



Importance of using the natural pozzolans on concrete durability

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Abstract

Natural pozzolans have become important because of their role in concrete durability. This situation has provoked an increase in the use of pozzolanic cement in concrete construction. This paper reports results of different portland–pozzolan cements containing different natural pozzolans, and they were compared with ASTM Types I, II and V cements. The pozzolanic activity and composition of each pozzolan were evaluated. The susceptibility to sulfate attack was studied by measuring the expansion in mortar bars at different ages (according to ASTM C 1012 Method) for 78 weeks. It was found that certain cements containing pozzolans with high activity or low alumina content improve resistance to sulfate attack, although the amount of pozzolan in the cement is important.

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1. Introduction

World requirements of quality assurance in the production of concrete have encouraged the development of supplementary cementing materials, which, combined with portland cement, allow us to manufacture different types of cement.

The use of pozzolanic materials in the construction industry has been a common practice for many years. The materials with the best pozzolanic characteristics have not always been used in a country where there are natural pozzolans of volcanic origin like tuff. The importance of using natural pozzolans in the cement industry requires a complete evaluation of their effects on concrete.

The use of supplementary materials like natural pozzolans has improved the durability of concrete [1].

Possible technological benefits from the use of natural pozzolans in concrete include enhanced impermeability and chemical durability, improved resistance to thermal cracking, and increase in ultimate strength [2].

One way to improve the sulfate resistance is to use pozzolanic-portland cement. This investigation was conducted to show which parameters govern on sulfate resistance.

In Mexico, there are regions where the sulfate concentrations are moderate and severe, according to ACI 201 (Guide to Durable Concrete), as shown in Table 1. They indicate sulfate concentrations in soils from 0.11% to 0.70% and in groundwaters and wastewaters from 288 to 10000 ppm. In the Pacific Coast, the sulfate content varies from 3500 to 6700 ppm, and in the Gulf of Mexico, it varies from 2500 to 5700 ppm. The contact of concrete with these soils and waters may cause expansion, chemical deterioration, and disruption, therefore, it is very important to consider using supplementary cementing materials in the concrete (that is subject to sulfate attack) to improve their resistance and reduce this type of attack.

Since natural pozzolans are available in Mexico, the exploitation of pozzolanic or both pozzolanic and cementitious properties of mineral admixtures, when used as a partial replacement for cement, can lead to a considerable economic benefit and durability.

2. Scope of investigation

The objective of this study was to document the performance of nine natural pozzolans used to produce cement in Mexico and to correlate the performance results with the pozzolanic activity, chemical analysis, and the petrographic characteristics. Tests performed according to ASTM 1012 “Standard Test Method for Length Change

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Table 1
Sulfate content in different regions of Mexico

| Place (Mexico) | Water-soluble sulfate (SO_4^{2-}) in soils [%] | Sulfate in water (SO_4^{2-}) [ppm] | ACI 201.2R-92 |
|--------------------------------|-----------------------------------------------------------|-----------------------------------------------|----------------------------------|
| Texcoco, Mex. | 0.11–0.18 | | 0.10–0.20% (exposure moderate) |
| Altamira, Tamps. | 0.70 | | 0.20–2.00% (exposure severe) |
| Coatzacoalcos, Ver. | 0.20–0.28 | | |
| Wastewater, Toluca, Mex. | | 760 | 150–1500 ppm (exposure moderate) |
| Groundwater, Progreso, Yuc. | | 1995 | 1500–10000 ppm (exposure severe) |
| Seawater, Pacific Coast | | 3500–6700 | |
| Seawater, Gulf of Mexico Coast | | 2500–5700 | |

of Hydraulic Cement Mortar Exposed to a Sulfate Solution” [3] on eight portland–pozzolan cements and ASTM Types I, II and V were conducted. The proportioning of the mortar remained constant at 1 part of cement and 2.75 parts of standard sand, and the bars were stored in 5% sodium sulfate solution. The ability of mortar made using portland cements and portland–pozzolan cements to resist attack by sulfates was examined. These include composition, reactivity, and amount of pozzolan used with the portland cement and amount of tricalcium aluminate in the cement.

The classification of every pozzolan includes its mineralogical–petrological characteristics, chemical composition, and pozzolanic activity index with lime and portland cement, and available alkalis were evaluated.

3. Experimental methods

3.1. Materials

3.1.1. Natural pozzolans

In this study, as shown in Fig. 1, representative samples from nine natural pozzolanic deposits located in different states of the Mexican Republic were used. These materials were dried at a temperature of 100 °C, ground, and fineness

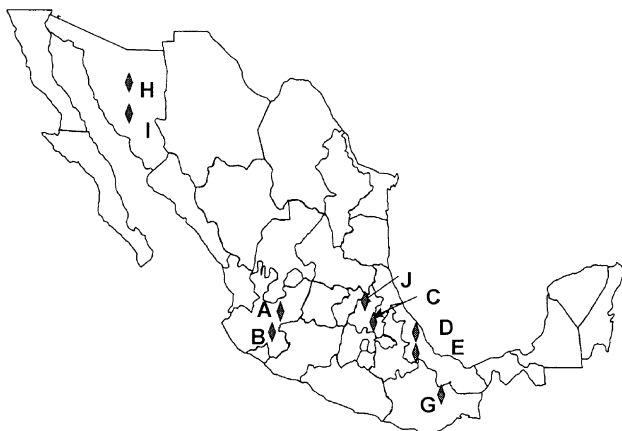


Fig. 1. Localization of natural pozzolans in Mexico.

was determined (amount of material retained in No. 325 sieve–45 μm) according to ASTM C 430 [4].

Their physical characteristics and mineralogical identification by XRD are shown in Tables 2 and 3. Physical and chemical properties as pozzolanic activity with lime and portland cement, and available alkalis are shown in the Table 4. They were determined according to ASTM C 311 [5].

3.1.2. Cements

The cements used included the following: three portland cements (Types I, II and V) and eight portland–pozzolan cements. These cements have different clinker, pozzolanic material, and amount of pozzolan. The physical properties and chemical analysis of the cements are given in Tables 5 and 6.

3.1.3. Standard sand

The graded standard sand in making the mortar mixtures complied with the ASTM C 778.

3.2. Test methods

3.2.1. Petrographic examination

In order to make the petrographic identification, thin layers of each sample were prepared and observed under the petrographic microscope.

3.2.2. X-ray diffraction

The identification of the clay fraction in pozzolans was done on a Siemens X-ray diffractometer; the powder method and radiation $\text{K}\alpha\text{Cu}$ were used.

3.2.3. Chemical analysis

The chemical compositions of cements and pozzolans were determined by wet chemical methods according to ASTM C 114 [6] (see Tables 4–6).

3.3. Tests performed according to ASTM C 1012 method

ASTM 1012 standard test method [3] covers the determination of the length change of mortar bars stored in 5% sodium sulfate solution. Mortar mixtures proportioned as 1 part of cement, 2.75 parts of sand, and W/C of 0.485 were

Table 2
Mineralogical and petrological characteristics of natural pozzolans

| Pozzolan/classification | Mineralogical (essential) | Special characteristics |
|----------------------------------------------------|--------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| PZ-A Tuff vitreous acid* | G and pumice lithics | • Pyroclastic texture • Voids and fluid structure |
| PZ-B Tuff crystal–vitreous Dacitic* | AN, Q, G, andesite, and dacite lithics | • Pyroclastic texture • Devitrification 20% • Andesite and dacite lithics altered by sericite 10% |
| PZ-C Tuff vitreous–lithic Rhyolitic* | G, Q, OL, and pumice | • Pyroclastic texture • Voids structure • Lithics sericitized and oxidized less than 10% |
| PZ-D Tuff lithic–andesitic* | AN and G | • Pyroclastic texture |
| PZ-E Tuff crystal–andesitic* | AN and G | • Trachytic texture • Voids structure |
| PZ-G Tuff vitreous–crystalline Dacitic | OL, AN, Q, G, and pumice and dacite lithics | • Pyroclastic texture • Lithics altered by chlorite and sericite • Devitrification 60% |
| PZ-H Tuff vitreous Rhyo-dacitic | OL, Q, G and andesite, dacite and pumice lithics | • Pyroclastic texture • Voids structure • Devitrification less than 30% • Lithics altered of dacite and andesite |
| PZ-I Tuff crystal–vitreous–lithics Andesitic | OL, AN, G, and volcanic lithics | • Pyroclastic texture • Voids and cracked structure • Devitrification 100% • Some crystal dissolution • Matrix quartz-feldspatic • Mafics altered to clay |
| PZ-J Tuff vitreous Rhyolitic* | G, Q, S, and OL | • Pyroclastic texture • Voids and fluid structure • Devitrification 10% |

OL: oligoclase; AN: andesine; G: glass; Q: quartz; S: sanidine; R: rock.

* Incoherent material.

used cast prismatic specimens $25 \times 25 \times 285$ mm in size. When pozzolanic cements were used, the water content was adjusted to keep flow of the mortar within $\pm 5\%$ of the obtained with W/C of 0.485. Specimens were cured until the mortar cube strength reached a value of 20 MPa. The results as expansions of mortar bars for 78 weeks are shown in Table 7.

4. Results and discussion

4.1. Natural pozzolans

4.1.1. Petrographic characteristics

Natural pozzolans in Mexico are materials of pyroclastic origin as a result of explosive volcanic eruptions, where eruptive fragments are transported by air to be finally deposited in the ground water, and once deposited as incoherent materials, they can be submitted to diagenetic processes transforming them into compacted rocks called tuffs.

In the case of Mexican pozzolans, they are indistinctly exploited as incoherent materials in the form of compact rocks. In the incoherent pozzolans, these correspond to similar deposits (like in the state of Hidalgo were they are close to each other) with very little lithological

variations causing small changes in the chemical composition. The products show an evident acid composition. In this respect, the pozzolan PZ-B, which is in another region, shows a low content of SiO_2 , which is a basic material but does not act in detriment to the pozzolanic activity index.

It is very common that these materials are found partially cemented with a vitreous paste with several degrees of alteration. The mineralogical–petrological characteristics and the diagenetic processes affecting reach deposit, in particular, can be found in Table 1.

Table 3
Mineralogical identification by X-ray diffraction of natural pozzolans

| Pozzolan | Minerals identified |
|----------|---------------------|
| PZ-A | F, Q, and Crt |
| PZ-B | F and Crt |
| PZ-C | F |
| PZ-D | F, H, and Crt |
| PZ-E | F, H, and Crt |
| PZ-G | H, Clp, F, and Cl-M |
| PZ-H | Cl-M, Q, Clp, and F |
| PZ-I | Q, Crt, F, and Clp |
| PZ-J | Crt and F |

Identification: Cl: chlorite; M: montmorillonite; Crt: cristobalite; Q: quartz; F: feldspar; H: heulandite; G: gmelinite; Clp: clinoptilolite.

Table 4
Physical properties and chemical analysis of some natural pozzolans

| | PZ-A | PZ-B | PZ-C | PZ-D | PZ-E | PZ-G | PZ-H | PZ-I | PZ-J |
|---------------------------------------------------------------------------------------------|------|------|------|------|------|------|-------|------|------|
| <i>Physical tests</i> | | | | | | | | | |
| <i>Fineness</i> | | | | | | | | | |
| Passing 45 μm , % | 93.9 | 93.6 | 93.6 | 93.8 | 93.5 | 94.7 | 93.8 | 94.5 | 94.6 |
| <i>Chemical Analysis, %</i> | | | | | | | | | |
| SiO ₂ (S) | 69.2 | 55.1 | 70.1 | 58.6 | 58.9 | 62.4 | 62.1 | 64.8 | 69.1 |
| Al ₂ O ₃ (A) | 13.6 | 19.9 | 13.9 | 19.7 | 20.8 | 16.0 | 11.6 | 14.1 | 14.7 |
| Fe ₂ O ₃ (F) | 2.8 | 6.4 | 2.2 | 5.2 | 5.0 | 2.8 | 2.8 | 1.5 | 2.1 |
| S + A + F | 85.6 | 81.4 | 86.2 | 83.5 | 84.7 | 81.2 | 76.5 | 80.4 | 85.9 |
| CaO | 1.8 | 6.4 | 1.0 | 6.7 | 6.4 | 2.3 | 5.8 | 3.1 | 1.7 |
| MgO | 1.0 | 3.9 | 0.5 | 3.0 | 2.9 | 1.3 | 1.7 | 0.6 | 0.8 |
| SO ₃ | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| Na ₂ O | 2.92 | 2.56 | 2.96 | 3.44 | 3.76 | 1.62 | 1.04 | 1.28 | 2.88 |
| K ₂ O | 3.20 | 2.44 | 5.98 | 1.68 | 1.30 | 3.12 | 1.94 | 1.76 | 5.20 |
| Equivalent alkalis (as Na ₂ O) | 5.02 | 4.17 | 6.89 | 4.55 | 4.62 | 3.67 | 2.32 | 2.44 | 6.30 |
| Loss on ignition | 5.0 | 4.2 | 3.3 | 1.7 | 1.5 | 11.0 | 13.3 | 10.7 | 3.6 |
| <i>Pozzolanic activity with portland cement</i> | | | | | | | | | |
| Activity index at 28 days | 90.9 | 90.9 | 98.5 | 80.9 | 83.3 | 91.8 | 103.1 | 97.3 | 94.6 |
| <i>Pozzolanic activity with lime</i> | | | | | | | | | |
| Compressive strength at 7 days, MPa | 6.58 | 4.78 | 5.75 | 5.1 | 5.40 | 6.10 | 5.93 | 5.98 | 5.64 |
| <i>Available alkalis</i> | | | | | | | | | |
| Na ₂ O | 0.55 | 0.24 | 0.42 | 0.41 | 0.37 | 0.07 | 0.26 | 0.12 | 0.43 |
| K ₂ O | 0.94 | 0.22 | 1.02 | 0.43 | 0.45 | 0.22 | 0.13 | 0.54 | 1.10 |
| Equivalent alkalis (as Na ₂ O) | 1.17 | 0.38 | 1.09 | 0.69 | 0.67 | 0.21 | 0.34 | 0.47 | 1.15 |
| Specification for ASTM C 618, Class N, maximum equivalent alkalis (as Na ₂ O) | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 | 1.50 |

Table 5
Physical properties and chemical analysis of portland cements

| | ASTM Type I cement | ASTM type II cement | ASTM type V cement |
|-------------------------------------------------|-----------------------|------------------------|-----------------------|
| <i>Physical tests</i> | | | |
| <i>Fineness</i> | | | |
| Passing 45 μm , % | 80.0 | 87.1 | 77.8 |
| Blaine, m ² /kg | 319 | 372 | 272 |
| <i>Compressive strength of 51-mm cubes, MPa</i> | | | |
| 3 days | 20.0 | 23.9 | 13.0 |
| 7 days | 25.8 | 33.3 | 19.5 |
| 28 days | 30.7 | 44.4 | 27.5 |
| <i>Chemical analysis, %</i> | | | |
| SiO ₂ | 20.8 | 20.6 | 20.7 |
| Al ₂ O ₃ | 5.8 | 5.1 | 4.9 |
| Fe ₂ O ₃ | 3.1 | 3.4 | 4.8 |
| CaO | 61.5 | 62.7 | 62.9 |
| MgO | 2.4 | 2.2 | 1.6 |
| SO ₃ | 2.4 | 2.6 | 2.4 |
| Na ₂ O | 0.41 | 0.09 | 0.22 |
| K ₂ O | 0.56 | 0.50 | 0.40 |
| Loss on ignition | 1.5 | 1.5 | 1.8 |
| <i>Bogue potential compounds composition, %</i> | | | |
| C ₃ S | 42.0 | 52.2 | 50.8 |
| C ₂ S | 28.0 | 19.7 | 21.1 |
| C ₃ A | 10.1 | 7.8 | 4.9 |
| C ₄ AF | 9.4 | 10.3 | 14.6 |

Mexican tuffs (compacted materials) used as pozzolans have a first characteristic in their components (pyroclastic and matrix) in which outstanding process is zeolitization, which shows the great capacity that volcanic materials have to produce this diagenetic transformation [7]. Zeolitic minerals identified (X-ray) in three (PZ-G, PZ-H, and PZ-I) of these pozzolans are clinoptilolite, heulandite, and gmelinite. It is clear that there exists an important association between the alteration of the vitreous matrix of these tuffs with the presence of a pair of mineralogical species of diagenetic origin of zeolite type, evidence that has been proved in laboratory tests by Sersale [8]. As in the case of incoherent materials, its characteristics are shown in Table 2.

4.1.2. X-ray diffraction

By means of the X-ray diffraction patterns, the following constituents were identified: feldspars, quartz, cristobalite, clay minerals as chorite–montmorillonite, and zeolitic compounds as clinoptilolite, heulandite, and gmelinite. Results are given in Table 3.

4.1.3. Chemical analysis

In the pozzolans, it is possible to find characteristics easily measurable and correlate with their activity. Among these characteristics, the chemical composition plays an important part. In the Table 4, it can be seen that the chemical composition of Mexican natural pozzolans have a

Table 6
Physical properties and chemical analysis of pozzolanic cements

| | CPZ-A | CPZ-B | CPZ-C | CPZ-DE | CPZ-G | CPZ-H | CPZ-I | CPZ-J |
|------------------------------------------|-------|-------|-------|--------|-------|-------|-------|-------|
| <i>Physical tests</i> | | | | | | | | |
| Fineness | | | | | | | | |
| Passing 45 μm , % | 93.6 | 90.2 | 97.4 | 89.5 | 89.1 | 95.5 | 97.1 | 88.6 |
| Blaine, m^2/kg | 488 | 444 | 394 | 414 | 380 | 434.5 | 387.5 | 380 |
| Compressive strength of 51-mm cubes, MPa | | | | | | | | |
| 3 days | 17.2 | 11.9 | 16.6 | 17.7 | 21.2 | 24.2 | 24.8 | 17.5 |
| 7 days | 22.2 | 16.4 | 20.6 | 22.3 | 24.2 | 28.2 | 27.6 | 24.2 |
| 28 days | 31.9 | 24.7 | 31.6 | 35.2 | 33.4 | 37.6 | 36.2 | 34.6 |
| <i>Chemical analysis, %</i> | | | | | | | | |
| SiO_2 | 39.7 | 38.2 | 36.1 | 26.7 | 29.5 | 31.2 | 29.8 | 37.6 |
| Al_2O_3 | 4.1 | 4.9 | 4.7 | 5.1 | 4.9 | 3.3 | 2.9 | 4.5 |
| Fe_2O_3 | 2.1 | 2.4 | 2.3 | 2.2 | 2.3 | 3.1 | 3.7 | 1.8 |
| CaO | 45.2 | 48.0 | 47.7 | 56.2 | 52.9 | 54.0 | 54.4 | 48.4 |
| MgO | 0.8 | 1.8 | 2.0 | 1.2 | 2.8 | 1.3 | 1.4 | 1.4 |
| SO_3 | 3.3 | 3.8 | 3.4 | 3.1 | 2.9 | 2.3 | 1.9 | 2.5 |
| Na_2O | 0.61 | 0.49 | 0.48 | 0.13 | 0.31 | 0.15 | 0.45 | 0.29 |
| K_2O | 0.82 | 0.66 | 0.45 | 0.30 | 0.86 | 0.60 | 0.70 | 0.66 |
| Loss on ignition | 2.7 | 3.4 | 2.4 | 4.8 | 3.0 | 3.6 | 3.2 | 2.3 |
| Amount of pozzolan | 30 | 22 | 21 | 10 | 16 | 19 | 14 | 24 |
| C_3A , % at clinker | 10.4 | 10.4 | 10.7 | 10.9 | 14.3 | 2.6 | 1.0 | 12.4 |

strong acid character, having a high ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) content ranging around 73.7–84% of the total. Between the two oxides, silica prevails in all cases. It reaches percentages greater than 55%. The importance of the content is clearly emphasized by the fact that the active vitreous phases of pozzolans generally are richer in silica and alumina content. Chemical composition of Mexican natural pozzolans is incoherent, and tuffs are rich in silica. It is important to emphasize that the total alkalis content in Mexican pozzolans is lower than 6.9%, whereas the loss on ignition is between 1.5% and 13.3%, and the content of other elements like lime is less than 7%.

The natural pozzolans to use as a mineral admixture in portland cement must meet certain chemical and physical requirements. For instance, ASTM C 618 Class N admix-

tures must have a minimum content of 70% in $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, whereas Mexican natural pozzolans have between 76.5% and 86.2%. This chemical requirement is arbitrary for the purpose and does not have direct relationship with properties of material. Although, the importance of the content ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) is emphasized by the fact that the active vitreous phases generally are richer in silica and alumina content. The Mexican natural pozzolans show a strong acidic character, having a ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) content ranging around 73.7–84% of the total. However, not all showed pozzolanic activity (Table 4).

4.1.4. Pozzolanic activity with lime

The evaluation of pozzolanic activity is essential in the consideration of the utility of a given pozzolan. Lea [9] has

Table 7
Results of ASTM C 1012 tests in portland and pozzolanic cements

| Cement | Expansion, % | | | | | | | | | | | |
|-------------------------------|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | Week | | | | | | | | | | | |
| | 1 | 2 | 3 | 4 | 8 | 13 | 15 | 16 | 26 | 39 | 52 | 78 |
| PC-I | 0.009 | 0.012 | 0.017 | 0.025 | 0.036 | 0.082 | 1.13 | | | | | |
| PC-II | 0.009 | 0.013 | 0.017 | 0.019 | 0.029 | 0.041 | 0.045 | 0.052 | 0.1 | 0.19 | 0.35 | |
| PC-V | 0.004 | 0.007 | 0.008 | 0.009 | 0.015 | 0.023 | 0.025 | 0.027 | 0.042 | 0.064 | 0.082 | |
| CPZ-A | 0.007 | 0.006 | 0.015 | 0.016 | 0.020 | 0.022 | 0.022 | 0.024 | 0.027 | 0.031 | 0.031 | 0.038 |
| CPZ-B | 0.014 | 0.018 | 0.023 | 0.028 | 0.035 | 0.039 | 0.041 | 0.043 | 0.055 | 0.072 | 0.084 | 0.11 |
| CPZ-C | 0.007 | 0.011 | 0.016 | 0.016 | 0.019 | 0.021 | 0.023 | 0.024 | 0.027 | 0.032 | 0.037 | 0.039 |
| CPZ-DE | 0.009 | 0.014 | 0.014 | 0.015 | 0.021 | 0.026 | 0.029 | 0.036 | 0.057 | 0.068 | 0.094 | |
| CPZ-G | 0.007 | 0.012 | 0.014 | 0.016 | 0.019 | 0.025 | 0.026 | 0.030 | 0.035 | 0.059 | 0.096 | 0.13 |
| CPZ-H | 0.003 | 0.007 | 0.008 | 0.007 | 0.009 | 0.011 | 0.013 | 0.013 | 0.016 | 0.025 | 0.033 | 0.034 |
| CPZ-I | 0.002 | 0.003 | 0.004 | 0.007 | 0.008 | 0.009 | 0.017 | 0.015 | 0.017 | 0.025 | 0.030 | 0.034 |
| CPZ-J | 0.009 | 0.013 | 0.019 | 0.019 | 0.020 | 0.022 | 0.025 | 0.025 | 0.024 | 0.037 | 0.042 | 0.044 |
| Specification for ASTM C 1157 | | | | | | | | | | | | |
| MS, maximum | | | | | | | | | 0.1 | | | |
| HS, maximum | | | | | | | | | 0.05 | | 0.1 | |

proposed different methods to evaluate it. Mechanical strength tests nowadays are a basic complement to the petrographic and chemical methods. Besides, the two fundamental pozzolan characteristics are: (a) ability to react with lime; and (b) ability to form products with binding properties [7].

According to the results shown in Table 4, the compressive strength of Mexican natural pozzolans ranged between 4.78 and 6.58 MPa, two cases were less than 5.39 MPa specified by the ASTM Standard C 618.

It is well known that one of the fundamental conditions for a rapid zeolitization is the structure of finely subdivided volcanic glass [10]. In fact, most easily, zeolitizable pozzolans are those that have a more marked hydraulic activity as those presented mainly in PZ-G and PZ-H deposits. This reaction produces neohydrated phases (hydrated calcium silicates and aluminates in excess of lime) that are important to form binding compounds, which are very advantageous when the material contains silica and alumina easily mobilized. This is typical of amorphous structures and particularly of acid glasses [10].

In this study, the materials containing zeolites were detected, and they presented more reactivity than those containing vitreous constituents, confirming work cited by Sersale [10]. This is due probably to the more open porous structure of the zeolites, which, therefore, is more likely to be attacked. Indeed, these pores allow chemical agents to penetrate, attacking their crystalline structure, destroying and liberating silica, alumina, and alkalis, the first of which combine with lime.

4.1.5. Pozzolanic activity with portland cement

Although the principal pozzolanic reaction is the chemical reaction involving lime and silica, cementitious products are also formed as a result of the chemical reactions between lime, alumina, or iron oxide. The essential difference between the pozzolanic reactions and the reactions involving the hydration of portland cement alone is not in the composition of the hydration products [1].

The behavior of the Mexican natural pozzolans shows different compressive strengths of the mortars' pozzolan–portland cement mixtures with regard to portland cement alone. Mechanical strength tests are still, today, the indispensable complement to chemical and physical methods. According to Table 4, strength activity index with portland cement ranging from 80.9% to 103.1% at 28 days old, which is over 75% as specified by ASTM standard C 618 [11]. The pozzolans that contain zeolitic minerals and present a marked increase in hydraulic activity are PZ-G (6.10 MPa) and PZ-H (6.58 MPa) with the presence of clinoptilolite.

4.1.6. Available alkalis

The chemical interaction of certain siliceous mineral constituents of aggregate with the alkalis in portland cement is known to cause expansion and cracking of

concrete. The commonly practiced method of reducing the risk of such involves the use of a low-alkali cement. When the use of a high-alkali portland cement ($>0.6\%$ Na_2O equivalent) in combination with an aggregate containing alkali-reactive constituents results in the expansion phenomenon, it may be controlled by incorporating into the concrete mixture a pozzolanic material that has proven in laboratory tests to be effective in reducing the alkali–aggregate expansion [1].

All natural pozzolans are not equally effective in combating alkali–silica expansion. It is important to consider the available alkalis to prevent this expansion although many natural pozzolans themselves show a high content. Most of the Mexican natural pozzolans present a high content of alkalis (until 6.90% Na_2O equivalent). However, the available alkalis content ranges between 0.38% and 1.22% Na_2O equivalent (which is less than 1.5% as specified by ASTM Standard C 618). Results are given in Table 4. Most of the Mexican pozzolans that contain zeolitic minerals present less than 1% Na_2O equivalent of available alkalis.

4.2. Results of tests performed according to ASTM C 1012 method

The primary cause of the sulfate attack in mortars or concrete is the reaction between the C_3A present in the portland cement and the sulfate ions (SO_4^{2-}) from the environment, resulting in the formation of expansive ettringite. The formation of gypsum, another expansive product, also takes place due to the reaction with $\text{Ca}(\text{OH})_2$, a by-product of cement hydration and the sulfates. An experimental program was performed on the sulfate resistance of portland–pozzolan cements, and reference mortars made with ASTM Types I, II and V cements. The results of the performance tests on mortar-bars-exposed sulfate attack

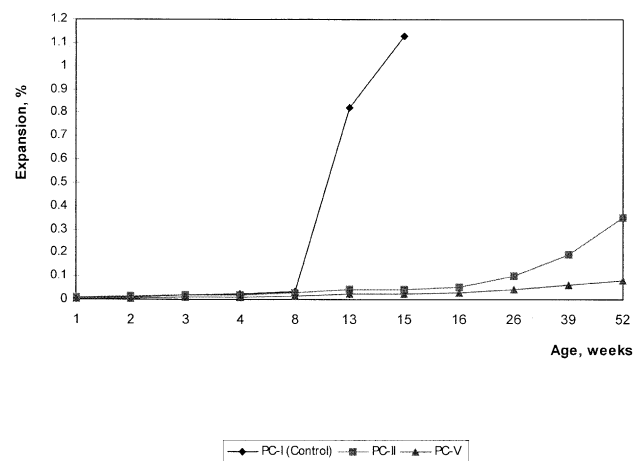


Fig. 2. Performance of portland-cements-exposed sulfate attack in 5% Na_2SO_4 solution.

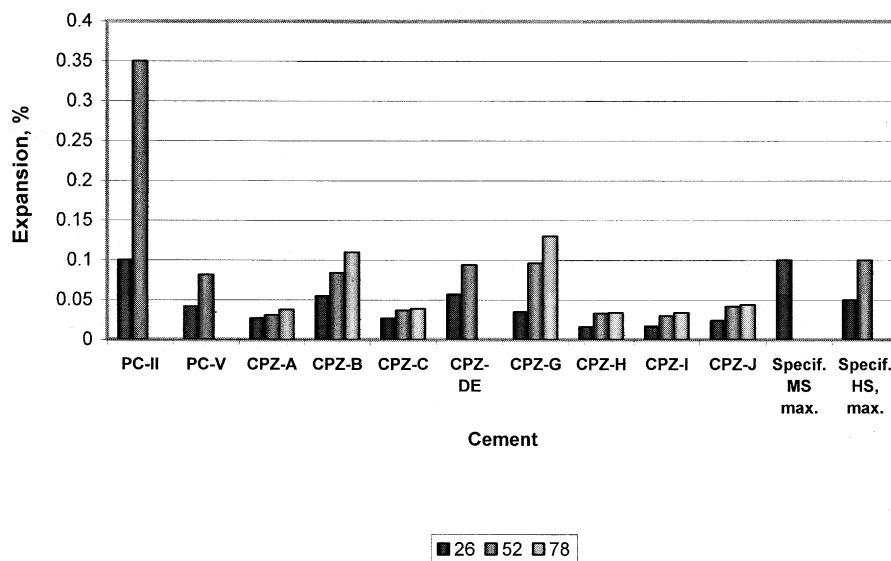


Fig. 3. Performance at portland- and pozzolanic-cements-exposed sulfate attack in 5% Na₂SO₄ solution at different ages.

in 5% solution over a period of 78 weeks for the pozzolanic cements are shown in Table 7. The portland–pozzolan cement (CPZ-H, CPZ-I, CPZ-A, and CPZ-C) mortars showed the lowest sulfate expansion at 26, 52, and 78 weeks (Fig. 3), followed by the of CPZ-J cement and the reference Type V cement mortar (Figs. 2 and 3), in that order.

These pozzolanic cements contain pozzolans with high pozzolanic activity with lime, greater than 5.93 MPa and portland clinker Type V (CPZ-H and CPZ-I) and Type I with C₃A between 10.2% and 12% and pozzolans with activity pozzolanic with lime greater than 5.64 MPa.

Instead, the reference Type II cement has a greater expansion than the pozzolanic cements CPZ-B and CPZ-G (Figs. 2 and 3) at 52 weeks. Besides, mortar bars showed little cracks.

The changes in length of the reference Types I and II are also illustrated in Fig. 2. ASTM Type I has very high expansion at early ages (after 8 weeks), and the mortar bars are curved and with big cracks. ASTM Type II showed great change length after 26 weeks. Obviously, ASTM Type I is not resistant to sulfate attack.

Large expansions due to water absorption by ettringite are registered only when the system loses its strength considerably. When the hydroxyl ions are replaced by the sulfate ion (a stage that is indicated by disappearance of CH and the appearance of gypsum in the cement paste), the C-S-H loses its adhesion and strength. This is the condition under which expansion of microcrystalline ettringite by osmotic forces will be possible [12].

5. Concluding remarks

The Mexican natural pozzolans are characterized to be of pyroclastic origin, with diagenetic processes in a different

scale; these processes were identified by means of the test methods as: devitrification, sericitization, chloritization, oxidation, and zeolitization.

Representative minerals of these lithological groups are: glass, oligoclase, andesine, quartz, pumice, and volcanic lithics mainly of acid composition.

The principal finding from this study is that substantial sulfate resistance can be achieved (equal to or greater than Types II and V) by using portland–pozzolan cements with clinker Type I or V. This is particularly significant because the pozzolans used that show high pozzolanic activity increase sulfate resistance when are added as a mineral admixture. Specifically:

- The pozzolanic cements containing Types I and V portland clinker and pozzolans with high pozzolanic activity have a better sulfate resistance than Type V cement, even after 52 weeks.
- The pozzolans containing alumina between 11.6% and 14.7% and high pozzolanic activity have in the cements the best sulfate resistance than those containing alumina with at least 16%.
- Pozzolanic cements with Type V clinker are more effective in increasing sulfate resistance, even containing levels of 14% of pozzolan.
- Pozzolanic cements with Type I clinker and pozzolans with pozzolanic activity less than 5.4 MPa are moderate sulfate resistance.

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