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Use of zeolite-bearing pozzolan to inhibit the reactivity of a sand from Argentina

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Abstract

Sands used as fine aggregate for concrete in the south of Buenos Aires province (Argentina) are composed of a high proportion of particles containing glassy materials (volcanic glass), exceeding the maximum content established in the standards. In a previous work, the potential reactivity against the alkali-silica reaction (ASR) of a sand sample exploited near Médanos locality was studied. It contains volcanic glass (4.5 %) and volcanic rocks (27.5 %), most of them with glassy mesostasis. The potential reactivity was confirmed by the petrographic method (IRAM 1649 - ASTM C295) and the accelerated mortar bar test (IRAM 1674 – ASTM C1260) (0.677 % at 14 days). Previous studies on an affected roundabout concrete pavement that only reached 20 % of its projected life confirmed the reactivity of the sand. In this work, results of the conventional concrete prism test (IRAM 1700 - ASTM C1293) and the accelerated concrete prism test (IRAM 1700 - RILEM AAR 4.1) performed on the same fine aggregate are presented. Considering that this sand is one of the main materials used as fine aggregate in the area, a zeolite-bearing pozzolan from Mendoza (Argentina) was used to inhibit the ASR. Expansions in the conventional and accelerated concrete prism tests confirmed the high reactivity of the sand (0.392 % and 0.391 %, respectively). The natural pozzolan was effective in inhibiting the ASR, allowing the use of the reactive sand while contributing to concrete sustainability by reducing the consumption of cement (30 % replacement by mass). Petrographic post-test studies on mortar bars showed that the aggregates containing glassy materials are responsible for the ASR. The pozzolanic reactivity of the mineral addition was confirmed by SEM-EDS.

***Keywords**: alkali-silica reaction; reactive sand; sustainable concrete; zeolite-bearing pozzolan*

1. INTRODUCTION

Sands from the south of Buenos Aires province (Argentina), used as fine aggregates for concrete, contain abundant volcanic glass (as individual particles or in volcanic rock mesostasis) [1]. Generally,

fine aggregates used in Bahía Blanca area are composed of more than 50 % of volcanic rocks. Many of those rocks present an unaltered glassy matrix or partially altered to clay minerals [2, 3]. In addition, unaltered volcanic glass particles are also frequent (5 % - 15 %).

In a previous work [4] the potential reactivity of ten samples of fine aggregates from quarries of Buenos Aires province were evaluated against the alkali-silica reaction (ASR) by the petrographic method (IRAM 1649 [5] - ASTM C295 [6]) and the accelerated mortar bar test (AMBT, IRAM 1674 [7] - ASTM C1260 [8]). All samples were qualified as potentially reactive by both methods. One of those samples, located near Médanos locality (Figure 1.1), was used as fine aggregate for a concrete pavement of a national route in the area. Before four years of its service life, the structure undergone important damage leading to the replacement of affected slabs. The concrete presented evidence of lixiviation processes and reaction rims in the aggregates, disturbance of mortar texture, and abundant microcracks. It was concluded that the early concrete deterioration was due to the ASR, the sand fraction being the reactive component [9].

In the present work, additional studies were performed on the fine aggregate from Médanos area by the conventional concrete prism test (CPT, IRAM 1700 [10] - ASTM C1293 [11]) and the accelerated concrete prism test (ACPT, IRAM 1700 [10] - RILEM AAR 4.1 [12]) to confirm the reactive behavior of this material. As this sand is one of the main materials used as fine aggregate for concrete in the area (due to its physical characteristics and availability), a zeolitized vitreous breccia from the south of Mendoza province (Argentina) was studied as natural pozzolan in different percentages of cement replacement to inhibit the ASR (preventive performance measure – IRAM 1512 [13]).

Zeolite-bearing materials can be effective in inhibiting the ASR for different reasons. Zeolites can decrease the alkaline ion concentration in the pore solution through ion exchange, adsorption, and pozzolanic reaction [14]. In addition, their reactivity appears to be related to the large external specific surface and metastability, which favor their dissolution into the saturated lime solution and the successive precipitation of hydrated calcium silicate (± Al) phases [15-17].

Figure 1.1: Geographical location of Médanos locality in Buenos Aires province and of pozzolan deposit (1) in Mendoza province (Argentina).

2. MATERIALS AND METHODS

The fine aggregate was extracted from a stockpile in a quarry located near Médanos locality (Figure 1.1), in the south of Buenos Aires province (40 km SW of Bahía Blanca, Argentina). This material was previously qualified as potentially reactive by the AMBT (0.677 % at 14 days) and the petrographic method (4.5 % of volcanic glass as individual particles and 27.5 % of volcanic rocks, most of them with glassy mesostasis).

Additional studies to assess the potential reactivity of this material were conducted by the CPT and the ACPT. After being demolded, concrete prisms were wrapped in damp cotton cloth covered with polyethylene film, placed in a nylon bag with 5 ml of distilled water, and hermetically sealed before being placed in the storage containers. In addition, in the ACPT 420 kg/m^3 of cement was used with 5.25 kg/m^3 total alkali content in concrete, instead of 440 kg/m^3 of cement and 5.5 kg/m^3 total alkali content as specified in RILEM AAR-4.1 standard. Non-reactive coarse aggregates and an ordinary portland cement class 40 (OPC 40) from Argentina were used for the tests. According to Argentine standard, expansion limit to consider an aggregate as potentially reactive is 0.04 % both in the CPT and the ACPT at 52 weeks and 13 weeks, respectively [10].

To inhibit the ASR in the fine aggregate, a natural pozzolan (zeolitized vitreous breccia) from the south of Mendoza province (Argentina) was used [18]. The pozzolanic activity of the material was confirmed in previous studies [19, 20]. Although this material was previously characterized [18-20], new analyses were performed for the present work considering the possible geological heterogeneity of the deposit. The pozzolan was analyzed by X-ray diffraction (XRD) using a Rigaku D-Max III-C diffractometer, working at 35 kV and 15 mA, using Cu $K\alpha_{1,2}$ radiation (λ = 1.541840 Å) filtered with a graphite monochromator in the diffracted beam, from 3º to 60º 2θ with increments of 0.04° 2θ and a counting time of 1 s per step. Additional chemical studies were performed by X-ray fluorescence (XRF) using Rigaku RIX 2000 equipment at the Instituto de Geología y Minería (Jujuy, Argentina).

To test the potential inhibitory effect of the pozzolan on the reactive fine aggregate, mortar bars were made according to the AMBT [7]. The expansion limit to consider an aggregate as potentially reactive is 0.1 % at 14 days in 1N NaOH solution at 80 °C, according to the Argentine standard. Test time was extended up to 26 days to evaluate the evolution of expansion. Mortar bars with 10 %, 20 % and 30 % cement replacement (by mass) with natural pozzolan were prepared and compared to reference mortars without the mineral addition. After tests, mortars with 30 % replacement of cement were studied by petrography using a Leica DM750P polarizing microscope on thin sections and scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) with a LEO EVO 40-XVP microscope on gold-coated thin sections working at 20 kV.

Finally, the inhibitory effect of the natural pozzolan was also evaluated by the CPT and ACPT [10] using the same percentage of replacement (30 %). In this work, preliminary results are shown for the CPT, as the samples have not achieved yet the testing time required to evaluate the reactivity.

3. RESULTS AND DISCUSSION

3.1 Pozzolan characterization

The XRD pattern of the natural pozzolan is shown in Figure 3.1. The material is composed of mordenite (zeolite) with minor K-feldspar and plagioclase. A background hump was observed between 20º and 30° 2θ, indicating the presence of amorphous material (volcanic glass). These components were also observed by petrography and SEM-EDS. Previous studies [20] indicated that the amorphous phase content was ~70 % - 75 %, while mordenite content was ~25 %. Additional accessory phases (<5 %) were also found in the deposit [18] such as clinoptilolite, smectites, opal C-T, Fe-Ti oxides, and colloform silica.

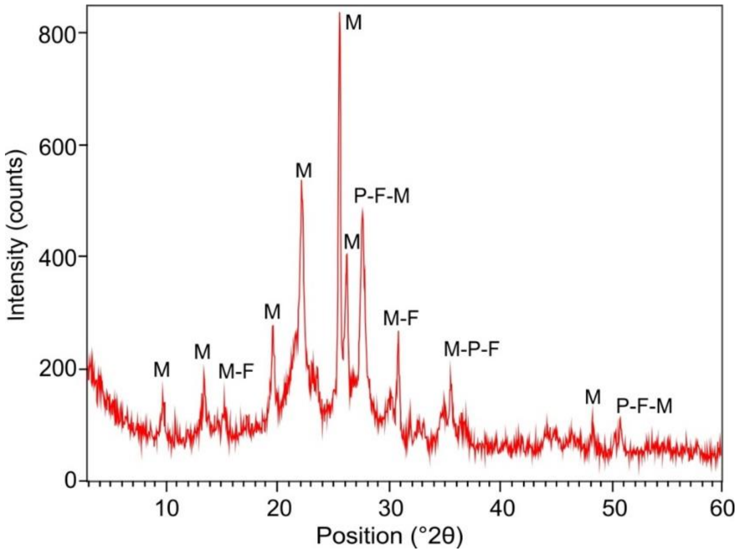

Figure 3.1: XRD pattern of the natural pozzolan. M: mordenite, F: K-feldspar, P: plagioclase.

Table 3.1 lists the chemical composition of the pozzolan. It can be observed that the content of SiO_2+Al_2O_3+Fe_2O_3 (82.5 %) is greater than 70 %, the loss on ignition is less than 10 %, and SO_3 content is very low (< 0.1 %), meeting the chemical requirements of ASTM C618 [21] for natural pozzolan Class N.

Table 3.1: Chemical composition of the pozzolan (%). LOI: loss on ignition.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI
70.62	0.11	10.98	0.90	0.02	0.39	2.34	1.69	2.49	0.01	0.07	9.85

3.2 CPT and ACPT

Expansion results obtained by the CPT and ACPT using the fine aggregate from Médanos locality are presented in Tables 3.2 and 3.3. It can be observed that expansion exceeds the limit of 0.04 % at 52 weeks (0.392 %) and 13 weeks (0.391 %) respectively, giving evidence of the high reactivity of the fine aggregate.

Table 3.2: Expansion in the CPT at 38 ºC [10].

Weeks	1	2	4	8	13	18	26	39	45	52
Expansion (%)	0.012	0.012	0.020	0.091	0.220	0.295	0.351	0.383	0.392	0.392

Table 3.3: Expansion in the ACPT at 60º C [10].

Weeks	5	8	10	13	15	20
Expansion (%)	0.322	0.352	0.359	0.391	0.395	0.371

3.3 AMBT

The Argentine standard IRAM 1512 [13], following FHWA [22] and AASHTO [23] recommendations, suggests verifying the behavior of the studied aggregate in the AMBT and CPT prior to evaluating the inhibitory effect of the active mineral addition. Effectiveness of the natural pozzolan in inhibiting the ASR can be verified by the AMBT if expansion results of CPT at 1 year and of AMBT at 14 days (without addition) fall in the region delimited by the two lines in Figure 3.2a (Annex D of IRAM 1512 standard [13]). In the present work, 0.729 % of expansion (Figure 3.2b) was measured at 14 days in the AMBT (without mineral addition). This value is slightly higher than that previously determined (0.677 % at 14 days [4]) due to heterogeneities of the sand deposit.

Considering the results obtained, the AMBT can be used to evaluate the effectiveness of natural pozzolan in inhibiting the ASR, as the expansion values fall whiting the limits of the field defined in Figure 3.2a.

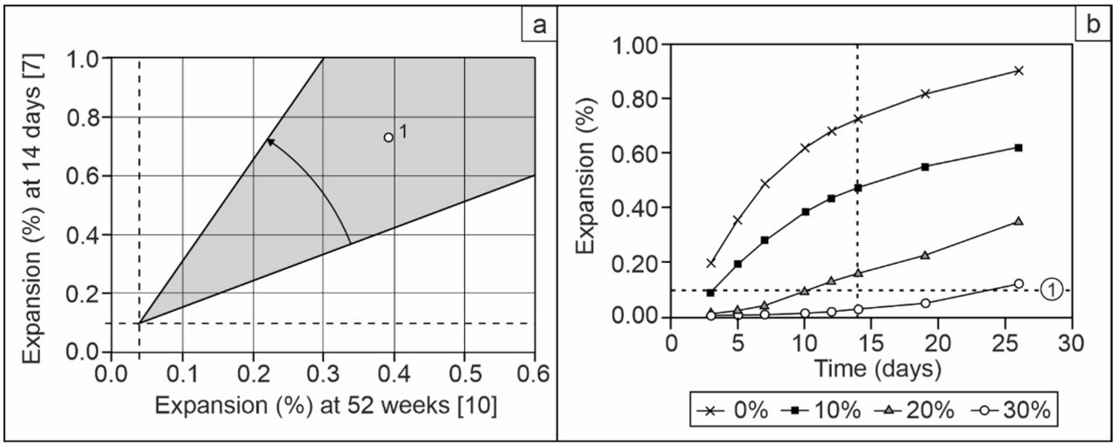

Figure 3.2: a) Comparison between expansion of reactive fine aggregate from Médanos locality (1) in the AMBT at 14 days and the CPT at 52 weeks (IRAM 1512, Annex D [13]). b) Expansion results of the reactive fine aggregate in the AMBT [7] with different replacement of cement by natural pozzolan (0 %, 10 %, 20 %, 30 %). 1: expansion limit of 0.1 % at 14 days in 1N NaOH solution.

Expansion curves of Médanos sample with different percentages of cement replacement by natural pozzolan (10 %, 20 % and 30 %) are shown in Figure 3.2b. At 14 days expansion results were 0.475 %, 0.162 %, and 0.030 % respectively. Considering these results, an additional test was performed using 25 % of natural pozzolan, obtaining 0.117 % of expansion. Therefore, 30 % of the mineral addition was enough to inhibit the ASR.

3.4 Ongoing tests

Considering that the AMBT revealed that 30 % of cement replacement by natural pozzolan was effective in inhibiting the ASR, the same percentage of replacement was also used in the CPT and the ACPT in order to verify whether the reaction was also inhibited in those tests. In the case of the CPT the expansion at 18 weeks is 0.014 % compared to 0.295 % measured in the CPT without mineral addition at the same age. Although the expansion is considerably lower, the expansive behavior of the prisms must be evaluated up to 2 years of testing according to IRAM 1512 standard [13] to verify the effectiveness of the addition in inhibiting the reaction.

Regarding the ACPT, the expansion measured at 13 weeks is 0.003 %, therefore, the reaction is inhibited. Although this procedure to verify the inhibitory effect of the active mineral additions is not included in the standard, the results will help collect records and define limits in a near future.

3.5 Post-test microstructural-chemical study of mortar bars

3.5.1 Petrography

Photomicrographs of the mortar bars without mineral addition and with 10 %, 20 % and 30 % of cement replacement by natural pozzolan are presented in Figure 3.3. Abundant microcracks up to ~20 µm thick mainly associated with volcanic aggregate and quartzitic aggregates are observed, except for the mortar bar with 30 % of cement replacement. Those microcracks link the sand aggregates through the cement paste and the cement-aggregate interface, or crosscut the aggregates, and are partially filled with ASR products. The mortar bar with 30 % of cement replacement shows no signs of deterioration. The cement paste is not affected (no microcracks were observed).

3.5.2 SEM-EDS

Figure 3.4a shows a pozzolan particle in the mortar bar with 30 % of cement replacement by the mineral addition after testing and Figure 3.4b, elemental profiles obtained by EDS crosscutting the pozzolan particle. In can be seen that the mineral addition presents a central sector with almost no chemical changes. Toward the edges of the particle there is a progressive decrease of Si and Al and an increase of Ca (from the cement paste). In the cement paste (very close to the pozzolan), a slight decrease of Ca and an increase of Si and Al are observed. This transitional change in the concentration of the elements at the interface has been previously described [20], revealing some chemical reaction between the cement paste and the pozzolan (pozzolanic reaction).

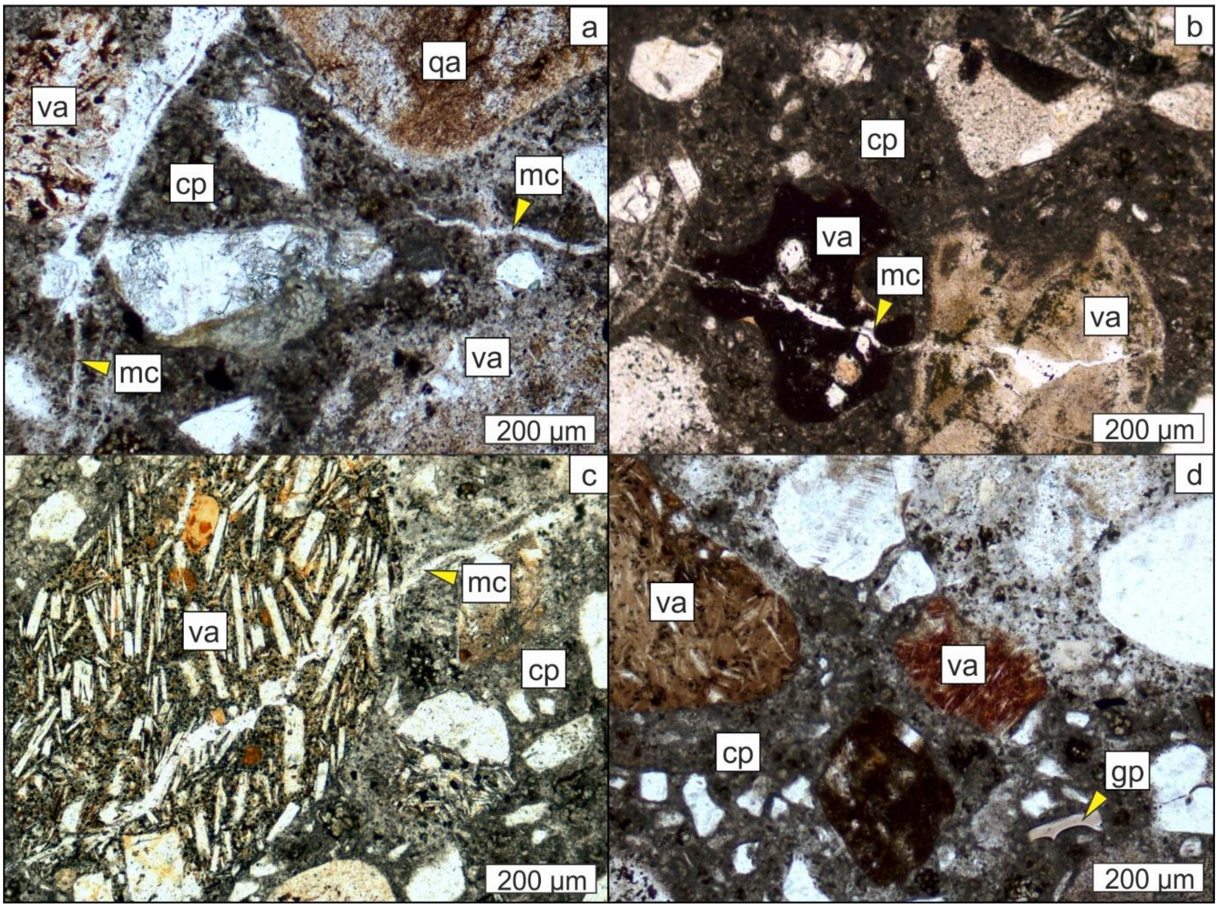

Figure 3.3: Photomicrographs. Mortar bars without pozzolan (a), with 10 % of pozzolan (b), 20 % of pozzolan and 30 % of pozzolan (d). cp: cement paste, mc: microcracks, va: volcanic aggregate, qa: quartzite aggregate, gp: volcanic glass particle.

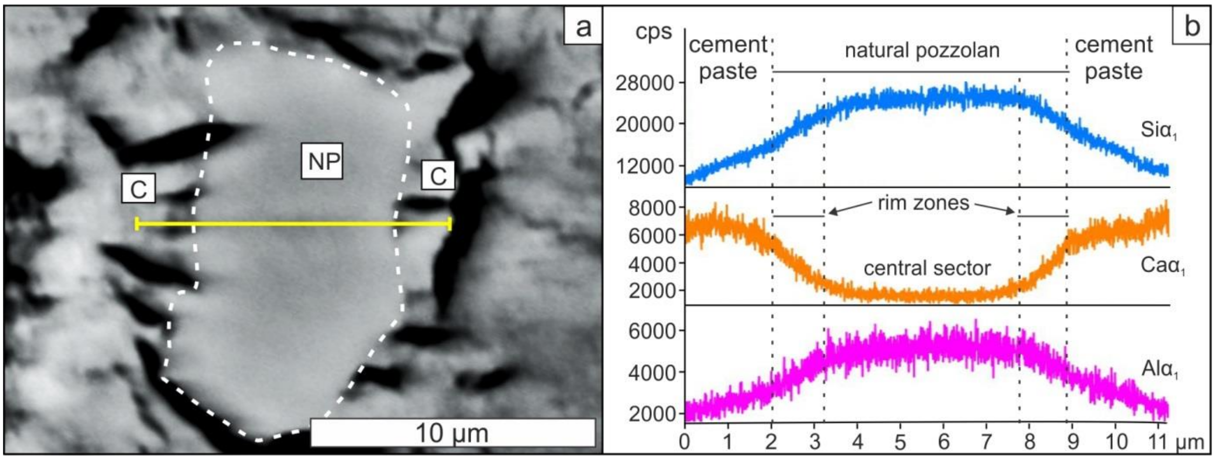

Figure 3.4: SEM-EDS. a) Backscattered electron image of a natural pozzolan particle in the mortar with 30 % replacement of cement. Yellow line indicates the sector where elemental profiles were obtained. C: cement paste, NP: natural pozzolan. b) Elemental profiles of Si, Ca, and Al obtained by EDS from the sector indicated in Figure 3.4a. cps: counts per second.

4. CONCLUSIONS

The mineral addition used as pozzolan corresponds to a zeolitized vitreous breccia rich in mordenite from the province of Mendoza (Argentina).

To inhibit the reactivity of the sand located near Médanos locality (Buenos Aires, Argentina), 30 % of cement replacement by natural pozzolan was necessary. The preventive measure adopted was checked by performance in the AMBT according to IRAM 1512 standard specifications [13]. However, the effectiveness of the pozzolan in inhibiting the ASR is also being checked by the CPT (ongoing test). So far, the expansion at 18 weeks is lower than the expansion without the pozzolan at the same age. However, the expansion progress should be monitored up to 2 years (expansion < 0.04 %) according to the standard. In addition, the inhibition effectiveness was also checked by the ACPT to have more records and propose limit values for this test. At 13 weeks the reactivity was inhibited (0.003 % expansion).

After being tested, mortar bars with 30 % of cement replacement by natural pozzolan show no signs of deterioration by petrography (no signs of cement paste or aggregate deterioration). By SEM-EDS it was observed that the pozzolan-cement paste interface shows evidence of chemical reaction between both components, confirming the pozzolanic behavior of the zeolitized vitreous breccia.

5. ACKNOWLEDGEMENTS

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