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The effect of using natural zeolite on the properties and hydration characteristics of blended cements

Yilmaz Kocak[a,*], Eda Tascı[b], Unal Kaya[c]

[a] Dumlupinar University, Kutahya Vocational School of Technical Sciences, Department of Construction, Kutahya, Turkey
[b] Dumlupinar University, Faculty of Engineering, Department of Materials and Ceramic Engineering, Kutahya, Turkey
[c] Duzce University, Faculty of Technical Education, Department of Construction Duzce, Turkey

HIGHLIGHTS

- The zeolite consists mainly of cliniptilolite.
- The structures of cement and cliniptilolite are regular.
- FT-IR spectra can provide useful information on zeolite mineral structure.
- Zeolite contributes to the consumption of $Ca(OH)_2$ formed during the hydration of Portland cement.

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ABSTRACT

In this study, various properties and the hydration mechanisms of cements containing natural zeolite were investigated. In the first stage a complete physical, chemical, mineralogical, molecular characterization of the zeolite and cement was performed. In the second stage, the mechanical and physical properties of blended cements, incorporating 0%, 5%, 10%, 15% and 20% zeolite by weight were determined. Finally, the hydration rate and products of cement pastes were studied by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) at 28 days. As it is concluded, the examined zeolite consists mainly of cliniptilolite, which reacts with the $Ca(OH)_2$ generated during the hydration of Portland cement to form cement-like hydrated products. Finally, the addition of zeolite has affected the physical and mechanical properties of the blended cements depending on the amount of zeolite.

1. Introduction

Pozzolans are materials that consist predominantly of reactive SiO_2 and Al_2O_3 and are able to combine with portlandite ($Ca(OH)_2$), a by-product of cement hydration to form further gel products. Therefore, they have been widely used as an additive in cement in which portlandite is a major hydration product [1,2]. Their widespread use can be explained by their beneficial effect on the properties of concrete leading to technical, economical and ecological advantages [3–7]. It is widely accepted that pozzolans can increase the durability, reduce the heat of hydration, increase the resistance to sulfate attack and reduce the energy cost per cement unit [8–12]. One of the most widely used types of pozzolans is natural zeolites [13–17].

Zeolites, which form a large family of crystalline aluminosilicates, have been widely used as an additive in constructions since ancient times. Zeolites are microporous crystalline solids with well-defined structure that offer large (internal and external) surface areas, consisting of a three-dimensional network of silicon–oxygen SiO_4 and aluminum–oxygen AlO_4 tetrahedra [18]. The high surface area is the basis of high reactivity. Cliniptilolite and heulandite are the most common types of natural zeolite minerals on the earth. Heulandite is determined as the mineral with a ratio $Si/Al < 4$, while cliniptilolite has a ratio $Si/Al > 4$. Their structure is characterized by large, intersecting, open channels of ten and eight-member tetrahedral rings. The large, ten-member ring and the smaller, eight-member ring confine channels parallel to the *c*-axis. In natural zeolites, these channels are predominantly occupied by Na, K, Ca and H_2O. Previous works on the pozzolanic reactivity of zeolites as heulandite and cliniptilolite have shown that

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* Corresponding author. Address: Dumlupinar University, Kutahya Vocational School of Technical Sciences, Germiyan Campus Kutahya, Turkey. Tel.: +90 274 227 04 50; fax: +90 274 227 04 54.
E-mail address: yilmazkocak@dpu.edu.tr (Y. Kocak).

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the zeolitic minerals are able to react with lime, produce cementitious phases and improve concrete properties [19].

Natural zeolite is abundantly deposited in Turkey and it can be easily excavated and processed. The utilization of natural zeolite, when used as a partial replacement for cement, can lead to a substantial durability, economical and ecological benefits. Therefore, the aim of this study is to determine the effect of zeolite, coming from Gordes region of Manisa (in Turkey), on properties of blended cement, cement pastes and cement mortars using various testing methods.

2. Materials and methods

In this study, CEM II A–M (L–W) 42.5 R cement, zeolite, standard aggregate and water were used as materials. The cement was produced in the Izmir Cimentas Cement Factory. The composition of the cement is 8% fly ash, 7% limestone, 4.5% trass, 80.5% clinker and gypsum. The zeolite was excavated in Gordes region of Manisa which was obtained from the Rota Mining. For the preparation of mortar specimens, CEN standard aggregate, conforming to TS EN 196-1 [20], and city water of the province of Izmir were used.

In this study, the cement was used for the preparation of reference samples. Zeolite was blended in this cement at rates of 0%, 5%, 10%, 15% and 20%. Therefore, a total of five different cements were used and those were codified as R, 5ZC, 10ZC, 15ZC and 20ZC.

Chemical, physical, XRD, FT-IR and SEM analyses are conducted for the samples used in the experiments.

Chemical analyses of cement and zeolite are performed on ARL 8680 S X-ray diffraction. Surface areas are determined as Blaine values by Toni Technik 6565 Blaine and specific weights are determined by Quantachrome MVP-3. The mineralogical properties are determined by Rikagu miniflex XRD device using Cu Kα ($\lambda = 1.54$ Å) radiation. FT-IR analyses are conducted using Bruker Vertex 70 in the wave number range of 400–4000 cm^{-1}. Microstructure analysis of cement paste samples are determined by means of a JEOL branded JSM 6060LV variable pressure.

Cement paste and mortar mixtures are prepared in accordance with TS EN 196-1 [20]. The volume expansion values, water demands and setting time values of cement paste specimens are determined in accordance with the Le Chatelier method, conforming to TS EN 196-3 [21].

Mortar mixtures, used in flexural and compressive strength tests, each contained 450 g cement, 1350 g standard sand and 225 ml water, and mixed in a mortar-mixing machine, conforming to TS EN 196-1 [21]. The prepared mortars were poured into the 40 × 40 × 160 mm prismatic formworks. These mortar specimens were shaken for 1 min on a shaking table then settled into the formworks. These specimens were kept in a laboratory environment for 24 h. At the end of this duration, the specimens were taken out of the formworks and kept in a curing pool. The specimens were taken from the pool after 2, 7, 28 and 56 days and were tested for flexural and compressive strengths in accordance with TS EN 196-1 [21].

3. Experimental results and discussion

3.1. Chemical analysis

The results, obtained from the chemical analyses of cement and zeolite, are presented in Table 1.

According to the chemical analysis results, cement consists of CaO with higher proportion and Al_2O_3, Fe_2O_3 and SO_3 compounds with lower proportion. The main component of zeolite is SiO_2 and the ratio of SiO_2/Al_2O_3 (S/A) is 7.76 in weight. Cliniptilolite is identified as the mineral with a ratio Si/Al > 4 and very low Na and Ca contents [22,23]. From the chemical analyses study of the zeolite, it is concluded that the main mineral constituent belongs to cliniptilolite group (Table 1).

Table 1
Chemical composition of cement and zeolite.

Materials	Cement	Zeolite
Chemical composition: wt.%		
SiO_2 (S)	19.92	64.44
Al_2O_3 (A)	5.83	8.3
Fe_2O_3 (F)	3.15	1.66
CaO	58.16	1.77
MgO	1.37	0.07
SO_3	3.49	0.04
Na_2O	0.9	2.3
K_2O	0.86	2.24
Loss on ignition	4.99	18.95
S + A + F	28.9	74.4

Table 2
Physical specifications of cement and zeolite.

Materials	Range dimension (over sieve) (%)			Specific gravity (g/cm^3)	Blaine (cm^2/g)
	>200 μm	>90 μm	>45 μm		
Cement	0	0.1	2.7	3.04	4310
Zeolite	3.9	15.3	28	2.06	6130

3.2. Physical analysis

Physical specifications of cement and zeolite are presented in Table 2.

Particle size distribution, Blaine value and specific gravity are determined in the physical analyses. The particle size values of cement are smaller in comparison to the zeolite. The Blaine value of zeolite, on the other hand, is higher in comparison to cement. This indicates that zeolite has a porous structure. While the specific gravity of cement is 3.04 g/cm^3, the specific gravity of zeolite is 2.06 g/cm^3 (Table 2). When the zeolite with a low specific gravity is blended in cement, the specific gravity values of the obtained cement samples with zeolite substitution also decrease.

3.3. Mineralogical analysis

XRD analyses are conducted to determine the mineralogical structure of cement and zeolite (Fig. 1).

According to the XRD patterns, the main components of cement are tricalcium silicate ($3CaOSiO_2$), dicalcium silicate ($2CaOSiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$) and brownmillerite ($Ca_2(Al,Fe^{3+})_2O_5$). Zeolite consists of cliniptilolite ($(Na,K)_6[Al_6Si_{30}O_{72}]20H_2O$) and quartz ($SiO_2$). The XRD results indicate that the structures of cement and cliniptilolite are regular (crystal) (Fig. 1) [22].

3.4. FT-IR analysis

FT-IR analyses can be used to define molecule groups in a particle. In the FT-IR studies related to cement and pozzolan, the infrared spectrum is considered in mainly 4 wide band regions. They are composed of peaks corresponding to the deviations in Si–Al, S, C and OH bonds [24,25]. Besides, the difference in the number of vibrations in this wave length can be evaluated locally. Surface structures of the molecules are determined from the FT-IR results obtained from the analyses and shown in Fig. 2 schematically.

In FT-IR spectroscopy, vibration of the atoms forming solid cages and molecular vibrations are seen in 400–1600 cm^{-1} and 1600–4000 cm^{-1} region, respectively. Vibration peaks are observed at 492, 520, 658, 881, 1136, 1445 and 3655 cm^{-1} wave numbers from FT-IR analysis of cement (Fig. 2). Al–O bonds present with Si–O give vibration peaks of 492, 462 and 520 cm^{-1}. Si–O bonds in cage structures are in the form of a vibration peak at 881 cm^{-1} wave number. Sulfur–oxygen (S–O) bonds which show the plaster in cement is seen at 658 and 1136 cm^{-1}. C–O, on the other hand, is observed at 1445 cm^{-1}. Vibration peak of water ions and molecules in the structure is at 3455 cm^{-1} wave number [26–28].

FT-IR spectra can provide useful information on zeolite mineral structure. Vibration peaks are observed at 452, 603, 800, 1000, 1639, 3390 and 3600 cm^{-1} wave numbers from FT-IR analysis of zeolite (Fig. 2). Si–O–Si and Si–O–Al vibrations are observed in