# Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan

B. Uzal [a],[*],[1], L. Turanlı [b], H. Yücel [c], M.C. Göncüoğlu [d], A. Çulfaz [c]

[a] Department of Civil Engineering, Nigde University, Nigde, Turkey
[b] Department of Civil Engineering, Middle East Technical University, Ankara, Turkey
[c] Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey
[d] Department of Geological Engineering, Middle East Technical University, Ankara, Turkey

## ARTICLE INFO

## ABSTRACT

Pozzolanic activity of clinoptilolite, the most common natural zeolite mineral, was studied in comparison to silica fume, fly ash and a non-zeolitic natural pozzolan. Chemical, mineralogical and physical characterizations of the materials were considered in comparative evaluations. Pozzolanic activity of the natural zeolite was evaluated with various test methods including electrical conductivity of lime–pozzolan suspensions; and free lime content, compressive strength and pore size distribution of hardened lime–pozzolan pastes. The results showed that the clinoptilolite possessed a high lime–pozzolan reactivity that was comparable to silica fume and was higher than fly ash and a non-zeolitic natural pozzolan. The high reactivity of the clinoptilolite is attributable to its specific surface area and reactive SiO$_2$ content. Relatively poor strength contribution of clinoptilolite in spite of high pozzolanic activity can be attributable to larger pore size distribution of the hardened zeolite–lime product compared to the lime–fly ash system.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pozzolanic activity is defined as the ability of natural or by-product materials to produce components having binding property as a result of their reaction with calcium hydroxide (CH) in presence of moisture. The use of pozzolanic materials as partial replacement for Portland cement in blended cements and concrete has become almost unavoidable due to energy-saving concerns and other environmental considerations, such as CO$_2$ emission related to Portland cement-clinker production. The performance of supplementary cementing materials (SCMs) in blended cements and concrete mixtures depends on factors such as particle size distribution and specific surface area which controls water requirement, rheology and pozzolanic activity. Pozzolanic activity influences the ultimate compressive strength, permeability and chemical durability. The progress of pozzolanic reaction between lime and active phases of a pozzolan in the presence of water is monitored by measuring the amount of free lime consumed in the system which depends on the mineralogical composition and amount of pozzolanic phases, their SiO$_2$ content, and the curing age. The rate of pozzolanic reaction is affected by the specific surface area of pozzolan, water/solid ratio of the mix, and curing temperature [1].

Zeolites derived from either natural or artificial sources are aluminosilicates, with a skeletal crystal structure which contains voids occupied by ions and molecules of water having considerable freedom of movement that enables ion exchange and reversible dehydration [2]. In fact, the ability of ion exchange in lime–zeolite pastes leads to the pozzolanic reaction responsible for the strength development in a lime–zeolite system. Other pozzolanic materials such as silica fume, fly ash, rice husk ash and many natural pozzolans derive pozzolanic activity from non-crystalline silica which is the primary phase present in these materials.

Studies on pozzolanic activity of zeolitic natural pozzolans have shown that zeolitic tuffs have excellent pozzolanic activity [3], and they are more reactive than glassy materials with regard to lime fixation [1,4]. In a recent paper, Caputo et al. [5] investigated the pozzolanic activity of synthetic zeolites and reported that the less siliceous zeolite was more reactive with Ca(OH)$_2$ when compared to a more siliceous zeolite, whereas the more siliceous zeolite exhibited higher contribution to strength of the cementitious system. Therefore more research is needed to understand fully the reasons responsible for higher pozzolanic activity of zeolite minerals compared to natural siliceous pozzolanic materials. The published literature also lacks reports on evaluation of pozzolanic activity of natural zeolites in comparison with more active siliceous pozzolanic materials such as silica fume, and fly ash. One of the objectives of this study is to fulfill this need.

This paper reports the results of an investigation on evaluation of pozzolanic activity of clinoptilolite, a natural zeolite in comparison

---

* Corresponding author. Tel.: +90 388 2252240; fax: +90 312 2250112.
E-mail addresses: burakuzal@gmail.com, burak.uzal@nigde.edu.tr (B. Uzal).
[1] At the time of the study, the author was a PhD. student at the Department of Civil Engineering, Middle East Technical University, Ankara, Turkey.

**Table 1**
Chemical composition of the pozzolanic materials used.

| Definition | Gördes zeolite (clinoptilolite) | Silica fume | Sugozu fly ash | Non-zeolitic natural pozzolan |
|---|---|---|---|---|
| Notation | GZ | SF | FA | NZP |
| *Oxide analysis (%)* | | | | |
| $SiO_2$ | 69.32 | 95.2 | 57.86 | 61.56 |
| $Al_2O_3$ | 11.35 | 0.55 | 22.67 | 11.46 |
| $Fe_2O_3$ | 1.28 | 0.17 | 6.88 | 2.96 |
| CaO | 1.72 | 0.21 | 4.08 | 2.90 |
| MgO | 0.82 | 0.55 | 4.32 | 1.42 |
| $Na_2O$ | 0.95 | 0.17 | 0.77 | 3.76 |
| $K_2O$ | 3.96 | 1.03 | 1.82 | 2.39 |
| Loss on ignition | 8.90 | 1.11 | 2.76 | 4.83 |
| Total | 98.30 | 98.99 | 101.16 | 91.28 |
| Reactive $SiO_2$, % | 54.93 | 94.26 | 41.15 | 45.63 |
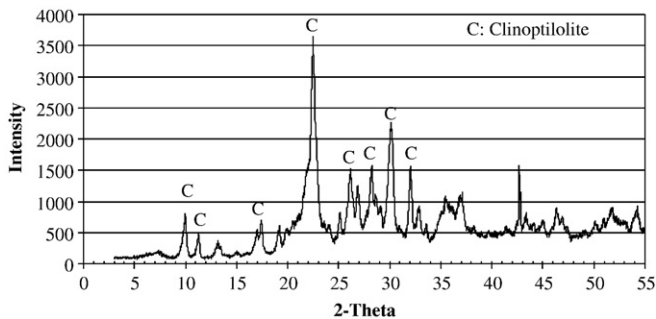


**Fig. 1.** Powder XRD pattern and identified phases of Gördes natural zeolite (Cu-Kα radiation).

non-zeolitic pozzolanic materials such as silica fume, fly ash and a natural mineral pozzolan. Pozzolanic activity of the clinoptilolite obtained from the Gördes (Manisa) deposits in Western Turkey (Manisa, Gördes) was compared to undensified silica fume (SF), class F fly ash (FA), and a non-zeolitic natural pozzolan (NZP). Early period of the pozzolanic reaction of Gördes zeolite (GZ) was evaluated by monitoring electrical conductivity and pH of lime–zeolite–water suspension, in comparison with lime–water suspensions of SF, FA

and NZP. The progress of the pozzolanic reaction at later ages was evaluated by measuring calcium hydroxide content, compressive strength development and pore size distribution of lime–pozzolan pastes. The data was analyzed to understand the differences between the Gördes zeolite and other pozzolanic materials with regard to their pozzolanic activity.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Clinoptilolite

The oxide composition of the clinoptilolite, as determined by ICP-MS (inductively coupled plasma-mass spectrometry) technique, is shown in Table 1. Reactive $SiO_2$ content of the clinoptilolite was also determined in accordance with EN 197-1 [6] and EN 196-2 [7]. In EN 197-1, reactive $SiO_2$ is defined as "the fraction of the silica which, after the treatment with hydrochloric acid (HCl), is soluble in boiling potassium hydroxide (KOH) solution". It is determined by subtracting the $SiO_2$ content of insoluble residue of the material after the treatment with HCl and KOH solutions from total $SiO_2$ content in accordance with the standard procedures specified in EN 196-2.

Powder X-ray diffraction pattern and identified phases of the Gördes zeolite are shown in Fig. 1. As seen from the pattern, clinoptilolite, a common zeolite mineral, is the major crystalline phase present. From mineralogical–petrographical analysis including polarized-light micros-copy of thin-sections of the rock as well as XRD analysis, the clinoptilolite content of the rock was estimated at 75 ± 5%. The rock also contains small amount of quartz, sanidine and biotite as crystalline phases as well as un-zeolitized glassy phase. Morphology of the zeolitic rock was examined under a scanning electron microscope (SEM), and prismatic clinoptilolite crystals were clearly observed as shown in Fig. 2.

The Gördes zeolite, henceforth abbreviated as GZ, was crushed and then ground in a ball mill until 80% particles passed through 45-μm sieve. Physical properties and particle size distribution of GZ and other pozzolanic materials used in this study are described next.

#### 2.1.2. Fly ash, silica fume, and non-zeolitic natural pozzolan

A class F fly ash (FA) from Sugozu Thermal Power Plant, a commer-cially available undensified silica fume (SF), and a non-zeolitic natural pozzolan (NZP) from a local deposit were used in the study for



**a) low magnification**　　　**b) high magnification**
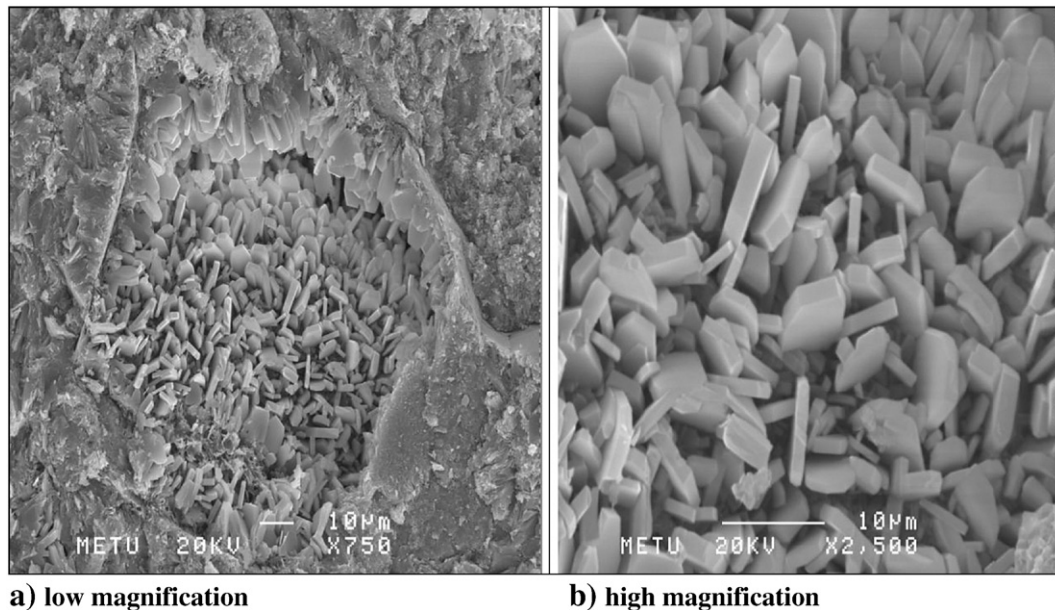
**Fig. 2.** SEM micrographs of the zeolite rock.

comparison purposes. SF and FA were used as received whereas NZP was ground to similar fineness as GZ, i.e. 80% passing through 45-μm sieve. The chemical composition and XRD patterns with identified phases are shown in Table 1 and Fig. 3, respectively. The XRD pattern of SF was completely amorphous, whereas FA and NZP contain some crystalline phases in addition to the glassy phase.
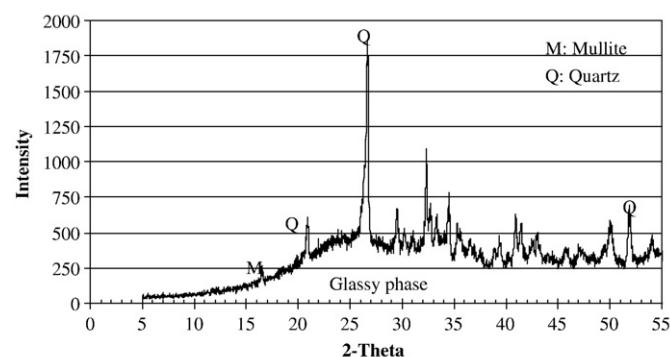
Particle size distributions of GZ and the other pozzolanic materials were determined by Malvern Mastersizer 2000 laser particle size analyzer and distribution curves are given in Fig. 4. In order to disperse the flocculated SF particles due to their extremely small particle size (<1 μm), SF sample was subjected to ultrasound application for a prolonged time before particle size analysis. Physical properties of finely-ground natural zeolite and the other pozzolanic materials are given in Table 2.
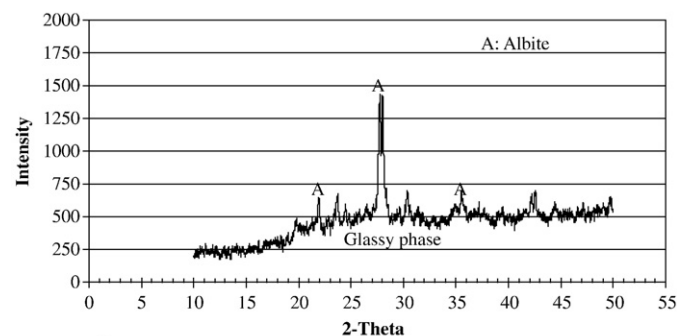
### 2.1.3. Hydrated lime

A technical-grade Ca(OH)$_2$ was used to prepare lime–pozzolan pastes, and the calcium hydroxide content was 84% by mass as TGA (thermo-gravimetric analysis). In addition, an analytical-grade Ca
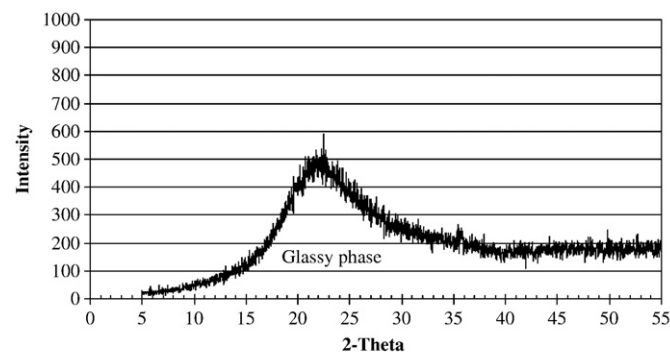


**Fig. 4.** Particle size distribution curves of the pozzolanic materials.

(OH)$_2$ was used to prepare lime–pozzolan–water suspensions prepared for electrical conductivity measurements.

### 2.2. Methods

#### 2.2.1. Particle size distribution

Particle size distributions of GZ and the other pozzolanic materials were determined by Malvern Mastersizer 2000 laser particle size analyzer and distribution curves are given in Fig. 4. In order to disperse the flocculated SF particles due to their extremely small particle size (<1 μm), SF sample was subjected to ultrasound application for a prolonged time before particle size analysis.

#### 2.2.2. Electrical conductivity measurements

Evaluation of pozzolanic activity of finely divided materials by electrical conductivity measurement of lime–pozzolan–water suspension is a rapid method, which was first proposed by Luxan et al. [8]. The method provides a rapid indication of pozzolanic activity by determining the drop in electrical conductivity of lime–water solution after addition of finely-ground pozzolanic material. The reaction between Ca(OH)$_2$ and pozzolanic material results in a reduction in electrical conductivity of aqueous suspension, which is attributed to fixation of dissolved Ca(OH)$_2$ by pozzolan particles. Therefore the magnitude of reduction in conductivity can be used as a measure of pozzolanic activity. However this method is not useful for the pozzolanic materials which contain considerable amount of soluble ions, such as fly ash because they contribute to conductivity of the aqueous solution. In order to overcome this issue, Paya et al. [9] improved the Luxan's method and they suggested an enhanced conductivity technique including a correction procedure considering the effect of soluble ions in pozzolanic materials on the conductivity value.



**Fig. 3.** XRD patterns and identified phases of the pozzolanic materials. Powder XRD pattern identified phases of a) SF, b) FA, and c) NZP (Cu-Kα radiation).
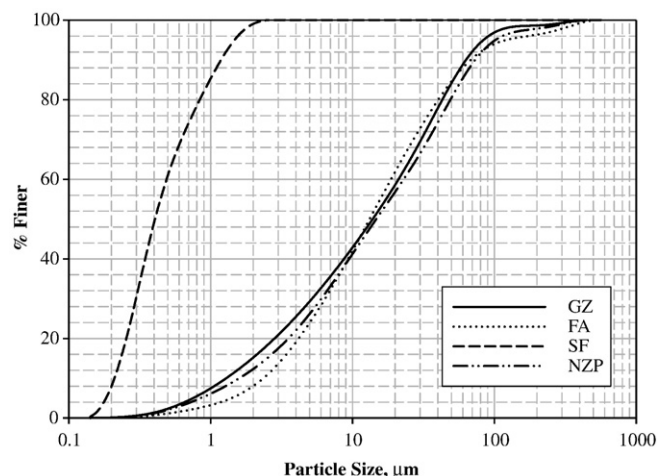
**Table 2**
Physical properties of the pozzolanic materials.

| Definition | Gördes zeolite | Silica fume | Sugozu fly ash | Non-zeolitic natural pozzolan |
|---|---|---|---|---|
| Notation | GZ | SF | FA | NZP |
| *Physical properties* | | | | |
| Specific gravity | 2.16 | 2.18 | 2.37 | 2.36 |
| Fineness | | | | |
| Passing 45-μm (%) | 80 | 100 | 84 | 79 |
| Blaine fineness (m$^2$/kg) | 995 | 5684 | 388 | 615 |
| BET surface area (m$^2$/kg) | 35,500 | 18,780 | 3380 | 24,650 |

An experimental set-up which is similar to the one proposed by Paya et al. [9] was used for evaluation of early-age pozzolanic activity of GZ in comparison with other pozzolanic materials.

The following procedure was used.

An unsaturated $Ca(OH)_2$ solution was prepared in a beaker with solution of 200 mg of analytical-grade $Ca(OH)_2$ in 250 ml of deionized water. The beaker was then placed in a constant-temperature water bath to hold the temperature of the solution at $40 \pm 1$ °C. The solution was continuously mixed by a small electrical mixer. Electrical conductivity, pH and temperature of the solution were continuously recorded by a digital conductivity-meter and a pH meter. After the lime–water system reached a constant conductivity, 5 g of pozzolanic material was added to the beaker. Conductivity and pH values of the solution were recorded at regular time intervals after adding the pozzolanic material, and conductivity vs. time curve was plotted for the lime–pozzolan–water system. The same procedure was repeated for the pozzolan–water systems at $40 \pm 1$ °C. For this purpose, 5 g of pozzolanic material is added into 250 ml of deionized water, and conductivity vs. time curve and pH vs. time curves were obtained. This was done because the contribution of the pozzolanic material to conductivity should be subtracted from the conductivity of lime–pozzolan–water system.

Corrected conductivity–time curves for each lime–pozzolan–water system were obtained by subtracting the contribution of pozzolanic material to conductivity of lime–pozzolan–water suspension. Finally, for an effective comparison, relative loss in corrected conductivity was calculated as percentage with respect to initial conductivity value of lime–water solution before addition of pozzolanic material. A higher loss in conductivity is attributable to higher amount of lime fixation by the pozzolanic material.

### 2.2.3. $Ca(OH)_2$ depletion in lime–pozzolan pastes

In order to evaluate the direct pozzolanic activity of the studied natural zeolite and the other pozzolanic materials, $Ca(OH)_2$ depletion in lime–pozzolan pastes was monitored by TGA conducted at various ages. Lime–pozzolan pastes were prepared by using a technical-grade $Ca(OH)_2$, with 1:1 lime:pozzolan ratio and 0.55 water-to-solid ratio. Fresh pastes were filled into plastic syringes to prevent moisture loss and carbonation, and then the pastes in syringes were cured at $50 \pm 1$ °C to accelerate the pozzolanic reaction.

The amount of reacted lime in the lime–pozzolan pastes were determined by TGA analysis of the hardened pastes at 3, 7, and 28 days of age. The initial amount of $Ca(OH)_2$ for each lime–pozzolan paste at age zero was calculated from the TGA data of the lime and the specific pozzolan as percent by total ignited weight of the components. The amount of free lime in hardened lime–pozzolan pastes for the specified test ages was determined by TGA as percent by the ignited weight of the paste. The amount of reacted lime, for a specific age, was calculated from the difference between the initial and the final amounts of free lime, expressed as percentage of the initial amount.

### 2.2.4. Compressive strength of lime–pozzolan pastes

Measurement of compressive strength of lime–pozzolan pastes is another test method which gives a direct indication of the pozzolanic activity on potential strength contribution. Lime–pozzolan pastes were prepared with the zeolite and other pozzolanic materials by using 1:1 lime:pozzolan ratio and 0.55 water-to-solid ratio by mass. A technical-grade $Ca(OH)_2$ was used for this test. Fresh pastes were cast into 2.5 cm cubic molds, sealed with stretched-film and cured at $50 \pm 1$ °C until testing age. Compressive strengths of hardened lime–pozzolan paste specimens were determined at 3, 7, and 28 days after casting.

### 2.2.5. Pore size distribution of lime–pozzolan pastes

Pore size distributions of hardened lime–pozzolan pastes were determined at age 28 days. The hardened lime–pozzolan pastes, which were prepared for thermal analyses and compressive strength tests, were also used for mercury intrusion porosimetry analyses in order to determine their pore size distributions.

The hardened pastes were crushed to particle size range of approximately 3–5 mm and immersed in acetone for 24 h to replace free water. The samples were then subjected to vacuum drying at 55 °C in a vacuum oven for 24 h. The pretreated samples were analyzed by a mercury intrusion porosimeter with 55,000 psi maximum injection pressure for pore sizes in the range between 3–10,000 nm (0.003–10 μm). In calculating the pore size distribution from mercury intrusion data, the contact angle was assumed as 142°. For all the samples, a completely identical sample preparation and measurement procedure was applied.

## 3. Results and discussion

### 3.1. Electrical conductivity of lime–pozzolan system

In order to use for correction of conductivity values of lime–pozzolan suspensions in water, conductivity and pH of the pozzolan–water suspensions at $40 \pm 1$ °C were determined as a function of time and the results are given in Fig. 5. As can be seen from Fig. 5, addition of the pozzolanic materials into de-ionized water resulted in increase in conductivity of the suspensions due to incorporation of some ions into water from the pozzolanic materials. Conductivity of suspension
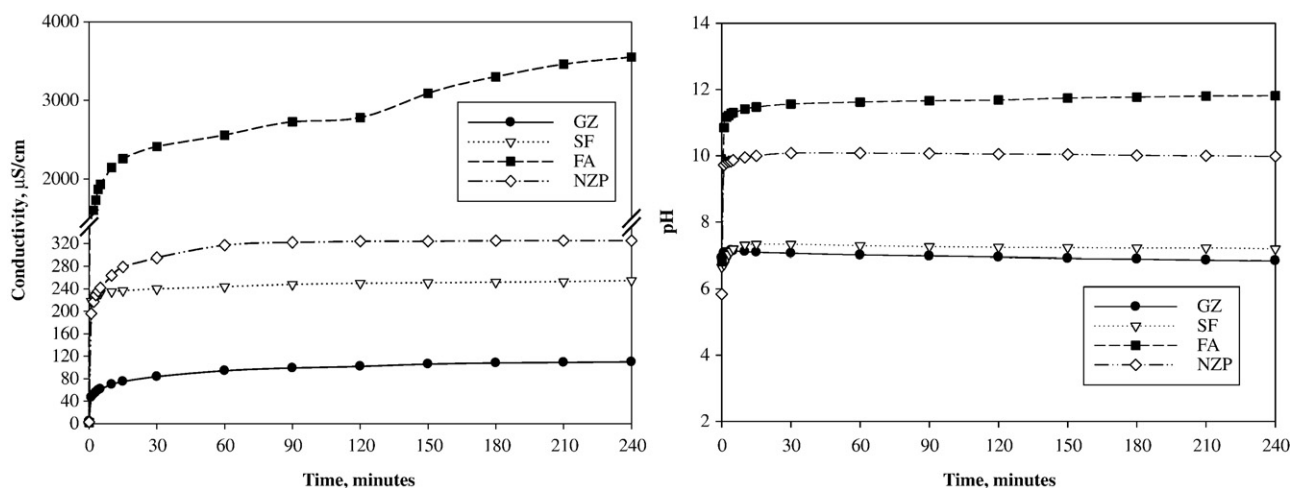


**Fig. 5.** Conductivity and pH variation curves with time for pozzolan–water suspensions at $40 \pm 1$ °C.

of GZ was lower than those of the other pozzolanic materials. The slight increase in conductivity of the zeolite–water suspension can be associated with the release of cations such as $Na^+$, $K^+$ and/or $Ca^{+2}$ as a result of cation exchange with $H^+$ ions, as experimentally showed by Rivera et al [10]. The fly ash–water system showed extremely higher conductivity than the other suspensions even within a few minutes which indicated that the fly ash clearly differed from the zeolite and other pozzolans due to significantly higher content of water-soluble ions.

Comparing the influence of the pozzolanic materials on pH of their suspensions, it was observed that it matched with their effect on conductivity of suspensions, that is, increase in the pH of zeolite–water suspension was less than those of SF, FA, and NZP suspensions (Fig. 5). The reason for small increase in pH of zeolite–water suspension is the same as the reason for the increase in conductivity, i.e. cation exchange decreasing the concentration of $H^+$ ions as experimentally showed by Rivera et al. [10]. Increase in pH of the SF, FA and NZP suspensions can be attributed to leaching of $Na^+$, $K^+$ and or $Ca^{++}$ from vitreous aluminosilicate fractions because the hydrolysis of aluminosilicates would increase the $(OH)^-$ concentration of the solutions [9]. The net relative loss in conductivity of the lime–pozzolan–water suspensions as a measure of lime fixation by the pozzolanic material is shown in Fig. 6 for each pozzolanic material.

Loss in conductivity of all the suspensions increased with time due to lime fixation as a result of pozzolanic reactivity. GZ exhibited a considerably higher reactivity than the other pozzolanic materials at early ages of testing, which is attributed to relatively higher BET surface area of GZ (Table 2). By the end of 240-minute testing period, it was observed that reactivity of GZ was similar to SF but higher than FA and NZP. From the slope of the curve of SF suspension, it was expected that SF would show higher reactivity than GZ for longer testing durations. This can be attributed to the higher reactive $SiO_2$ content (Table 1) of SF when compared to the zeolite and other pozzolanic materials.

Consequently, reactivity of the natural zeolite with $Ca(OH)_2$ in a suspension, measured by electrical conductivity technique, was found to be comparable to the silica fume and higher than the fly ash as well as the non-zeolitic natural pozzolan. For the first few minutes of the pozzolanic reaction in suspensions, it was observed that the specific surface area was another governing parameter together with reactive $SiO_2$ content for the lime fixation ability of the pozzolanic materials because GZ exhibited significantly higher reactivity than SF in first stages of test period. However, for the later periods, the amount of active phases in the pozzolanic material (such as reactive $SiO_2$ content) seems to become a dominant factor in determining the pozzolanic activity. Thus, pozzolanic activity of Gördes zeolite, which
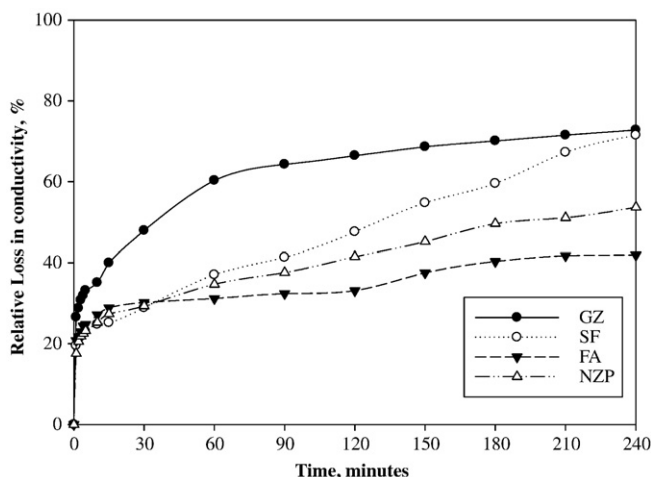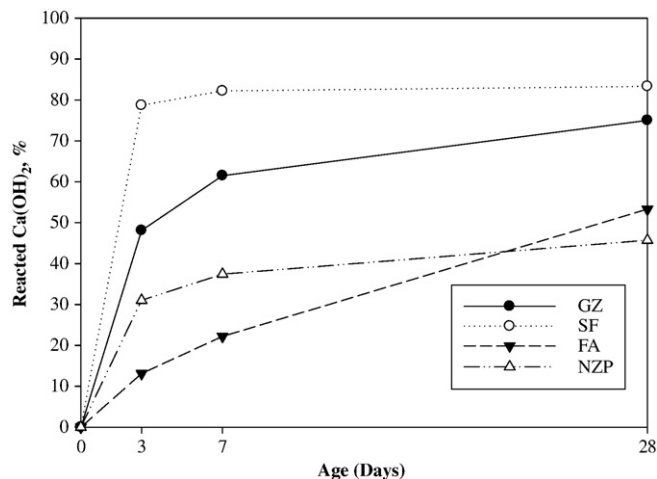


Fig. 7. Amounts of reacted $Ca(OH)_2$ in lime–pozzolan pastes.

is higher than those of the fly ash and the non-zeolitic pozzolan, can be attributed to the combined effects of relatively high BET surface area and reactive $SiO_2$ content of GZ.

### 3.2. $Ca(OH)_2$ depletion in lime–pozzolan pastes

The amounts of reacted $Ca(OH)_2$ in lime–pozzolan pastes as percent of the initially available $Ca(OH)_2$ are illustrated in Fig. 7.

The data in Fig. 7 indicated that the studied zeolite, GZ, consumed significantly higher amount of $Ca(OH)_2$ than the fly ash and the non-zeolitic natural pozzolan, but lower than the silica fume, for all test ages. At the end of 28 days, GZ consumed 75% of the initially available $Ca(OH)_2$, whereas the consumption values were 83%, 53%, and 46% for SF, FA, and NZP, respectively. These results confirm the pozzolanic activity evaluation results from the electrical conductivity measurements of lime–pozzolan suspensions.

It should be noted that the rate of $Ca(OH)_2$ consumption of FA between the ages of 7 days and 28 days was higher than that of GZ, whereas the reverse was true for the rate before the age 7 days. It confirms the slow pozzolanic reaction of fly ash particles, also reported by other authors [1,8]. This is due to the slow pozzolanic reaction at the surface of fly ash particles initially, and a relatively faster reaction later with the interior glassy phase of ash.

In regard to the effect of properties of pozzolanic materials on ability to fix $Ca(OH)_2$, the test results from lime–pozzolan pastes (Fig. 8) showed a clear relationship between the reactive $SiO_2$ content of pozzolans and the amount of $Ca(OH)_2$ consumed at early ages (3 days and 7 days). However, at later ages other factors, such as delayed pozzolanic reaction in the case of fly ash and high-calcium-ion exchange ability in the case of zeolite, also became important.
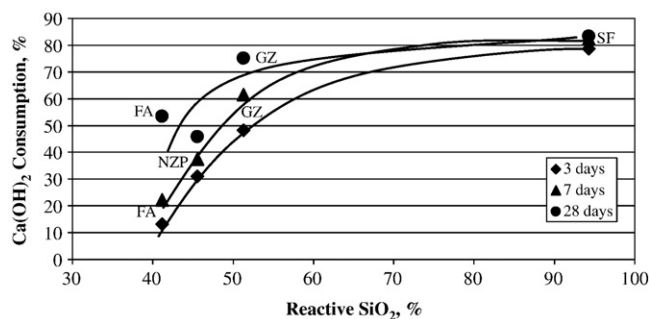


Fig. 6. Relative loss in corrected conductivity of lime–pozzolan–water suspensions.



Fig. 8. Relationship between reactive $SiO_2$ content and $Ca(OH)_2$ consumption.

Fig. 9. Compressive strength of lime–pozzolan pastes.



Fig. 11. Pore size distributions of lime–pozzolan pastes as determined by mercury intrusion porosimetry.
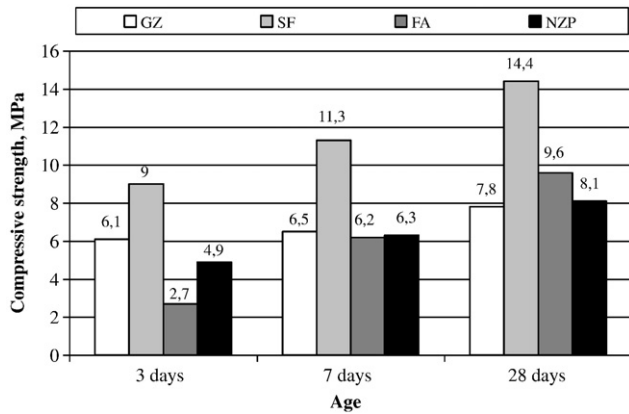
### 3.3. Compressive strength of lime–pozzolan pastes

Although the strength of a lime–pozzolan paste increases as the amount of reacted lime increases, there is no direct correlation between the two parameters for different pozzolanic materials [1]. Therefore, in the construction practice, the compressive strength of lime–pozzolan mixtures is generally accepted as one of the methods for evaluation of field performance of pozzolanic materials.

The above results had shown that the GZ's potential to react with $Ca(OH)_2$ was higher than FA and NZP. However this does not insure that GZ would produce higher mechanical strength in lime–pozzolan pastes when compared to FA and NZP.

The compressive strength of the lime–pozzolan pastes at 3, 7, and 28 days of age are shown in Fig. 9. The strength of lime–GZ paste was lower than that of lime–SF paste at all test ages. Only at age 3-days the lime–GZ paste exhibited higher compressive strength than FA and NZP pastes, however the difference in strength at 7 and 28 days of age between the three pozzolans were not considered significant. The mechanical strength produced as a result of pozzolanic reaction is controlled by the microstructure of the hydration products, rather
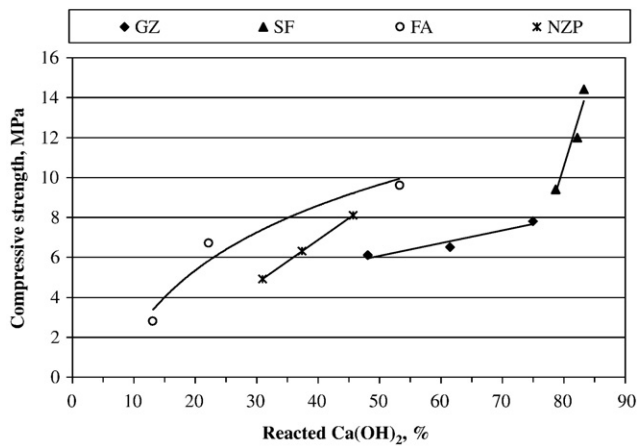
than the amount of reacted $Ca(OH)_2$. The lack of a general correlation between the amount of reacted $Ca(OH)_2$ and the compressive strength of lime–pozzolan pastes is illustrated by Fig. 10. In Table 3, the 28-day compressive strengths of lime–pozzolan pastes are shown for each percent of reacted $Ca(OH)_2$. The results confirm that the hydration product by the lime–pozzolan reaction is stronger with amorphous-silica type pozzolans (SF, FA, and NZP) than zeolitic pozzolan (GZ).

### 3.4. Pore size distribution of lime–pozzolan pastes

Pore size distributions of the lime–pozzolan pastes as determined by mercury intrusion porosimetry (MIP) are illustrated in Fig. 11. Bulk



Fig. 10. Relationship between the amount reacted $Ca(OH)_2$ and the strength of lime–pozzolan pastes.

**Table 3**
Compressive strength of pastes per each percent of reacted $Ca(OH)_2$.

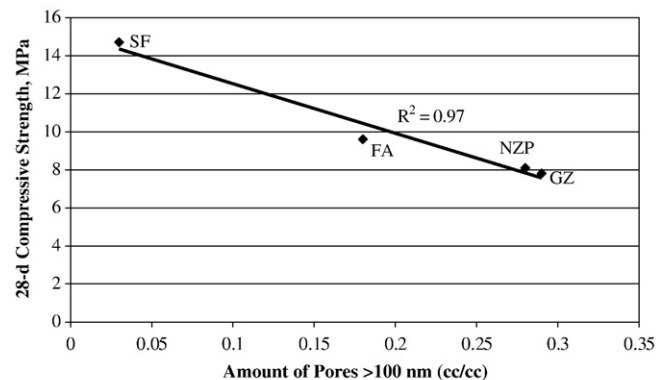|  | GZ | SF | FA | NZP |
|---|---|---|---|---|
| 28-day compressive strength of lime–pozzolan pastes per each percent of reacted $Ca(OH)_2$, MPa | 0.10 | 0.17 | 0.18 | 0.18 |
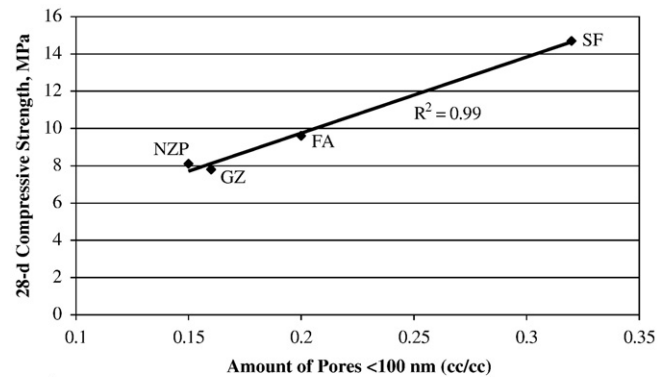


a) Amount of pores <100 nm vs. 28-day compressive strength of lime-pozzolan pastes



b) Amount of pores >100 nm vs. 28-day compressive strength of lime-pozzolan pastes

Fig. 12. Correlation between the amount of pores (a. <100 nm and b. >100 nm) and 28-day compressive strength of lime–pozzolan pastes.

density of the hardened pastes was measured and used to convert the pore volumes from cc/g to cc/cc and distributions are illustrated for cc/cc units.

It is reported that relatively small pores (<50 nm) in hardened cementitious systems are commonly attributed to gel pores and micropores which do not adversely affect the mechanical strength [11]. The GZ–lime paste, when compared to SF–lime and FA–lime pastes, not only produced considerably higher total porosity but also a higher volume of pores larger than 100 nm size, which adversely affect the mechanical strength. This is supported the data in Fig. 12 which shows plots of 28-day compressive strength vs. volume of pores (<100 nm and >100 nm).

Although the clinoptilolite used in this study showed relatively low strength performance in lime pastes, the same material had shown a very good strength performance when used in concrete mixtures as a supplementary cementing material in a previous study carried out by Uzal et al. [12]. Therefore strength contribution performance of the clinoptilolite and its mechanism when used together with Portland cement will be investigated in further studies on blended Portland cements containing clinoptilolite.

## 4. Conclusions

Based on the experimental results, the following conclusions can be drawn on comparative evaluation of pozzolanic activity of the clinoptilolite and the non-zeolitic pozzolanic materials used in this study.

1) Electrical conductivity measurements of lime–pozzolan suspensions in water showed that, in first minutes of contact with lime, pozzolanic activity of the zeolite was comparable to the silica fume, but was higher than the fly ash and the non-zeolitic natural pozzolan. The high pozzolanic activity seems directly related to the specific surface area and the reactive $SiO_2$ content of the pozzolan.

2) Direct measurements of free lime consumption of lime–pozzolan pastes showed that the zeolite consumed much more $Ca(OH)_2$ when compared to fly ash and the non-zeolitic pozzolan, which confirmed the results obtained by the electrical conductivity measurements. A linear relationship is indicated, especially at early ages, between the reactive $SiO_2$ content of the pozzolanic materials and their ability to fix lime.

3) Although the zeolite showed a higher potential to react with $Ca(OH)_2$ than the fly ash and the non-zeolitic natural pozzolan, the 28-day strength of the lime–zeolite paste was significantly lower than the lime–fly ash paste. In fact, both predominantly crystalline pozzolanic materials (i.e., the clinoptilolite zeolite and the non-zeolitic natural pozzolan) produced significantly lower 28-day strengths in the lime–pozzolan pastes than predominantly non-crystalline pozzolans (i.e., silica fume and fly ash).

4) Microstructural differences in the hydration products associated with the pozzolanic reaction seem to be responsible for the strength differences. Compared to the pastes containing either silica fume or fly ash with lime, the lower 28-day strengths of the pastes containing either the zeolite or the non-zeolitic natural pozzolan can be attributed to a relatively higher volume of pores >100 nm size.

5) The results of this study confirms that direct testing of strength of lime–pozzolan pastes is a better indication of the potential strength contribution of the pozzolans in cementitious products than conventional pozzolanic activity tests.

## Acknowledgements

## References

[1] F. Massazza, Pozzolana and pozzolanic cements, in: P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, 4th Edition, Elsevier Ltd., London, 1998.
[2] G.V. Tsitsishvili, Natural Zeolites, E. Horwood, New York, 1992.
[3] B. Drzaj, S. Hocevar, M. Slokan, Kinetic and mechanism of reaction in the zeolitic tuff–CaO–H$_2$O systems at increased temperatures, Cem. Concr. Res. 8 (1978) 711–720.
[4] R. Sersale, Zeolite tuff as a pozzolanic addition in the manufacture of blended cements, in: D.W. Ming, F.A. Mumpton (Eds.), Natural Zeolites '93: Occurrence, Properties and UseInternational Committee of Natural Zeolites, New York, 1995, pp. 603–612.
[5] D. Caputo, B. Liguori, C. Colella, Some advances in understanding the pozzolanic activity of zeolites: the effect of zeolite structure, Cem. Concr. Compos. 30 (2008) 455–462.
[6] EN 197-1, Cement — Part 1: Composition, specifications and conformity criteria for common cements, The European Committee for Standardization, 2000.
[7] EN 196-2, Methods of Testing Cements—Part 2: Chemical Analysis of Cement, The European Committee for Standardization, 1994.
[8] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cem. Concr. Res. 19 (1989) 63–68.
[9] J. Paya, M.V. Borrachero, J. Monzo, E. Peris-Mora, F. Amahjour, Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity, Cem. Concr. Res. 31 (2001) 41–49.
[10] A. Rivera, G. Rodriguez-Fuentes, E. Altshuler, Time evolution of a natural clinoptilolite in aqueous medium: conductivity and pH experiments, Microporous Mesoporous Mater. 40 (2000) 173–179.
[11] P.K. Mehta, P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials, Third EditionMcGraw-Hill, 2006.
[12] B. Uzal, L. Turanli, P.K. Mehta, High-volume natural pozzolan concrete for structural applications, ACI Mater. J. 104 (2007) 535–538.