



Na₂O, K₂O, SiO₂ and Al₂O₃ release from potassic and calcic–sodic feldspars into alkaline solutions

Francisco Locati^{a,*}, Silvina Marfil^b, Edgardo Baldo^a, Pedro Maiza^c

^a CICTERRA - CONICET - UNC, Av. Vélez Sarsfield 1611, (X5016GCA) Córdoba, Argentina

^b Departamento de Geología, Universidad Nacional del Sur, Researcher at CIC de la Provincia de Buenos Aires - INGEOSUR, San Juan 670, (8000) Bahía Blanca, Buenos Aires, Argentina

^c Departamento de Geología, UNS, Researcher at CONICET - INGEOSUR, San Juan 670, (8000) Bahía Blanca, Buenos Aires, Argentina

ARTICLE INFO

Article history:

Received 21 December 2009

Accepted 19 April 2010

Keywords:

C. Alkali release

D. Feldspars

B. Microstructure

D. Alkalies

C. Alkali–aggregate reaction

ABSTRACT

The potential release of elements from potassic and calcic–sodic feldspars into the concrete pore solution was evaluated by ICP-MS using 1 N NaOH and KOH solutions at 80 °C in accordance with the conditions set in the chemical test method. Materials were characterized by petrography, XRD and by XRF analysis. The influence of textural and microstructural characteristics on the leaching process was also analyzed by immersing polished plates of each mineral in 1 N NaOH at 80 °C for 7 days. Optical microscope and SEM observations indicate that microstructural characteristics, such as cleavage zones, twins, grain–grain contact and the finer and less abundant phases in perthites, play a key role in the leaching process under alkaline conditions. Na₂O, K₂O, SiO₂ and Al₂O₃ are supplied by hydrolysis, although the participation of other processes cannot be ruled out.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

A significant percentage of the rocks used as aggregates in concrete come from metamorphic and igneous basement areas containing rocks such as migmatites, gneisses, schists and different types of granitoids. These rocks contain minerals of the feldspar group in varying proportions. They are found worldwide and especially abundant in the “Sierras Pampeanas de Córdoba,” Argentina. Due to their physical and mechanical characteristics, most of them can be used as concrete aggregates. However, feldspars rich in sodium and potassium are a potential source of alkalis that may be released into the concrete pore solution and contribute to trigger the alkali–aggregate reaction (AAR). Predicting the potential alkali supply from different minerals under conditions similar to those of concrete by controlled laboratory tests has aroused great interest and is a problem that has been dealt with by a large number of researchers. Some of the most recent papers are those by Bérubé et al. [1–3], Constantiner and Diamond [4], Leemann and Holzer [5], Lu et al. [6], Shi [7] and Wang et al. [8,9], although this subject has been under study for 50 years.

Constantiner and Diamond [4] suggested that feldspars can contribute alkalis to the concrete pore solution and that if alkali-reacting aggregates contain feldspars, the released alkalis can actively

participate in the AAR. This is highly important since the use of low-alkali cements is one of the requirements to mitigate such reactions. However, this can be ineffective if alkalis are supplied by the minerals in the concrete aggregates.

Although Constantiner [10] suggests that in general alkali-containing aggregates release more sodium than potassium (as a function of temperature and fragment grain size), in the case of feldspars the likelihood of contributing alkali ions depends on their chemical composition. Thus, potassic feldspar seems to contribute K⁺ ions, sodic feldspars (plagioclase) Na⁺ ions [4] and presumably, feldspars such as anorthoclase can contribute both. However, as will be discussed further on, the type of alkali ion released not only depends on the chemical composition of the attacked feldspar.

Alkali release by the aggregates is a complex process and depends on many factors, such as the minerals containing alkalis, the mineral proportion in the aggregate, the type of alkali ion present in the pore solution (from sources other than that of alkali minerals), aggregate grain size, its texture, pore solution volume and its relation to the cement alkali content and pH [8,9].

One of the first authors who referred to alkali release by aggregates was Hansen [11], who suggested that certain alkali-bearing minerals could release alkalis into the liquid phase of concrete when their alkali content was very low. This was corroborated by Wang et al. [8] after many decades, and they determined that alkali contribution from aggregates decreases when high alkali content cements are used.

For instance, if the chemical equilibrium between the cement liquid phase (pore solution) and solid phase (hydration products) is broken, the alkalis can migrate from one phase to the other [12]. AAR

* Corresponding author. UNC - FCEfyN - Cátedra de Geología General, Av. Vélez Sarsfield 1611, (X5016GCA) Córdoba, Argentina. Tel.: +54 351 4344980/4981 (113); fax: +54 351 4334139.

E-mail addresses: flocati@efn.uncor.edu (F. Locati), smarfil@uns.edu.ar (S. Marfil), ebaldo@com.uncor.edu (E. Baldo), pmaiza@uns.edu.ar (P. Maiza).

could be the process that causes such disequilibrium due to consumption of the solution alkalis [11], promoting the release of alkalis from the aggregates.

Both the microstructure and the texture of the aggregate are key factors in dissolution processes. According to Worden et al. [13], Waldron et al. [14], Lee and Parsons [15], and Lee et al. [16–18], cleavage, dislocations and exsolutions in potassic feldspars seem to be the zones where dissolution processes start under acid pH conditions.

In this work the role played by both microstructural and textural arrangements at the initial stage of feldspar dissolution under alkaline conditions is analyzed in order to evaluate the alkali contribution from these minerals to the concrete pore solution, using the conditions prescribed in the chemical test method [19].

2. Feldspar characteristics

Feldspars belong to the tectosilicate group and can be grouped into two series: alkali feldspars (KAlSi_3O_8 – $\text{NaAlSi}_3\text{O}_8$) and plagioclases ($\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$). It is worth noting that the silica content decreases and the aluminum content increases at the calcic member of the plagioclase series.

The alkali feldspar series undergoes complete solid solution only at high temperatures. When the temperature drops, sodium and potassium segregation occurs due to the size requirements of the structure surrounding them, and unmixing of potassic feldspar hosting lamellae of sodic plagioclase (perthite) takes place. Something similar can occur in certain compositional ranges of the plagioclase series also forming very fine unmixing textures with the development of sodium-rich and calcium-rich zones, which usually cannot be observed under the optical microscope [20]. Three types of unmixing in the plagioclase series can be mentioned. *Peristerite intergrowths* that develop in the compositional range An_2 to An_{15} , *Bøggild intergrowths* (between An_{47} and An_{58}) and *Huttenlocher intergrowths* (between An_{60} and An_{85}), although there may be variations in the above-mentioned limits [21,22].

The nature of the interface of the different compositional sectors of a segregation is determined by the crystal structure of the two minerals involved. If they are similar, the crystal lattice matching across the boundary is good, resulting in a low-energy *coherent* interface, where the only distortions are elastic (no broken bonds due to homogeneous deformation).

A less perfect fit results in higher-energy *semicoherent* and *incoherent* interfaces containing dislocations due to inhomogeneous deformation [20,23].

The difference between submicroscopic and coarse perthites is particularly important because it roughly agrees with the differences between *coherent* or *semicoherent* and *noncoherent* perthites, respectively [23].

The intracrystalline deformation level in a perthitic potassic feldspar depends mainly on how fine exsolutions are and their relative amount in each phase. Thus it is observed that fine lamellar perthites are more strongly deformed than coarse perthites, and that the less abundant phases in an intergrowth tend to be more deformed [24].

3. Characterization of the materials studied

Feldspars from the Sierras Pampeanas de Córdoba, Province of Córdoba, Argentina, (samples LSR1, LSR3 and FB) and from Sierra de Maz, Province of La Rioja, Argentina, (sample AN) were used in this study.

LSR1: Potassic feldspar from a pegmatitic body (Fig. 1a). It is composed of 12.84% K_2O and 2.54% Na_2O . The pink mineral shows well-marked cleavage and development of perthites with irregular boundaries approximately 50 to 150 μm in width, which together

cover about 25% of the total surface area of the thin section analyzed (Fig. 2a). The theoretical formula of potassic feldspar is KAlSi_3O_8 .

FB: Potassic feldspar from a pegmatitic body (Fig. 1b). It is composed of 11.64% K_2O and 3.32% Na_2O . The white mineral exhibits well-marked cleavage. It shows development of lamellar lenticular perthites, net boundaries and spindle-like ends that bifurcate and occasionally cross cut each other. They are approximately 500 μm in width and together cover about 29% of the total surface area of the thin section analyzed. Perthites less than $\sim 4 \mu\text{m}$ in width develop in the potassic zone between larger grain size perthites.

LSR3: Saccharoidal aggregate of intergrown crystals of sodic plagioclase from a pegmatitic body (Fig. 1c). It is composed of 10.30% Na_2O and 1.06% CaO . The white mineral exhibits good cleavage. Straight grain boundaries and varying grain sizes (1 to 2 cm) are microscopically observed (Fig. 2c). The theoretical formula of albite is $\text{NaAlSi}_3\text{O}_8$.

AN: Gray to white plagioclase (labradorite) aggregate from anorthosite (Fig. 1d). It is composed of 90% plagioclase (consisting of 9.67% CaO and 5.23% Na_2O) and the remaining 10% consists of garnet, amphibole, biotite, chlorite, muscovite, epidote, calcite, quartz, titanite, apatite and opaque minerals. In previous work [25] on the same kind of rock, compositional ranges Ab_{42-76} An_{24-57} $\text{Or}_{<1.5}$ for plagioclase were reported. They are crystals $\sim 1 \text{ mm}$ in size (although some reach $\sim 6 \text{ mm}$) that form a polygonal mosaic with irregular to straight boundaries (Fig. 2d). Plagioclase individuals exhibit good cleavage and polysynthetic twinning. The theoretical formula of labradorite is $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$.

The four samples show high crystallinity evidenced by the good resolution and intensity of reflections in the XRD diagrams (Fig. 1).

4. Methods

The chemical analyses of major elements of the samples studied were made by XRF [at Activation Laboratories (ACTLABS), Canada]. Complementary mineral identification was performed by XRD, using a Rigaku D-Max III diffractometer with Cu ($\text{K}\alpha$) radiation and a graphite monochromator, at 35 kV and 15 mA, at a scan rate of 3 at 60° 2 θ .

Mineral descriptions were made using an optical microscope with polarized light on thin sections. For the determination of the approximate percentage of sodic plagioclase in perthites within potassic feldspars, ImageJ [26] was used; this software allows working with digitalized images of thin sections and determining percentages by color contrast between the two mineral phases.

In order to evaluate the potential alkali release, the samples were crushed and sieved to pass through a 300 μm mesh (sieve No 50) and retained on 150 μm mesh (sieve No 100). Then they were repetitively washed with water to remove adhered particles and unwanted material of lower specific weight (micas, organic particles, etc.). They were subsequently washed with alcohol, dried in a heater at approximately 105 $^\circ\text{C}$, and the magnetic minerals were extracted with a magnet.

Twenty-five grams of each sample was immersed in a 1 N NaOH solution at 80 $^\circ\text{C}$ for 24 h. At the end of the test time, each solution was filtered, a 10-ml aliquot was taken and made up to 200 ml. The same procedure was applied with a 1 N KOH solution at 80 $^\circ\text{C}$ to determine the sodium released from the different samples following the procedure proposed by Bérubé et al. [1]. Then the concentration of SiO_2 , Al_2O_3 , K_2O , Fe_2O_3 , CaO , MgO , MnO (in the NaOH solution) and Na_2O (in the KOH solution) was determined by ICP-MS (ACTLABS).

Although there are different criteria for the characteristics that the solutions to test alkali release from aggregates [1–3,6–8,27–31] should have, it was decided to use a NaOH solution since it is employed both in the chemical test method [19] and in the mortar bar accelerated test method [32] to assess aggregate reactivity.

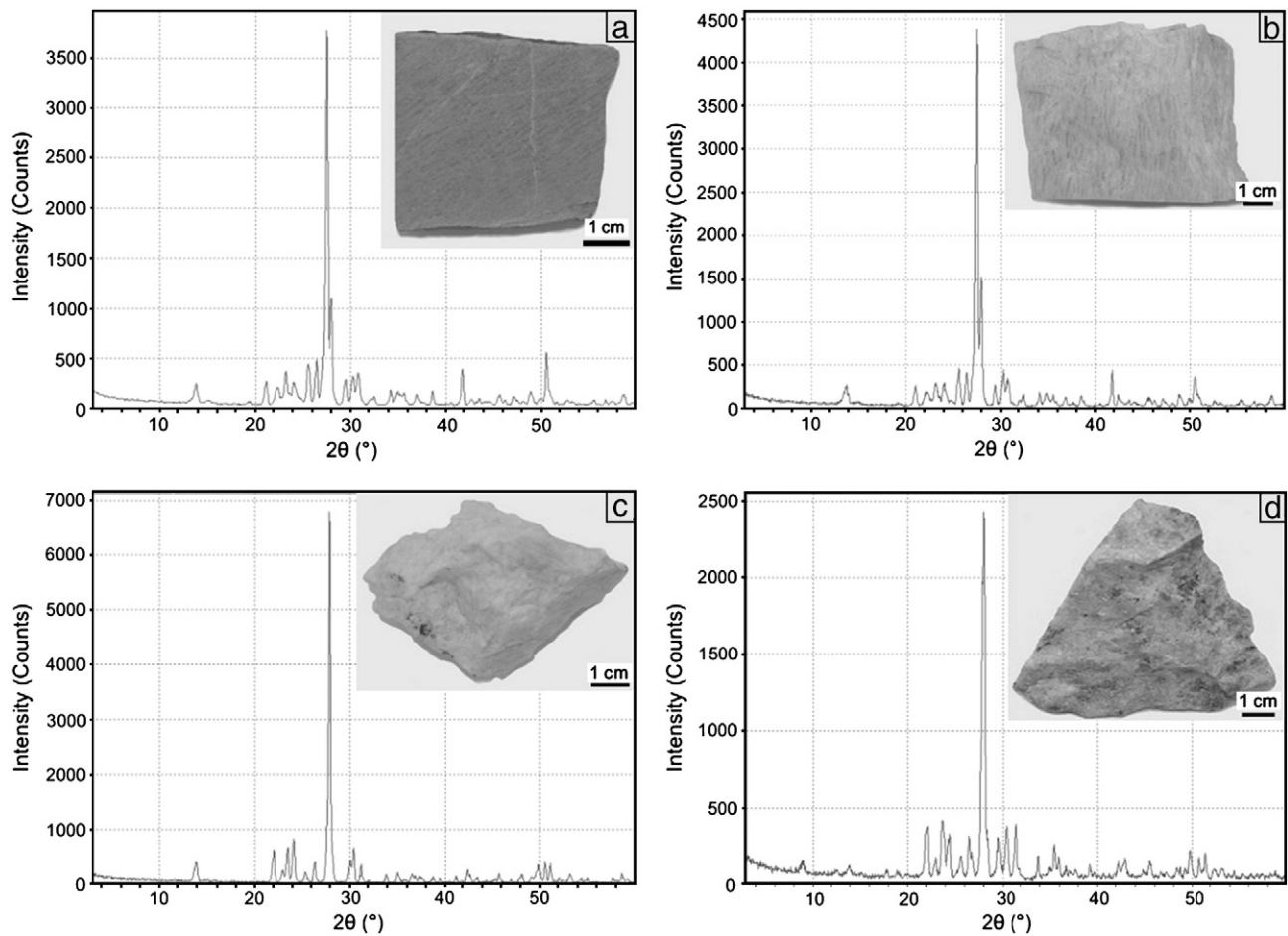


Fig. 1. XRD diagrams and macroscopic photographs of samples LSR1 (a), FB (b), LSR3 (c) and AN (d).

Since this is a first stage of research, the role of calcium in the alkali release process was not evaluated, so it was not taken into account to prevent its interference in the different tests.

In order to evaluate surface attack in an alkaline medium, 2×6 cm cuts were made and polished until perfect mirror-like surfaces were achieved. A portion of each sample was kept as reference and the other was immersed in the 1 N NaOH solution at 80 °C for 7 days.

Once the test time was complete, the samples were removed from the heater and washed. Images were then taken at 15 kV with SEM EVO 40XVP Leo (CCT-Bahía Blanca-UAT), and the reference surfaces and those attacked by NaOH were compared.

Both for the determination of the materials chemical composition and the performance of dissolution studies, it was necessary to separate feldspars from the accessory minerals to prevent interference in the chemical analyses.

5. Results

In Table 1 chemical analyses of the materials studied by XRF are shown and compared with the theoretical values for pure minerals. The samples used are chemically very near theoretical values [33]. Potassic feldspars have a higher Na_2O content, which ranges between 1.49% (LSR1) and 2.28% (FB), than the theoretical values with $\text{Ab}_{16.89}\text{Or}_{83.11}$ composition in the LSR1 sample, and $\text{Ab}_{22.5}\text{Or}_{77.5}$ composition in the FB sample. Plagioclases are $\text{An}_{9.33}$ (LSR3) and $\text{An}_{64.90}$ (AN) in composition.

Table 2 lists the results from the chemical analyses of the solutions after a 24-hour test time. By comparing the values of the elements released into the solution from the different samples (Fig. 3), it is observed that the samples that release more K_2O are FB (10.5 mg/l) and

LSR1 (7.93 mg/l); the sample that releases more Na_2O is AN (13.75 mg/l), and the one that releases more SiO_2 is LSR3 (52.55 mg/l). The Fe_2O_3 , CaO, MgO, MnO values are relatively low and sometimes cannot be detected. The Al_2O_3 values shown were recalculated based on the Si:Al ratio in each sample (Table 1) as they exceeded the detector limit (>7.56 mg/l).

Figs. 4 and 5 show how these materials respond to the alkali attack on polished surfaces (SEM images before and after the alkali attack). The LSR1 sample does not show great variation except for some localized dissolution zones (Fig. 4b). The FB sample shows a generalized alkali attack that has left feldspar cleavage planes exposed (Fig. 4d); before the alkali attack (Fig. 4c) random cracks and other cracks that use those cleavage planes can be seen. The alkali attack of the LSR3 sample is localized in preexisting microcracks (Fig. 5a) and in cleavage planes (Fig. 5b). The AN sample exhibits a more homogeneous alkali attack on the surface, although in some zones it is localized in cleavage planes and shows microcrack development (Fig. 5d).

6. Discussion

As we mentioned before, the content of alkalis released from aggregates into the concrete pore solution is a complex process and depends on many factors.

Wang et al. [9] studied the alkali release of different aggregates and their results suggest that using low water/cement ratio and preventing water from entering the concrete could effectively restrain alkali release from aggregates. They also showed that using low water/cement ratio and lower cement content in normal concrete, the pore solution/aggregate ratio will decrease significantly. Thus, a decrease in the amount of the pore solution produces an increment of the

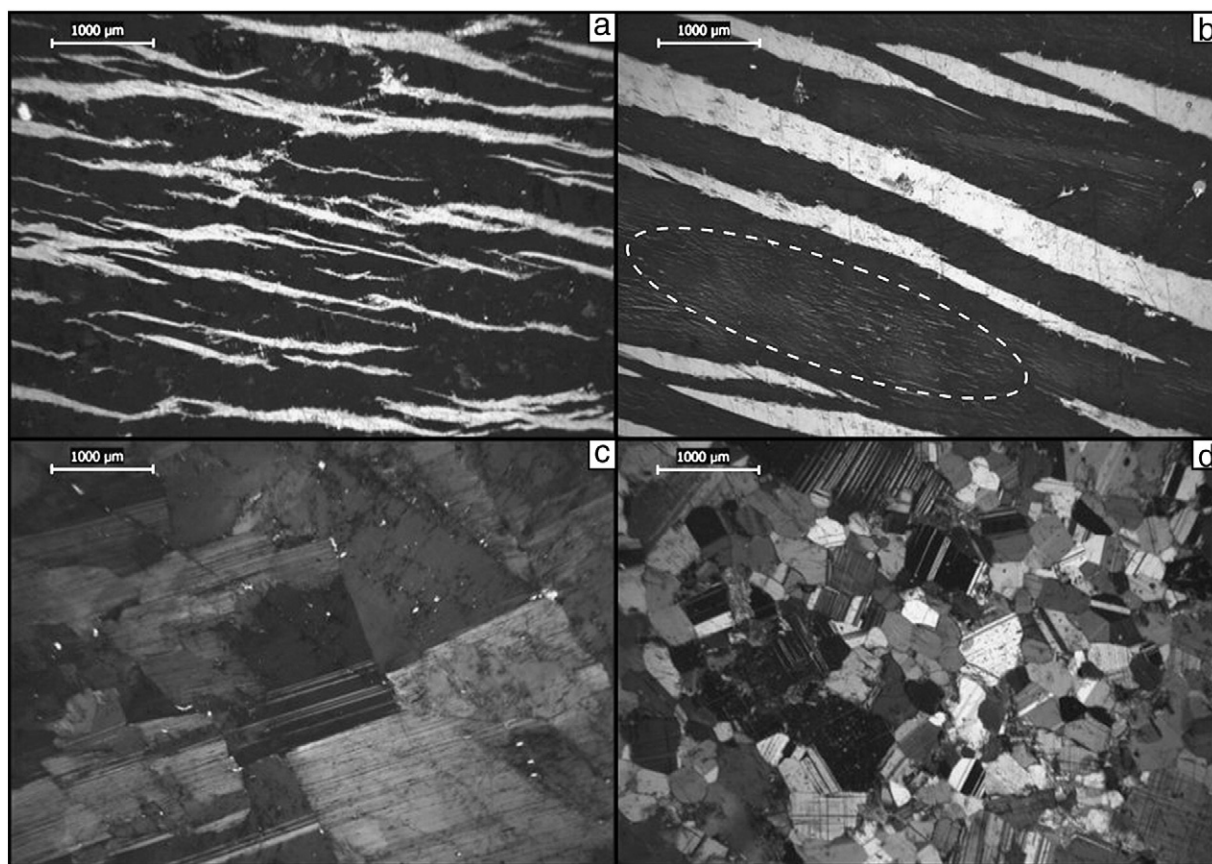


Fig. 2. Photomicrographs under crossed nicols. a) LSR1 sample: It shows development of lamellar perthites with irregular boundaries; b) FB sample: It shows development of lamellar lenticular perthites with net boundaries and spindle-like ends. An area where smaller grain size perthites have developed is enclosed in a dotted line; c) LSR3 sample: It shows intergrown crystals of plagioclase with straight boundaries; and d) AN sample: Plagioclase crystals arranged in a polygonal mosaic.

concentration of alkalis, which decreases the decomposition reaction rate of alkaline minerals in concrete. Their results showed that the maximum released alkali content was increased by 40 times when the pore solution/aggregate ratio was increased from 0.05 to 2.

The alkali content of the cement may also influence the alkali release by the aggregates. According to Wang et al. [8] the higher the alkali concentration in the initial pore solution, the lower the amount of alkali release from aggregates (at least for nepheline- and feldspar-bearing aggregates). This possibly occurred because the alkali release by the aggregate depend on the saturation condition of the solution.

Table 1

Chemical analysis of major elements in the materials used in the tests.

	LSR1		FB		LSR3		AN	
	*	**	*	**	*	**	*	**
SiO ₂	64.73	65.39	65.08	65.39	66.34	68.71	53.90	45.88
Al ₂ O ₃	18.59	18.45	18.46	18.45	20.30	19.63	26.98	34.31
K ₂ O	12.84	14.76	11.64	14.76	0.29	0.03	0.71	0.11
Na ₂ O	2.54	1.08	3.32	1.08	10.30	11.72	5.23	0.82
CaO	0.07	–	0.06	–	1.06	0.22	9.67	18.28
Fe ₂ O ₃	0.08	–	0.09	–	0.07	–	0.71	–
MgO	<0.01	–	<0.01	–	<0.01	–	0.04	–
MnO	<0.01	–	<0.01	–	<0.01	–	0.01	–
TiO ₂	0.01	–	<0.01	–	0.01	–	0.11	–
P ₂ O ₅	0.09	–	0.04	–	0.07	–	0.02	–
Cr ₂ O ₃	<0.01	–	<0.01	–	<0.01	–	<0.01	–
LOI	0.24	–	0.22	–	0.30	–	1.37	–
Total	99.19	99.68	98.91	99.68	98.74	100.31	98.75	99.4

* Weight percent measured in the sample.

** Theoretical weight percent of the mineral identified in the sample (after Anthony et al. [34]).

In general, alkalis in the concrete pore solution are mostly supplied by the cement, but chemical admixtures, mineral admixtures, aggregates, mixing water, and a moist external environment may also contribute alkalis to the pore solution [9]. For example, depending on their compositions, the supplementary cementing materials (SCMs) that are used to depress the level of alkalinity of the concrete pore solution could release alkalis into the solution [34] if the concentration drops due to alkali consumption by another process such as the alkali–aggregate reaction [12].

In this work we focus on to alkali release from potassic and calcic-sodic feldspars into alkaline solutions in order to understand the role played by each feldspar species, its composition and its microstructural and textural characteristics in the process.

Table 2

Oxides released into NaOH solution at 24-hour test time. Alumina values (*) were recalculated from the original values of Table 1 since they exceeded the detector limit (>7.56 mg/l). The Na₂O content was determined in the KOH solution.

	LSR1 (mg/l)	FB (mg/l)	LSR3 (mg/l)	AN (mg/l)	DL
SiO ₂	27.98	24.35	52.55	21.15	0.427
Al ₂ O ₃	*8.04	*6.91	*16.08	*10.59	0.008
K ₂ O	7.93	10.50	1.57	3.90	0.072
Na ₂ O	8.47	9.43	7.82	13.75	0.013
Fe ₂ O ₃	0.40	0.11	0.11	0.09	0.029
CaO	ND	ND	0.98	1.12	0.979
MgO	0.09	0.09	0.09	0.09	0.002
MnO	ND	ND	ND	ND	1.3 10 ^{−4}
Na ₂ O _{eq} in the solution	0.014	0.016	0.009	0.016	

DL: Detection limit. ND: not detected.

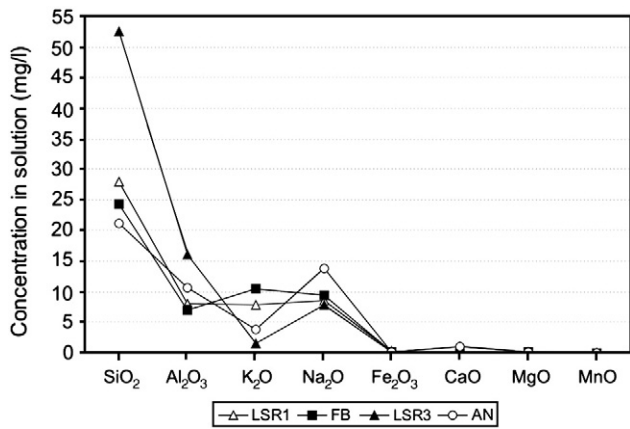


Fig. 3. Comparison of oxide concentrations in solution for the different samples studied (values taken from Table 2).

Although in his PhD thesis Constantiner [10] already warned about the difficulty in applying data from geochemical studies on mineral weathering to systems similar to those of cement, the publication of new papers and the reinterpretation of previous studies are useful for both analyzing the stability of different feldspars and studying the process of alkaline solution attack and the role played by mineral microstructures in such process.

According to some authors, the process of alkali release into the concrete pore solution may be linked to the ion exchange between the solution and the minerals. Others, however, suggest that alkali contribution occurs by hydrolysis or dissolution of the minerals

contributing even alumina and silica to the concrete pore solution [2,4–8,35–37].

Currently, there are numerous geochemical studies that have been conducted to analyze the conditions under which the dissolution of feldspars occurs during natural processes at different temperatures and in a wide range of pH. A summary of previous work on this subject can be found in the paper by Zhang and Lüttge [38].

According to Hellmann et al. [39,40] sodium from plagioclases is released by ion exchange with the potassium present in the alkaline solution (KOH) due to the influx of aqueous species into the mineral structure. This process would supposedly open up the mineral structure so that hydrolysis by attack of the hydroxyls from the solution at the Al–O–Si and Si–O–Si bonds can occur.

Hellmann [40] analyzed the albite–water system in a temperature range between 100° and 300 °C and a wide pH range, and found that there is strong evidence of nonstoichiometric dissolution at elevated temperature and basic pH (he mainly used KOH as alkaline solution). At the beginning, sodium release is much higher than aluminum and silicon release, reaching depths of about 1227 Å. The higher the solution alkalinity is, the greater the preferential release of aluminum results due to its high reactivity under these conditions. At the initial stage, a fast release rate of sodium and then silicon and aluminum was observed on the feldspar surface. As the distance between the boundary and the inside of the crystal grew, the solution diffusion became more difficult and hence the release rate decreased. In general, the depth of sodium release is one order of magnitude higher than that of aluminum.

Such incongruent dissolution process was reported by Wang et al. [8] for feldspars under conditions similar to those of concrete, but in a less marked way and restricted to the most superficial zones of the aggregates.

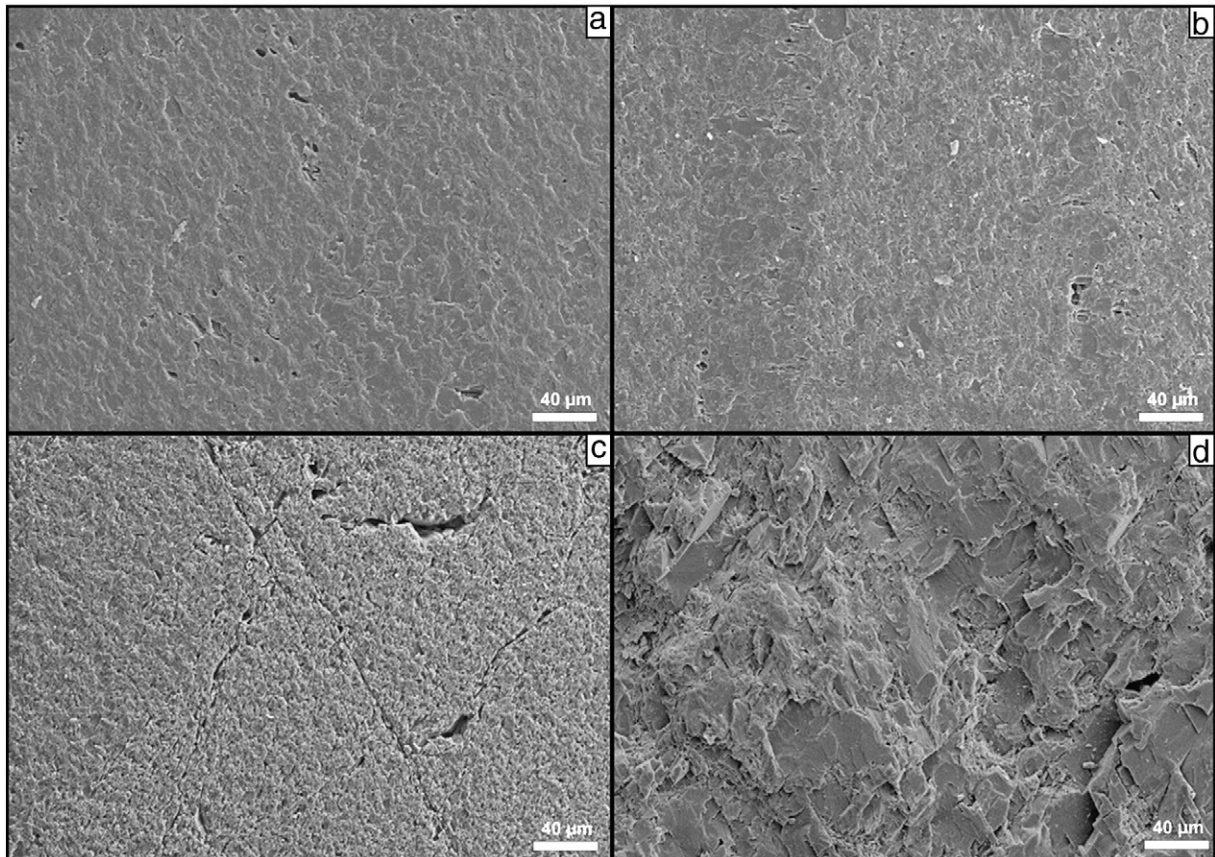


Fig. 4. SEM images of reference samples and samples attacked by NaOH solution. a) Reference sample LSR1; b) Attacked sample LSR1; c) Reference sample FB; and d) Attacked sample FB.

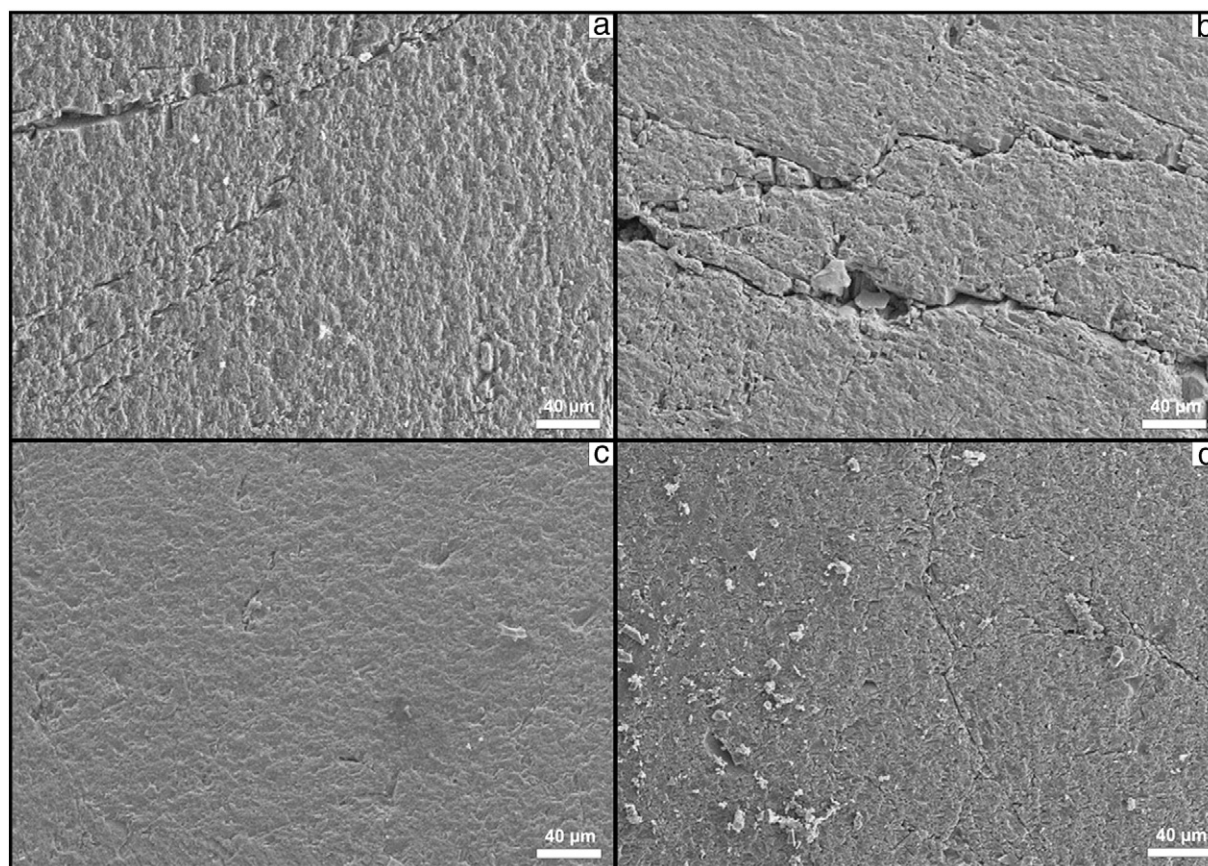


Fig. 5. SEM images of reference samples and samples attacked by NaOH solution. a) Reference sample LSR3; b) Attacked sample LSR3; c) Reference sample AN; and d) Attacked sample AN.

Although the Al_2O_3 values of the samples studied were recalculated, one of them showed a behavior similar to the above-mentioned. If silica and alumina release were stoichiometric, the FB sample would release ~ 6.91 mg/l alumina. However, concentrations >7.56 mg/l were found in the chemical analyses. This could be indicating nonstoichiometric release processes.

Moreover, the alkalis released into the solution (Na_2O and K_2O), together with silica and alumina contribution, would support the theory of bond rupture and ion release according to a surface hydrolysis process for feldspars, but the action of other processes cannot be ruled out. However, there is no complete agreement yet about the processes that cause alkali release from aggregates and the major role played by each of them.

Based on the total alkali contribution to the solution ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), the following order of alkali release was determined: $\text{FB} > \text{AN} > \text{LSR1} > \text{LSR3}$. As was mentioned above, according to Wang et al. [8,9], this order will be influenced by many factors involved in the alkali release from each mineral and not only by the type of mineral species or their chemical composition.

An important aspect to be considered in the alkali release process is the microstructural characteristics of feldspars. In this work it was found that crystal intergrowths create areas susceptible to alkali attack both in potassic feldspars and in plagioclases.

It is quite understandable that sodic plagioclase (LSR3) releases much more sodium than calcium because it is near albite in composition ($\text{An}_{9.33}$), but why calcic plagioclase (AN) releases approximately 12 times more sodium than calcium considering that it is composed of almost twice as much calcium as sodium?

The greater release of sodium than calcium in calcic plagioclase could be because sodium is more easily exchangeable with potassium from the solution than calcium owing to the one-to-one charge

balance. Likewise, sodium release would be easier than that of calcium due to the strong double bond of the latter in the mineral structure.

Another factor to be taken into account is the greater internal deformation of the less abundant phases in feldspar intergrowths, as has been reported by Blasi and De Pol Blasi [24]. Such microstructures are more susceptible to be dissolved because of their high internal energy. The AN sample has an approximate composition $\text{An}_{69.90}$ so a *Huttenlocher intergrowth* with calcium-rich and sodium-rich zones would be expected. Thus the sodic phase within plagioclase of the AN sample will possibly be more susceptible to be dissolved because it is the most scarce phase, hence accounting for the supply of significant amounts of sodium to the solution.

In addition, the great release of silica as compared to that of alumina from sodic plagioclase (relative to calcic plagioclase) is possibly due to the original Si:Al ratio of 3:1 for the sodic end and 2:2 for the calcic end.

In potassic feldspars intergrowth development is also a key factor in dissolution processes. Teng et al. [41] have analyzed homogeneous, gem-type potassic feldspar crystals without perthitic exsolution and suggest that the dissolution process is stoichiometric. However, in the cases studied in this work the two feldspars analyzed (LSR1 and FB) are nonhomogeneous perthitic feldspars where albitic zones would undergo a nonstoichiometric dissolution process, as proposed by Hellmann [40].

According to Wollast [42] the alteration of potassic feldspars under alkaline conditions would start by ion exchange with K^+ from the crystal structure. However, potassic feldspar has a slower absolute dissolution rate than albite, presumably due to K^+ reabsorption at cation sites stabilizing the surface more strongly than Na^+ . This also implies that the dissolution rate of feldspar under alkaline conditions is strongly influenced by the concentration of any cations that can

effectively compete for cation-exchange sites on the feldspar surface [43].

Using TEM, Lee and Parsons [15] and Lee et al. [16–18] also observed this preferential dissolution behavior of albite relative to potassic feldspar in perthitic intergrowths but for acidic conditions.

The pH dependence on the dissolution rate of albite and potassic feldspar can be observed in the diagram presented by Blum [43], who worked with data available from different research papers (see papers cited therein) (Fig. 6).

In general, the dissolution rate for the two types of feldspars is higher in acidic conditions than in basic conditions, and it increases both with higher pH and lower pH, being lower in neutral conditions. This behavior is similar to that observed by Wang et al. [9], where in most cases the pH increase in the pore solution results in an increase in alkalis released from the minerals, with some exceptions for dawsonite, leucite and nepheline.

Perthitic potassic feldspars can release potassium and important amounts of sodium into highly alkaline solutions, as reported by Lu et al. [6] and as observed in LSR1 and FB samples. The release rate seems to increase with the solution alkalinity, albite being more susceptible to be leached than potassic feldspar in perthitic intergrowths.

It is important to also explain why the two potassic feldspars analyzed (LSR1 and FB samples) have similar chemical composition (Table 1), give similar XRD diagrams (Fig. 1 a and b) and both exhibit development of perthite (Fig. 2 a and b), but the FB sample releases more sodium and potassium than the LSR1 sample (Table 2). Additionally, it shows a higher degree of attack under SEM (Fig. 4). The reason seems to be related to the microstructural characteristics of the intergrowths in each feldspar. Images from the optical microscope (Fig. 2) indicate that the FB sample shows development of very thin lamellae ($\sim 4 \mu\text{m}$) between lenticular perthites of greater size (Fig. 2b). According to Blasi and De Pol Blasi [24], they would be the result of higher deformation and hence, be more unstable and susceptible to be attacked by alkaline solutions. The great influence of preexisting microcracks and mineral cleavage on the disaggregation process should also be taken into account.

7. Conclusions

Microstructural and textural characteristics appear to play an important role in controlling the initial stage of feldspar dissolution under alkaline conditions. The results of this work are summarized as follows.

- The analysis of thin sections with the optical microscope and of polished surfaces by SEM shows that the leaching phenomenon under alkaline conditions mainly occurs at cleavage zones, twins,

grain–grain contact and, in the case of perthites, in the finer and less abundant phases.

- Both potassic feldspars and plagioclases showed susceptibility to alkali attack, releasing Na_2O and K_2O and even SiO_2 and Al_2O_3 into the concrete pore solution. Such contribution will depend on many factors that influence the alkali release from each mineral, especially microstructural characteristics, and not only on the type of mineral species and/or chemical composition.
- The presence of silica and alumina in the solution indicates that a surface hydrolysis process of feldspars has occurred, and although further research is needed to gain better understanding of this process, some evidence indicates nonstoichiometric release.

Acknowledgements

The authors thank Universidad Nacional de Córdoba, Universidad Nacional Sur, Comisión de Investigaciones Científicas de la Prov. de Buenos Aires and CONICET for their support. The authors would like to acknowledge W.S. Rasband from the National Institutes of Health, Bethesda, Maryland, USA, for his continuous development and support of ImageJ. Finally we are grateful to Keith Baldie (Managing Editor) and anonymous reviewers for their comments that have improved the manuscript.

References

- [1] M.-A. Bérubé, J. Duchesne, J.F. Dorion, M. Rivest, Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity, *Cem. Concr. Res.* 32 (2002) 1215–1227.
- [2] M.-A. Bérubé, J. Duchesne, J.F. Dorion, M. Rivest, Reply to the discussion by C. Shi of the paper “Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali–silica reactivity”, *Cem. Concr. Res.* 34 (2004) 897–899.
- [3] M.-A. Bérubé, J. Duchesne, J.F. Dorion, M. Rivest, 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”, *Cem. Concr. Res.* 34 (2004) 903–904.
- [4] D. Constantiner, S. Diamond, Alkali release from feldspars into pore solutions, *Cem. Concr. Res.* 33 (2003) 549–554.
- [5] A. Leemann, L. Holzer, Alkali–aggregate reaction–identifying reactive silicates in complex aggregates by ESEM observation of dissolution features, *Cem. Concr. Compos.* 27 (2005) 796–801.
- [6] D. Lu, X. Zhou, Z. Xu, X. Lan, M. Tang, B. Fournier, 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 (2006) 1157–1165.
- [7] C. Shi, 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. Bérubé, J. Duchesne, J.F. Dorion, M. Rivest, *Cem. Concr. Res.* 34 (2004) 895.
- [8] Y. Wang, M. Deng, M. Tang, Alkali release from aggregate and the effect on AAR expansion, *Mater. Struct.* 41 (1) (2008) 159–171.
- [9] Y. Wang, G. Yu, M. Deng, M. Tang, D. Lu, The use of thermodynamic analysis in assessing alkali contribution by alkaline minerals in concrete, *Cem. Concr. Compos.* 30 (4) (2008) 353–359.
- [10] D. Constantiner, Factors affecting concrete pore solution: (A) alkali fixation by drying and carbonation and (B) alkali release from feldspars, PhD thesis, Purdue University, 1994.
- [11] W.C. Hansen, Release of alkalis by sands and admixtures in portland cement mortars, *ASTM Bull.* (1959) 35–38.
- [12] M.H. Shehata, M.D.A. Thomas, Alkali release characteristics of blended cements, *Cem. Concr. Res.* 36 (2006) 1166–1175.
- [13] R.H. Worden, F.D.L. Walker, I. Parsons, W.L. Brown, Development of microporosity, diffusion channels and deuteric coarsening in perthitic alkali feldspars, *Contrib. Mineral. Petrol.* 104 (1990) 507–515.
- [14] K. Waldron, M.R. Lee, I. Parsons, The microstructures of perthitic alkali feldspars revealed by hydrofluoric acid etching, *Contrib. Mineral. Petrol.* 116 (1994) 360–364.
- [15] M.R. Lee, I. Parsons, Microtextural controls of weathering of perthitic alkali feldspars, *Geochim. Cosmochim. Acta* 59 (21) (1995) 4465–4488.
- [16] M.R. Lee, M.E. Hodson, I. Parsons, The role of intragranular microtextures and microstructures in chemical and mechanical weathering: direct comparisons of experimentally and naturally weathered alkali feldspars, *Geochim. Cosmochim. Acta* 62 (16) (1998) 2771–2788.
- [17] M.R. Lee, D.J. Brown, C.L. Smith, M.E. Hodson, M. MacKenzie, R. Hellmann, Characterization of mineral surfaces using FIB and TEM: a case study of naturally weathered alkali feldspars, *Am. Mineral.* 92 (2007) 1383–1394.

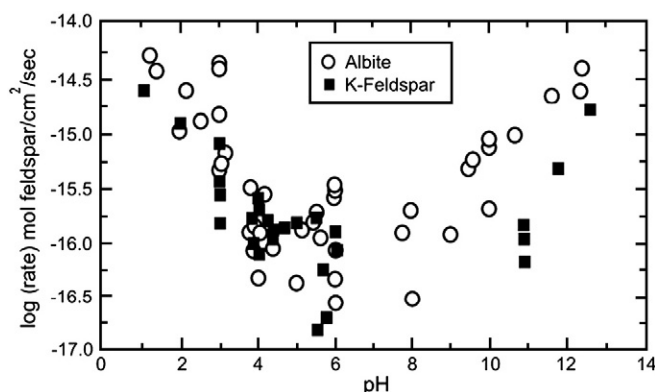


Fig. 6. Comparison between the dissolution rate of albite and potassic feldspar as a function of pH (after Blum [43]).

- [18] M.R. Lee, M.E. Hodson, D.J. Brown, M. MacKenzie, C.L. Smith, The composition and crystallinity of the near-surface regions of weathered alkali feldspars, *Geochim. Cosmochim. Acta* 72 (2008) 4962–4975.
- [19] ASTM C 289, Potential Alkali–Silica Reactivity of Aggregates (Chemical Method), Annual Book of ASTM Standards, ASTM Publication Office, Philadelphia, PA, 1994.
- [20] R.H. Vernon, A Practical Guide to Rock Microstructure, Cambridge Univ. Press, United Kingdom, 2004.
- [21] W.A. Deer, R.A. Howie, J. Zussman, An introduction to the Rock-Forming Minerals, 2nd Ed. Longman, London, 1992.
- [22] C. Klein, C.S. Hurlbut Jr., 4th Ed, Manual de mineralogía (basado en la obra de J.D. Dana), vol. II, Reverté, Barcelona, 1997.
- [23] R.A. Yund, J. Tullis, Subsolidus phase relations in the alkali feldspars with emphasis on coherent phases, in: P.H. Ribbe (Ed.), Feldspar Mineralogy, 2nd Ed, Reviews in Mineralogy, vol. 2, Mineralogical Society of America, 1983, pp. 141–176, Chapter 6.
- [24] A. Blasi, C. De Pol Blasi, Aspects of alkali feldspar characterization: prospects and relevance to problems outstanding, in: I. Parsons (Ed.), Feldspars and their Reactions, NATO ASI Series, C421, Kluwer Academic Publishers, Dordrecht, 1994, pp. 51–103.
- [25] C. Casquet, R.J. Pankhurst, C.W. Rapela, C. Galindo, J. Dahlquist, E. Baldo, J. Saavedra, J.M. González Casado, C.M. Fanning, Grenvillian massif-type anorthosites in the Sierras Pampeanas, *J. Geol. Soc. London* 162 (2004) 9–12.
- [26] W.S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://rsb.info.nih.gov/ij/>, 1997–2009.
- [27] S. Diamond, ASR–Another look at mechanisms, in: K. Okada, S. Nishibayashi, M. Kawamura (Eds.), 8th ICAAR, Kyoto, 1989, pp. 83–94.
- [28] J.H.P. van Aardt, S. Visser, Formation of hydrogarnets: calcium hydroxide attack on clays and feldspars, *Cem. Concr. Res.* 7 (1) (1977) 39–44.
- [29] J.H.P. van Aardt, S. Visser, Calcium hydroxide attack on feldspars and clays: possible relevance to cement–aggregate reactions, *Cem. Concr. Res.* 7 (6) (1977) 643–648.
- [30] J.H.P. van Aardt, S. Visser, Reaction of $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at various temperatures with feldspars in aggregates used for concrete making, *Cem. Concr. Res.* 8 (6) (1978) 677–681.
- [31] H.C. Visvesvaraya, A.K. Mullick, G. Samuel, S.K. Sinha, R.C. Wason, Alkali reactivity of granitic rock aggregates, in: FINEP (Ed.), Proc. of the 8th International Congress on the Chemistry of Cement, vol. 5, 1986, pp. 208–213, Rio de Janeiro, Brasil.
- [32] ASTM C 1260, Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), Annual Book of ASTM Standards, American Society for Testing and Materials, West Conshohocken, Pennsylvania, 2005.
- [33] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy, vol. II, Mineral Data Publishing, Tucson, Arizona, 1995.
- [34] M. Kawamura, M. Koike, K. Nakano, Release of alkalis from reactive andesitic aggregates and fly ashes into pore solution in mortars, in: K. Okada, S. Nishibayashi, M. Kawamura (Eds.), 8th ICAAR, Kyoto, 1989, pp. 271–278.
- [35] O. Batic, J. Sota, P. Maiza, Montmorillonite included in some aggregates. A principal factor of A.A.R, in: A.B. Poole (Ed.), 9th ICAAR, vol. 1, 1992, pp. 53–60, London.
- [36] R. Goguel, Alkali release by volcanic aggregates in concrete, *Cem. Concr. Res.* 25 (4) (1995) 841–852.
- [37] D. Savage, K. Bateman, P. Hill, C. Hughes, A. Milodowski, J. Pearce, E. Rae, C. Rochelle, Rate and mechanism of the reaction of silicates with cement pore fluids, *Appl. Clay Sci.* 7 (1992) 33–45.
- [38] L. Zhang, A. Lüttge, Theoretical approach to evaluating plagioclase dissolution mechanisms, *Geochim. Cosmochim. Acta* 73 (2009) 2832–2849.
- [39] R. Hellmann, C.M. Eggleston, M.F. Hochella Jr., D.A. Crerar, The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions, *Geochim. Cosmochim. Acta* 54 (1990) 1267–1281.
- [40] R. Hellmann, The albite–water system: part II. The time–evolution of the stoichiometry of dissolution as a function of pH at 100, 200 and 300 °C, *Geochim. Cosmochim. Acta* 59 (9) (1995) 1669–1697.
- [41] H.H. Teng, P. Fenter, L. Cheng, N.C. Sturchio, Resolving orthoclase dissolution processes with atomic force microscopy and X-ray reflectivity, *Geochim. Cosmochim. Acta* 65 (20) (2001) 3459–3474.
- [42] R. Wollast, Kinetics of the alteration of K-feldspar in buffered solutions at low temperature, *Geochim. Cosmochim. Acta* 31 (1967) 635–648.
- [43] A.E. Blum, Feldspars in weathering, in: I. Parsons (Ed.), Feldspars and their Reactions, NATO ASI Series, C421, Kluwer Academic Publishers, Dordrecht, 1994, pp. 595–630.