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The Heat Storage Capacities of Mortars Containing Clinoptilolite Blended Cements

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Abstract

Recently, the studies on the heat storage capabilities of building materials for energy efficient building design are becoming more widespread. In this study, the heat storage capacities of mortars produced with blended cement containing clinoptilolite that is the most valuanle of the natural zeolite minerals were investigated. The clinoptilolite which is used as replacement material and has the highest purity rate (96% purity) in the world was obtained from Manisa-Gördes region. Firstly, the mortar samples containing clinoptilolite blended cements at 0, 10, 30 and 50% replacement ratios were produced. And then, the physical, chemical, mechanical, petrographic properties, thermal conductivity and heat storage capacities of clinoptilolite rock were determined. The compressive strengths and thermal performance tests were performed on the mortar samples containing clinoptilolite blended cements. The test results were compared amongst themselves and with each other. According to the test results, it was concluded that heat storage capabilities of the mortars containing clinoptilolite blended cements could be improved.

Key words: Clinoptilolite, blended cement, heat storage, mortar, zeolite

1. Introduction

The renewable energy sources are economic and environmental technologies. They have been becoming more widespread in the construction sector that uses energy intensively. The rational using of solar energy which is one of the renewable energy sources is transformed into applications in energy efficient building designs. One of these applications is the storage of solar energy on building materials. Solar energy is a source of energy that has continuity in nature, can be effective only during the day and can be variation seasonal effect. Therefore, it has become an essential requirement developing a storage method. At the first applications of solar energy using in history, it is seen that the houses in the hot climatic zones are built with very thick walls that has large thermal masses, The heat collected during the day by walls releases at night and emitting coolness throughout the day. In order to use it at the appropriate time and store of solar energy in buildings, the researches are conducted on the thermal capabilities of building materials. Rocks containing zeolite minerals have positive properties such as high heat storage capacity and pozzolanic activity, low energy grindability, natural and local formation and reserve status. In addition, it is understood from the literature that the strength and durability of mortar/concrete samples containing certain amounts of zeolite improve. Some of these studies are given below. Basyigit [1] used blended cement containing clinoptilolite as replacement material with 0, 5, 10 and 15% ratios in concrete. It was measured thermo-mechanical properties of concrete in the study. And, it was found that

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decreased by zeolite additive of thermal conductivity in concrete. Öcal [2] studied the effect of high temperature on some properties of natural zeolite blended concrete. In this context, 7 different concrete mixtures were prepared in 0, 5, 10, 15, 20, 30 and 40% replacement ratios by using natural zeolite. It has been concluded that the natural zeolite additive reduces the thermal conductivity coefficient of concrete. Özkahraman et al. [3] investigated thermal insulation effect on using as building material of tuffs containing analcime that is zeolite mineral at 15% ratio. They concluded that the zeolite tuff with 40% pore rate would obtained save up to 60% in term of air conditioning compared to the concrete on the outer walls of buildings. Bilgin [4] showed that natural zeolite mineral could be used in solar energy storage systems depending on adsorption and ion exchange properties. It mentioned that clinoptilolite and chabasite could be used as a heat exchanger and for heating small buildings. Dincer and Rosen [5] stated that zeolites are highly efficient materials in various thermal storage and solar-related air-conditioning activities thanks to their ability such as highly heat-absorbing and maintain structural stability while being hydrating/dehydrating. Karakurt et al. [6] used natural zeolite (clinoptilolite) as aggregate and binding factor in aerated concrete. According to the results, the thermal conductivity of the natural zeolite blended samples was lower than the control samples. Thus, it was concluded that the low-density material and a higher building insulation performance would be achieved by using aerated concretes containing natural zeolite in wall blocks. Sallı Bideci et al. [7] examined on the properties of cement mortar by using 0, 5, 10, 15 and 20 ratios of zeolite. In the study, the most suitable values in terms of blended cement properties were obtained from 10% zeolite blended cement mortars. Thus, it has been concluded that natural zeolite blended cement will contribute positively to energy saving and environmental pollution. Ahmadi and Shekarchi [8] compared the usability of zeolite obtained from Iran in concrete as pozzolan with silica fume. According to the results of the study, zeolite did not exhibit pozzolanic property as much as silica fume, but it contributed to mechanical strength more than silica fume.

The aim of this study is to determine how will effect of the heat storage capacities and the physical-mechanical properties of mortars containing natural and local zeolite (clinoptilolite) blended cements.

2. Materials and Method

The natural zeolite mineral, clinoptilolite, was replaced by Portland cement. The clinoptilolite (C) which is natural zeolite type was obtained from Manisa/Gördes regions of Turkey. The cement used in tests was CEM I 42.5 R type of Portland cement (PC) produced in accordance with EN 197-1 [9]. 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 [10] was used. In lime-pozzolan mixtures, slaked lime ($Ca(OH)_2$) was used as specified in TS 25 [11]. It was used melamine-based modified polymer superplasticizer (at 1, 1.5 and 2% ratios) complying with EN 934-2 [12] by adding to mixture water to recover of adverse effect on mortar consistency of natural zeolite. In production of all samples, the water that does not contain organic substances, harmful minerals or salts was used. The natural zeolite (clinoptilolite) sample was obtained by finely grinding in a ball mill so as to provide approximately 70% passing value through 45 μm sieve. The amounts of zeolite used in mixtures were 0 (none), 10 (low), 30 (medium) and 50 (high)% of cement weight. The samples were produced with the labels PC, C10, C30, C50 for blended cement mixtures and MPC, MC10, MC30 MC50 for mortars. Density-specific surface (Blaine) of natural zeolite and cements were determined according to EN 197-1 and EN 196-6 [13], respectively. The tests for determination of pozzolanic activity of natural zeolite were made by mechanical test method which is determined with average compressive strengths of lime-pozzolan mixtures in accordance with TS 25. Chemical composition of zeolite 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 zeolite. 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 zeolite 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 thermal properties of mortars were performed by 20x 60x150 mm molds at 28 days. The compressive strengths of mortars were determined by 50x50x50mm cube molds at 28 days. The strength developments of mortars were carried out in accordance with the EN 196-1. The results obtained from the test series were compared amongst themselves and with each other.

2.1. Determination tests of thermal conductivity and heat storage

The prepared mortar mixtures were poured into steel molds produced in accordance with the probes. They were kept in molds for 24 hours under laboratory conditions. Samples were cured in water for 28 days. The mortar samples were tested with thermal conductivity and heat storage value (heat capacity) meter, which is referred to with ISOMET 2104 code, in the Laboratory of Dicle University Mining Engineering Department. The thermal conductivity values (k) and heat storage capacity values of mortars-rocks were determined as a result of the experiments carried out according to the principles of TS EN ISO 8990 [14] and ISO 6946[15] standards. The measuring device uses the hot wire method according to DIN 51046 [16], TS EN 993-15 [17]. The measurements were made at 22-25 °C and five different points on each sample. The ISOMET 2104 is capable of measuring the heat conduction coefficient at a sensitivity of 5% in the range 0.04-0.06 W/mK and the volumetric specific heat at a sensitivity of 15% in the range 4.0x104-4.0x106 J/m^{3}K. It has three different solid surface probes developed for the determination of thermal properties of hardened materials such as natural stones, rocks, mortar and concrete [18].

3. Results and Discussion

3.1. Some properties of Portland cement, blended cements and natural zeolite

Some properties of Portland cement (PC), blended cements and natural zeolite are given Tables 1-3. The density of clinoptilolite is 32.37% lower than PC. The specific surface area of clinoptilolite is 27.07% higher than PC. This situation depends on mineral structure, porosity and fragilement properties of zeolite. The cumulative passing (%) of 45 µm sieve for Portland cement, clinoptilolite are 67.11%, 68.64%, 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 and chemical compositions of natural zeolite

Chemical composition	Clinoptilolite (wt.%)	Physical properties	
SiO_2	64.70		Clinoptilolite
Al_2O_3	11.21	Density, (g/cm^3)	2.11
Fe_2O_3	1.38	Blaine fineness (cm^2/g)	4079
CaO	2.08		
MgO	0.79	Over sieve (%)	
Na_2O	0.38	45µm	31.36
K_2O	3.78	90 µm	11.51
Loss of ignition	11.80	200 µm	2.57

Table 3. Physical properties of blended cements

Physical properties	PC	C10	C30	C50
Specific surface (cm^2/g) Blaine fineness	3210	3408	3664	3898
Density, (g/cm^3)	3.12	2.75	2.72	2.46

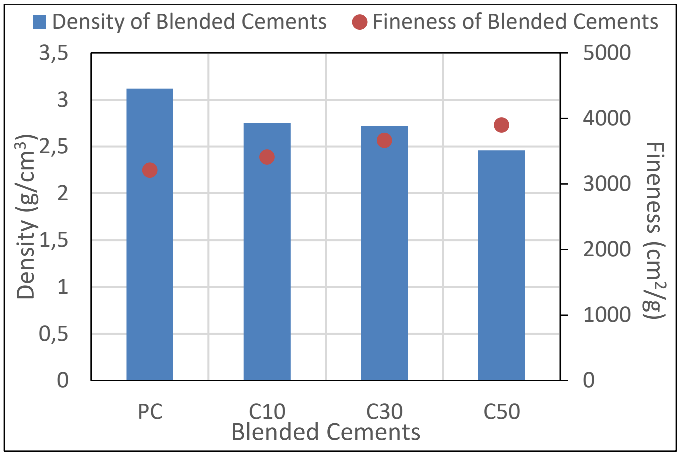

Figure 1. The density-fineness for blended cements

3.2. Pozzolanic activity of natural zeolite

The pozzolanic activity of natural zeolite 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 [19]. 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 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 value of natural zeolite (clinoptilolite) is given Table 5.

Table 4. The amounts of materials for tests on pozzolanic activity

	TS 25	The amounts for tests
		Clinoptilolite
Slaked lime ($CaOH_2$)	150g	150g
Pozzolan	2x150x(density of poz. /density of $CaOH_2$) (g)	2x150x(2.11/2.15)= 294.42g
Standard sand	1350g	1350g
Water	0.5x (150+pozzolan) (g)	0.5x(150+294.42) =222.21g

Table 5. Pozzolanic activity values of natural zeolite

TS 25 limit values	Clinoptilolite
Lime-pozzolan mix. 7 days compressive strength >4MPa	9.02MPa
$SiO_2+Al_2O_3+Fe_2O_3$ wt. content >70%	77.30%
Specific surface area > 3000cm^2/g	4079 cm^2/g

According to Table 5, in TS 25, one of the conformities 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 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 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 pozzolan which is used in this study were found to be 4079 cm^2/g for clinoptilolite. It is seen that; the fineness of natural zeolite is higher than that of Portland cement. And, the content of silica and alumina are above of 70%. 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 results show that the zeolite used in the study have usable potential as a pozzolan.

3.3. Mineralogical analysis of natural zeolite

The results of mineralogical analysis of natural zeolite are given below. XRD diffraction patterns and SEM images of zeolite are presented Figs. 2-3. The clinoptilolite sample was obtained from Gördes Zeolite Company. 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. When the diffractogram and SEM image of zeolite are examined, as seen that zeolite contains clinoptilolite as dominant minerals. And, it has crystal structure.

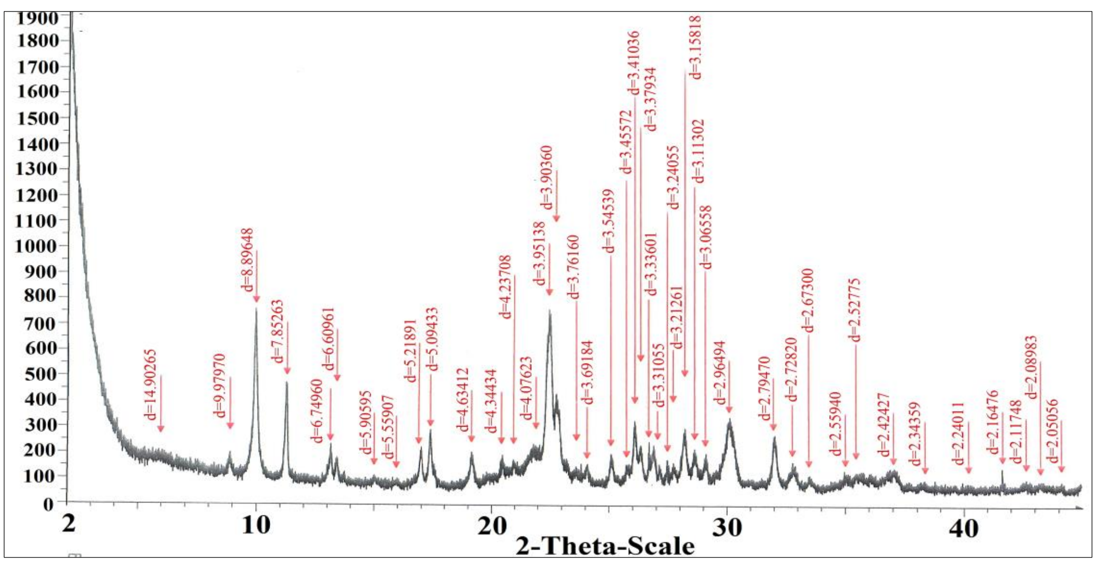

Figure 2. XRD patterns of clinoptilolite (Gördes Zeolite Company)

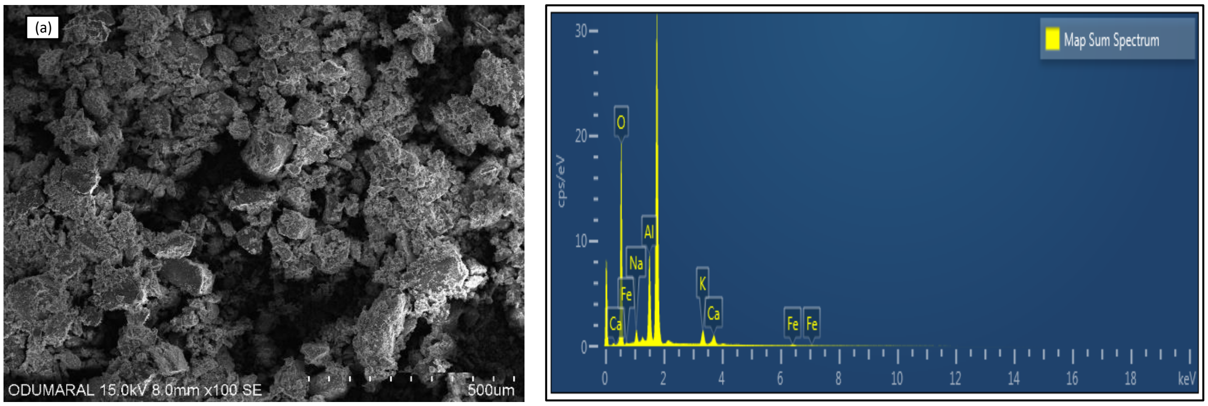

Figure 3. SEM image (a) and EDS (b) of clinoptilolite sample

3.4. The compressive strengths of mortars

The compressive strengths and densities of mortars are given in Table 6. The variation graphs of their are given in Fig. 4. According to the Table 6, the densities of the mortars containing clinoptilolite blended cements decrease with the increasing of clinoptilolite ratios due to the low density of clinoptilolite. The compressive strengths of mortars meet the minimum strength value specified in TS EN 197-1 up to 10% replacement ratio.

Table 6. The compressive strengths and densities of mortars

Mortars	Density (g/cm^3)	Compressive strength (MPa)
MPC	2.32	54.96
MC10	2.16	50.79
MC30	2.15	41.08
MC50	2.01	24.97

(b)

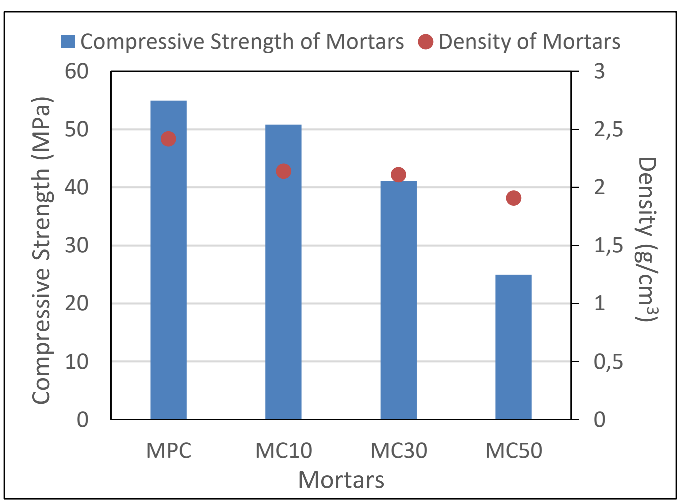

Figure 4. The compressive strengths and densities of mortars

3.5. Thermal conductivity and heat storage of clinoptilolite rock

For solid materials used in heat storage, density (ρ), (kg/m^3), specific heat (c_p), (J/kgK), thermal conductivity (k), (W/mK) and thermal diffusivity (α), (m^2/s) are important factors that determine heat storage capability. In the calculation of thermal conductivity coefficient (k), q; heat flow through section A, ΔT; temperature difference in thickness ΔL. It is determined by $k = q.(\Delta L / \Delta T)$ equation. The smaller the thermal conductivity coefficient (k) of a material, the better the insulation. The thermal diffusivity coefficient which is a thermophysical property shows how fast the heat is dissipated in the material. In the calculation of the thermal diffusivity coefficient (α), k; thermal conductivity coefficient, ρ; density, c_p; specific heat. It is determined by $\alpha = k / (\rho.cp)$ equation. Low thermal diffusivity means that most of the heat is absorbed by the material and very little amount is transmitted [20]. The $C=\rho.cp$ equation used in heat transfer is called the heat capacity of a material. Heat capacity indicates the heat storage ability of a material. The density, thermal conductivity (k), specific heat (c_p), heat capacity (C) and thermal diffusivity coefficient (α) obtained from the thermal performance tests performed on the clinoptilolite rock are given in Table 7.

Table 7. Thermal properties of clinoptilolite rock

Natural zeolite	Density (ρ) (kg/m^3)	Thermal conductivity (k) (W/mK)	The specific heat (c_p) (J/kg.K)	The heat capacity $C=(\rho.c_p)x10^{-6}$ ($J/m^3.K$)	Thermal diffusivity coefficient ($\alpha=k/(\rho.c_p)x(10^{-6})$) ($m^2/s$)
Clinoptilolite	2110	0.61	777.25	1.64	0.37

3.6. Thermal conductivity and heat storage values of mortars

Thermal conductivity and heat storage values of mortars are given in Table 8. The heat capacities-specific heats and thermal conductivity-density of mortars are given in Fig. 5-6.

Table 8. Thermal properties of mortars

Mortars	Density (ρ) (kg/m^3)	Thermal conductivity (k) (W/mK)	The specific heat (c_p) (J/kg.K)	The heat capacity $C=(\rho.c_p)x10^{-6}$ ($J/m^3.K$)	Thermal diffusivity coefficient ($\alpha=k/(\rho.c_p)x(10^{-6})$) ($m^2/s$)
MPC	2300	2.75	730.43	1.68	1.64000
MC10	2230	2.72	865.47	1.93	1.40933
MC30	2170	2.48	811.06	1.76	1,40909
MC50	2110	2.31	810.17	1.71	1.35087

According to the results, the thermal conductivity (k) values of mortars containing zeolite blended cement decrease as the zeolite replacement ratio increases. On the other hand, in all replacement ratios, the heat capacity of zeolite blended mortars are higher than that of Portland cement blended mortars. Accordingly, it is possible to say that the thermal insulation and heat storage ability of mortars containing zeolite blended cement is improved. The thermal diffusivity coefficients of mortars containing zeolite blended cement are lower than that of mortars containing Portland cement. This means that most of the heat is absorbed by the material and very little is transmitted.

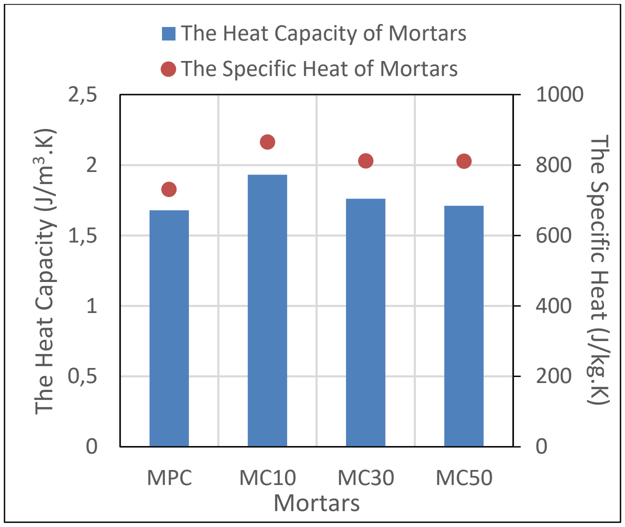

Figure 5. The heat capacities-specific heats of mortars

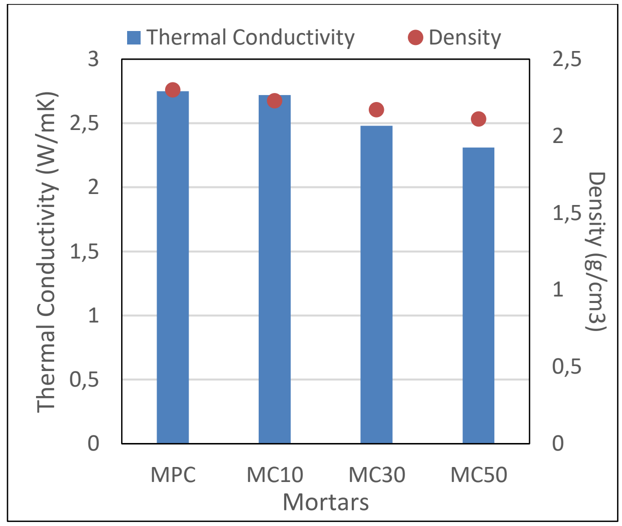

Figure 6. Thermal conductivities-densities of mortars

Conclusions

The pozzolanic activity of natural zeolite clinoptilolite determined according to TS 25 is 9.02 MPa. In mortar samples, compressive strengths of mortars decrease when natural zeolite replacement ratios increase. The compressive strength of mortar containing clinoptilolite blended cement at 10% replacement ratio is achieved an acceptable value. The heat capacities of mortars containing clinoptilolite blended cement are higher than that of mortars containing Portland cement. The thermal conductivity (k) values of mortars containing zeolite blended cement decrease as the zeolite replacement ratios increase. Accordingly, it is possible to say that the thermal insulation of mortars containing zeolite blended cement is improved. The thermal diffusivity coefficients of mortars containing zeolite blended cement are lower than that of mortars containing Portland cement. The low thermal diffusivity means most of the heat is absorbed by the material and very little is transmitted. The heat storage ability (highest specific heat value) of mortars containing natural zeolite clinoptilolite was observed in MC10 test series. In summary, the blended cement production containing natural zeolite clinoptilolite that has pozzolanic properties provides some advantages in terms of heat storage. And, when heat capacities and compressive strengths of mortars containing zeolite both evaluated together, it is thought that to be 10% of optimum replacement ratio.

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