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# Effect of Natural Pozzolans on the Alkali-Silica Reaction of Aggregates in Real Concrete Specimens

**Foroughi, M. [1], Tabatabaei, R.[2] and Shamsadeini, M. [2]**

[1] Islamic Azad University, Bardsir Branch, Chemistry Department, Iran
[2] Islamic Azad University, Kerman Branch, Civil Engineering Department, Iran

**ABSTRACT**

In this paper, alkali-silica reaction potential of aggregates was investigated in experimental real concrete specimens including natural pozzolans by using mortar bar method. Pozzolans samples from four famous sources around the Kerman province were collected for this investigation.
Several aggregates show medium ASR potential reaction. Comparison of alkali-silica gels in concrete samples with those from mortar bar specimens pointed-out several important factors, such as the time factor, external parameters, and effect of the ASR. Replacing the percentage of portland cement with natural pozzolan was successful in reducing expansion potentials. Finally, specifications for using pozzolan in different categories including ASR mitigation in the concrete mixture are prepared.
**Keywords:** alkali-silica reactivity (ASR); natural pozzolan; cementitious materials; pozzolanic effect; siloxane networks.

## 1. INTRODUCTION

Identifying the alkali-silica reaction (ASR) in concrete is one of the most recognized harmful phenomena in concrete. ASR is a chemical reaction between the reactive silica contained in the aggregates and the alkalis within the cement paste [1, 2 and 3]. The result is an alkali-silica gel that absorbs water and increases in volume. If the gel is confined by the cement paste, it builds up pressure as it grows causing internal stresses that eventually could crack the concrete [4, 5]. It should be noted that three important alkalis that occur commonly in cement are sodium, potassium and calcium ($Na^+$, $K^+$ and $Ca^{2+}$). Sources of alkali in concrete pore solution are alkali sulfates in cement, mix water, supplementary cementitious materials and deicing salts. It is predicted based on experiments that alkalis in the form of sodium and potassium are adsorbed and do not chemically form the structure of alkali-silica gel [6].

In recent years some innovative tests have been appeared for identifying aggregates subject to ASR, but each has its limitations [7]. Most researchers have been studied ASR in the portland cement concretes without mineral admixtures. Soon after ASR was first identified as the cause of several concrete failures, it was found that the use of mineral admixtures as a replacement of a portion of the cement in concrete could reduce the ASR effects on concrete [8, 9]. The most commonly used admixtures are fly ash, silica fume, and slag. Factors that influence the effectiveness of mineral admixtures in mitigating ASR consist of the composition of the cement and admixture, levels of replacement and the fineness of admixture [10]. Thomas found that when high alkali fly ash was used to replace 20% or more of the weight of cement in concrete specimens containing a very reactive aggregate, ASR was greatly reduced and very little evidence of the reaction was recorded [11]. Blackwell showed that a class of fly ash with 4.0% equivalent $Na_2O$ was effective in preventing excessive ASR expansions in concrete specimens made with a reactive greywacke and high alkali content concrete [12].

Several natural pozzolans such as calcined clay have also been reported effective in mitigating the ASR effects. The use of air entrainment and lithium admixtures in concrete has been proven to potentially mitigate the effects of ASR. Effective mitigation methods need to be available for use with aggregates that are prone to ASR. In order to reduce the cost of construction, it is important that reactive aggregate sources be used as effectively as possible [13]. Alkali-silica reactivity potential of quartz sands and gravels was tested using modified mortar bar and gel pat tests [14, 15].

It is of note that use of reactive aggregate beyond the pessimum proportion can reduce the ASR effect. This can be attributed to the decrease in calcium hydroxide and alkali hydroxide available per aggregate particle. Research by Ichikawa concludes that for a fixed volume of reactive aggregate in a mix, increase in particle size increases ASR expansion but reduces the rate of ASR. Also, very fine reactive aggregate sizes tend to mitigate ASR by pozzolanic effect [16].

A comprehensive of alkali-silica reaction conclude that the process of alkali-silica reaction involves alkali cations, calcium ions, hydroxyl ions and reactive silica phases in aggregate was presented by Ichikawa [16]. Research by Ichikawa concludes that for a fixed volume of reactive aggregate in a mix, increase in particle size increases ASR

***Corresponding Author:** Tabatabaei, R., Assistant Professor, P.O Box 76175-6114, Kerman-Iran.
Email: tabatabaei@iauk.ac.ir

expansion but reduces the rate of ASR. Also, very fine reactive aggregate sizes tend to mitigate ASR by pozzolanic effect.

As determined by Scanning Electron Microscopy (SEM) exposed, Alkali-silica reaction (ASR) is a reaction that takes place between the reactive silica contained in aggregates and the alkalis in the cement paste. For the reaction to take place in concrete, three conditions must exist: high pH, moisture, and reactive silica. Various types of silica present in aggregates react with the hydroxyl ions present in the pore solution in concrete. First, Alkalis and hydroxyl ions break the siloxane networks in aggregate particle to form Alkali-silica gel. Then, the gel is restrained by the surrounding mortar; an osmotic pressure is generated by the swelling. Once that pressure is larger than the tensile strength of the concrete, crack occurs leading to additional water relocation or absorption and additional gel swelling as shown in Fig.1 (see chemical details in Ref. [13]).

Application of a non-reactive aggregate is one way to reduce ASR phenomena. It is noted that, this method is based on important parameters such as geography, geology, and cost of aggregate production. Today regarding production of natural aggregate, new criteria can be offered for providing mix design of concrete with high stability. Reducing cement alkalies such as sodium, potassium and calcium ( $Na^{+}$ , $K^{+}$ and $Ca^{2+}$ ) is another possible method to avoid ASR. Conversely, it too has several major limitations. Low-alkali cements in the concrete are suffer from some drawbacks due to increasingly cost to production. Furthermore, in most cases, using the Low-alkali cements are not sufficient to diminish highly reactive aggregates. Alkalies can also be supplied by production of artificial admixtures. In addition, electrochemical methods of corrosion protection, such as cathodic protection may attend alkalies in the concrete mixture [17, 18].


Fig. 1: Physical distress mechanisms of ASR [17].

Several pozzolans such as coal fly ash, granulated slag, silica fume, lithium nitrate and calcined clay have been effective in controlling ASR expansions in cement concrete at levels of cement replacement between 15 and 25 percent by weight. The pozzolans are all byproducts of other industries and the chemical characteristics of these are silicates or aluminosilicates that have been shaped as amorphous or glass phases in high temperature blast furnace followed by rapid cooling under various conditions [17].

Since pozzolan is recognized as a powerful admixture to avoid ASR phenomena, the chemical activities of pozzolan is an ongoing topic. The results obtained from hardened pastes of cement with pozzolan admixtures have shown the pozzolanic reaction can be processed in several phases. In general, as determined by Scanning Electron Microscopy (SEM), the hydration reaction of the Portland cement, the tricalcium silicate ($C_3S$ ) and dicalcium silicate ($C_2S$ ) react to form calcium silicate hydrates ($C-S-H$ ). Simultaneously, the pH of the water increases to more than 12. Consequently, the silicate network structure of the pozzolan is ruptured in to smaller units, and these units react with the calcium hydroxide to form more calcium silicate hydrate ($C-S-H$ ) gel. Regarding its economy and consuming energy potential among rock materials, it has very technical advantages including decrease of heat cracks from cement hydration. Furthermore, the XRD test clearly has confirmed better durability against ASR potential and high final compressive strength. However, it is recognized that addition of a large quantity of the natural pozzolan decreases the strength of concrete; consequently the optimum quantity is necessary to achieve the maximum compressive strength [20].

In this study, natural pozzolans haven been used in an extensive testing program. The natural pozzolans used in this study have obtained from Iranian mines and the physical properties consist of pumice, diatomaceous and perlite that are mineralogical material containing large quantities of $SiO_2$ and $Al_2O_3$ with small particles, high porosity. Guidelines for predicting the potential alkali-silica reaction of aggregates are developed and recommendations for minimizing concrete damage due to ASR are given.

## 2. MATERIALS

Materials used were in line with the research objectives. Aggregates used were natural sand and coarse aggregate. For the testing program, these aggregates were obtained from ten different aggregate producers providing a total of four aggregates of which ten were coarse, five were fine, and one was mixed sand and gravel. These materials had different field performances as far as ASR performance.

All aggregates were thoroughly washed and oven dried before use in the experiments. The sand was sieved and batched as per the gradation requirements of Standard ASTM C 1260 procedure. ASTM C 1260 requires that all aggregates be graded as per Table 1. Therefore, all aggregates had to be separated into the required sieve sizes, washed over a #100 sieve, and then combined using the specified quantities for each sieve.

Table 1. ASTM C 1260 Aggregate Grading Requirements

| Sieve Size | | |
|---|---|---|
| **Passing** | **Retained on** | **Mass, %** |
| 4.75 mm (No. 4) | 2.36 mm (No. 8) | 10 |
| 2.36 mm (No. 8) | 1.18 mm (No. 16) | 25 |
| 1.18 mm (No. 16) | 600 μm (No. 30) | 25 |
| 600 μm (No. 30) | 300 μm (No. 50) | 25 |
| 300 μm (No. 50) | 150 μm (No. 100) | 15 |

Type II high alkali cement was used for preparing mortar specimens. Kerman Type II High alkali cement has an equivalent alkali content of 0.82%. The reagent grade chemicals used in pure state were 1N sodium hydroxide solution and de-ionized water.

### 2.1 Study Area Description for the Pozzolans

The area chosen for this study, a part of Kerman province in the south east of Iran is an extraordinary case due to the unusually high number of  Pozzolans mines.

The Pozzolan mines constitute one of the largest groups of minerals known with more than 50 distinct natural species recognized and more than 100 species having no natural counterparts have been synthesized in the laboratory. The natural Pozzolans occur in a variety of geologic settings and ages such as deposits formed in: (a) hydrologically closed systems of volcanic materials in saline/alkaline lakes, (b) open systems of fresh water lakes and groundwater; (c) low grade burial metamorphic formations; (d) hydrothermal or hot water activities; (e) deep marine volcanoclastic sediments; and (f) weathered soil from volcanic materials.

Table 2. Compositions of selective natural pozzolans

| Pozzolan Category | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $CaO$ | $MgO$ | $SO_3$ | $K_2O$ | $Na_2O$ | $Cl$ | $LOI$ | Blaine $m^2/Kg$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **A** | 56.75 | 23.86 | 4.60 | 3.42 | 1.72 | 0.19 | 2.84 | 3.04 | 0.05 | 1.98 | 286 |
| **B** | 57.12 | 20.05 | 3.54 | 2.46 | 1.95 | 0.25 | 1.40 | 1.20 | 0.08 | 2.22 | 315 |
| **C** | 61.57 | 18.00 | 4.93 | 6.69 | 2.63 | 0.10 | 2.95 | 3.65 | 0.04 | 2.15 | 310 |
| **D** | 55.24 | 22.64 | 5.03 | 4.39 | 3.15 | 0.14 | 2.83 | 2.85 | 0.05 | 1.87 | 287 |

The natural pozzolans with different physical and chemical properties in different regions of Kerman City located in the south eastern part of Iran were collected from four sources. Natural pozzolans used in this work, were obtained from Rafsanjan, Sirjan and Sharbabak areas. The obtained pozzolans were firstly characterized for their chemical and mineralogical compositions and also pozzolanic activity. The results of chemical analysis were determined according to ASTM standard and the values of specific surface area determined by Blain air-permeability apparatus are shown in Table 2.

## 3. Accelerated Mortar Bar Method: ASTM C 1260

This test is being thoroughly investigated all over the world. In contrast to the results of the C 227 test method, it was found that 14-day expansions decrease with decreasing water-cement ratio. Since, in this test, mortar bars are immersed in a 1N $NaOH$ solution, the pore solution of the bars is controlled by the concentration of the solution and the migration of the alkali ions in the bars is likely to decrease with decreasing water-cement ratio. It was also found that even though the test was capable of detecting numerous aggregates.  It was too severe for many aggregates that have performed well when tested using the concrete prism method and that have performed well in the field. In general, most of the researchers agreed that this test is a good ASR predictor; however, it is too severe for some aggregates that have had good field performances.

## 4. Experimental Study

Standard ASTM C 1260 and Mortar Bar Test Methods were used for predicting expansion potential in mortar bars subjected to different natural pozzolans. In these tests, the potential of an aggregate to cause alkali silica reaction was verified. It should be mentioned that reactivity of aggregate was established by expansion greater than 0.1% after immersing the mortar bars in soak solution for 14 days.

Mortar mix was prepared using aggregates and cement as per test matrix of this research. Aggregates were graded as per the requirements mentioned in the procedure. Cement (type II) was sieved through 850 µm (No. 20) sieve to avoid any lumps. Mortar specimens of the size were cast. Quantitative details of each ingredient of mortar mix to be prepared per batch are as below:

Aggregate to cement ratio: 2.25

Water- cement ratio: 0.47 % by mass (Water-cement ratio was adjusted based on the % water absorption of the aggregate).

Mixture proportions for the completed procedures are shown in Table 3. In the following table, ASTM C 138 was used to measure the unit weight, yield, and air content and ASTM C 109 was used to measure the flow. All weights shown were calculated on a four-mortar bars basis.

Table 3. Mortar Mixtures Used for ASTM C 1260

| Mix ID | Graded Aggregate Dry Weight, $Kg$ | Cement, $Kg$ | Water, $Kg$ | $W/Cm$ water to cement ratio | $\gamma$ (unit weight) $Kg/m^3$ | Pozzolan[1] % | Flow | Total Air Content % |
|---|---|---|---|---|---|---|---|---|
| **P-1** | 878 | 350 | 200 | 0.47 | 2274.3 | 0 | 36.0 | **2.49** |
| **P-2** | 878 | 350 | 200 | 0.47 | 2251.9 | 5 | 78.5 | **0.48** |
| **P-3** | 878 | 350 | 200 | 0.47 | 2237.6 | 10 | 45.0 | **1.11** |
| **P-4** | 878 | 350 | 200 | 0.47 | 2224.1 | 20 | 75.0 | **1.71** |
| **P-5** | 878 | 350 | 200 | 0.47 | 2215.7 | 35 | 82.0 | **1.89** |
| **P-6** | 878 | 350 | 200 | 0.47 | 2054.8 | 35 | 0.0 | **1.70** |

**Note 1: Replacing % of the Portland cement weight with Pozzolan**

The mortar mix was prepared, mixed and cast into the moulds as per the requirements of the Standard. Mortar specimens in moulds were allowed to cure for 24 hrs and then removed from the moulds. Zero-day reading was taken at the end of 24 hrs and specimens were subjected to 1N Sodium hydroxide solution ( $NaOH$ ) at 80°C in a temperature-controlled room at 38°C. The moisture room was kept in less than 50%. Ratio of volume of solution to volume of mortar specimens was considered as 4.0.

The average of three bars for four pozzolan categories was used to get the final expansion result of the testing procedures. The results are presented in Figs. 2 to 5. Mixture proportions used for these tests are listed in Table 3 that includes mixture properties including unit weight, flow number, % pozzolan (replacing the cement with % pozzolan) and air content. In this study, expansion data were recorded after zero-day of curing and then every 3, 7 and 14 days.

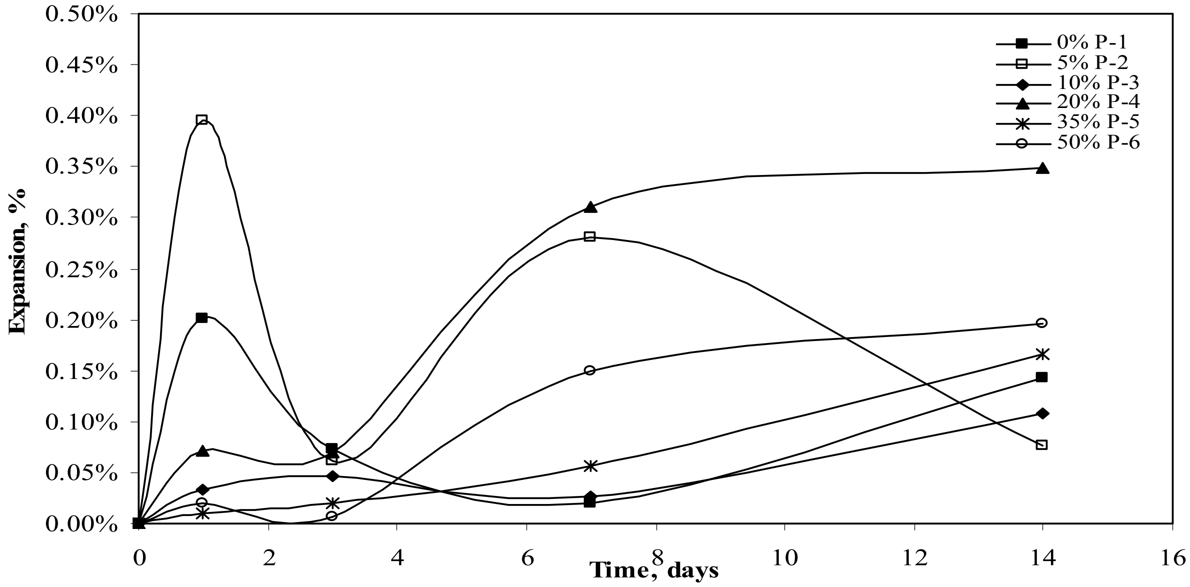


Fig. 2: ASTM C 1260 Expansions for Category A Pozzolan

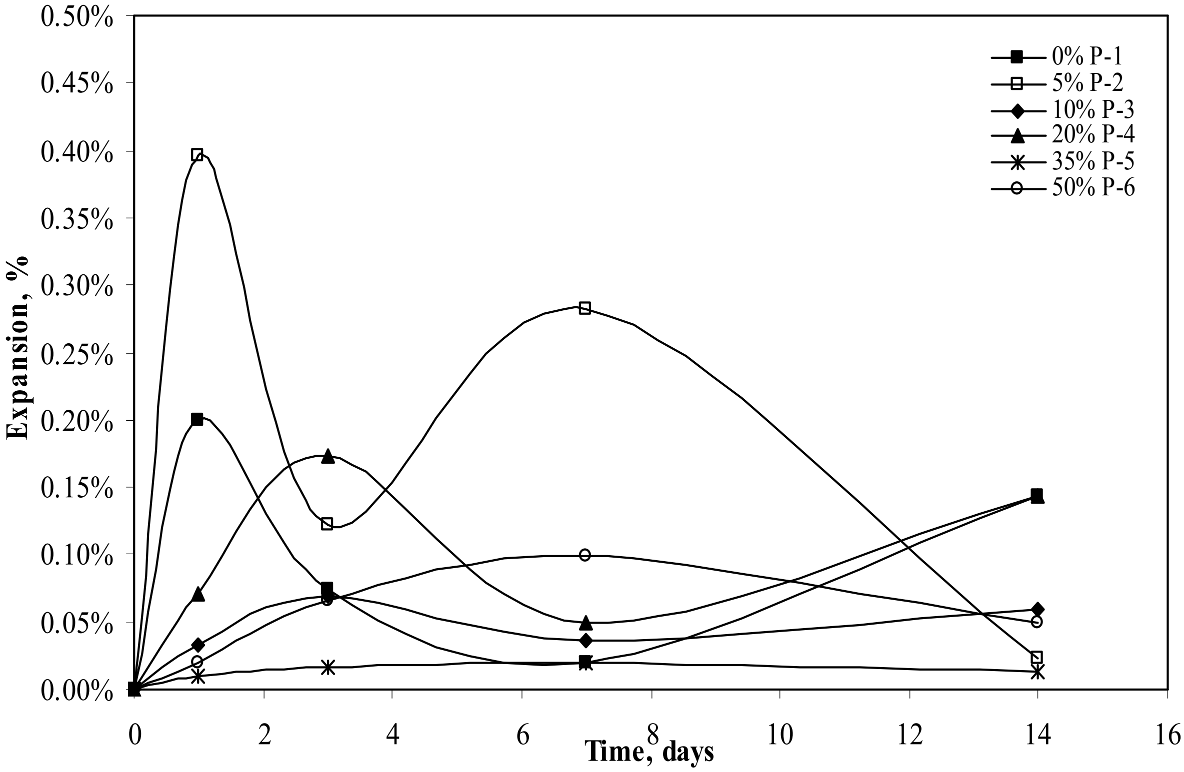


Fig. 3: ASTM C 1260 Expansions for Category B Pozzolan

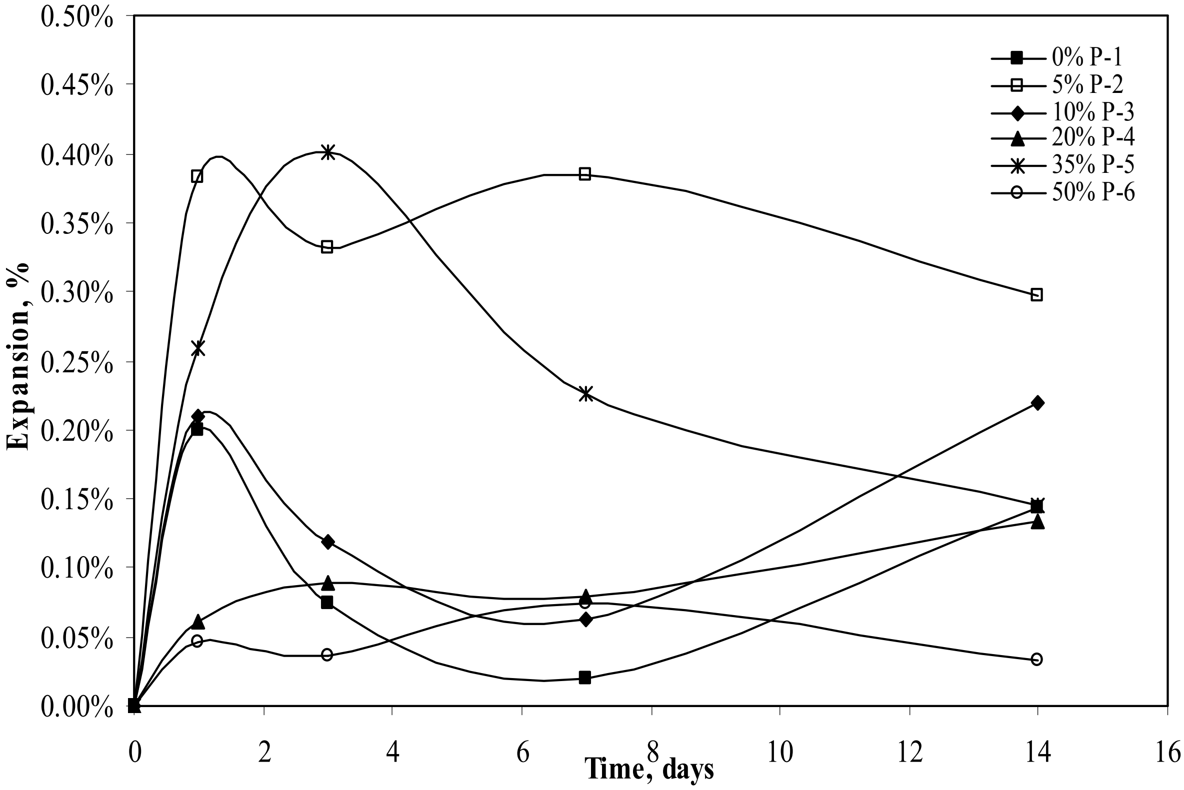


Fig. 4: ASTM C 1260 Expansions for Category C Pozzolan

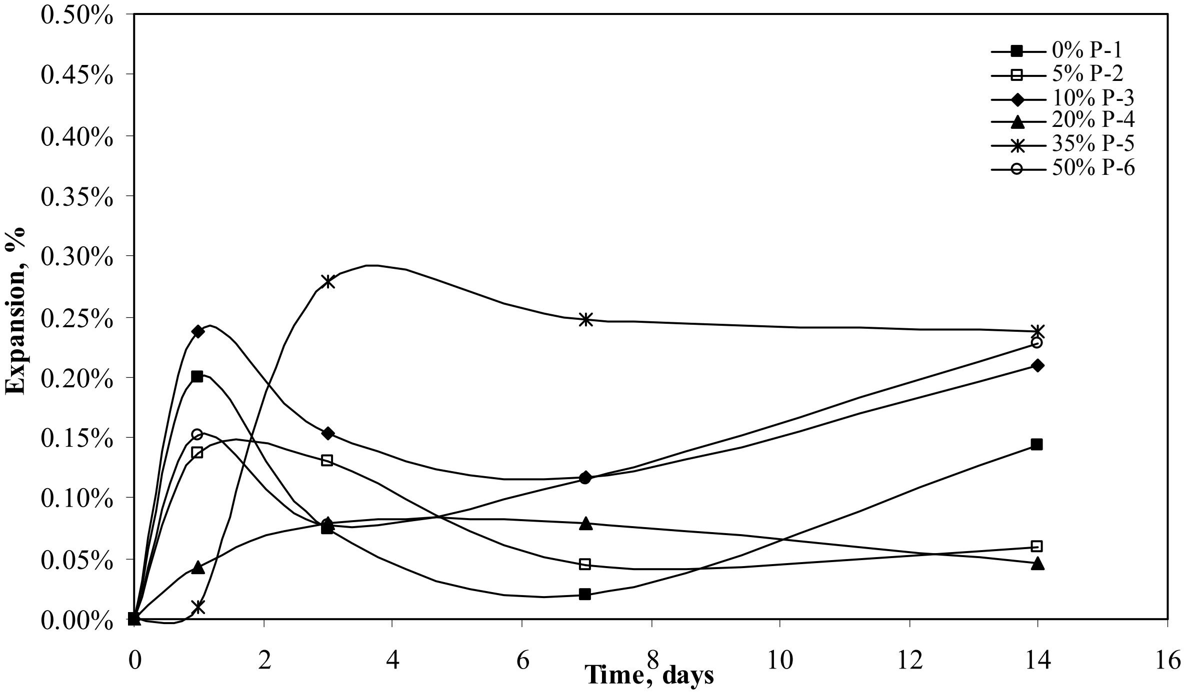


Fig. 5: ASTM C 1260 Expansions for Category D Pozzolan

Criteria proposed in the standard ASTM C 1260 document to determine the reactivity of aggregates are as follows: 14-day expansions lower than 0.10% are considered innocuous, 14-day expansions between 0.10% and 0.20% are considered inconclusive, and 14 -day expansions greater than 0.20% are considered reactive. Based on the results of the study conducted by the Strategic Highway Research Program (SHRP C-343), it was concluded that aggregates showing 14-day expansions higher than 0.08% are considered reactive and 14-day expansions lower than 0.08% are considered innocuous. As a result, the 0.10% criterion was adopted throughout this study for the interpretation of the ASTM C 1260 results [19, 15].

The average mortar expansions of category B contain less than 2.5% alkalis show that all percentages of this pozzolan truly improve the ASR effect. This matter is illustrated in Fig. 3.

As shown in Fig. 4, the average results of category C indicate that low values of about 10% of the pozzolan contains more than 5% calcium oxide ($CaO$) actually worsen the ASR problem. Replacing 50% (by weight) of the Portland cement with this pozzolan has found to mitigate ASR in concrete. Consequently, if the calcium content of the pozzolan increases, the amounts of the pozzolan used in the concrete should also be increased.

The expansion results obtained of both categories A and D are shown in graphs of Figs. 1 and 5. These graphs indicate other than the alkali availability that contributes to efficiency of natural pozzolans in reducing ASR damage.

## 5. Conclusion

The mortar mixes with different natural pozzolans were examined for the evaluation of the expansion due to ASR potential. The effective alkali contribution of the mixture depends upon the nature of the reactive aggregate and the levels at which the weight of cement is replaced with the natural pozzolan. Replacing the cement with about 5% natural pozzolan contains less than 2.5% alkalis (such as category B) was effective in reducing expansions. As a result, it was noted that the natural pozzolan has a positive effect in reducing damage due to ASR and does more then just dilute the alkalis in the cement. Using the same reactive aggregate but replacing higher than %5 of the cement with natural pozzolan contains more than 5% calcium oxide (such as categories C) resulted in an increase in expansions for a given cement alkali content. It was determined that 5% of the total alkalis in the pozzolan contributed to the expansions of concrete specimens. Furthermore, it is inappropriate to use a singular value to estimate the contribution of the alkalis of the pozzolan to the rate of ASR. It is dependent upon the aggregate nature and levels of replacements. Specifications for using pozzolan as an ASR mitigation alternative should take into consideration that highly reactive aggregates require higher amounts of pozzolan in the mixture. As the calcium content of the pozzolan increases (category C), the amounts of the pozzolan used in the concrete should also be increased.

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