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A Comparative Study: Blended Cements Containing Analcime and Clinoptilolite

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Setting times,
Strength,
Zeolite

Abstract: The demand to blended cements is increasingly widespread due to clean environment and energy saving. In the future, this demand will not be met by currently additives on the market. For this reason, alternative additives will always be needed. The aim of this study is to provide a contribution for additive variety used in sustainable blended cement productions. Therefore, in this study, natural zeolite type clinoptilolite (C) which is widely used in blended cement production and different natural zeolite type analcime (A) are compared. These zeolites are natural pozzolans with volcanic tuff origin. Firstly, pozzolanic activities, mineralogical structures, physical and chemical properties of zeolites were determined. And then, the heat of hydration, setting times and compressive strength tests were performed on samples prepared by using Portland cement (PC) and natural zeolite blended cements. The replacement ratios of zeolites used in test samples are 0, 10, 30 and 50% of Portland cement weight. According to results of pozzolanic activity tests, the compressive strengths of lime-zeolite (pozzolan) mixtures were determined as 6.30MPa for analcime and 9.02MPa for clinoptilolite. The heats of hydration of blended cements containing analcime were lower than that of blended cements containing clinoptiloite and that of Portland cement at all replacement ratios. The setting times of blended cements containing analcime were determined as shorter than that of blended cements containing clinoptiloite and that of Portland cement. The compressive strengths of mortars containing analcime blended cements were slightly higher than that of mortars containing clinoptilolite blended cements. The optimum strength values of mortars containing both zeolite blended cements were obtained at 10% replacement ratio. According to the results obtained from the study, analcime exhibits similar properties to clinoptilolite. In some cases, due to these similar properties, analcime may be an alternative additive to clinoptilolite which is widely used in blended cement industry.

Karşılaştırmalı Bir Çalışma: Analsim ve Klinoptilolit İçeren Katkılı Çimentolar

Anahtar Kelimeler
Analsim,
Klinoptilolit,
Hidratasyon ısısı,
Priz süreleri,
Dayanım,
Zeolit

Özet: Temiz çevre ve enerji tasarrufu nedeniyle katkılı çimentolara olan talep, giderek yaygınlaşmaktadır. Gelecekte, bu talep piyasadaki katkı maddeleri tarafından karşılanamayacaktır. Bu nedenle, alternatif katkı maddelerine her zaman ihtiyaç duyulacaktır. Bu çalışmanın amacı, sürdürülebilir katkılı çimento üretiminde kullanılan katkı çeşitliliğine bir katkı sağlamaktır. Bu nedenle, bu çalışmada, katkılı çimento üretimlerinde yaygın olarak kullanılan doğal zeolit tipi klinoptilolit (K) ve farklı doğal zeolit tipi analsim (A) karşılaştırılmıştır. Bu zeolitler volkanik tüf kökenli doğal puzolandırlar. Öncelikle, zeolitlerin puzolanik aktiviteleri, mineralojik yapıları, fiziksel ve kimyasal özellikleri belirlendi. Ardından Portland çimentosu (PC) ve doğal zeolit katkılı çimentolar kullanılarak hazırlanan numuneler üzerinde hidratasyon ısısı, priz süreleri ve basınç dayanımı testleri gerçekleştirildi. Test numunelerinde kullanılan zeolitlerin yer değiştirme oranları Portland çimentosu ağırlığının 0, 10, 30 ve %50' sidir. Puzolanik aktivite testlerinin sonuçlarına göre, kireç-zeolit (puzolan) karışımlarının basınç dayanımları analsim için 6.30 MPa ve klinoptilolit için 9.02 MPa olarak belirlendi. Analsim içeren katkılı çimentoların hidratasyon ısıları, tüm yer değiştirme oranlarında, klinoptilolit içeren katkılı çimentolardan ve Portland çimentosundan daha düşüktür. Analsim içeren katkılı çimentoların priz süreleri klinoptilolit içeren katkılı çimentolardan ve Portland çimentosundan daha kısa olarak belirlendi. Analsim katkılı çimentolar içeren harçların basınç dayanımı, klinoptilolit katkılı çimentolar içeren harçlardan biraz daha yüksektir. Her iki zeolit karışımlı çimento içeren harçların optimum dayanım değerleri %10 yer değiştirme oranında elde edilmiştir. Çalışmadan elde edilen sonuçlara göre, analsim klinoptilolite benzer özellikler sergilemektedir. Bazı durumlarda, bu benzer özelliklerden dolayı, analsim çimento endüstrisinde yaygın olarak kullanılan klinoptilolite alternatif bir katkı maddesi olabilir.

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1. Introduction

Cement is a building material that needs to environmental (less CO_2 emissions) and economical (less energy) solutions due to its production techniques [1]. The easiest solution of this problem is to produce blended cement by using additive materials. Zeolites that have pozzolanic property are one of these additives. Zeolites include more than forty minerals types which naturally occur. Clinoptilolite, analcime, heulandite, chabazite and mordenite are the most common types of natural zeolite minerals on the earth [2]. Clinoptilolite which is the most valuable mineral of zeolite group is commonly used in blended cement productions. Therefore, there are many studies on clinoptilolite. But, although the analcime is known as second valuable zeolite mineral after from clinoptilolite. There are a limited number of detailed and comparative studies on analcime. For example, Özen et al., [3] examined the pozzolanic action of five natural zeolite rich materials (three different clinoptilolite, one each mordenite and analcime) obtained from Turkey. The effectiveness of the pozzolanic action was monitored by XRD and FTIR analyses on zeolite samples. The blended cements with the five zeolite rich rocks were prepared and the compressive strengths were measured as a function of the curing time. The researchers reported that clinoptilolite rich rocks gave the best results with respect to pozzolanic action. Cobzaru et al., [4] studied the kinetics of the ion exchange process with Cu^{2+} ions on clinoptilolite and analcime-based zeolites with particle size within 0.5-0.6 mm at different temperatures. The results indicated that the optimum temperature favors the sorption process of zeolites with Cu^{2+} ions. Akgün et al., [5] determined the pozzolanic activity of analcime which is the natural zeolite mineral and investigated how the setting time and volume expansion parameters of the blended cement will be affected when used analcime in blended cement production. They found that the obtained results were within the limit values of standards. Akgün in another study [6] defined some properties for analcime and clinoptilolite such as fineness, density, chemical-physical property, mineralogical structure, pozzolanic activity and abrasion. They announced that analcime has the potential to be an alternative to clinoptilolite which is more widely used in cement productions. According to these studies, The more detailed and comparative studies should be performed for analcime with similar properties to clinoptilolite.

The clinoptilolite is a natural zeolitic mineral with chemical formula $(Na_3K_3)(Al_6Si_{30}O_{72})24H_2O$, which is rich in silica and contains alkali and earth alkaline cations. On the other hand, analcime is a feldspathite mineral with a very large amount of hydrated sodium aluminosilicate $(Na(AlSi_2O_6).H_2O)$ in its structure. Also, the natural zeolites formed by the alteration of the vitric pyroclastic deposits are more reactive materials than the fly ash and furnace slags between mineral additives [7]. It is known that they show considerable pozzolanic activity despite their distinct crystalline structure [8]. 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 [9,10].

Generally, some of the studies on zeolites are presented below. Kocak et al., [11] reported that as the replacement ratio of zeolite increases, the water demand of cement paste increases. This increment is explained by the micro gaps in zeolite and its high specific surface area. In another study, Kocak et al., [12] investigated the effect of the surface properties of Portland cement, diatomite and zeolite on the performance of concrete composites. In their study, reference (Portland cement), 10-20% diatomite, 10-20% zeolite, 5+5%-10+10% diatomite and zeolite were substituted for Portland cement. Ultrasonic pulse velocity, capillary water absorption and compressive strength tests were performed on the hardened concrete for 28, 56 and 90 days. As result, they identified that both the zeolite and diatomite substitution has a positive effect on the performance of concrete. Gerengil et al., [13] assessed the electrochemical impedance of reinforcing steel in concrete containing diatomite and zeolite exposed to sodium chloride. They were declared that reinforcement in the reference concrete was the most corroded compare to concretes containing zeolite and diatomite. Perraki et al., [14] used zeolite as replacement material in the blended cement. According to test results, all zeolite blended samples were not exceed early age compressive strength values of Portland cement. But, they were exceed the 28 and 90 days strength values. In another study on the samples with clinoptilolite content of 5, 10, 20 and 40% of Portland cement weight. Yılmaz et al., [15] obtained the highest compressive strength in 20% zeolite blended cement. Ramezanianpour et al., [16] determined that strengths of concretes contained 15% natural zeolite were almost similar to or slightly lower than that of reference concretes. In a study carried out by Canpolat et al., [17] it was determined that early age compressive strength of concretes containing 15% zeolite blended cement increased. Uzal et al., [18] stated out that the pozzolanic activity of clinoptilolite is higher than silica fume and fly ash. Caputo et al., [19] studied on blended cements prepared by mixing together ordinary Portland clinker to investigate the pozzolanic activity of zeolites. And, pozzolanic activity was demonstrated to depend on zeolite structure. Mertens et al., [20] studied the pozzolanic reaction between portlandite and different types of nearly pure natural zeolites. They determined that finer grain sizes or higher specific surface areas of pozzolans yield a higher short-term pozzolanic activity and mainly the external surface area are important for zeolites. Liguori et al., [21] evaluated the feasibility of some widespread zeolite rich tuffs 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-day curing. The good pozzolanic behaviour proved by all the tuffs, coupled with their low cost, makes very promising the use of zeolitic tuffs for the production of eco-sustainable blended cements. Jonatka et al., [22] tested sulphate resistance and passivation ability on the mortars containing zeolite. The increased sulphate resistance of pozzolan cement relative to that of PC was found. Steel was not corroded in the mortars made with pozzolan cement containing up to 35% of zeolite. They said that steel was protected against corrosion by this pozzolan cement in the same measure as the reference PC. Karakurt et al., [23] studied about using natural zeolite (clinoptilolite) as an aggregate and bubble-generating agent in autoclaved aerated concrete (AAC) production. They were experimentally investigated effects of particle size, replacement amount (25, 50, 75 and 100%) and curing time on the AAC properties. They were found that usage of natural zeolite, especially with a coarser particle size, has beneficial effect on the physical and mechanical properties of AAC. Bilim [24] presented a study of the properties and behavior of cement mortar with clinoptilolite. In the study, six mortar mixtures were prepared by replacing the Portland cement with 0, 5, 10, 15, 20 and 30% clinoptilolite by weight. Test results showed that compressive and flexural strength of the mortars containing clinoptilolite were higher than the control mixture. Uzal and Turanlı [25] investigated the properties and hydration characteristics as well as paste microstructure of blended cements containing 55% by weight zeolitic tuff composed mainly of clinoptilolite mineral.

In this study, i) pozzolanic activities of analcime and clinoptilolite, ii) mineralogical structures, physical and chemical properties of blended cements, iii) heat of hydration developments of blended cements containing clinoptilolite and analcime iv) compressive strengths of mortars containing analcime and clinoptilolite blended cements were investigated. The aim of these investigations is to compare between blended cements containing analcime which is potential mineral additive and blended cements containing clinoptilolite which is commonly used. The other comparison in this study is made between blended cements and Portland cement. After these comparisons in the study, it is aimed to contribute to additive variety in the market with preliminary tests on analcime that is natural and local pozzolan.

2. Materials and Methods

The natural zeolite minerals, clinoptilolite and analcime, were replaced by Portland cement. The analcime (A) and clinoptilolite (C) which are natural zeolites type were obtained from Ordu/Perşembe and Manisa/Gördes regions of Turkey, respectively.
The cement used in tests was CEM I 42.5 R type of Portland cement (PC) produced in accordance with EN 197-1 [26]. The PC was obtained from Unye Cement Company. In pozzolanic activity tests and strength tests of mortars, CEN (the European Committee for Standardization) standard sand in accordance with EN 196-1 [27] was used. In lime-pozzolan mixtures, slaked lime ($Ca(OH)_2$) was used as specified in TS 25/T1 [28]. It was used melamine-based modified polymer superplasticizer (at 1, 1.5 and 2% ratios) complying with EN 934-2 [29] by adding to mixture water to recover of adverse effect on mortar consistency of natural zeolites. In production of all samples, the water that does not contain organic substances, harmful minerals or salts was used. Two different natural zeolite (analcime and clinoptilolite) samples were obtained by finely grinding in a ball mill so as to provide approximately 70% passing value through 45 μm sieve. The amounts of zeolites used in mixtures were 0 (none), 10 (low), 30 (medium) and 50 (high)% of cement weight. The samples were produced with the labels PC, A10, A30, A50, C10, C30, C50 for blended cement mixtures and MPC, MA10, MA30, MA50, MC10, MC30 MC50 for mortars. Density-specific surface (Blaine) of natural zeolites and cements were determined according to EN 197-1 and EN 196-6 [30], respectively. The tests for determinations of pozzolanic activities of natural zeolites were made by mechanical test method which is determined with average compressive strengths of lime-pozzolan mixtures in accordance with TS 25/T1. 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 in laboratory of "General Directorate of Mineral Research And Explorations" coded as "MTA". 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 images for microstructure 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 "Ordu University, Central Research Laboratory" coded as "ODUMARAL". For SEM investigations, it was made gold plating to provide conductivity on zeolite samples which have fineness used in the study. For this, the surface of sample on the carbon

band of the gold plating device (sputter) was plated with gold at a thickness of approximately 10-20nm with 20-30 mA. Mortar samples were prepared by applying the standard mixing, molding and curing procedures stated in EN 196-1. Samples were prepared in laboratory environment where temperatures are 20±2ºC and relative humidity is 60±5%. The sand-to-cement ratio of mortars was constantly 3. The water-to-cement ratio of mortars was constantly 0.5. The flow values of mortar mixtures are about 150 ± 20 mm. The compressive strengths of mortars were determined by 50 mm cubes at 2, 7 and 28 days. The compressive strength developments of mortars were carried out in accordance with the EN 196-1. Also, determinations of the normal consistency and setting times, volume expansion values of blended cements (containing natural zeolite at different ratios) and Portland cement were carried out in accordance with the EN 196-3 [31] by using Vicat and Le Chatelier test sets. In this study, the tests for heats of hydration and hydration rates determinations were made in accordance with CEN/TR 16632 [32]. The heat of hydration determination was carried out with TAM AIR Isothermal Calorimeter at 20°C constant temperature and 0.5 water/cement ratio on the samples prepared at the determined mixture ratios. The results obtained from the test series were compared amongst themselves and with each other.

3. Results and Discussions

3.1 Some properties of Portland cement, blended cements and natural zeolites

Some properties of Portland cement (PC), blended cements and natural zeolites are given Tables 1-3. The differences at chemical/mineralogical structure effect to densities of zeolites. The densities of clinoptilolite and analcime are 32.37% and 26.92% lower than PC, respectively. The specific surface areas of clinoptilolite and analcime are 27.07% and 48.91% higher than PC, respectively. This situation depends on mineral structure, porosity and fragilement properties of zeolites. The cumulative passing (%) of 45 µm sieve for Portland cement, clinoptilolite and analcime are 67.11%, 68.64% and 70.80%, respectively. The densities of blended cements have decreased with increasing of zeolite ratios. The fineness of blended cements containing zeolite has increased with increasing of zeolite ratios (Fig. 1).

Table 1. Chemical composition, physical and mechanical properties of Portland cement (PC)

Chemical composition	(wt.%)	Physical and mechanical properties of Portland cement			
SiO_2	19.53	Density, (g/cm^3)	3.12	Clinker sample (%)	
Al_2O_3	5.33	Initial set, (h)	2.50	C_3S	54.94
Fe_2O_3	3.56	Final set, (h)	4.15	C_2S	18.52
CaO	62.26	Volume expansion, mm	2.00	C_3A	8.39
MgO	0.99	Specific surface (Blaine) (cm^2/g)	3210	C_4AF	11.26
SO_3	3.02	The compressive strengths (MPa)	2 days	7 days	28 days
Na_2O	0.95		32.30	44.60	53.00
K_2O	0.73	Over sieve (%)	45µm	90 µm	200 µm
Loss of ignition	3.06		32.89	12.15	2.73

Table 2. Physical properties of blended cements

Physical properties	PC	C10	C30	C50	A10	A30	A50
Specific surface (cm^2/g) Blaine fineness	3210	3408	3664	3898	3752	3918	4449
Density, (g/cm^3)	3.12	2.75	2.72	2.46	2.79	2.75	2.71

Table 3. Physical properties and chemical compositions of natural zeolites

Chemical composition	Clinoptilolite (wt.%)	Analcime (wt.%)	Physical properties		
SiO_2	64.70	46.71		Clinoptilolite	Analcime
Al_2O_3	11.21	17.24	Density, (g/cm^3)	2.11	2.28
Fe_2O_3	1.38	9.21	Blaine fineness (cm^2/g)	4079	4780
CaO	2.08	3.03		Over sieve (%)	
MgO	0.79	5.29			
Na_2O	0.38	4.84	45µm	31.36	29.20
K_2O	3.78	4.08	90 µm	11.51	9.80
Loss of ignition	11.80	7.00	200 µm	2.57	2.15

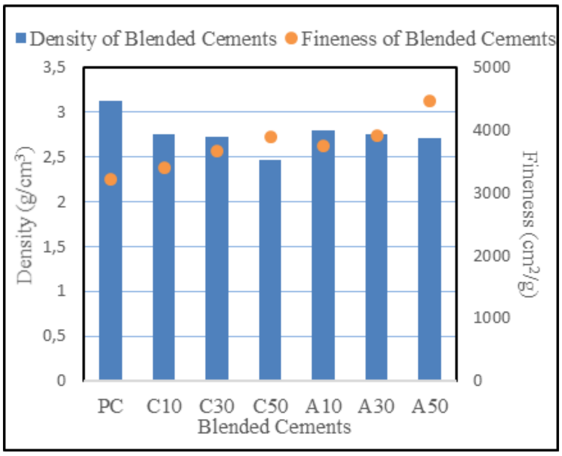


Figure 1. The density-fineness for blended cements

3.2. Pozzolanic activity of natural zeolites

The pozzolanic activity of natural zeolites depends on their chemical and mineralogical composition. Pozzolans are defined as materials with silica and alumina. The SiO_2 and Al_2O_3 contents of natural zeolites 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 hardened cement, strength of mortar/concrete is improved and the mortar/concrete becomes more impermeable [33]. In TS 25/T1, 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 and calcium hydroxide ($Ca(OH)_2$). The amounts of materials required to prepare three test samples for tests on pozzolanic activity are given in Table 4. Pozzolanic activity values of natural zeolites are given Table 5. According to Table 5, in TS 25/T1, one of the conformity criterias for pozzolans is the 7 days compressive strength of samples prepared with lime-pozzolan mixture. The limit value of the compressive strength is at least 4 MPa. In tests performed for pozzolanic activity, the average compressive strength values for the lime-zeolite (pozzolan) mixture samples were determined as 6.30 MPa for analcime and 9.02 MPa for clinoptilolite. It has also been emphasized that the sum of SiO_2 + Al_2O_3 + Fe_2O_3 in TS 25 should be at least 70% by mass. The value of this total was found to be 73.16% for analcime and 77.3% for clinoptilolite. At the same time, the specific surfaces of the pozzolans should be greater than 3000 cm^2/g. The specific surfaces of pozzolans which are used in this study were found to be 4780 cm^2/g for analcime and 4079 cm^2/g for clinoptilolite. It is seen that, the finenesses of natural zeolites are higher than that of Portland cement. And also, the contents of silica and alumina are above of 70%. Due to the this 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 results show that the zeolites used in the study have an usable potential as a pozzolan.

3.3. Mineralogical analysis of natural zeolites

The results of mineralogical analysis of natural zeolites are given below. XRD diffraction patterns and SEM images of zeolites are presented Figs. 2-5. The clinoptilolite sample was obtained from Gördes Zeolite Company. The analcime sample was obtained from Ordu-Perşembe region of Turkey. The main component in the sample (>50%) 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 (Silicate-Zeolite Group Mineral) (80-85%), Opal-CT (Opal-Kritobalite/Tridimite) (Silicate-Silice Group Mineral) (10-15%), Quartz (Silicate-Silice Group Mineral (% <2)), Feldspar (Na and K-Felspat) (Silicate-Feldspate Group Mineral) (<2%), Illite-Mica (Silicate-Clay-Mica Group Mineral) (% <5). As other minerals; opal-CT is a certain rate, illite mica, quartz and feldspar are low and trace rates. According to the mineral ratios at the mineralogical composition results determined by the X-ray diffraction analysis (XRD) of clinoptilolite sample, the sample is characterized by zeolite industrial raw material. The analcime rock is a vitric tuff and consists of glass splinters and crystal components. Glass splinters are 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 and they are in the form of amorphous crystals. The rock is heavily affected by alteration and chloritization and zeolite are common. Very little carbonation has been detected and is not widespread. Silicification was detected in binding material. When the diffractograms and SEM images of zeolites are examined, as seen that zeolites contain analcime and clinoptilolite as dominant minerals. They have crystal structure. The similar microstructure formation is seen at the same magnification of the SEM images of zeolites.

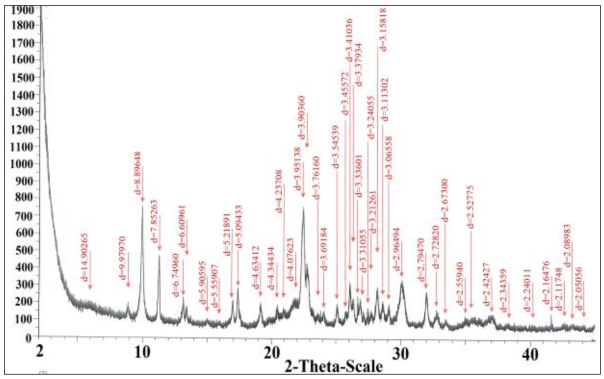


Figure 2. XRD patterns of clinoptilolite (Gördes Zeolite Company

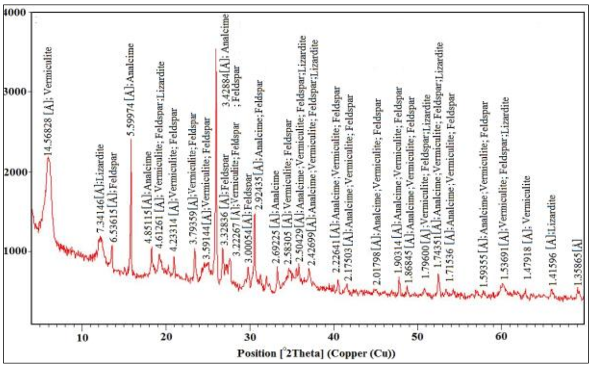


Figure 3. XRD patterns of analcime (MTA)

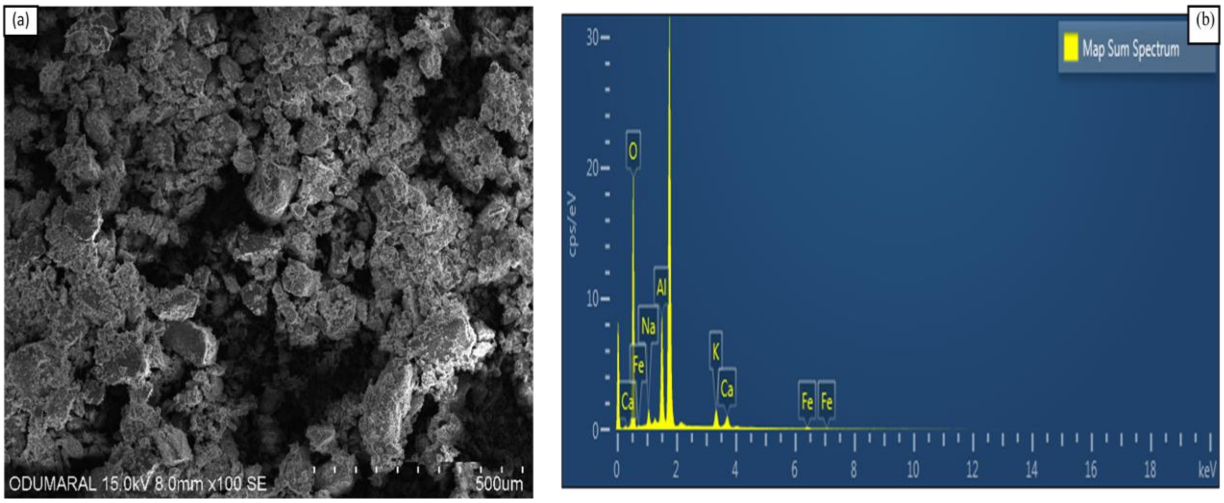


Figure 4. SEM image (a) and EDS (b) of clinoptilolite sample

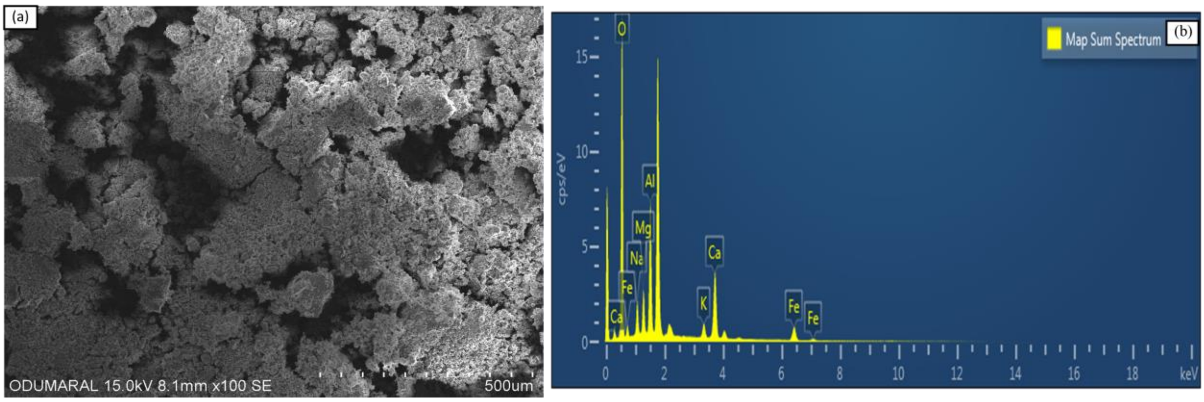


Figure 5. SEM image (a) and EDS (b) of analcime sample

3.4. The water demand, setting times and volume expansion of cements

The water demands (water/binder ratio for normal consistency), setting times and volume expansion values of all cements are given in Table 6. As seen in the Table 6, the water demands of blended cements containing natural zeolites increased with increasing of replacement ratio due to their fineness and micropores inherently found in their structures. It has been found that initial and final setting times of blended cements containing natural zeolites were shorter than that of Portland cement due to the increase of amount of zeolite content. Actually, according to expected situation in the literature, setting times should be extended with increasing of replacement ratio and with decreasing in the amount of Portland cement. Probably, this adverse case depends on the decrease of cement paste consistency due to continuous water adsorption of zeolite particles after the preparation of cement paste. There are such behaviors of some natural pozzolan for blended cements in literature [34-35]. The amount of natural zeolite in the cement directly affected the volume expansion. As the ratio of natural zeolite increased, the volume expansion values also increased. The volume expansion values of blended cements containing analcime were found to be higher than that of blended cements containing clinoptilolite. Accordingly, it has been determined that the setting times and volume expansion values of all blended cements containing natural zeolite considered in this study are within limits in EN 197-1.

3.5. Heats of hydration of blended cements

The hydration reactions occur when water is added to the cement. This reactions are mostly exothermic. That is, the reactions generate heat. The amount of heat and the releasing rate of heat can create a inconvenient situation. The rate at which the heat of hydration is released depends on the rate of chemical reactions between water and cement components. And, the most important factor affecting hydration is time. We can get by monitoring heat values and the its releasing rate at which heat is evolved using a technique called conduction calorimetry. The heat evolution graphs obtained from results of calorimeter measurements are shown in Figs. 6-11. At the graphs, the heat of hydration (cal/g) refers to the heat value released by one gram of cement at a defined time during the hydration of the cement. The hydration rate (mW/g) refers to the releasing rate of heat resulted from hydration reactions. The results obtained from the test series were compared amongst themselves and with each other by using maximum values. According to the results obtained from performed tests on cements, the heat of hydrations (cal/g) of blended cements (A10, A30, A50, C10, C30 and C50) are 5%, 12%, 30%, 5%, 6% and 30% are lower than that of Portland cement, respectively. The hydration rates (mW/g) of blended cements (A10, A30, A50, C10, C30 and C50) are 0%, 24%, 30%, 0%, 22% and 40% lower than that of Portland cement, respectively. If it is compared with each other of zeolites, the decline at heat of hydration of analcime blended cement was higher than that of clinoptilolite blended cement for 30% replacement ratio. The decline of heat of hydration eliminates adverse effects such as irregular internal stress distribution, shrinkage and crack formation caused by heat released during hydration of cement. As replacement ratio increases, the heat of hydration and hydration rate of blended cements containing zeolite are lower than that of Portland cement. Because, zeolite blended cements consist less clinker and zeolites have water in their microstructural pores. The results of the calorimetric measurements for blended cements in the study are consistent with the literature [36-38].

Table 6. The water demands, setting times and volume expansion values of all cements

Cements		PC	C10	C30	C50	A10	A30	A50
Water demand (%)		30	36	39	42	32	34	36
Setting times (Vicat)	Initial (h)	2.83	2.66	2.42	2.33	2.25	2.00	1.92
	Final (h)	4.25	4.00	3.75	3.00	3.50	3.25	2.75
Volume expansion (mm)		2.00	3.00	4.50	5.00	4.50	6.50	7.50

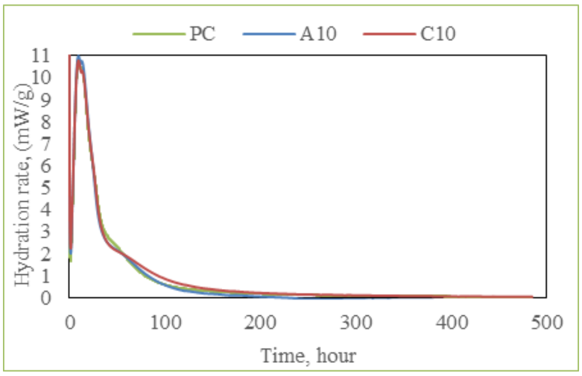


Figure 6. Hydration rate-time graph (A10, C10)

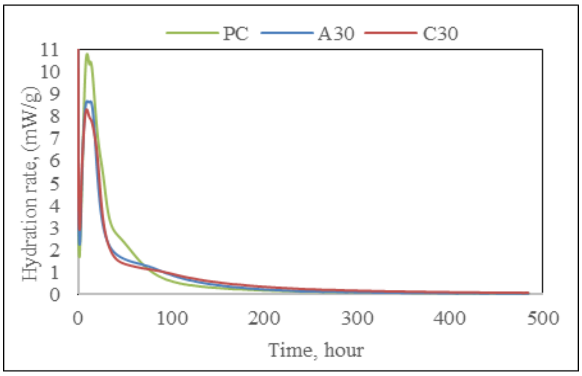


Figure 8. Hydration rate-time graph (A30, C30)

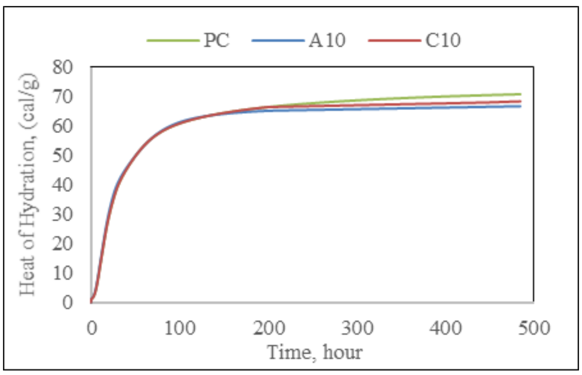


Figure 7. Heat of hydration-time graph (A10, C10)

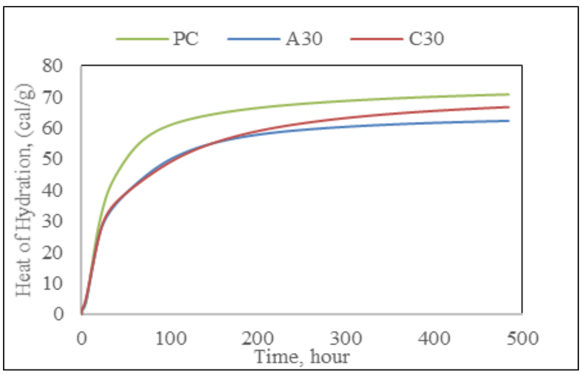
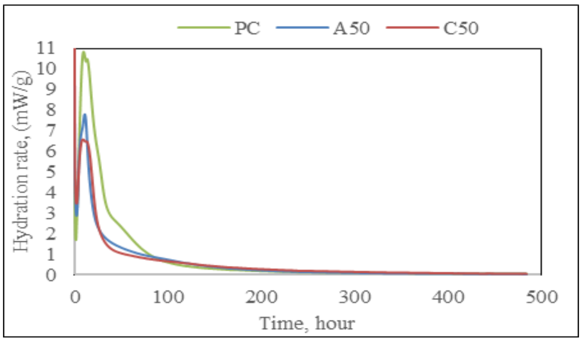


Figure 9. Heat of hydration-time graph (A30, C30)



Figyre 10. Hydration rate-time graph (A50, C50)

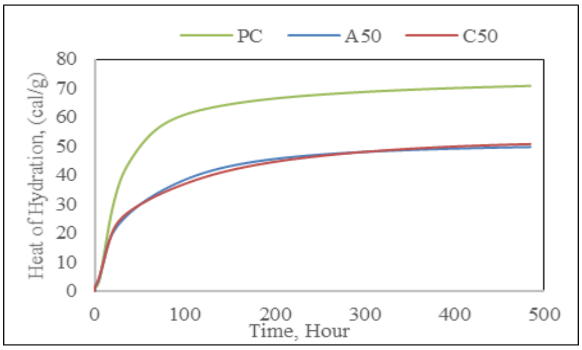


Figure 11. Heat of hydration-time graph (A50, C50)

3.6. The compressive strengths of mortars

The amounts of materials required to prepare of mortar samples are given in Table 7. The average compressive strength development (MPa) and density (g/cm³) of cement mortars are given in Table 8. The average compressive strength and density for mortars are illustrated in Figs. 12. As seen from Table 8 that the compressive strengths of mortars containing analcime blended cements were slightly higher than that of mortars containing clinoptilolite blended cements. Because, the specific surface area of analcime was a little higher than that of clinoptilolite. Due to the low densities of both natural zeolite additive type, the densities of mortars containing blended cements decrease with increasing of replacement ratio. The zeolite additives affected the fresh behaviors of blended cement pastes but they did not have significant effect on compressive strengths of mortars. It is possible to explain the cause of this situation as follows. As known that pozzolans sometimes decelerate the rate of strength development of the sample depending on the structure of the used pozzolan. But, in later ages, the strength increases by recovering with through additional binders due to pozzolanic activity [14, 39, 40]. There are many studies about long-term strength improvements of zeolites in the literature. Some of these are given below. Canpolat et al., [17] investigated the effecs of zeolite as Portland cement replacement materials on the properties of cement. In the study, the compressive strengths of cement mixtures containing zeolite (with 5, 10, 15, 20, 25, 30 and 35%) were determined at 2, 7, 28 and 90 days. It was seen that the strengths of mixtures at 90 days were higher than that of mixtures at 28 days with the range 6-22% various ratios due to amount of replacement. Ahmadi et al., [41] evaluated the effectiveness of zeolite in mechanical and durability properties of concrete and also compared with other pozzolanic admixtures such as silica fume and fly ash. Based on results of the study, the compressive strengths of concretes containing 15% zeolite blended cements improved at 28 days. And, even the compressive strengths of concretes containing 15% zeolite blended cements gradually increased to strengths of concretes prepared with silica fume replacements (10-12.5%) at 90 days. Considering studies in the literature and similar findings of zeolites used in the study it is an expected result that it will be increase of compressive strengths of mortars at longer-term tests in samples of present study. The optimum strength values of mortars containing both analcime and clinoptilolite blended cements were obtained at 10% replacement ratio. The compressive strengths of mortars at 28 days decrease at 30 and 50% replacement ratio. This situation is a result of decreasing in the amount of cement with increasing of replacement ratio.

Table 7. The amount of material for mortar

Components	Replacement ratio (%)			
	0 (none)	10 (low)	30 (medium)	50 (high)
Sand (g/cm³)	1350	1350	1350	1350
Cement (g/cm³)	450	405	315	225
Natural zeolite (g/cm³)	-	45	135	225
Water (g/cm³)	225	225	225	225
Plasticizer (%)	-	1	1.5	2

Table 8. The average compressive strength and density of mortars

Cement Mortars	MPC	MC10	MC30	MC50	MA10	MA30	MA50
Density (g/cm³) for cubes (28 days)	2.42	2.14	2.11	1.91	2.16	2.13	2.10
Standard deviations	1.720	1.711	1.731	1.610	1.522	1.625	1.497
Ave. comp. strengths (MPa) (2 days)	36.83	29.79	21.11	11.80	41.84	28.84	12.63
Standard deviations	1.679	1.742	1.558	1.521	1.733	1.589	1.797
Ave. comp. strengths (MPa) (7 days)	45.35	42.00	27.56	14.35	45.64	35.49	20.04
Standard deviations	1.765	1.595	1.496	1.644	1.565	1.553	1.966
Ave. comp. strengths (MPa) (28 days)	54.96	50.79	41.08	24.97	52.72	41.96	25.52
Standard deviations	1.831	1.757	1.663	1.942	1.790	1.583	1.834

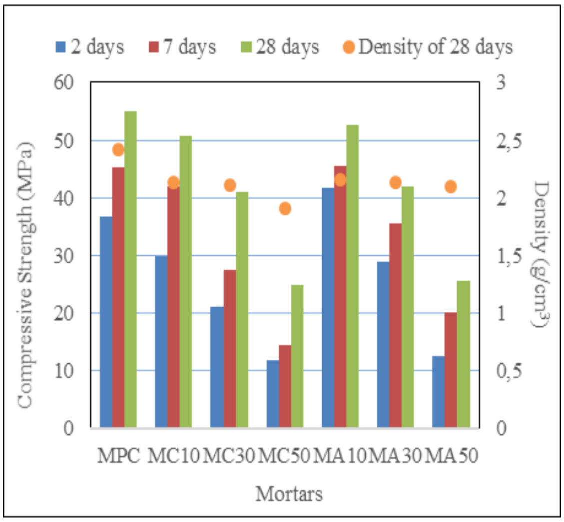


Figure 12. Compressive strength-density of mortars

4. Conclusions

- The water demand of blended cements containing natural zeolite with increasing of replacement ratio linearly increased due to micropores inherently found in their structures. The setting times of blended cements containing natural zeolites were shorter than that of Portland cement. As the ratio of natural zeolite increased, the volume expansion values also increased.

- The heats of hydration of blended cements containing both natural zeolite decreased at all replacement ratio. But, the decline at heat of hydration of analcime blended cement was higher than that of clinoptilolite blended cement for 30% replacement ratio.

- The compressive strengths of mortars containing analcime blended cements were slightly higher than that of mortars containing clinoptilolite blended cements at all replacement ratio. The optimum replacement ratio for compressive strengths of mortars containing both analcime and clinoptilolite blended cements was 10%.

- The results of the present study carried out with preliminary tests should be supported by strength and durability tests for later ages.

- In summary, the analcime have similar positive properties to clinoptilolite such as high silica-alumina content, mineralogical structure, setting times, volume expansion, low density, filler effect, high pozzolanic activity, low heat of hydration and compressive strengths of mortar. Therefore, due to these similar properties, natural zeolite analcime has an usage capacity like clinoptilolite which is more widely used in sustainable cement productions.

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