quarry is sited 300 meters from failure of Laza [26], with dextral displacement touching the right stirrup, which makes the aggregate affected by the ductile shear failure [27]. Petrography composition of the aggregates is a granite, oriented, with predominance of plagioclases over potassium feldspars (granodiorite), according ASTM C294, plutonic rocks (16.1) [28]. The modal composition of the aggregates is shown in Table 2. The mineral phases have a specific crystallochemistry [29]. According with these characteristics this granodiorite is considered as reactive aggregate, due to the idiomorphic texture with fenocrystals of plagioclases (>3 mm) that favors the reactivity of the alkaline phases (big grains are more susceptible to development fissures y deformations), being altered to sericite and illite phases [30]. In Figure 1 texture of K-feldspars, Na-feldspar and quartz are shown. Petrologically is a Hercynian granodiorite calc-alkaline oriented with two micas [26].

Porosimetry by mercury intrusion

Total porosity of the three samples was determined by mercury intrusion porosimetry with equipment Micromeritics Autopore IV. Conditions of measurement are: penetrometer volume is 3.50 ml, maximum volume of intrusion is 0.5 ml/g and range of pressure between 0.50 and 33 000 psi. The total porosity of aggregate samples S1C3, S2C1 and S2C3 are 0.86%, 0.83% and 0.90%, respectively, that is very low. Also, have high density, the average bulk density are 2.60 g/mL. Most of the pores have a diameter centered on 0.2 μm . The granodiorite rock is very dense, with low porosity and small size of pores.

Backscattering electron microscopy and energy dispersive X-ray (BSE-EDX)

Granitic aggregates were analyzed by BSE-EDX identifying the main components and the distribution of its analyzing the elemental mapping associated with the images. Microscopic analysis have made with a microscopy JEOL 5400 and with a microanalysis OXFORD Link.

In the microstructural analysis different phases are observed that correspond to Na-feldspars, K-feldspars and quartz. However some other minority compounds are observed corresponding to calcium phosphates (apatite) and ferromagnesian phyllosilicates minerals. In Figure 2 a BSE image of the alkaline feldspars is shown with Na-feldspars and K-feldspars of the granodiorite. The potential change in composition of the alkaline feldspars is analyzed by EDX microanalysis after their exposition to extraction solutions. Were observed and analyzed by BSE-EDX the three aggregate samples in each extraction solution and also a reference from each of them. A minimum of ten EDX analysis were taken from each sample and each type of feldspar to obtain an average value of the different atomic elements present in the aggregates. The initial composition (reference) is compared later with the composition at the end of the extraction tests.

2.2 Concrete samples from dam

Samples of the concrete dam were analyzed to compare their composition with the composition of alkali feldspars before and after the alkaline extraction test. In the dam there is an area mainly affected by ASR, that it is located in the upper right side [21]-[23]. Some concrete samples were taken from the ASR affected concrete and some other from without affection, to analyze the composition of alkaline feldspars. The interior part of the coarse aggregates are considered as reference, because due to the low porosity of the granite aggregates we consider that the pore solution has not penetrated more than 3 or 4 centimeters in depth. Alkali feldspars composition has been analyzed by EDX microanalysis interior zones of the aggregate and exterior zones close to the cement paste. The interior zones are considered as reference and the exterior zones are exposed to the pore solution. Samples taken from concrete affected by ASR are nominated as C0 and samples taken from concrete without alteration are nominated as C3. All the samples are taken at least 3 meters in deep from the central part of the structure to avoid carbonation.

2.3 Alkaline extraction test

Three types of granodiorite aggregates were tested (S1-C3, S2-C1 y S2C3). Cubes of aggregates were cut with dimensions 30x30x30 mm. Also, the analysis face was prepared by mirror polished. At the end of the

polish the samples were cleaned in an ultrasonic bath with water to remove polish material and dust. The polish face (to be analyzed by BSE-EDX) is sited perpendicular to the bottom part of the recipient to avoid accumulation of material over it. The test cubes are completely immersed in the test solution with a relationship 2:1 solid to liquid in polyethylene recipients, and were closed hermetic to avoid evaporation.

The temperature of test was 40°C and the samples were tested by 750 days. The high exposition time and the exposition surface of the aggregates permits to simulate the action of concrete pore solution in contact for long time with aggregates like in the concrete dam. Six alkaline extraction solutions with high pH were used. These solutions permits to analyze the action of single ions and combination of it's, and evaluate the influence of these mixes. The ion concentrations permit to obtain high pH values similar to the concrete pore solutions [18]-[20]. In Table 3 is shown the composition of the different test solutions and the pH value before and after the test period. At the end of the test the samples were extracted to the solutions and cleaned with a spray of desionized to eliminate rest of the solutions or deposits. Later the samples were dried with air and were prepared to be analyzed by BSE-EDX.

3 RESULTS

3.1 Analysis of alkaline feldspars exposed to extraction solutions

In general a pH decrease is observed in all solutions except in D1 (1M NaOH) that shown a pH increase. The pH decrease is associated with the need to maintain the ionic equilibrium in the liquid phase and the electroneutrality of it. Some ions can migrate from the aggregates and ions from the solutions can combine with the solid and the pHs vary to equilibrate these processes Mio.

The polish aggregate surfaces were analyzed by BSE-EDX before and after the test with alkaline extraction solutions. In each case, at least ten EDX microanalyses were taken from the Na-feldspars and from de K-feldspar in order to have an average composition of them. The main elements were determined by percentage, sodium, potassium, aluminum, silicon and calcium. Also, the Al/Si ratio was determined to evaluate the potential migration of siliceous phases to the extraction solution. In Table 4 the average elemental composition (% oxides) of alkaline feldspars are shown for each simple and for each extraction solution, and Al/Si ratio (atomic %).

The values of the Al/Si ratio in alkaline feldspars remain practically constant with respect to the initial stage in all cases. This indicate that there no alteration in the siliceous phases of the alkaline feldspars. Although, this granodiorite is qualified as reactive and it was observe the formation of ASR reaction products. Due to this the formation of siliceous gels of ASR are associated with the alteration of deformed quartz of the granodiorite. With respect to the calcium no significant variations are observed. Only a slight increase of calcium in the alkaline feldspars is observed with extraction D4, D5 and D6 that contain mixes of alkaline ions and lime saturated. This slight increase of calcium can be due to an ionic interchange with sodium or potassium or to equilibrate the migration of some of these ions. On the other hand, a release of alkalis (sodium and potassium) is observed in general with respect to the initial stage. It is observe that proportionally the higher migration is produced in the minority ion in each of the alkali feldspars, sodium in K-feldspar and potassium in Na-feldspar. In Figure 3 is shown the variation of percentage of Na₂O and K₂O with respect to the initial stage for Na-feldspar and K-feldspar, and the release of Na₂O_{eq} for each granodiorite sample. Also, it is observed that the Na-feldspars have more migration of alkalis to the test solution. With respect to the extraction solutions it is observed that solution D1 (1M NaOH) don't have migration in Na-feldspars and there are an increase of sodium in these feldspars. The behaviour of the solutions D2 (1M KOH), D4 (0,2M NaOH + Ca(OH)₂ Sat.) and D5 (0,5M KOH + Ca(OH)₂ Sat.) has variation with the sample, but in general there is more extraction of sodium. On the other hand the most effective extraction solutions are D3 (Ca(OH)₂ Sat.) and D6 (0,1M NaOH + 0,6M KOH + Ca(OH)₂ Sat.). With these solutions alkali release is observed in all cases. With D3 extraction solution an ionic interchange (Na-Ca or K-Ca) can be produced, while D6 extraction solution is more similar to the pore solution and more representative of the concrete situation. And, also D6 extraction solution is the most effective to extract the alkalis from this aggregate.

3.2 Analysis of alkaline feldspars in the concrete dam

Aggregates from concrete dam were analyzed by BSE-EDX. These aggregates are in contact with the pore solution for more than fifty years. Concrete samples from areas with alteration by ASR and without alteration are analyzed. In the concrete affected by ASR reaction products have been observed, mainly gels (with high concentration in silicon and calcium) and needle like crystals (with high concentration in sodium and less silicon). In Figure 4 an aggregate with Na-feldspar and K-feldspar is observed. In the interface with cement paste there are vitreous gel, formed close to the K-feldspar, and needle like crystals, formed close to the Na-feldspar. Different particles of alkaline feldspar from the concrete areas affected or not by ASR are analyzed by EDX microanalysis. And, also the Al/Si ratio has been calculated. The average compositions of these analyses are shown in Table 5, comparing these results with the initial stage. There no significant variation in the Al/Si ratio, as has been observed in aggregates tested in extraction solutions. This indicate that there no alteration of the siliceous phases of the alkali feldspars. On the other hand, some migration of alkalis from the aggregates has been observed, mainly in K-feldspars. The average variation of alkalis with respect to the reference area of the aggregates is shown in Figure 3 (expressed as %Na₂O and %K₂O). And, also the extraction of Na₂O_{eq} for Na-feldspars and K-feldspars is shown in this Figure 3.

4 DISCUSSION

The petrography analysis of the granodiorite shown more than a 20% of deformed quartz, with extinction angles >15% that confirm the reactivity of this phase [32]. This justified the appearance of siliceous gels in concrete dam. The alkaline feldspars have an idiomorphic textures that promote the reactivity of the alkaline phases, due to a potential formation of fissures and deformations [30]. It is observe some extraction of alkalis from plagioclase and K-feldspars in long time tests.

This granodiorite have not variations of Al/Si ratio in any case. Although, in aggregates as nepheline decrease in Al/Si ratio and reaction products formation is observed when are tested with a solution 0.1 mol/l KOH A2. The constancy of Al/Si ratio permits to analyze the migration of alkalis to the test solution or to the concrete. Maximum value of alkalis release observed is around 2.5% (express as %Na₂O_{eq}). This value is similar to others granites and granitic gneiss, but much smaller than others aggregates as siliceous sandstone (Potsdam) y dolostone limestone (Kingston) that have values higher that 20% of extraction of Na₂O_{eq} A1. The higher migration is observed in Na-feldspars due to the instability of plagioclase. Moreover it is noteworthy that always the minority alkali ion have the relatively high migration. This is due to that feldspars are unmixing solutions and promote that the minority ions are going out, because the net is distorted. The migration of minority alkaline ions is more evidence with sodium ion, due to that it ionic radius (0.95Å) permits it substitution by Ca (with ionic radius 0.99Å), while the ionic radius of potassium is much higher (1.33Å). Due to the higher ionic radius is more difficult substituting potassium than sodium and stabilize it crystalline net [34]-[36].

With relation to the extraction solution the more efficiencies are D3 (Ca(OH)₂ sat) y D6 (Na-K-Ca) that extract alkalis in all samples tested and in K-feldspars and Na-feldspars. The extraction solution D6 is the most adequate to test alkali release of aggregates because it composition is similar to the pore solution and permits to reduce the duration of test [17]. Although, the extraction solution D3 shown results closer to the field concrete and it is more common used. Duyou Lu found that this solution is more effective than the distilled water [37]. But other authors consider that lime saturated solutions produce an ionic interchange [38]. On the other hand, some authors consider that it is difficult to dissolve alkalis come from feldspars [7],[8]. But others works have proved the alkalis extraction from feldspars analyzing the pore solution of mortars [4]. In the present work the migration of alkalis from feldspars has been observed in field concrete dam, after more than fifty years of exposition to pore solution.

The analysis of the concrete dam in zones affected and none affected by ASR permits corroborate the alkali migration of alkalis from alkaline feldspars and a certain influence in the ASR development. The migration of alkalis from aggregates of the field concrete is, although more moderate that from alkalis tested with alkaline extraction solutions (D3 and D6) for long time. The difference between alkali migration in

concrete dam with ASR and without is more significant in Na-feldspars than in K-feldspars. This is due to the higher instability of plagioclases that has been also observed in the accelerated tests with extraction solutions. The characteristics of this granodiorite can promote the generation of seed point that favors the microcracking and the water penetration and cleaning of soluble phases, as portlandite, that is a common phenomena in concretes made with granitic rocks [39].

On the other hand, the migration of sodium from the plagioclase produces a preferential growth of needle like crystals (rich in sodium) in some paste aggregate interface. While in others zones it is observe the presence of siliceous gels. The silicon came from the quartz particles that have undulate extinction and a crystalline net high deformed. But the difference between alkali migration in zones with ASR and without in concrete dam may be insufficient to justified the different behavior of the concrete with the time. And, special analysis on the cement phase shall be considered.

5 CONCLUSIONS

In the alkali feldspars of the granodiorite alkali release is produced, but there aren't changes in Al/Si ratio. This indicates that siliceous gels found in concrete dam came from the deformed quartz.

Alkalis release is observed in feldspars. There is a preferential release of minority alkali element in each feldspar, which is Na in K-feldspar and K in Na-feldspar. This is associated with the stability of the crystalline nets of the feldspar. Sodium migration occurs more easily for their ionic radius similar to the calcium.

In accelerated test the higher extraction of total alkalis is produced in Na-feldspar. This is due to the instability of the plagioclase.

The most efficiency extraction solutions are D3 (Ca(OH)₂ sat.) and D6 (0,1M NaOH + 0,6M KOH + Ca(OH)₂ Sat.). The D6 extraction solution is more representative of pore solution and extracts more alkalis than the rest of solutions. This can overestimate the potential extraction of alkalis, but on the side of safety.

In the concrete of the dam the higher migration of alkalis from feldspar is observed in the zone with alterations by ASR. Although there are no significant differences between the areas with and without ASR. Formation of needle like crystals, with a high content of sodium, and siliceous gels are observed in concrete affected by ASR. The products rich in sodium are formed close to the sodium feldspar possibly by the influence of these. Although, the siliceous gels are formed by the alteration of the deformed quartz.

Also other factors different of the alkalis migration from feldspars as cement composition shall be taken into account to justify the differences between areas with and without ASR in the dam.

6 ACKNOWLEDGEMENT

This work has been development under the Project HOREX, leader by Iberdrola and co-funded by Centre for the Technological and Industrial Development (CDTI) under Project IDI-20070472.

7 REFERENCES

- [1]. Van Aardt, J.H.P., Visser, S. (1997): Formation of hydrogarnets: Calcium hydroxide attack on clays and feldspars. *Cement and Concrete Research*. (7): 39-44
- [2]. Y. Kawabata1, K. Yamada, H. Matsushita (2008): Alkali-silica reactivity and expansion of mortar incorporating glassy andesite in alkaline solution. 13th ICAAR Conference Proceedings: Ed. M.A.T.M. Brockmans & B.J. Wigum, Trondheim, Norway
- [3]. Van Aardt JHP, Visser S (1977): Calcium hydroxide attack on feldspars and clays: possible relevance to cement-aggregate reactions. *Cement and Concrete Research*. 7(6): 643-648
- [4]. Constantíner D, Diamond S (2003): Alkali release from feldspars into pore solutions. *Cem. and Conc. Res*, 33(4): 549-554
- [5]. Bérubé, M.A, Dorion, J.F., Rivest, M, (2000): Distribution of alkalis in concrete structures affected by ASR, contribution by aggregates A. In: Proc. 11th ICAAR Conference Proceedings: Québec City, Canada: 139-148
- [6]. Bérubé, MA, Dorion J.F., Rivest M (2002): Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by ASR. *Conference Proceedings* 32(8):1215-1227
- [7]. Wang, Y, Mo, L, Deng, M, Tang, M (2004): Thermodynamic analysis on decomposition of feldspar mineral under alkali condition. 12th ICAAR Conference Proceedings, Beijing, China: 211-220
- [8]. Wang, Y., Deng M., Tang, M. (2008): Alkali release from aggregate and the effect on AAR expansion. *Materials and Structures*. (41):159-171

- [9]. Grattan-Bellew P.E., Beaudouin J.J. (1980): Effect of phlogopite mica on alkali-aggregate expansion in concrete. *Cement and Concrete Research* 10(6):789–797
- [10]. Shayan, A. (2004): Alkali-aggregate reaction and basalt aggregate. 12th ICAAR, Beijing, China: 1130–1135
- [11]. Gillott, J.E., Rogers C.A. (1994): Alkali-aggregate reaction and internal release of alkalis. *Mag. Concrete Research*. 46(167):99–112
- [12]. Durand, B. (2000): A note about alkali contribution from aggregates in concrete affected by ASR. 11th ICAAR, Québec City, Canada: 169–177
- [13]. Bérubé, M.A., Duchesnea, J., Doriona, J.F., Rivest, M. (2004): A reply to the discussion by Mingshu Tang of the paper “Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity”, *Cement and Concrete Research* (34):903–904
- [14]. Mingshu, T (2004): A discussion of paper “Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity by M.-A. Berube, J. Duchesne, J.F. Dorion and M. Rivest. *Cement and Concrete Research* (34):901
- [15]. Constantiner, D., Diamond, S. (2003): Alkali release from feldspars into pore solutions. *Cem. and Conc. Res.* (33):549– 554
- [16]. Duchesne, J., Bérubé, J.M.A. (1994): Effect of supplementary cementing materials on the composition of cement hydration products, *Advance Cement Based Materials* (2):43–52
- [17]. Menéndez, E., Prendes, N., Aldea, B., Márquez, C. (2011): Analysis of alkalis release by granites using different alkaline solutions and evaluation of their influence on the concrete dam affected by ASR. Sent to publish.
- [18]. Longet, P. Longuet, L Burglen, Zelwer, A. (1973): The Liquid Phase of Hydrated Cement. *Revista Mat. Const.* 676:35-41
- [19]. Moragues, A., Macias, A., Andrade, C. (1987): Equilibria of the chemical composition of the concrete pore solution. Part I: Comparative study of synthetic and extracted solutions, *Cement and Concrete Research*. 17:173-182
- [20]. Moragues, A, Goni, S., Andrade, C. (1990): Chemical characterization of synthetic concrete pore solutions, *Ceram. Trans* 16:57-65
- [21]. Gil, A., Cajete, J. (1991): Study on The Interaction Aggregate-paste in the Concrete at the San Esteban Dam. Dix-septième Congrès des Grands Barrages. Vienne, Commission Internationale des Grands Barrages: 65-88
- [22]. Cajete, J., Delgado, C. (1989) : Regeneración e impermeabilización del hormigón de la Presa de San Esteban, Orense (España). Conferencia sobre Potenciación y Remodelación de Plantas Hidroeléctricas. Zurich: 7-15
- [23]. Menéndez, E., Prendes, N., Márquez, C., Aldea, B. (2011), Analysis of the concrete of San Esteban dam. HOREX Project. Inform 19.346-F6
- [24]. ASTM C 227-10, Standard Test Method for Potential Alkali-Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)
- [25]. ASTM C 1260-07, Standard test method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)
- [26]. Mapa Geológico de España E. 1:50.000 y Memoria explicativa. Hoja Nogueira de Ramuin (1974). Segunda serie. Primera Edición. IGME. D.L. 5.612-1974:37
- [27]. Iglesias Ponde de León, M., Choukroune, P (1980). Shear ones in the Iberian Arc. *Journal of Structural Geology*, 2:63-68
- [28]. ASTM C 294-86. Standard Descriptive Nomenclature for Constituents of natural Mineral Aggregates:167-173
- [29]. Reacción Alcali-Árido en Presas de Hormigón. Ideas Generales y Recomendaciones (1994): Monografías 17. Colegio de Ingenieros de Caminos, Canales y Puertos. Comité Español de Grandes Presas:112
- [30]. Mather, C. (1966): Petrographic examination. Hardened concrete. Symposium on significance of properties of concrete and concrete making materials:125-143
- [31]. Salinas, J.L. (1983): Recomendaciones para una normalización del Estudio Petrológico de los Áridos. Documentos del laboratorio de Carreteras Vicente Escario:105-124
- [32]. Grattan-Bellew, P.E. (1993): Is high undulatory extinction in quartz indicative of alkali-expansivity of granitic aggregates?. Institute for research in Construction National Research Council of Canada. Ottawa, Ontario Canada:434-439
- [33]. Bérubé, M.A., Duchesnea, J. Doriona, J.F. Rivest, M. (2002): Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity. *Cement and Concrete Research* 32: 1215–1227
- [34]. F.J. Turner, J. Verhoogen (1978): *Petrología ígnea y metamórfica*. Ed. Omega. Barcelona
- [35]. V. Araña Saavedra, J. López Ruiz (1974): *Volcanismo. Dinámica y Petrología de sus Productos*, Ed. Istmo, Colegio Universitario. Sta. Cruz de Tenerife
- [36]. N.N. Greenwood (1970): *Cristales iónicos, defectos reticulares y no estequiometría*, Ed. Alhambra, S.A. Madrid
- [37]. 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. *Cement and Concrete Research*: 36:1157–1165
- [38]. Shi, C (2004): A discussion of the paper “Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity” by M.A. Berube, J. Duchesne, J.F. Dorion and M. Rivest, *Cement and Concrete Research* 34: 895
- [39]. Pitts, J. (1987). The role of petrography in the investigation of concrete and its constituents. *Concrete*:5-7

TABLE 1: Chemical composition of aggregates by XRF and LOI by gravimetry.

<i>Compound</i>	<i>S1-C3</i>	<i>S2-C1</i>	<i>S2-C3</i>
SiO ₂ (%)	58,42	60,63	57,50
Al ₂ O ₃ (%)	11,67	12,74	12,68
K ₂ O (%)	4,33	4,49	4,53
Na ₂ O (%)	2,91	3,06	2,55
Fe ₂ O ₃ (%)	1,00	1,03	1,32
CaO (%)	0,58	0,65	0,76
P ₂ O ₅ (%)	0,41	0,38	0,51
MgO (%)	0,27	0,24	0,30
SO ₃ (%)	0,23	---	0,02
TiO ₂ (%)	0,16	0,15	0,24
Rb ₂ O (%)	0,04	0,03	0,04
Cr ₂ O ₃ (%)	0,02	0,03	
MnO (%)	0,01	0,01	0,02
LOI (%)	0,77	0,85	0,71

TABLE 2: Petrography characterization of aggregates by think section.

<i>Minerals</i>	<i>Phases</i>	<i>Range (%)</i>	<i>Characteristics of phases</i>
Essentials	Na feldspars (Plagioclase)	34.7 – 31.6 %	Partly altered rims
	K feldspars	25.2 - 21.6 %	Altered to clays (Chlorites, etc.)
	Quartz	22.4 - 18.5%	Wavy extinction (> 26%)
	Micas (Biotite)	18 - 12%	Pleocroisme. Laminar texture
	Muscovite	9 - 4%	Leafy structure. Green color, partially altered
Accessories	Chlorites	3.3 - 0,7%	High interference colors
	Apatite	0.4 - 0,01%	Pseudo-hexagonal dark points
	Opaque	1.1 – 0.1%	Sulfides phases

TABLE 3: Chemical composition of the extraction solutions and initial and final pH.

<i>Denomination</i>	<i>Chemical composition</i>	<i>Initial pH value</i>	<i>Final pH value</i>
D1	1M NaOH	13,63	13,71
D2	1M KOH	14,13	13,97
D3	Ca(OH) ₂ Sat.	12,07	10,72
D4	0,2M NaOH + Ca(OH) ₂ Sat.	13,81	13,38
D5	0,5M KOH + Ca(OH) ₂ Sat.	13,96	13,9
D6	0,1M NaOH + 0,6M KOH + Ca(OH) ₂ Sat. (*)	13,71	13,53

TABLE 4: Alkaline feldspar composition by EDX and aluminum-silicon ratio in the different extraction solutions.

	Extrac solut.	Na-feldspar							K-feldspar						
		Na ₂ O (%)	K ₂ O (%)	Na ₂ O _{eq} (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	CaO (%)	Al/Si ratio	Na ₂ O (%)	K ₂ O (%)	Na ₂ O _{eq} (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	CaO (%)	Al/Si ratio
Aggregate S1C3	Initial stage	11,20	1,47	12,17	18,50	66,77	0,53	0,28	0,93	16,51	11,79	17,54	64,41	0,26	0,28
	D1	13,12	0,54	13,48	17,92	66,53	0,43	0,28	1,08	16,64	12,03	17,37	64,21	0,18	0,28
	D2	11,42	1,70	12,54	18,19	66,50	0,58	0,28	0,78	16,42	11,58	17,49	63,93	0,20	0,28
	D3	11,15	1,35	12,04	18,12	67,54	0,78	0,27	0,90	15,34	10,99	17,05	64,61	0,39	0,27
	D4	11,59	0,65	12,02	17,69	67,78	0,64	0,27	1,23	16,60	12,15	16,73	64,72	0,40	0,27
	D5	9,95	1,56	10,98	18,37	68,10	0,85	0,28	0,77	16,44	11,59	16,71	64,66	0,64	0,26
	D6	9,80	0,98	10,44	17,84	67,89	0,93	0,27	0,80	16,27	11,51	16,91	64,61	0,76	0,27
Aggregate S2C1	Initial stage	11,67	1,23	12,48	18,67	68,28	0,45	0,28	1,12	16,40	11,91	17,66	64,27	0,18	0,28
	D1	13,28	0,58	13,66	18,09	67,27	0,43	0,28	1,41	15,78	11,79	17,52	64,04	0,15	0,28
	D2	10,64	1,49	11,62	18,30	67,51	0,35	0,28	0,89	17,30	12,27	17,74	63,06	0,16	0,29
	D3	11,26	0,72	11,73	18,42	67,98	0,50	0,28	0,84	16,31	11,57	17,84	64,49	0,20	0,28
	D4	11,72	0,63	12,13	18,60	68,01	0,54	0,28	1,17	16,42	11,97	17,71	64,21	0,16	0,28
	D5	9,73	1,37	10,63	18,14	68,10	0,79	0,27	0,87	16,49	11,72	17,00	64,10	0,46	0,27
	D6	9,31	1,10	10,03	17,89	68,58	0,73	0,27	0,86	16,22	11,53	17,93	63,99	0,63	0,29
Aggregate S2C3	Initial stage	11,82	1,82	13,02	18,75	67,78	0,46	0,28	1,07	16,31	11,80	17,96	64,38	0,33	0,29
	D1	12,43	0,72	12,90	18,62	67,24	0,45	0,28	1,20	14,56	10,78	17,84	64,13	0,29	0,29
	D2	11,39	1,91	12,65	18,65	67,69	0,40	0,28	0,98	16,40	11,77	17,62	63,76	0,26	0,28
	D3	11,72	0,61	12,12	18,14	65,99	0,43	0,28	0,71	16,07	11,28	17,69	64,10	0,40	0,28
	D4	12,45	0,58	12,83	18,70	66,41	0,76	0,29	1,11	16,53	11,99	17,89	63,48	0,49	0,29
	D5	11,76	1,82	12,96	18,17	66,91	0,89	0,28	0,64	15,36	10,75	17,49	64,47	0,46	0,28
	D6	11,65	0,65	12,08	18,72	66,14	0,84	0,29	0,75	15,76	11,12	17,96	64,55	0,55	0,29

TABLE 5: Variation of alkalis with respect to the initial stage in Na-feldspars and K-feldspar

Concrete zone	Extraction solutions	Na-feldspar						K-feldspar					
		Na ₂ O (%)	K ₂ O (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	CaO (%)	Al/Si ratio	Na ₂ O (%)	K ₂ O (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	CaO (%)	Al/Si ratio
C0	Initial stage	12,56	0,33	18,57	67,12	0,14	0,28	0,81	16,10	17,98	63,59	0,00	0,29
	Aggregate close to paste	12,34	0,30	18,45	66,97	0,18	0,28	0,43	16,39	17,93	62,49	0,00	0,29
C3	Initial stage	11,76	0,19	18,95	67,27	0,19	0,29	0,83	17,89	17,66	61,81	0,00	0,29
	Aggregate close to paste	11,58	0,16	19,05	67,98	0,09	0,29	0,49	18,15	17,79	62,55	0,00	0,29

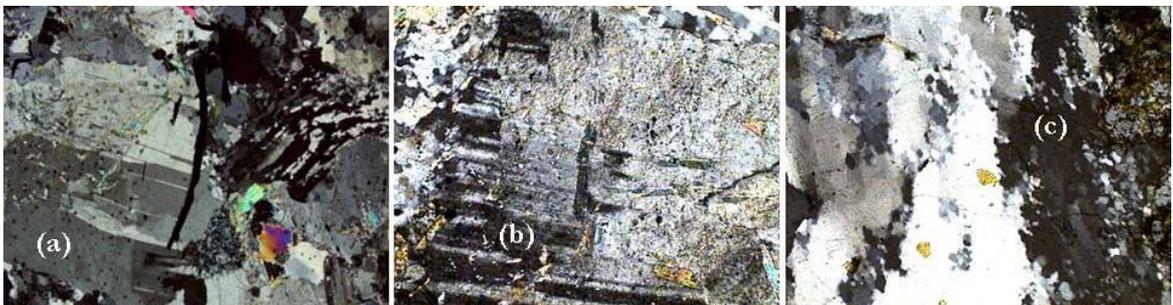


FIGURE 1: Granodiorite petrography analysis, (a) Na feldspars (plagioclase), (b) K feldspars and (c) sarcoid quartz.

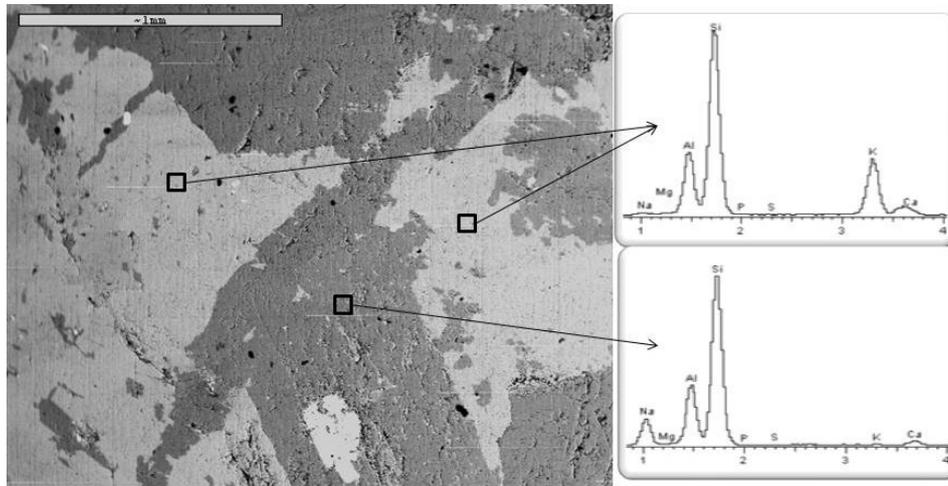


FIGURE 2: Microstructural and microanalytical aspect of alkaline feldspar.

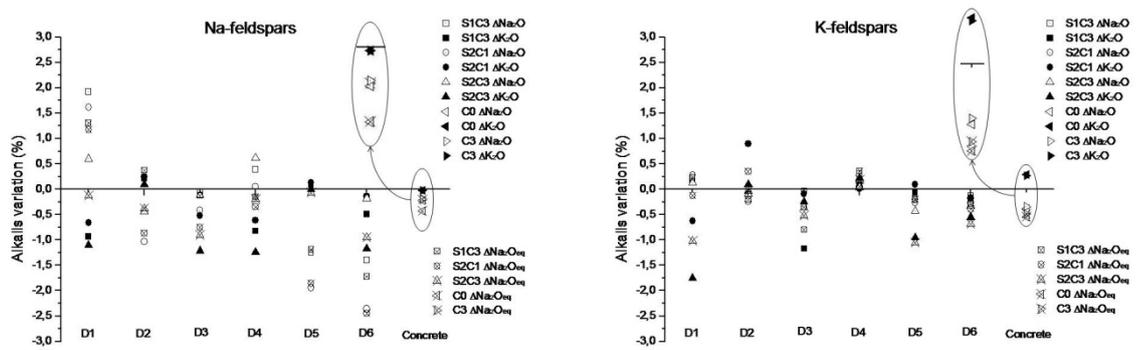


FIGURE 3: Variation of alkalis with respect to initial stage for tested aggregates and for aggregates from the concrete dam. And, $\text{Na}_2\text{O}_{\text{eq}}$ extracted for each sample.

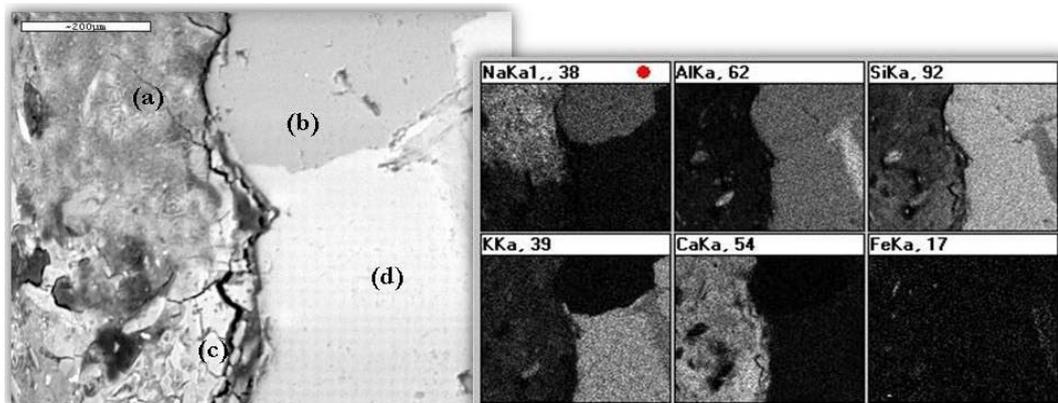


FIGURE 4: Paste-aggregate interface with ASR products, microcrystals (a) and gel (c), close to Na-feldspar (b) and K-feldspar (d).