EXPERIMENTAL RESEARCH ON ALTERNATIVE POZZOLAN ANALCIME TO CLINOPTILOLITE

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In the future, depending on the increasing demand of cement, the additives in the market may not be able to meet the demand or there may be a need to use high amounts of additives. So, there is a need to new alternative additive materials. The aim of this study is to evaluate the potential of analcime which may be alternative to clinoptilolite. Therefore, it was performed some tests on mortars/concretes containing analcime and clinoptilolite. The amounts of natural zeolites (analcime, clinoptilolite) which were used for blended cements were 0, 10, 30 and 50% of Portland cement weight. In the study, i) physical, chemical, mineralogical, pozzolanic properties of natural zeolites, ii) strength, abrasion resistance and capillarity on samples containing analcime and clinoptilolite blended cements, iii) the energy evaluations for cements/concretes used in the study were investigated. According to the results, analcime has been showed similar properties to clinoptilolite. In some cases, due to these similar properties, it has been concluded that analcime may be an alternative pozzolan to clinoptilolite which is widely used in blended cement industry.

Keywords: *natural zeolite, analcime, clinoptilolite, pozzolan, concrete*

1. Introduction

Although cement is indispensable in the construction industry, there are some problems in terms of its production techniques. The productions of Portland cement are responsible for 7-8% of CO_2 emissions of world. 1 kg of Portland cement clinker releases 0.87 kg of CO_2 to atmospheres [1]. And the non-renewable energy sources with significant quantities are consumed at production stages such as grinding of cement raw materials and calcination of clinker. To solve these problems of cement, the use of natural and local pozzolanic additive has become increasingly common. Since the pozzolans with high activity affects positively to performance of cement, the use of blended cement is especially inevitable for performance-based mortar/concrete designs [2]. On the other hand, it is known that the demand for cement will increase in the future depending on the population [3]. So, to meet this demand, there is need to new additives alternative to present additives in market.

It is known that the clinoptilolite which is a mineral of natural zeolites is commonly used in blended cement productions [4-11]. Zeolite group of minerals currently include more than forty naturally occurring species [12]. Clinoptilolite, analcime, heulandite, chabazite, and mordenite are the most common types of natural zeolite minerals on the earth [13]. These different minerals need to be worked on to ensure their widespread use as cement additives. The analcime is known as second valuable zeolite mineral after from clinoptilolite in zeolite minerals.

Natural zeolites are crystalline aluminosilicates composed of a three-dimensional arrangement of silicon–oxygen (SiO_4) and aluminum–oxygen (AlO_4) tetrahedra. The zeolites formed by the alteration of the vitric pyroclastic deposits are more reactive materials than the fly ash and furnace slags between mineral additives [14]. It is known that they show considerable pozzolanic activity despite their distinct crystalline structure [15]. And zeolites contribute to the formation of cement-like hydrated products during the hydration of cement and to $Ca(OH)_2$ consumption occurred during the hydration process. Zeolite pozzolans are preferred in production of hydraulic cement for some important applications. Because the zeolites contain silica at high ratios. Therefore, they provide neutralization of lime released in during solidification of concrete [16]. Due to the zeolites used as additives are the slowing down and decrease of heat evolution during hydration of cement, they are beneficial in the construction of large structures [17-18]. Some of the studies on zeolites are given below. Perraki et al. [19] were studied on zeolite as replacement material in blended cement and they stated that zeolite blended cements were not exceeded early age compressive strengths of Portland cement, but they were exceeded the 28- and 90-days strengths. Kocak et al. [20] reported that as the replacement ratio of zeolite increases, the water demand of cement paste increases. They explained that the reason of this increment is the micro gaps of zeolite and high specific surface area of its. Yılmaz et al. [21] studied on the blended cements with clinoptilolite content of 5, 10, 20 and 40 wt.% of Portland cement. And they found that the highest compressive strength was in 20% zeolite blended cement. Ramezanianpour et al. [22] determined that addition of zeolite delayed the strength development during the first 7 days after which concretes having 10% zeolite provided

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almost similar compressive strength to that of reference concretes. Canpolat et al. [23] stated that 15% of zeolite additive increases early compressive strength. Uzal et al. [24] declared that the pozzolanic activity of clinoptilolite is higher than silica fume and fly ash. Mertens et al. [25] studied the pozzolanic reaction between portlandite and different types of nearly pure zeolites. They pointed out that finer grain sizes or higher specific surface areas of pozzolans yield a higher short-term pozzolanic activity and mainly the external surface area is important for zeolites. Liguori et al. [26] evaluated that the feasibility of some widespread zeolite-rich tuffs to act as pozzolanic material for manufacturing blended cements by chemical and mechanical characterization. Mechanical characterization was carried out by measuring compressive strength of blended mortars after 28-days curing. They explained the good pozzolanic behavior proved by all the tuffs, coupled with their low cost, makes very promising the use of zeolitic tuffs to produce eco-sustainable blended cements. Jonatka et al. [27] evaluated sulphate resistance and passivation ability of the mortars containing zeolite. They determined the increased sulphate resistance of pozzolan blended cement relative to that of PC and steel was not corroded in mortars made with pozzolan cement containing up to 35 wt.% of zeolites. Most of the above studies and the others in the literature are studies on clinoptilolite mineral of zeolite group. But a comprehensive study on the second valuable mineral analcime of zeolite group is not available in the literature. In the author's previous paper, the preliminary tests were performed on analcime and clinoptilolite and some properties of the two pozzolans and of the blended cements containing analcime and clinoptilolite were determined [28]. The present study consists strength results at the later ages of concretes containing analcime and clinoptilolite, some durability tests and energy evaluations of blended cements containing analcime and clinoptilolite. In the study, it was determined that whether analcime has potential to be an alternative to clinoptilolite by comparison of obtained results. Thus, it has been aimed to contribute to variety of present additive in the market.

2. Materials and Methods

The zeolite minerals were analcime and clinoptilolite. The analcime (A) and clinoptilolite (C) were obtained from Ordu/Perşembe and Manisa/Gördes regions of Turkey, respectively. They are natural pozzolans with volcanic tuff origin. The cement was CEM I 42.5 R type of Portland cement (PC) in accordance with EN 197-1 [29]. CEN standard sand in accordance with EN 196-1 [30] was used for samples at pozzolanic activity tests. In lime-pozzolan mixtures of pozzolanic activity tests, slaked lime ($Ca(OH)_2$) was used as specified in TS 25 [31]. In mortar samples of abrasion tests, the sand-to-cement ratio and water-to-cement ratio of mortar samples were constantly 3 and 0.5, respectively. It was used melamine-based modified polymer superplasticizer for all test samples (as 3, 4, 5% ratios at 10, 30, 50% replacement ratios, respectively). In strength tests, the water-to-cement ratio of concretes was 0.5. The maximum grain size of aggregate was 16 mm. The aggregates were lime based crushed stone and sand. The ratios of coarse aggregate and sand were 55% and 45%, respectively. The slump of concretes was 7-8 cm.

Analcime and clinoptilolite were obtained by finely grinding in a ball mill to provide approximately 70% passing value through 45 μm sieve. The ratios of zeolites used in mixtures were 0 (none), 10 (low), 30 (medium) and 50 (high)% of cement weight. Density-specific surface of zeolites and cements were determined according to EN 197-1 and EN 196-6 [32], respectively. The pozzolanic activity of zeolites were made by mechanical test method. Chemical composition of zeolites was determined by X-ray fluorescence (XRF) analysis. This analysis was carried out by using desktop XRF (EDXRF) device as percentage (%) with loss of ignition (LOI) amount on samples prepared as pellet. X-Ray Diffraction (XRD) analysis was performed to determine mineralogical composition of zeolites. This analysis was performed using a ‘‘Bruker D8 Advance’’ diffractometer (with CuKα-radiation and Ni filter) at 40 kV and 40 mA. The samples were scanned from 2θ, 2 to 45°, at a scanning speed of 2°/min. The petrographic findings were determined under a polarization microscope in Black Sea Technical University, Mining Engineering Laboratory. The microstructure images of zeolites were obtained using a Scanning Electron Microscope (SEM) that is brand of Hitachi, model of SU 1510 with EDX - (Energy Dispersive X-ray Spectroscopy) sensor. In SEM investigations, zeolite samples which have fineness used in the study was made gold plating to provide conductivity. Some tests have been carried out to determine conformity with current standards of blended cements used in the study. The blended cement samples were produced with the labels PC, A10, A30, A50, C10, C30, C50. The density-specific surface (Blaine) of blended cements and Portland cement were determined in accordance with the EN 197-1 and EN 196-6, respectively. The determinations of the water demand, setting times (initial-final) and volume expansion tests of blended cements and Portland cement were carried out by using Vicat and Le Chatelier test sets. The compressive-flexural strengths of concretes were determined by 150 mm cube and 150x150x525 mm prism molds, respectively. The concrete samples were produced with the labels CPC, CA10, CA30, CA50, CC10, CC30, CC50.

In abrasion tests on mortars, three cube molds of 70.7 mm were used. The abrasion losses of the samples were determined by Bohme surface abrasion tests in accordance with EN 1338/AC [33]. The mortar samples were produced with the labels MPC, MA10, MA30, MA50, MC10, MC30, MC50. The capillarity coefficients of concretes prepared with 100 mm cube molds were determined by capillarity action tests in accordance with EN 772-11 [34].

3. Results and Discussions

3.1 Properties of cements/zeolites/aggregates

Some properties of cements/zeolites/ aggregates are given Tables 1-4. The densities of analcime and clinoptilolite were determined as 26.92 and 32.37% lower than that of PC, respectively. The cumulative passing (%) of 45 µm sieve for Portland cement, clinoptilolite and analcime were 67.11, 68.64 and 70.80%, respectively. The fineness of analcime and clinoptilolite were approximately like each other. The densities of blended cements decreased with increasing of zeolite ratios. The fineness of blended cements containing zeolite increased with increasing of zeolite ratios. The determined values of aggregates complied with standard aggregate values for concretes in EN 12620 [35]. The results of conformity tests for blended cements containing analcime and clinoptilolite were performed in above mentioned author's previous paper. It were determined that setting times and volume expansions of blended cements were within limits in EN 197-1. And the water demands of blended cements increased with increasing of replacement ratio.

3.2 Pozzolanic activity

The pozzolanic activity depends to chemical and mineralogical composition of pozzolans. The SiO_2 and Al_2O_3 contents of pozzolans react with calcium hydroxide released during the hydration of cement and convert it into CSH (Calcium-Silicate-Hydrate) gels and aluminates. Thus, due to the microstructure of

Table 1

Properties of Portland cement

Chemical	(wt.%)	Physical and mechanical properties			
SiO_2	19.53	Density (g/cm^3)			3.12
Al_2O_3	5.33	Specific surface (Blaine) (cm^2/g)			3210
Fe_2O_3	3.56	Sieves (µm)	45	90	200
CaO	62.26	Over sieve (%)	32.89	12.15	2.73
MgO	0.99	Initial set (min)	170		
SO_3	3.02	Final set (min)	255		
Na_2O	0.95	Vol. exp. (mm)	2.00		
K_2O	0.73	Days	2	7	28
LOI	3.06	Comp.str. (MPa)	32.30	44.60	53.00
Clinker components (%)		C_3S	C_2S	C_3A	C_4AF
		54.94	18.52	8.39	11.26

Table 2

Physical properties of blended cements

Physical properties	PC	C10	C30	C50	A10	A30	A50
Density, (kg/m^3)	3120	2750	2720	2660	2790	2750	2710
Specific surface (cm^2/g) (Blaine)	3210	3408	3664	3898	3752	3918	4449

Table 3

Properties of natural zeolites

Chemical composition	Analcime (wt. %)	Clinoptilolite (wt. %)	Physical properties		
SiO_2	46.71	64.70		Analcime	Clinoptilolite
Al_2O_3	17.24	11.21	Density, (kg/m^3)	2280	2110
Fe_2O_3	9.21	1.38	Blaine fineness (cm^2/g)	4780	4079
CaO	3.03	2.08			
MgO	5.29	0.79	Over sieve (%)		
Na_2O	4.84	0.38	45µm	29.20	31.36
K_2O	4.08	3.78	90 µm	9.80	11.51
LOI	7.00	11.80	200 µm	2.15	2.57

Table 4

Properties of aggregates

Aggregates	Dry density (kg/m^3)	Saturated density (kg/m^3)	Visible density (kg/m^3)	Water absorption (%)
Coarse (≥4mm)	2500	2560	2650	2.19
Fine (≤4mm)	2550	2600	2690	1.97

Table 5

Materials for pozzolanic activity tests

Materials	In TS 25	Analcime	Clinoptilolite
Slaked lime ($CaOH_2$) (g)	150	150	150
Pozzolan (g)	2 x 150 x (density of poz. /density of $CaOH_2$)	318.14	294.42
Standard sand (g)	1350	1350	1350
Water (g)	0.5x (150+pozzolan)	234.07	222.21

Table 6

Pozzolanic activity of natural zeolites

Limit values	Analcime	Clinoptilolite
Lime-pozzolan mix. 7 days compressive strength> 4 MPa	6.30	9.02
$SiO_2 + Al_2O_3 + Fe_2O_3$ wt. % content> 70%	73.1	77.30
Specific surface area> 3000 cm^2/g	4780	4079

hardened cement, strength of mortar/concrete is improved. And the mortar/concrete becomes more impermeable [36]. In TS 25, the pozzolanic activity test is defined as a characteristic determined in terms of compressive strength of mortar obtained by mixing natural pozzolan, water, standard sand, calcium hydroxide (Ca $(OH)_2$). The amounts of materials required to prepare three test samples for tests on pozzolanic activities of zeolites were given in Table 5, Pozzolanic activity of zeolites was given Table 6. As seen in Table 6, the eligibility criterions of the standard are met by the zeolites in the study. Due to these values, the reaction which is between pozzolan and lime is increased. It is thought that, this situation is caused an increment at the value of pozzolanic activity. The test results are showed that the zeolites used in the study have usable potential as a pozzolan in terms of pozzolanic activity.

3.3 Mineralogical and petrographic analysis

The results of analyzes performed on natural zeolites were given in previously paper [28]. They are summarized below. The main component (>50%) in clinoptilolite sample is "clinoptilolite" that is a zeolite group mineral and is a member of hoylandite-clinoptilolite isomorphic series. The ratio of clinoptilolite in the sample is 80-85%. Clinoptilolite sample is volcanic glass with less amounts crystal and rock fragments. It was altered to zeolites and other minerals. The rock of analcime is a vitric tuff. And it consists glass splinters and crystal components. Glass splinters have been converted to zeolite and chlorite which are heavily altered. Crypto crystalline silica formations are present in binding material. The crystalline constituents are composed of heavily fragmented augite (pyroxene) and very little biotite. Opaque minerals are present in less than 5% of the rocks. Very little carbonation has been detected and is not widespread. Silicification was detected in binding material. And both natural zeolites have crystal formation and contain analcime and clinoptilolite as dominant minerals. The morphology of natural zeolites samples analyzed by SEM [28] revealed the morphologic similarities to each other of both zeolites observed at the equal magnification of the SEMs of zeolites. On the other hand, the EDS quantitative analysis data confirms that the zeolite samples used in the study are different types of zeolites due to different Si/Al ratios. The different Si/Al ratios of zeolites depend on their chemical compositions [37]. The Si/Al ratios for analcime and clinoptilolite were determined as 2.25 and 4.15, respectively.

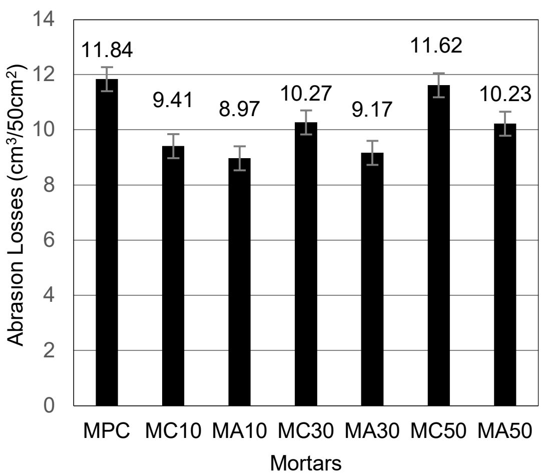

Fig. 1 - Abrasion losses for samples.

3.4 Abrasion losses

In Bohme surface abrasion tests for abrasion losses. The volumetric abrasion losses (ΔV) in samples were determined. ΔV was calculated by Eq. (1): where denotes ΔV ($cm^3/50cm^2$); volumetric abrasion loss corresponding to ~ 50cm^2 abrasion surfaces of samples, Δm (g); weight loss at end of 16 cycles, ρ (g/cm^3); density.

$$\Delta V = \Delta m / \rho \quad (1)$$

Abrasion losses are presented in Fig. 1. The abrasion losses mortars of containing clinoptilolite and analcime blended cements (MC10, MC30, MC50, MA10, MA30 and MA50) were 20.52, 13.26, 1.86, 25, 23 and 14% less than that of mortars containing PC (MPC), respectively. At all replacement ratios, the abrasion resistances of mortars containing analcime blended cements were higher than that of mortars containing clinoptilolite blended cements. The mortars containing 10 % analcime blended cements have been showed the best performance. It has been thought that the reason of this positive effect in abrasion resistance is probably an increase in performance at aggregate-cement paste interface and cement paste due to pozzolanic reactions of zeolites.

3.5 Capillarity tests

The concretes were subjected to capillary test in accordance with the EN 772-11 standard. After the samples of 10 cm cube taken from the curing pool were kept at 105 °C for 24 hours and reaching the standard dryness, the edges of the samples around the 3-4 cm base were made waterproofed with paraffin. Thus, the samples were only absorbed from the bottom. The weights of samples were determined at 1, 4, 9, 16, 25, 36, 49, 64, 81, 100, 121 and 144 min. And the capillarity coefficient was calculated by Eq. (2). Where, Q is the amount of water adsorbed in (cm^3); A is the cross section of sample (cm^2); t is time (s); k is the capillarity coefficient of the sample ($cm/s^{1/2}$).

$$Q/A = k \sqrt{t} \quad (2)$$

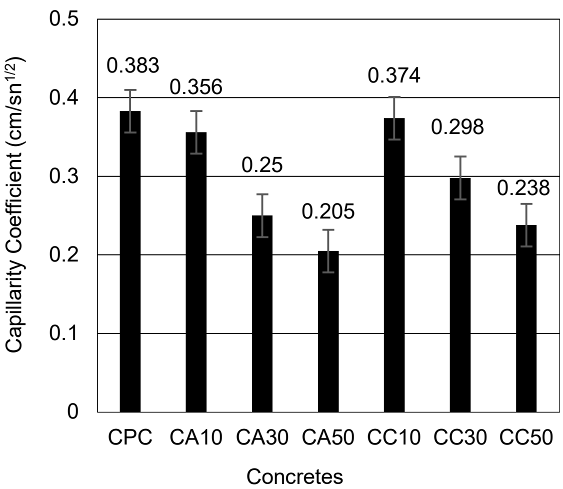

Fig. 2 - The capillarity coefficients of concretes.

The capillarity coefficients of concretes are presented in Fig. 2. The capillarity coefficient depends on pore structure of material. The capillarity of concretes containing both zeolites improved with increasing of replacement ratio. But the capillarity coefficient of concretes containing analcime blended cements was slightly more improved than that of concretes containing clinoptilolite blended cements. The situation is a result of improvement of the pore structure of the cement paste phase and the reduction of the pore diameters due to fineness of both zeolites [38].

3.6 Compressive-flexural- strengths

The mix design is given in Table 7. The strengths are illustrated in Figs. 3, 4. According to

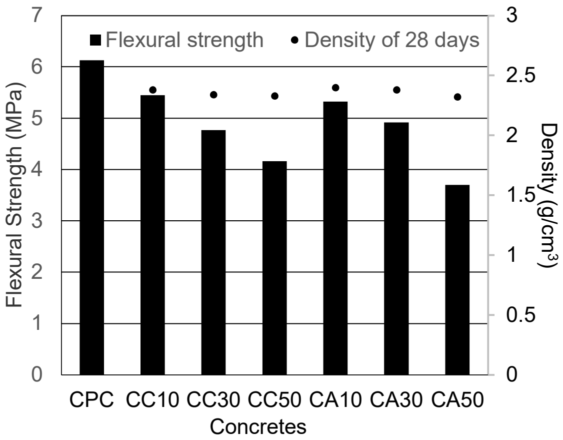

Fig. 3 - Flexural strength-density for concretes.

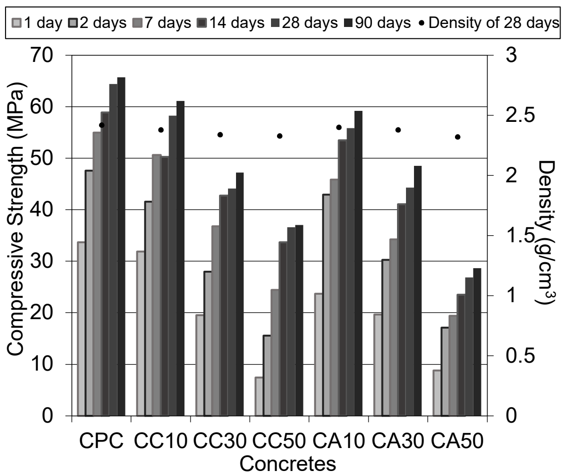

Fig. 4 - Compressive strength-density for concretes

Table 7

Mix design of concretes

Components	CPC	CA10	CA30	CA50	CC10	CC30	CC50
Portland Cement (kg/m^3)	350	315	245	175	315	245	175
Natural Zeolite (kg/m^3)	-	35	105	175	35	105	175
Water (kg/m^3)	175	175	175	175	175	175	175
Water / Cement	0.50	0.50	0.50	0.50	0.50	0.50	0.50
0-4 mm Aggregate (kg/m^3)	789.99	787.99	783.99	778.31	787.99	783.99	778.31
4-8 mm Aggregate (kg/m^3)	351.11	350.22	348.44	345.91	350.22	348.44	345.91
8-16 mm Aggregate (kg/m^3)	614.44	612.88	609.77	605.35	612.88	609.77	605.35
Plasticizer (kg/m^3)	-	10.5	14	17.5	10.5	14	17.5

strength results, as the zeolite replacement ratios increased, the compressive-flexural strengths of concretes containing both blended cements decreased. The declines at strengths of concretes were high at early ages. But the amount of the declines decreased with long curing period. Despite this decline at strengths, the compressive strengths of concretes containing blended cements at even 14 and 28 days had still a structural concrete class characteristic up to 30% replacement ratio although not as much as those containing Portland cement. Moreover, for both zeolites at 10% of replacement ratio, the 90-days strengths of concretes containing blended cements were approached to that of concretes of containing PC thanks to the long curing period and the additional binders developed at later ages with pozzolanic activity of zeolites. As known, that pozzolans sometimes decelerate the rate of strength development of samples. But, in later ages, depending on the structure of the used pozzolan and its pozzolanic activity, strength of samples increases due to additional binders [12, 17, 20]. The strengths of all concretes continued to improve up to the later ages like 90 days. The flexural strengths of concretes containing both blended cements showed similar trends with their compressive strengths.

3.7 Energy demand evaluations

The energy demand of blended cement and performance energy of concrete containing blended cement could be approximately calculated by Eq. (3) and Eq. (4) [39]. Where, E is the energy demand (in kWh), C_c and C_p are the proportions of Portland cement and pozzolan, respectively, $E_{process\ of\ cement}$ and $E_{grinding\ of\ cement}$ are the energy consumption (in kWh/t) of the cement manufacturing process (950 kWh/t) [40] and the finish grinding of the clinker (50 kWh/t) [41], respectively, $E_{grinding\ of\ zeolite}$ is the energy consumption (in kWh/t) for the grinding of the zeolites due to approximately lower hardness with clinker (35 kWh/t) [42], $E_{performance}$ is the performance energy relative to the compressive strength of the concrete containing the blended cements, strength is the compressive strength of the concrete with composition $C_c + C_p$.

$$E = C_c\,(E_{process\ of\ cement} + E_{(grinding\ of\ cement)} + C_p\,(E_{grinding\ of\ zeolite}),\ \text{(in kWh/t)} \quad (3)$$

$$E_{performance} = E / \text{strength},\ \text{(in kWh/t. MPa}^{-1}\text{)} \quad (4)$$

The energy demand of cements and the performance energy of concrete are given in Figs. 5,6, respectively. As seen, the energy demands of blended cements were lower than that of Portland cement. Because zeolite does not need thermal treatment. And grinding energy of zeolite is lower than that of clinker. The performance energies of concretes containing zeolite blended cements were lower than that of concretes containing Portland cement. The performance energy evaluations of concretes show more meaningful results in later ages like 90 days (Fig. 6).

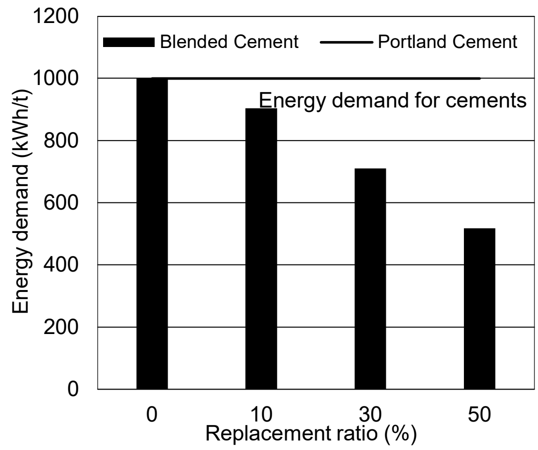

Fig. 5 - The energy demand for cements.

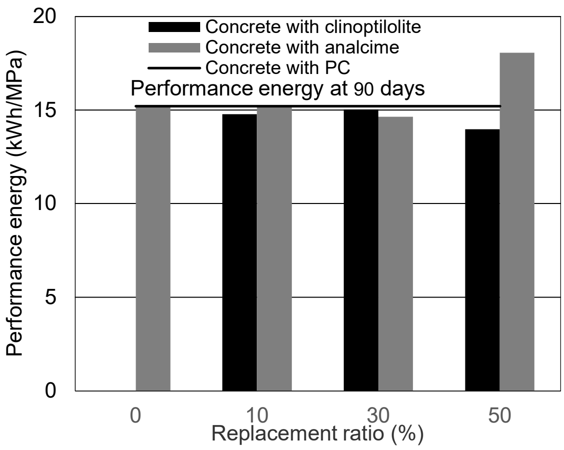

Fig. 6 - The performance energy for concretes.

4. Conclusions

The determined properties such as high silica-alumina content, mineralogical structure and pozzolanic activity for analcime have been showed that analcime could be used as pozzolan for blended cement productions.

The abrasion resistances, compressive and flexural strengths of samples containing analcime blended cements were slightly higher than that of samples containing clinoptilolite blended cements at all replacement ratios. For both zeolites at 10% of replacement ratio, the 90-days strengths of concretes containing blended cements were approached to that of concretes of containing PC thanks to the long curing period.

The capillarity of concretes containing both zeolites was improved. But the capillarity coefficients of concretes containing analcime blended cements were slightly more improved than that of concretes containing clinoptilolite blended cements.

The optimum replacement ratio in terms of strengths, abrasion losses, capillarity of samples containing both analcime and clinoptilolite blended cements was determined 10%.

At all replacement ratios and for both type zeolites, the energy demand of blended cement was lower than that of Portland cement due to absence of calcination process and low grinding energy of zeolites. It is possible to say that to produce zeolite blended cement and to use zeolite additive in concrete productions will make important contribution to world energy policies.

Lastly, it is known that the cement industry needs to alternative pozzolans, therefore, to increase pozzolan diversity, it should be studied on different minerals of zeolites. According to the results of this study, the analcime has been exhibited similar properties to clinoptilolite. These similarities indicate the potential to be alternative to clinoptilolite additive of analcime additive. In later studies, it will be worthwhile to investigate the microstructure details and other durability tests not discussed in this paper on analcime samples to be obtained from different regions to increase use of analcime in the blended cement industry.

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