

USE OF NATURAL ZEOLITES AS ASR INHIBITOR IN BASALTIC ROCKS

Francisco Locati ⁽¹⁾, Darío Falcone ⁽²⁾, Silvina Marfil ^{(3)*} and Belén Raggiotti ⁽⁴⁾

(1) CICTERRA (CONICET-UNC), Argentina

(2) UNLP - LEMIT - CIC (Prov. de Bs. As.), Argentina

(3) UNS - CIC (Prov. de Bs. As.) - INGEOSUR, Argentina

(4) UTN - FRC/CINTEMAC, Argentina

* smarfil@uns.edu.ar

Abstract

The capacity of a natural zeolite from the province of La Rioja (Argentina) to inhibit the alkali-silica reaction (ASR) was studied. The pozzolanic material corresponds to a mixture of clinoptilolite zeolite with minor gypsum, quartz and feldspar discarded in spoil heaps in a quarry. An alkali-reactive basaltic aggregate from a quarry in the Argentine Mesopotamia region was used for the study. Two series of tests according to the accelerated mortar bar method (IRAM 1674) were carried out. One set with 0% (control specimen), 10%, 15% and 20% replacement of cement by natural zeolite and another with the same percentages but using milled zeolite. To monitor the reaction process, mortar bars were studied after the test by stereomicroscopy, polarizing microscopy and SEM-EDS. After 16 days of testing, a reduction in expansion (~42 %) was detected in the mortars with 20% replacement by natural zeolite. However, their behaviour was still reactive. On the other hand, the mortars with 20% replacement by milled zeolite produced a 90% reduction in expansion at 16 days, below the limit prescribed by the standard. A simple milling process transforms this material into a good pozzolanic material inhibiting the alkali-reactivity of basaltic aggregates.

1. INTRODUCTION

Basaltic rocks from Argentina have been widely used as asphalt and concrete aggregates in different structures. Although generally it is a group of rocks of good physico-mechanical performance, when used as concrete aggregates some types can cause alkali-silica reactions due to the presence of volcanic glass, micro-cryptocrystalline silica and expansive clays in variable proportions [1]. Sometimes, this type of rock is the only one available as source of concrete aggregates in the area so, it is necessary to implement strategies in order to avoid this kind of reaction. One attractive option is the use of natural pozzolans.

In a quarry located in the province of La Rioja (Argentina), a volcanic material containing ~50% zeolite (a highly porous aluminosilicate) is accumulated and discarded in spoil heaps. Recently, this material has demonstrated to be a good admixture to improve the physico-mechanical behaviour of concrete [2-4].

Natural materials with a high content of zeolites are currently used in many countries as pozzolanic admixtures to improve not only the strength but also the durability properties of concrete [5].

In addition, the replacement of part of the cement by natural zeolitic materials has a positive impact on the environment due to the reduction in CO₂ emissions and energy consumption by the cement industry.

The aim of this study was to evaluate the use of a natural zeolite from the province of La Rioja as ASR inhibitor when reactive basaltic rocks are used as concrete aggregates.

2. MATERIALS

2.1 Cement

An ordinary portland cement (type I according to ASTM C 150), with Na₂O_{eq} = 0.86 %, was used to make the mortars.

2.2 Aggregates

The coarse aggregates are basaltic rocks of known reactivity both in laboratory tests [6,7] and structures [8]. The rocks are composed of plagioclase phenocrysts, augite and titaniferous augite with minor K-feldspar, apatite, iron and titanium oxides. In addition, a glassy material is present in the intergranular zones. In some sectors this material is altered to clays and micro-cryptocrystalline silica [9].

2.3 Natural zeolite (NZ)

The zeolitic material used in this study is a mixture of a natural clinoptilolite-Na (~50%) zeolite, with quartz, plagioclase, biotite and gypsum in variable proportions. It comes from a quarry in the province of La Rioja (Argentina) and is a secondary product accumulated in spoil heaps. According to ASTM C618 [10] classification, it is a class F pozzolan, although with higher loss on ignition (7.5%) and SO₃ (~8%) values.

2.4 Milled zeolite (MZ)

It is the same as NZ (Section 2.3) but hand-milled in a porcelain mortar until all material passes the #70 sieve (210 μm). Specific surface area = 374 m²/kg.

3. METHODS

3.1 Particle size distribution

The particle size distribution of NZ was determined in two stages. The coarse fraction (>1000μm) was sieved through standard sieves (#7, #8 #14, #16 #18), and the fine fraction (≤ 1000 μm) was determined by a particle size distribution analyzer based on laser diffraction (Partica 1A-950V2, HORIBA). The particle size distribution of the MZ sample was determined through the second procedure due to its fineness.

3.2 IRAM 1674

The reactivity of basaltic aggregates was determined according to the accelerated mortar bar method (IRAM 1674 [11], which is equivalent to ASTM C1260 [12]). For this purpose, mortar bars (25×25×285 mm) were cast and cured in a fog room for 24 h, then demoulded and immersed in water at 23 °C in a sealed container, and placed in a heater at 80 °C for 24 h. Subsequently, the initial length was measured and the mortars were immersed in a 1 N NaOH solution at 80 °C for 14 days (a total of 16 days). The tests were extended up to 28 days. Two series of tests were performed replacing part of the cement by 10%, 15% and 20% of zeolite. This replacement was carried out using NZ and MZ, and both were compared with the control specimen (CS, mortar without zeolite addition). According to IRAM 1674 standard, expansions below 0.10% at 16 days indicate aggregates of innocuous performance, expansions above 0.20% a potentially deleterious behaviour and expansions between 0.10% and 0.20% aggregates with uncertain behaviour.

3.3 Stereomicroscopy

Macroscopic observations were performed on mortar bars after the test by a Leica S6 E stereomicroscope (40x magnification). For this propose, mortar slabs (2 x 2.5 x 1 cm) were cut and polished with silicon carbide (abrasive size up to 9 µm).

3.4 Petrography

Petrographic descriptions on thin sections (~20 µm thick) of the mortars after the test were performed using a Leica DM EP polarizing microscope (500x magnification) in plane-polarized light (PPL) and cross-polarized light (XPL). Mortar slabs were impregnated with a fluorescent adhesive (Bohle - UV Adhesive - B 665-0) before making the thin sections. Therefore, additional petrographic observations were carried under epifluorescence by a Nikon ECLIPSE 50i POL polarizing microscope.

3.5 SEM-EDS

The mortar slabs (2 x 2.5 x 1 cm) used for the stereomicroscopic observations were polished with alumina (abrasive size up to 0.3 µm) and carbon-coated. Textural and chemical studies were performed using a Carl Zeiss high resolution FE (Field Emission)-Sigma SEM microscope equipped with an EDS detector. Compositional maps (Si, Ca and K) were obtained working at 8 kV. Secondary electron (SE) images and backscattered electron (BSE) images were obtained.

4. RESULTS

4.1 Particle size distribution

The NZ has a multimodal distribution and is composed of 40.62% of particles bigger than 1000 µm (Figure 1a) and 59.38% of particles smaller than or equal to 1000 µm (Figure 1b). The MZ has a quasi-unimodal distribution. It is composed of particles smaller than 175 µm and only ~14% of the particles are bigger than 45 µm, being this value within the limit established by the ASTM C618 [10] standard (Figure 2).

4.2 IRAM 1674

Mortars with 10%, 15% and 20% replacement of cement by NZ (Figure 3a) and with 10 and 15% replacement of cement by MZ (Figure 3b) suffered lower expansions than the CS

(0.41% at 16 days and 0.48% at 28 days) but always over the limit established by the standard (0.1% at 16 days of testing). On the other hand, the mortar with 20% replacement of cement by MZ (Figure 3b) shows expansions below the limit (<0.1%) at 16 days and even at 28 days.

4.3 Stereomicroscopy

At macroscopic level the control specimen (mortar without zeolite addition) presents intense deterioration. Cracks in the cement paste, in the cement–aggregate interface and inside the aggregates (Figure 4a) are frequent (empty or filled with a white or transparent massive reaction material, ~25 μm thick). Air voids are in general empty or partially filled with massive or crystalline materials. Some aggregates show the development of a reaction rim where a massive transparent material is recognized (Figure 4b).

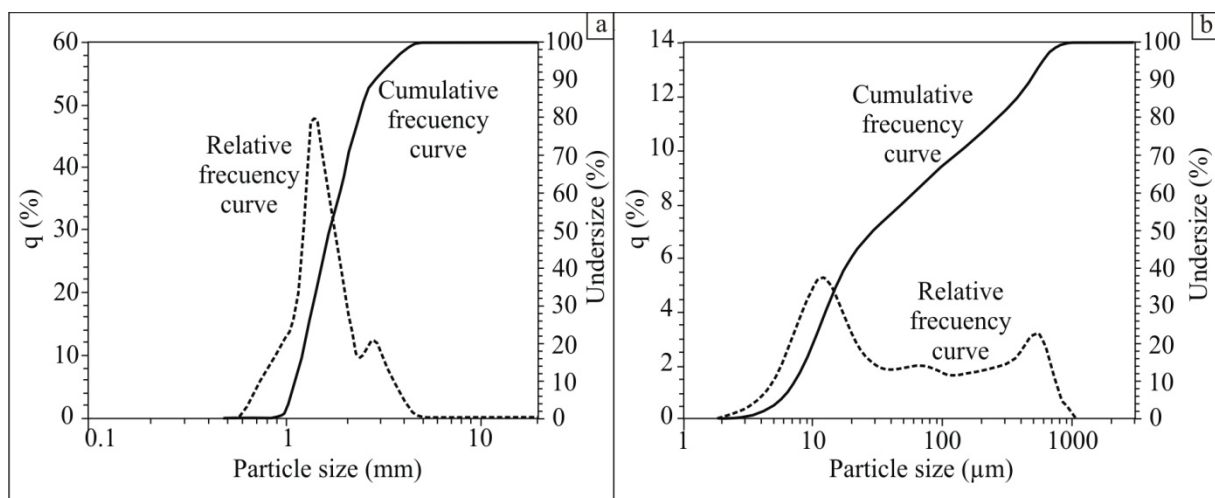


Figure 1: Particle size distribution curves of the particles >1000 μm (a) and $\leq 1000 \mu\text{m}$ (b) in the natural zeolite sample.

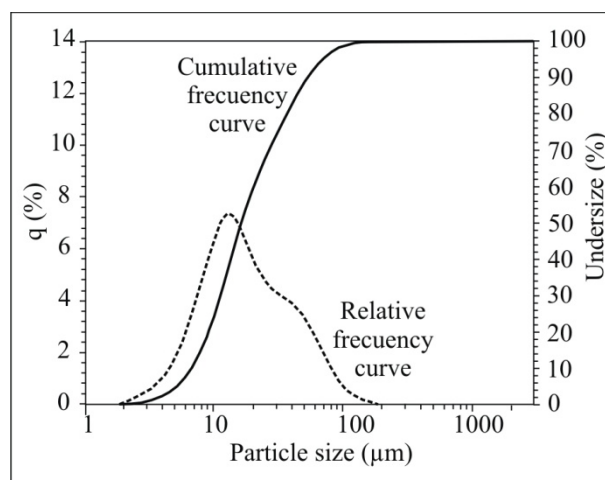


Figure 2: Particle size distribution curves of the particles (MZ).

In Figures 4c-f the mortar with 20% replacement of cement by NZ and 20% by MZ are compared. In the mortar with NZ the microcracks are empty or filled with a white material

(<10 μm) mainly in the cement paste and the cement–aggregate interface (Figure 4c). Some microcracks are associated with the zeolitic particles. Air voids are generally empty. Many zeolitic particles present a decolourized rim, $\sim 30 \mu\text{m}$ thick (Figure 4d). The mortar with MZ presents scarce microcracks (<10 μm), which are empty or filled with a transparent massive material (Figure 4e), in the cement paste, in the cement–aggregate interface and inside the aggregates (although less frequent). Air voids are mainly empty or partially filled with a transparent massive material. In general, the microstructure of the mortar is well preserved (Figure 4f).

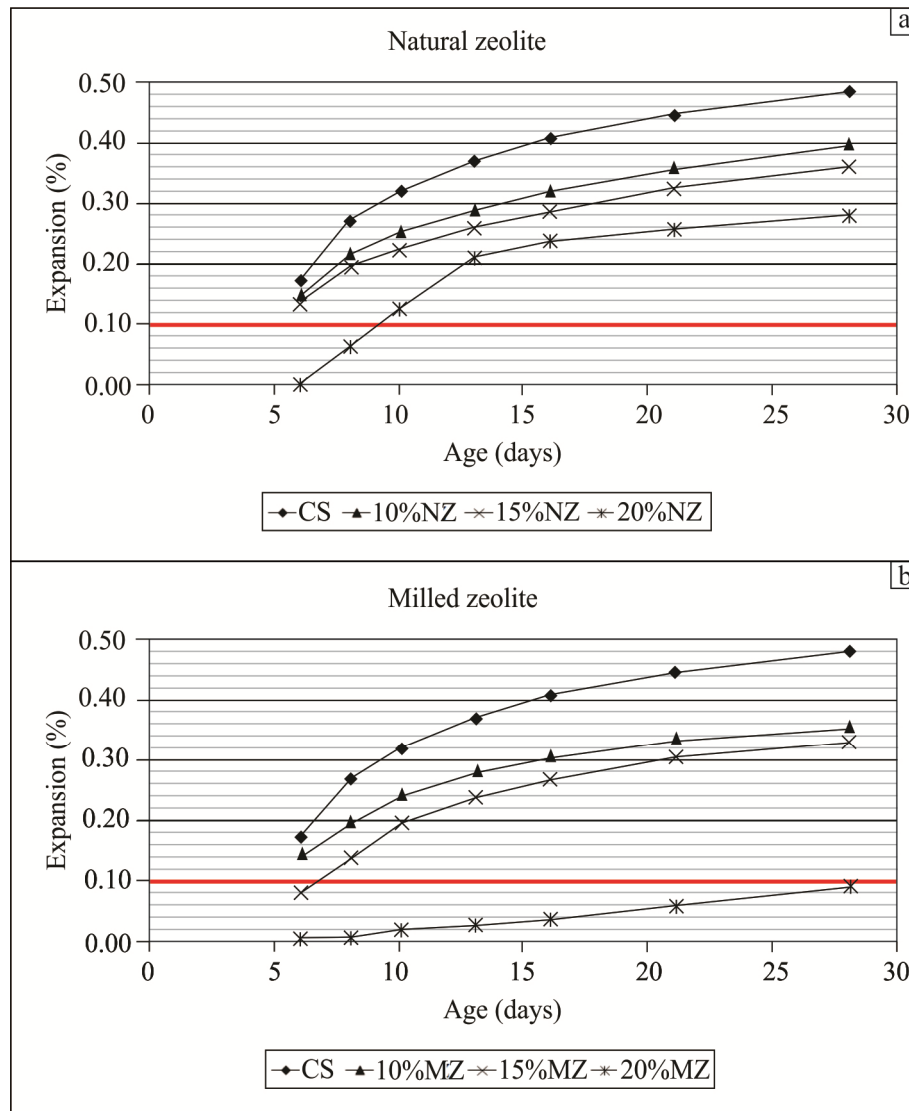


Figure 3: Mortar bar expansions with NZ (a) and MZ (b).

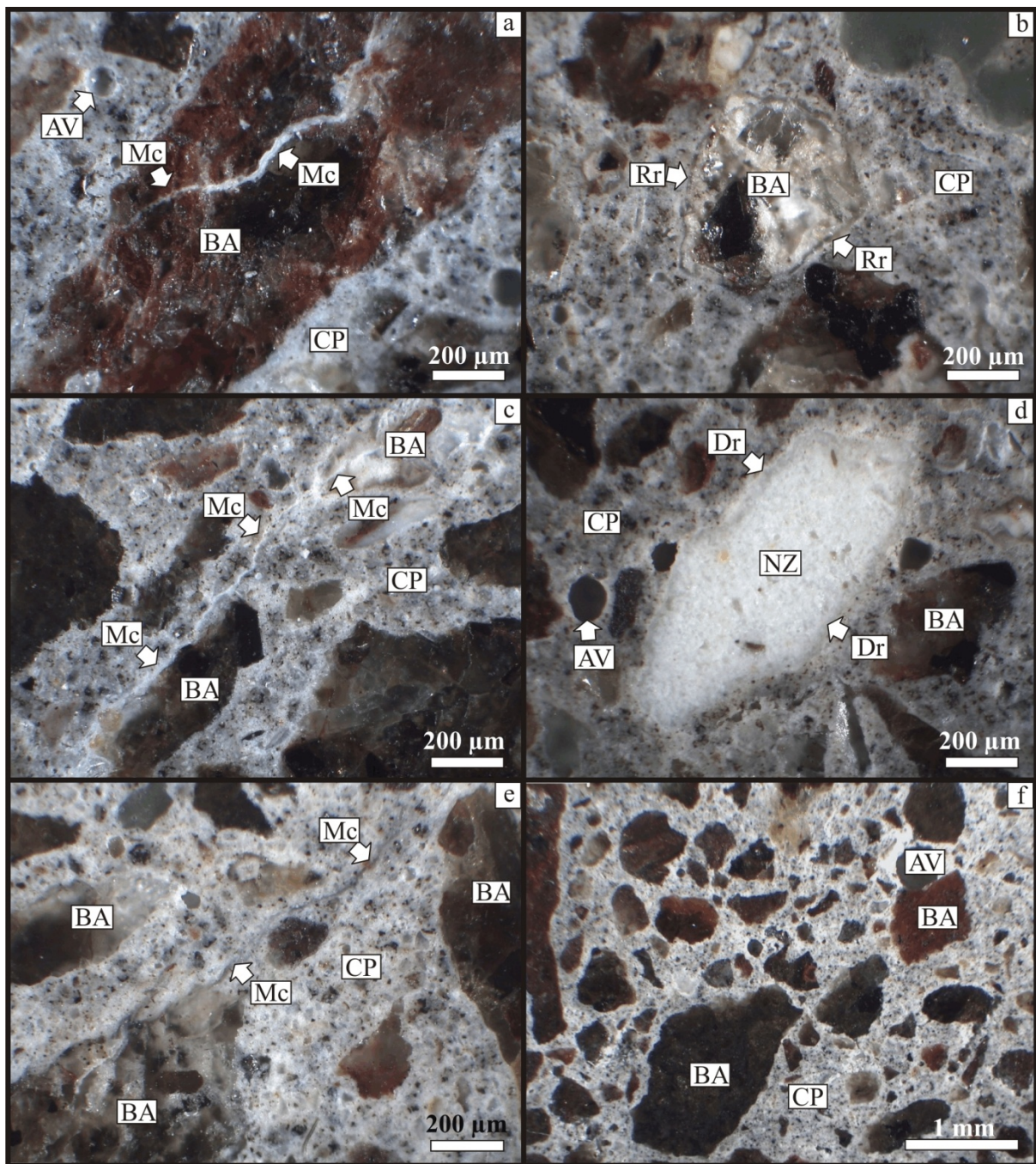


Figure 4: Macroscopic observations. a, b) CS (without zeolite addition). c, d) Mortar with 20% replacement of cement by NZ. e, f) Mortar with 20% replacement of cement by MZ. AV: air void, BA: basaltic aggregate, CP: cement paste, NZ: natural zeolite. Mc: microcrack, Rr: Reaction rim, Dr: Decolourized rim.

4.4 Petrography

At microscopic level the CS shows clear evidence of deterioration. Microcracks in the cement paste, in the cement–aggregate interface and affecting the basaltic aggregates are observed. They are empty or filled with a massive material of low interference colour (black

to grey) deposited in layers (banded) (Figure 5a, b). Air voids are partially filled with a material of similar characteristics.

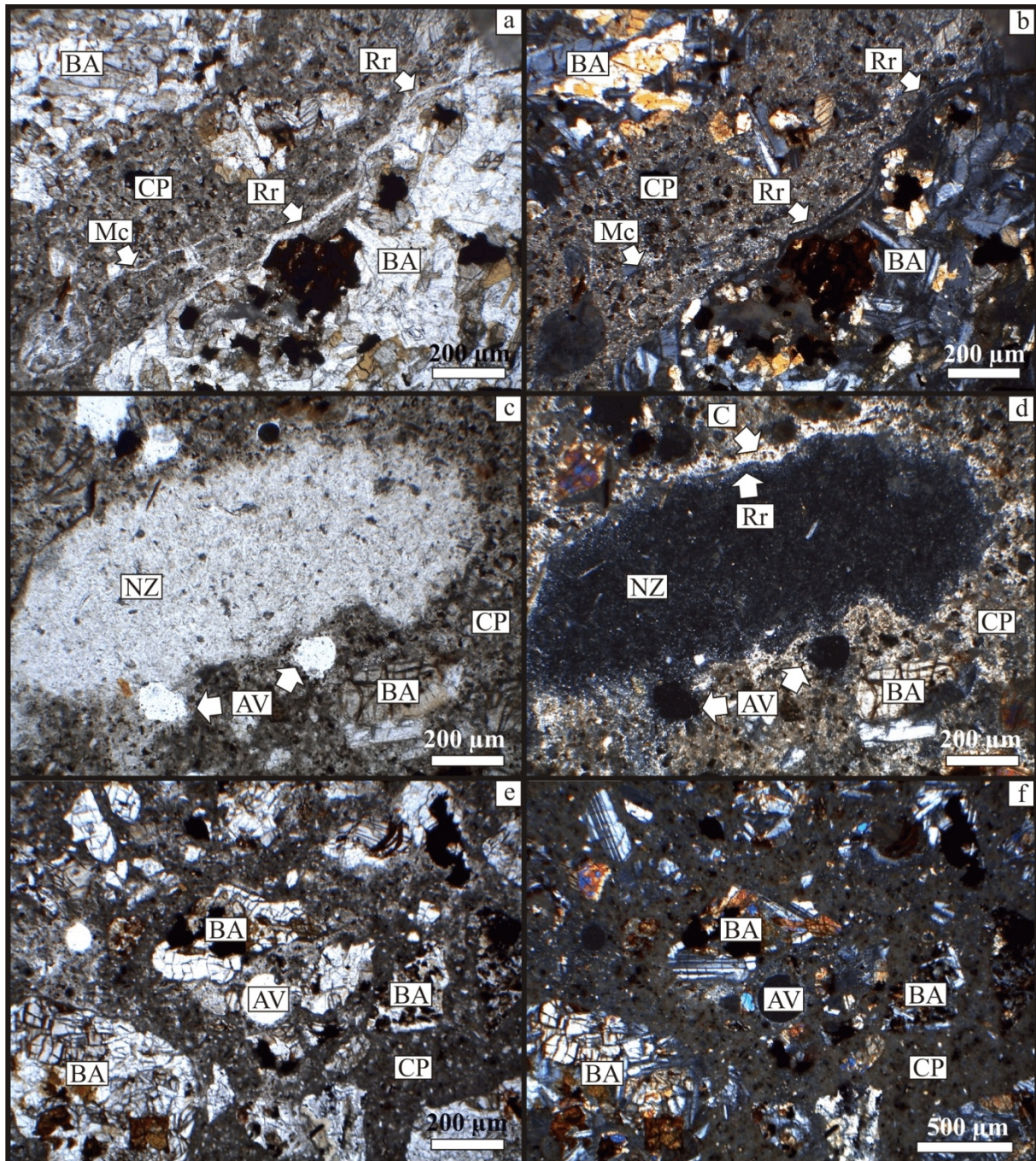


Figure 5: Microscopic observations (a, c, e: PPL; b, d, f: XPL). a, b) CS (without zeolite addition). c, d) Mortar with 20% replacement of cement by NZ. e, f) Mortar with 20% replacement of cement by MZ. AV: air void, BA: basaltic aggregate, CP: cement paste, NZ: natural zeolite. Mc: microcrack, Rr: Reaction rim, C: carbonated cement paste.

Mortars with NZ and MZ (20%) are less affected. Both mortar bars present empty microcracks or filled with a massive material of low interference colour mainly in the cement paste and the cement–aggregate interface. Air voids are mainly empty or partially filled with a similar material (black, grey or white). In the mortar with NZ, the zeolitic particles are clearly visible. Usually they have a ~30 μm thick reaction rim (Figure 5c, d) where a material of low interference colour (grey) is observed. Next to this zone, the cement paste is slightly carbonated (probably produced after test) due to the high porosity of the zeolitic particles (Figure 5d). However, the remainder of the paste is non-carbonated. In the mortar with MZ, the zeolitic particles could not be observed (Figure 5e, f).

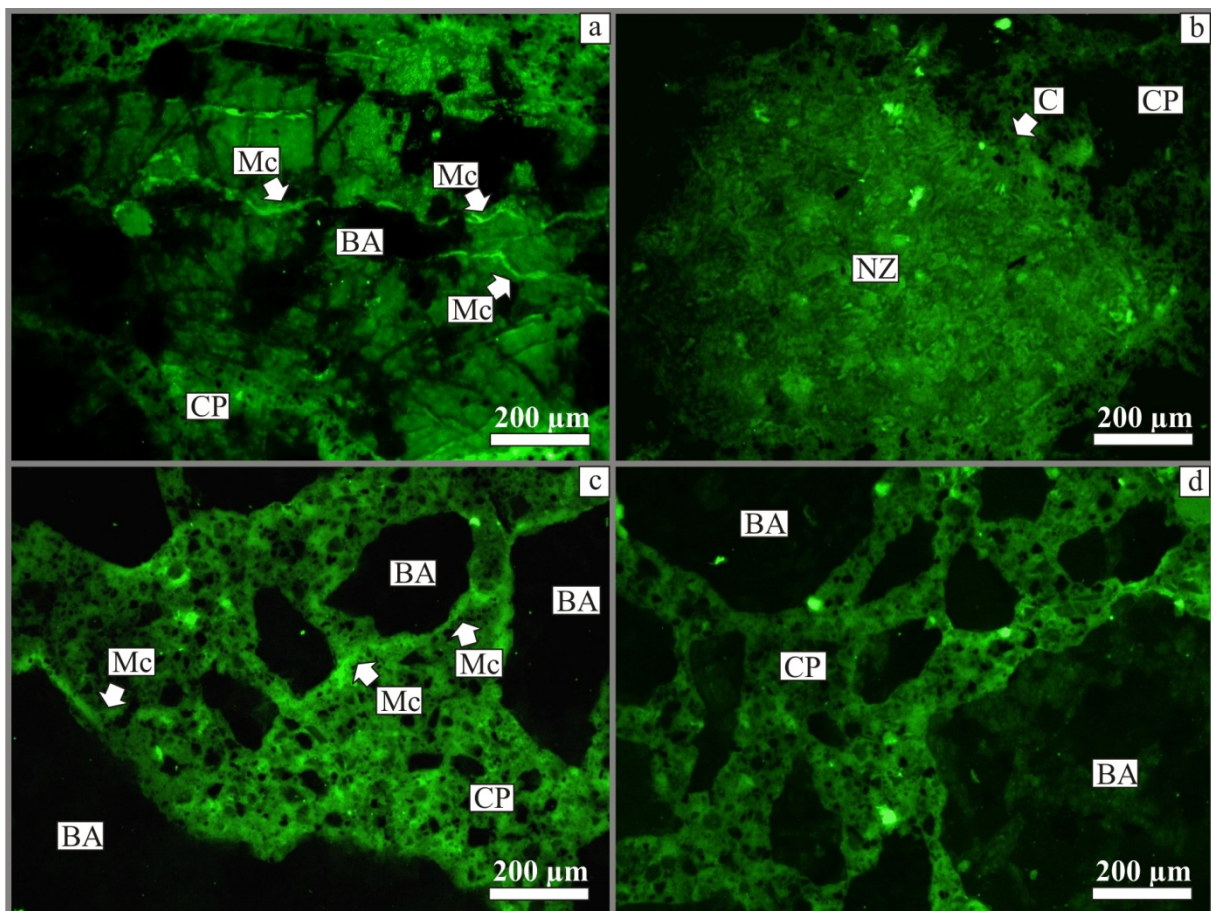


Figure 6: Microscopic observations (epifluorescence). a) CS (without zeolite addition). b) Mortar with 20% replacement of cement by NZ. c, d) Mortar with 20% replacement of cement by MZ. BA: basaltic aggregate, CP: cement paste, NZ: natural zeolite. Mc: microcrack, C: carbonated cement paste.

4.5 SEM-EDS

ASR products were recognized in all samples. They are mainly massive (Figure 7a) and consist of silicates (possibly hydrated) with variable contents of K, Na, Ca, Mg, and Al (Figure 7b, c).

Zeolitic particles in the mortars with NZ addition are easily identified through backscattered electrons images (Figure 7d) or by a combination of Si, Ca and K compositional

maps (Figure 7e, f, g). Coarse zeolitic particles are almost unmodified except in some sectors in the boundary where they began to react with the calcium from the cement paste.

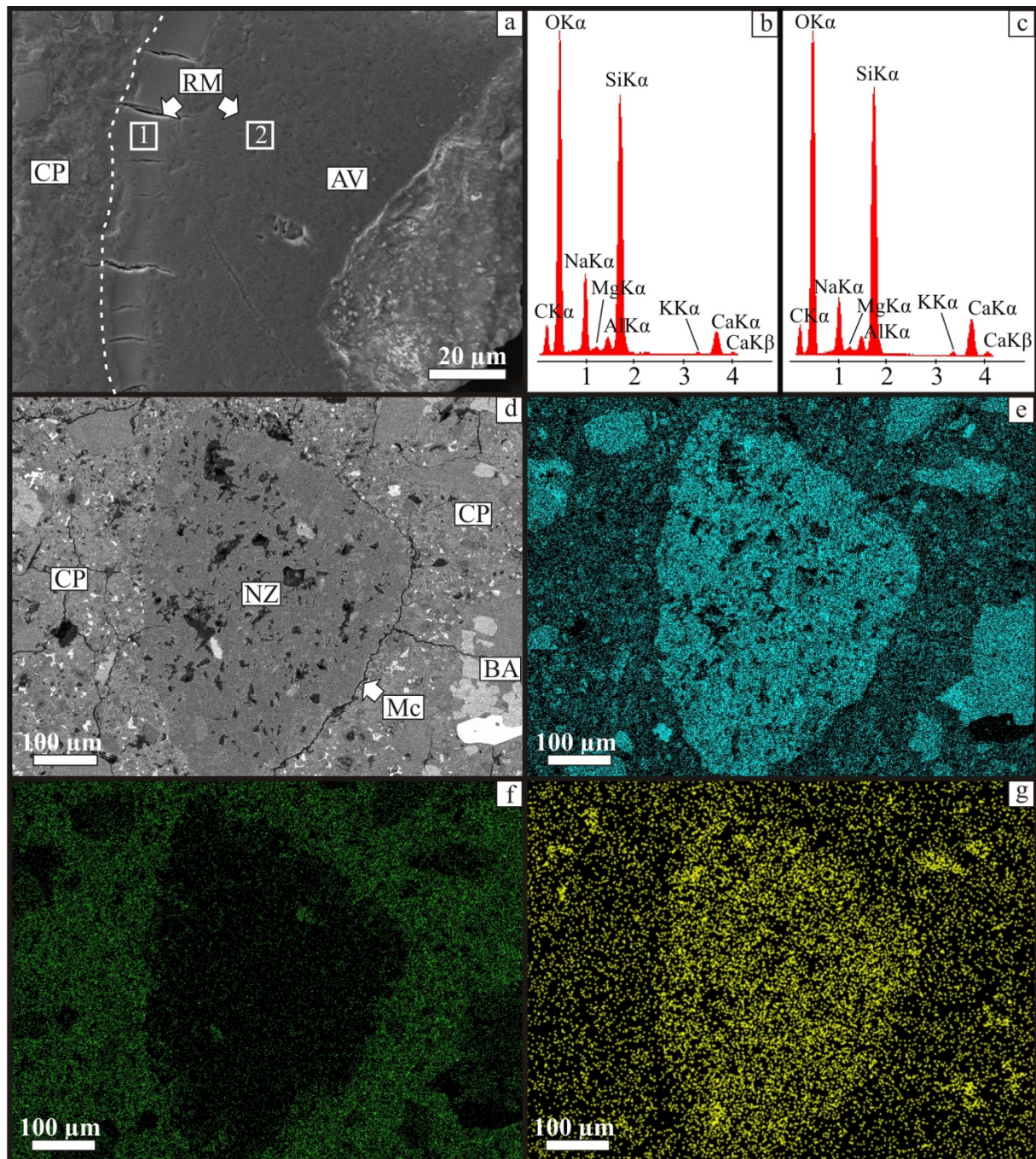


Figure 7: SEM-EDS. a) Secondary electron image of the ASR product filling an air void in the CS. b) EDS spectrum of ASR product in sector 1. c) EDS spectrum of ASR product in sector 2. d) Backscattered electron image of a zeolitic particle in the mortar with 20% replacement of cement by NZ. e-g) Compositional maps of Si (e), Ca (f) and K (g). CP: cement paste, AV: air void, RM: reaction material, NZ: natural zeolite, Mc: microcrack.

In the mortars with MZ addition, the zeolitic particles are not so easily identified, even in backscattered electron images (Figure 8a). The cement–zeolite interface is irregular and diffuse, and zeolitic particles are only visible at high zooms and combining compositional maps (Figure 8b, c, d). In this sample, it can be seen that the reaction between the zeolitic particles and the cement paste is not only restricted to the boundary but also to the interior of the aggregate.

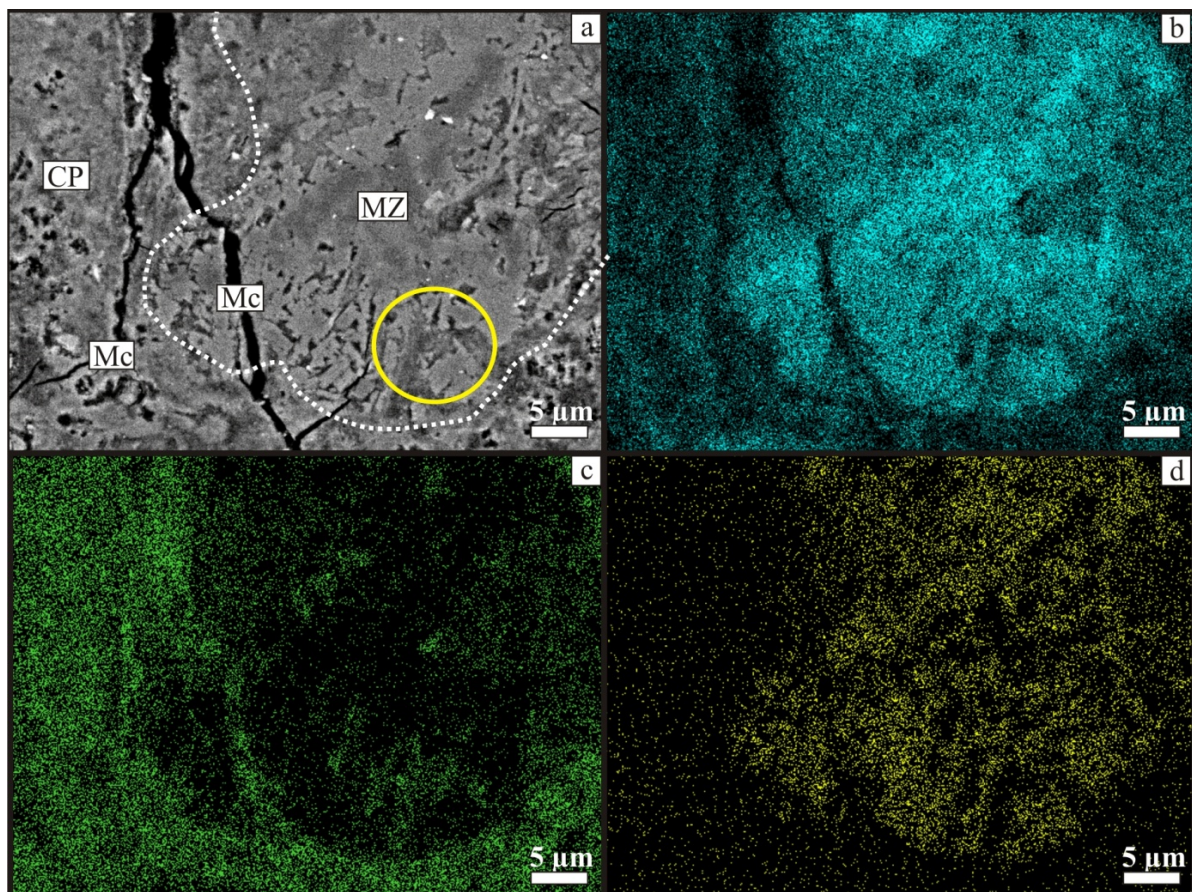


Figure 8: SEM-EDS. a) Backscattered electron image of a zeolitic particle in the mortar with 20% replacement of cement by MZ. b-d) Compositional maps of Si (b), Ca (c) and K (d). CP: cement paste, MZ: milled zeolite, Mc: microcrack. Yellow circle: reaction in zeolitic particle.

5. DISCUSSION

The fineness of the zeolitic particles from the province of La Rioja notably influences their behaviour as a pozzolanic concrete admixture. After 16 days of testing, a reduction in expansion (~42 %) was detected in the mortars with 20% replacement by NZ. However, the behaviour was still reactive. It was seen through macro and micro-observations that although the coarse zeolitic particle shows some reaction, it is restricted to the boundaries of the aggregate. Therefore, the pozzolanic process is not enough to inhibit the ASR. On the other hand, the mortars with 20% replacement by MZ produced a 90% reduction in expansion at 16 days (and it continued to be non-reactive till 28 days), below the limit prescribed by the standard. In this case, only microstructural and chemical observations through SEM-EDS

allow identifying zeolitic particles and the reaction processes, which are not only restricted to the boundaries but also inside the aggregate. Therefore, controlling the fineness of the zeolitic admixture is essential in order to properly inhibit the ASR in concrete, in agreement with other studies [13].

Some studies [14,15] have shown that when supplementary cementing materials (SCM) are not fine enough, not only its inhibitor capability is lost but also ASR can be potentiated due to coarser particles of SCM can also act as potentially reactive particles. In addition, previously ground SCM can lead to inhibition or exacerbation of the alkali-silica reaction (ASR), depending on the percentage used. In this study, a dosage of 20% replacement of cement by MZ appears to be a good strategy not only to inhibit the ASR when reactive basaltic aggregates are used as concrete aggregates but also to improve the physico-mechanical behaviour of concrete, as suggested by other studies [16]. The mechanism by which natural zeolites may act as ASR inhibitor is by decreasing the alkaline ion concentration in the pore solution through ion exchange, adsorption and pozzolanic reaction [17]. In addition, zeolite reactivity appears to be related to its large external specific surface and metastability, which favor its dissolution into the saturated lime solution and the successive precipitation of hydrated calcium silicate and hydrated calcium aluminate phases [18].

6. CONCLUSIONS

A simple milling process transforms the natural zeolite into a good pozzolanic material (~86% of the particles $\leq 45 \mu\text{m}$) inhibiting the ASR.

- The reaction of the zeolitic particles is limited to the boundaries in the NZ, while the reaction continues inside the aggregates in the MZ. The smaller the grains are, the bigger the specific surface and the possibility to ingress into the aggregate become.
- Although scarce microcracks and gel were observed in the samples with 20% replacement of cement by MZ, the microstructure of the mortars is well preserved. Therefore, this dosage appears to be an appropriate percentage to inhibit the ASR (the samples were non-reactive at 16 days and even at 28 days).
- Although more studies are needed, we encourage people involved in construction to use this kind of material accumulated in spoil heaps in quarries as concrete admixtures since these materials can act as good pozzolans and simultaneously have a positive impact on the environment.

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