Sakarya University Journal of Science

ISSN : 2147-835X
Publisher : Sakarya University

Vol. 28, No. 3, 480-495, 2024
DOI: https://doi.org/10.16984/saufenbilder.1245404

Research Article

Investigation of Usability of Sepiolite as a Pozzolan in Production of High Performance Cementitious Composites

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ARTICLE INFO

ABSTRACT

Keywords:
Sepiolite
Pozzolanic activity
Calcination
Strength

Article History:
Received: 08.02.2023
Accepted: 09.02.2024
Online Available: 06.06.2024

The continuous growth of population and urbanization in the world significantly increases the demand for cement. In terms of sustainability, the cement industry needs to develop new and effective pozzolans with the appropriate recycling of alternative raw materials. It is also important to evaluate sepiolite, which has very limited resources in the world compared to other industrial minerals and whose economic deposits are limited to Spain and Türkiye. In this study, the usability of sepiolite as a pozzolan in cement and its effects on physical, mechanical and durability properties were investigated. First of all, the chemical and physical properties of sepiolite in Eskisehir region were investigated. Crude and ground sepiolite calcined at 500 ºC, 700 ºC and 900ºC were substituted for CEM I 42.5 R class standard Portland cement at 5-10-15% and 20% ratios. The pozzolanic activities of produced sepiolite substituted cement were determined according to ASTM C-311. As a result, crude sepiolite retains more water than calcined sepiolite, thus negatively affecting the strength properties of the concrete. Additionally, sepiolite is considered suspicious (harmful-harmless) in terms of alkali silica reactivity except 10%-15%-20% crude sepiolite substitutions. Overall, It has been observed that sepiolite does not have sufficient pozzolanic properties in cementitious composites.

1. Introduction

The most important component of concrete production is undoubtedly cement. As a result of the high demand for concrete in the construction sector, the cement industry performs the most intensive production worldwide. Due to such intensive production, cement is among industrial productions that harm the environment. In recent years, the need for energy efficiency has prompted researchers to produce sustainable solutions within the cement industry [1]. The cement industry is faced with making more durable and sustainable production using less energy without sacrificing the mechanical properties of the material to be produced. For this reason, blended cement production has been one of the most common developments compared to normal cement production [2]. Additives such as blast furnace slag, fly ash, silica fume and natural pozzolans are used in the production of blended cement because of having economic and technical advantages [3, 4]. Pozzolans reduce the participation rate of clinker to the cement, thus improving the economy of cement and some of its properties according to needs. In addition, pozzolan-added cements also make cement more environmentally friendly material [5-7].

Cite as: R.C. Saka, S. Subaşı (2024). Investigation of Usability of Sepiolite as a Pozzolan in Production of High Performance Cementitious Composites, *Sakarya University Journal of Science*, 28(3), 480-495. https://doi.org/10.16984/saufenbilder.1245404

Sepiolite is a clay mineral in the sepiolite-palygorskite group consisting of magnesium hydrosilicate. Sepiolite with fibrous structure is formed by the alignment of octahedral and tetrahedral oxide layers. In addition, there are channel spaces along the fiber [8]. According to Nagy-Bradley, the chemical formula of sepiolite clay is $Si_{12}Mg_9O_{30}OH_6(OH_2)_4.6H_2O$ [9]. Sepiolite has a temperature sensitive structure. Zeolitic and adsorbed water molecules are lost as the temperature increases. In addition, when interacting with acids, its crystal structure may be partially destroyed. Temperature and acid effects make sepiolite changes its porosity and surface properties. Thus, it is possible to change the colloidal, catalytic and absorptive properties of their most important features. Spain produces almost all of the world's sedimentary sepiolite production. The highest quality meerschaum in the world is provided from the provinces of Eskisehir and Konya.

Kavas et al. added 3-5-10-15-20% and 30% sepiolite in addition to 5% gypsum to Portland cement clinker and tried to improve the properties of the mixture. Expansion tests, initial and final sets, bending and compressive strength tests were performed on the produced mixtures, and it was investigated at what rate the sepiolite substituted for cement improved these properties. As a result of the study, it was observed that 10% sepiolite substitution in concrete improved the mechanical properties of the mixtures and did not cause any negative effects on other properties [10].

In another study they carried out, the structural properties of cementitious mixtures containing sepiolite and the optimum mixing ratios were examined. Addition of 10% sepiolite improved the physical and mechanical properties of the mortar. Compared to the Portland cement mixture, the compressive strength values on the 2nd, 7th and 28th days, respectively, were found as 3.5-6.2% and 7.7% higher, and the flexural strength values were 12.7%-5.7% and 6.3% higher, respectively. According to SEM images, it was seen that the reason for this improvement was the formation of a network structure between the sepiolite fibrous structure and the cement matrix [11].

Fuente et al. demonstrated that it is possible to produce corrugated roofing from fiber concrete containing sepiolite [12, 13]. Andrejkovičová et al. prepared lime-based mortars with 10, 20% and 30% metakaolin and 5% fine sepiolite additives in order to facilitate the preparation of repair mortar in low humidity conditions. Mechanical properties and dynamic elastic modulus were examined after 28, 90 and 180 days of curing. It has been observed that as the amount of metakaolin increases in lime mortars, the mechanical strength after 90 days increases. The addition of sepiolite to blended air lime/air lime-metacaolin mixtures led to an improvement in compressive and bending strengths, especially in later wet curing, due to its microfibrous morphology and adsorption properties. 5 wt% fine sepiolite and 20 wt% metakaolin appear to be an optimal mixture for air lime mortars. [14].

Martinez-Ramirez et al. studied the carbonation properties of lime mixture containing sepiolite and found that It was observed the mechanical properties of less than 5% sepiolite substituted mixtures did not change and the carbonation process in lime mortars slowed down due to the water absorption feature of sepiolite [15]. In the study carried out on physical and mechanical properties of sepiolite-substituted cementitious mortars, mortars were formed by substituting 0-10-20% and 30% Eskisehir region sepiolite by weight instead of CEM I 42.5R cement. The mechanical and physical properties of the produced sepiolite added mortars on the 7th, 28th and 56th days were examined. As a result, it was recommended that the sepiolite additive ratio should not exceed 10% of the cement. It has been stated that the use of sepiolite at higher rates is suitable only in the applications of non-bearing walls and leveling concretes [16].

With the widespread use of aerated concrete, which is one of the wall materials, researches have gained importance. For this purpose, Savaş et al. studied the effect of sepiolite clay replacement on the compressive strength and thermal properties of quartzite, which is used as the main raw material in the production of aerated concrete material [17]. In the study, it is planned to produce G2-04 class gas concrete, which is used as wall building material. Aerated concrete was produced by substituting 5-10-15-

20-25% of sepiolite obtained from Eskisehir Sivrihisar region instead of quartzite. After curing the samples at 60 ºC for 4 hours, they were autoclaved at 180 ºC under 11 bar pressure for 6,5 hours. Compressive strength and thermal conductivity values of the produced samples were determined. As a result, by increasing the sepiolite substitution ratio, the compressive strength values of the samples decreased, while an improvement in heat conduction was observed [17].

Pozzolans are silica and alumina materials that have little or no binding property on their own, but when finely grinded, they combine with CH in aqueous environments and gain binding property. Studies on sepiolite were also carried out to determine the pozzolanic activity properties. In a study, sepiolite was calcined at 370-570 and 830 °C, and the properties of cementitious mortars containing calcined and crude sepiolite were investigated by compressive strength and rheology tests after reaction at 40 °C for 2-7-28 and 91 days. As a result, it was seen that sepiolite is a very inactive pozzolanic material and its water requirement is high. From 370 °C to 570 °C, calcination does not increase significantly. It was observed that the most effective calcination temperature was 830 °C, which increased the compressive strength of the mortar by 84% compared to the compressive strength of the reference Portland cement (PC) mortar [18].

Pu et al. investigated the compressive-flexural strength and microstructure of metakaolin - fly ash geopolymer activated with sodium hydroxide and sodium silicate solutions containing 0-5-10-15-20% sepiolite by mass. While an increase was observed in the compressive strength values of the mixtures made by adding 10% sepiolite at the end of 7 days, a decrease was observed in the strength values due to the increase in sepiolite addition. Similarly, with the addition of sepiolite up to 10%, the curing-independent flexural strength was improved. Crack formations were observed in the sample with 20% sepiolite compared to samples containing 10% sepiolite [19].

In order to determine the effects of air entrainment on the pores of hardened mortars, the rheological properties of the cement mixture foamed with air entrained aluminum powder were examined. As a result, it was observed that fly ash in Portland cement combined with metakaolin and sepiolite caused the highest expansion rate [20].

In addition to the studies on the effect of sepiolite in cementitious mixtures, it was wondered how it behaves with binders in polymer structure, and the effect of polyurethane and polyvinylalcohol addition on the rheological properties of sepiolite mixtures was investigated in a study. The results showed that the polymer molecules bind to the surface of the sepiolite and stabilize the viscosity properties at certain densities. In addition, it was observed that polyurethane polymer covers the sepiolite surface faster than polyvinylalcohol, but polyvinylalcohol coating has a smoother structure [21]. When the literature is examined, it is thought that sepiolites are suitable for use in the production of cementitious materials both as a filling material and because of their pozzolanic character.

In this study, the usability of ground sepiolite from Eskisehir region in cementitious mixtures was investigated. In this context, the pozzolanic activity characteristic of the sepiolite material was determined and the hydration properties of the mixtures produced by sepiolite substitution were revealed. The effect of sepiolite substitution on cement paste and mortar mixtures was investigated.

2. General Methods

2.1. Materials

2.1.1. Cement

In the study, CEM I 42.5 R standard Portland cement produced in accordance with TS EN 197-1 standard and supplied from Bolu Cement Factory was used. The physical and chemical analysis values of cement are given in Table 1.

Table 1. Physical and chemical analysis values of cement.

Components (%)		CEMI 42.5R	TS EN 197-1
CaO		63.03	
Al_2O_3		4.77	C+S≥50%
SiO_2		29.12	-
Fe_2O_3		4.37	-
SO_3		2.99	Lim .≤5%
MgO		2.35	Lim .≤4%
Na2O		0.29	-
Cl-		0.0141	-
K2O		0.49	Lim .≤0.10%
LOI		1.30	Lim .≤5%
Insoluble Residue		0.46	Lim .≤5%
Physical Properties			**TS EN 197-1**
Set (Min.)	**Initial**	125	min. 60
	Final	202	-
Density (g/cm^3)		3.17	-
Blaine Fineness (cm^2/g)		4359	-
Total Volume expansion (mm)		1.5	max . 10
% 45 µm sieve		2,5	-
Compressive Strength (N/mm^2)	**2 days**	27.5	min. 20
	7 days	45.7	-
	28 Days	56.8	max . 62.5 min. 42.5

2.1.2. Sepiolite

Sepiolite clay used in the study was obtained from Eskisehir region and was used in mixtures by calcining at 500ºC, 700ºC and 900ºC temperatures as well as being used as crude. Sepiolite which was crude and calcined at 900ºC, was substituted for the cement at the rates of 0%, 5%, 10%, 15% and 20%. The values of the chemical analysis results of the sepiolite are presented in Table 2.

Table 2. Chemical analysis values of crude sepiolite

Chemical Content Values of Crude Sepiolite (%)			
MgO	23.1	**Fe_2O_3**	0.23
Al_2O_3	0.45	**Cr_2O_3**	0.001
SiO_2	26.34	**Na_2O**	0.07
SO_3	0.05	**Mn_2O_3**	0.0023
K_2O	0.20	**TiO_2**	0.05
CaO	14.59	**other**	35.75

2.1.3. CEN standard sand

CEN standard sand produced in different countries according to TS EN 196-1 is used to determine the strength value of cement [22]. The grain size distribution of natural silica sand with a silicon dioxide content of at least 98% and preferably spherical grains should comply with Table 3.

Table 3. Grain size distribution of CEN sand

Sieve opening (mm)	**% Remaining in cumulative sieve**
2.00	0
1.60	7
1.00	33
0.50	67
0.16	87
0.08	99

In the study, CEN standard sand in form of 1350±5 g bags in accordance with TS EN 196-1 was used in the mortar mixture.

2.1.4. Water

In the study, Düzce Municipality drinking water was used as mixing water in production of the samples.

2.2. Method

2.2.1. Experiments on powder samples

2.2.1.1.Density

Experiment was carried out with Micromeritics Accupyc II 1340 branded gas pycnometer. The device is a fully automatic gas pycnometer system that measures according to the gas displacement principle. It is also called helium pycnometer in the literature. Density measurements of crude sepiolite and samples that were calcined for 3 hours at three different temperatures (500°C, 700°C, 900°C) were measured at least 5 times.

2.2.1.2. Laser particle size analysis

Grain size measurement is one of measurements needed in many industries and engineering fields such as sand, clay, ceramics, cement, food, cosmetics, paint and soil mechanics. Although there are different methods to determine the grain size, the basic principle of the laser diffraction method is based on the inverse relationship between the grain sizes and the refraction angles of the rays. In this method, laser beams are sent on the particles, and the rays that are refracted by hitting the particles and reflected in the forward direction pass through a lens and fall on the detector. The rays coming on the detector are converted into grain size and dispersion percentage values with the help of computer.

In the study, calcination process was applied at 500 ºC, 700 ºC, 900 ºC and laser grain size analysis of crude powder sepiolite samples was performed with Malvern Mastersizer 3000 branded device.

2.2.1.3. Thermal analysis

Thermogravimetry is used to determine the mass loss or increase in material as a function of time or temperature. The test sample is heated at a constant rate and the mass change is measured depending on the temperature. In general, the reactions that cause the mass of test samples to change; Oxidation reactions occur as decomposition or evaporation of a component.

A graph of mass versus time or temperature is called the TG curve. The change in the mass of the material due to temperature and the range of this change are an indicator of the thermal stability of the material. In this study, the thermal analysis experiment of crude sepiolite was carried out at Düzce University - Scientific and Technological Research Application and Research Center.

2.2.1.4. Chemical analysis

X-Ray Fluorescence Analysis (XRF) is performed to determine the chemical properties of a material. In this analysis, it is possible to determine the elements in the material and the oxide percentages of these elements.

In this study, chemical analyzes on crude, powdered sepiolite samples calcined at 500 ºC, 700 ºC and 900 ºC were analyzed by Çimsa A.Ş.

2.2.1.5. FT-IR analysis

This analysis is used to determine the functional groups in the structure of the molecule. When infrared light interacts with the material, the chemical bonds are stretched, bent, and compressed. As a result, the functional groups in the structure absorb IR light of a certain wavelength independently from the rest. Fourier transform infrared device named spectroscopy can be abbreviated as FT-IR. Analyzes of sepiolite were carried out with the Shimadzu IRPrestige 21 branded device in Düzce University - Scientific and Technological Research Application and Research Center.

2.2.1.6. Calcination

The process of heating a material below its melting point in order to remove volatile substances such as moisture and carbon dioxide is called calcination. It is one of the most common operations to make the ore useful after the grinding process. Lime and cement are also obtained by calcining some materials.

In this study, crude sepiolite was calcined in a Ref -San branded muffle furnace at 500°C, 700°C and 900°C temperatures for 3 hours.

2.2.1.7. SEM and EDS analysis

SEM images of the microstructures of the crude and calcined sepiolite samples at 900 °C were obtained with the FEI QuantaFeg 250 branded varying pressure device at Düzce University, Scientific and Technological Research Application and Research Center. EDS analyzes were performed using EDAX Apollo X branded device.

2.2.2. Experiments on paste samples

2.2.2.1. Consistency test

In this experiment, 5%, 10%, 15% and 20% calcined and crude sepiolite were substituted for the cement at 900ºC, and the consistency test was carried out in accordance with TS EN 196-3 [23].

2.2.2.2. SEM and EDS analysis

In the experiment, a total of 9 paste samples were taken from 0%, 5%, 10%, 15%, 20% crude and calcined sepiolite substituted paste samples at 900ºC, which were removed from the water cure after 28 days. SEM images of the samples were obtained with FEI QuantaFeg 250 brand variable pressure device at Düzce University - Scientific and Technological Research Application and Research Center. EDS analyzes were performed using EDAX Apollo X branded device.

2.2.3. Experiments on mortar samples

2.2.3.1.Flow test

In the test performed according to the TS EN 459-2 standard, the flow diameter values of calcined and crude sepiolite substituted mortar samples at 0%, 5%, 10%, 15% and 20% were measured. The average of the measurements made with an accuracy of 1 mm was taken [24].

2.2.3.2. Alkali-silica reactivity by accelerated test method

According to ASTM C-1260-01 standard, the experiment was carried out by pouring mortar mixtures containing 0%, 5%, 10%, 15% and 20% substituted crude and calcined sepiolite into 2.5x2.5x28.5 cm molds [25]. After 24 hours, the samples removed from the molds were kept in distilled water at 80 ºC for one day and reference measurements were taken. The size changes at the end of the 3rd, 7th and 14th days were measured in the solution prepared by using NaOH 40g in pellet form with 99% purity for 1 liter of distilled water.

2.2.3.3. Compressive strength test

Compressive strength test was carried out in accordance with TS EN 196-1 standard. The water ratios were determined so that the mixtures replaced with 5%, 10%, 15% and 20% crude and calcined sepiolite had the same flow diameter as the 0% reference mixture. Total of 12 samples with 50x50x50 mm dimensions were prepared to be tested on the 7th, 28th, 56th and 90th days. In the experiment, a cement pressure test device with a loading capacity of 30 tons and variable loading speed was used, and the compressive strengths of the mortar samples were calculated according to Equation 1.

$$f_c = \frac{P_{max}}{A_c} \quad (MPa) \qquad (1)$$

Here;

A_c : Cross-sectional area of the sample (mm^2)

f_c : Compressive strength (MPa)

P_{max} : The highest load reached at the time of fracture (N)

2.2.3.4. Pozzolanic activity test

Pozzolanic activity is defined as the extent to which materials with pozzolanic properties can react with hydrated lime and water, and gain binding.

In order for pozzolanic materials to show sufficient activity, they must be amorphous and fine-grained, contain sufficient silica, alumina and iron oxide. The pozzolanic activity is found by calculating the value called “strength activity index” according to the ASTM C-311 standard. The calculation of the index is given in Equation 2 [26].

$$Strength\ activity\ index = \left(\frac{A}{B}\right) * 100 \qquad (2)$$

Here;
A= compressive strength of mortar samples containing pozzolan,

B= compressive strength of the control mortar samples without pozzolan.

3. Results and Discussion

3.1. Experiments on powder samples

3.1.1. Density

AccuPyc II 1340 fully automatic gas pycnometer measuring according to the gas displacement principle are given in Table 4.

Table 4. Densities of sepiolite samples calcined at different temperatures

Sample Name	Density (g/cm ^{3})
Crude Sepiolite	2.5319
Calcined at 500°C sepiolite	2.7044
Calcined at 700°C sepiolite	2,9603
Calcined at 900°C sepiolite	3.2546

When the table is examined, an increase in the density value was observed depending on the increase in calcination temperature. It was observed that the density of the crude sepiolite was the lowest, while the sepiolite calcined at 900°C had the highest density value. After the calcining process, the density value of the sample increased by 29% at 900°C.

3.1.2. Laser particle size analysis results

Laser particle size analysis was performed on calcined and crude sepiolite samples. The results are given in Figure 1 comparatively.

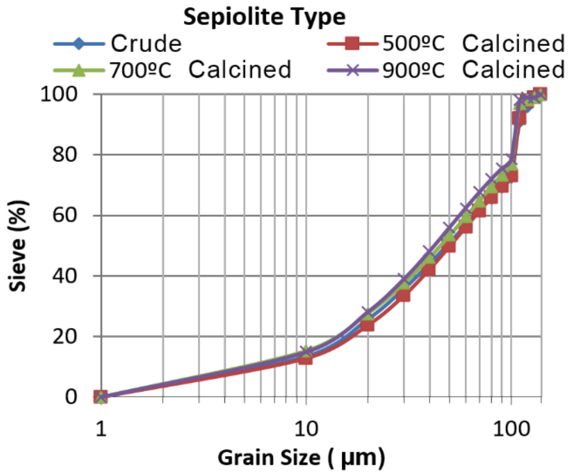

Figure 1. Laser particle size analysis results

The graph shows that the grain size distribution of the crude sepiolite is close to the sepiolite materials calcined at different temperatures. It was observed that the highest grain size of calcined and crude sepiolite was 130 micron meters. As a result, although the largest grain diameter of the sepiolite material decreased due to the increase in the calcined temperature during calcination, no significant difference was observed compared to the crude sepiolite sample.

3.1.3. Thermal analysis results

The thermal analysis values performed on the crude sepiolite sample are given in Figure 2.

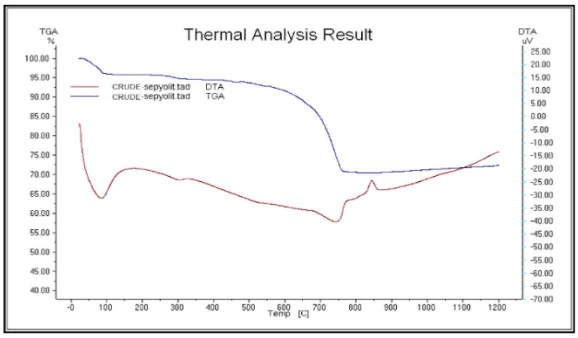

Figure 2. Thermal analysis results of crude sepiolite

While clear endothermic peaks were observed at 100 and 750°C temperatures from DTA curves, exothermic peaks were observed at 860°C. When the mass losses at different temperatures from the TG curve are examined, the dehydration of the chemical and physical water content between 0-200°C temperatures was in the order of 5%. Significant peaks showing the decarbonation of the carbonate phase were observed between 700-770°C. The mass loss in this section was determined to be around 15%. The total weight loss of sepiolite was 30% in the temperature range of 0-1200°C.

3.1.4. Chemical analysis results

The results of the chemical analysis are given in Table 5.

Table 5. Chemical analysis results of calcined sepiolites applied at different temperatures

	Sepiolite Type			
Chemical Comp.	**Crude S.**	**Calcined S. at 500°C.**	**Calcined S. at 700°C.**	**Calcined S. at 900°C.**
SiO_2	26.34	29.01	42.07	40
Al_2O_3	0.45	0.45	0.74	0.67
Fe_2O_3	0.23	0.27	0.35	0.36
CaO	14.59	16.68	18.96	22.68
MgO	23.06	26.26	31.34	35.35
SO_3	0.05	0.06	0.07	0.08
TiO_2	0.05	0.05	0.07	0.07
Cr2O3	0.001	0.001	0.0018	0.0017
Mn_2O_3	0.0023	0.0026	0.0044	0.0045
other.	35.75	27.3	6.6	0.5
Loss of Glow	36.9	31.1	4.31	1.40

When the chemical analysis values of the samples at different temperature values are examined, it is seen that all values increase with the increase in temperature, and the glow loss value of the crude sepiolite sample is 36.9%.

3.1.5. FTIR analysis results

FTIR analysis test with crude sepiolite is shown in Figure 3.

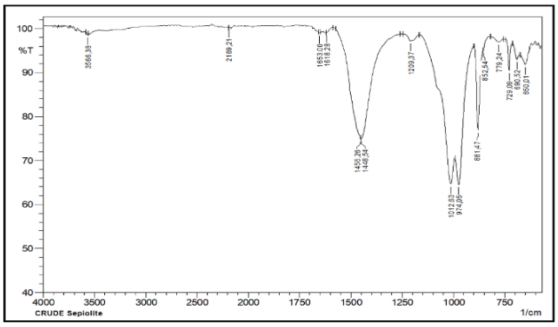

Figure 3. FTIR analysis graph of crude sepiolite

As a result of the FTIR analysis of the crude sepiolite material, open vibrations are observed at wave numbers of 650, 690, 729, 779, 881, 974, 1012, 1209, 1448, 1456, 1618, 1653 and 3566 cm^{-1}.· Wave numbers of 729, 881, 1448 and 1456 cm^{-1} indicate the presence of dolomite in the structure. Si-O bonds in the lattice structure are seen as asymmetric and symmetrical vibrations at wave numbers of 650, 690, 974, 1012 and 1209 cm^{-1}. The water ions and molecules in its structure are in the form of OH stretching vibrations at wave numbers of 3566 cm^{-1} and H-O-H bending vibrations at wavenumbers of 1618 and 1653 cm^{-1}.

3.1.6. SEM and EDS analysis results

In the study, SEM images obtained from the samples are given in Figure 4 and EDS analysis values are given in Figure 5.

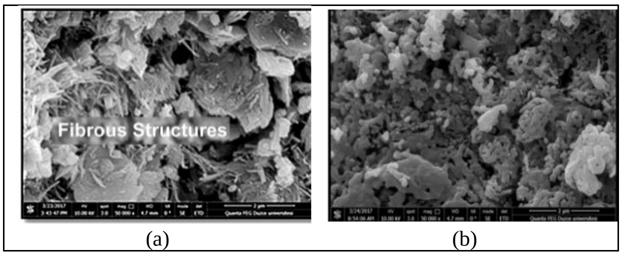

Figure 4. SEM analysis images a) Crude sepiolite b) Sepiolite calcined at 900 °C

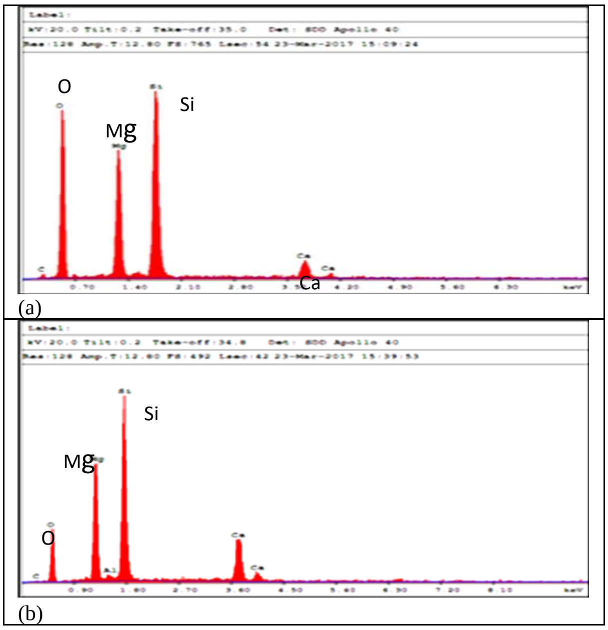

Figure 5. EDS analysis values a) Crude sepiolite b) Sepiolite calcined at 900°C

Fibrous structures of the crude sepiolite sample are seen. It is understood that the structure of the fiber structures changed after the calcination process and took an oval shape.

When the EDS results are examined, it is seen that the oxygen contained in the crude sepiolite is largely removed from the system after calcination process.

3.2. Experiments on paste samples

3.2.1. Consistency test results

The water requirement of paste mixtures containing different amounts of calcined and crude sepiolite was determined with the vicat instrument. The graph of the change in the W/B ratio depending on the amount of sepiolite is given in Figure 6, and the relationship between these values is given in Figure 7.

According to the results, it is seen that the water absorption value of the crude sepiolite is higher than the calcined sepiolite material, and the water demand increases with the increase of sepiolite content in the paste mixture. Compared to the control sample, the water requirement increased by 59% with the 20% crude sepiolite substitution, while the 20% calcined sepiolite substitution increased the water requirement of the mixture by 28%. From this, it is concluded that the crude sepiolite material absorbs more water than the calcined sepiolite.

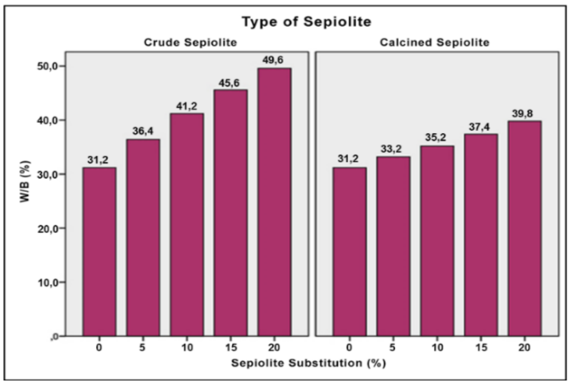

Figure 6. Graph of W/B ratios depending on the amount of sepiolite

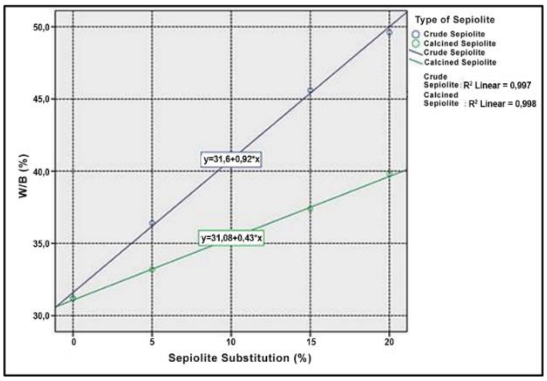

Figure 7. Graph of the relationship between sepiolite substitution rates and W/B value

3.2.2. SEM and EDS analysis results

CSH is a hydration product that gives strength to cement. As a result of the examinations carried out with the electron microscope, information about the structure of C-S-H can be obtained. These structures can generally be in two different states as fibrous and thin plates. With the increase of CSH products over time, boards and fibers develop and get into each other and increase the strength values of cement [27, 28]. In the study,

SEM and EDS analyzes of 0% control, 20% crude and 20% calcined substituted samples are given in Figure 8, Figure 9 and Figure 10.

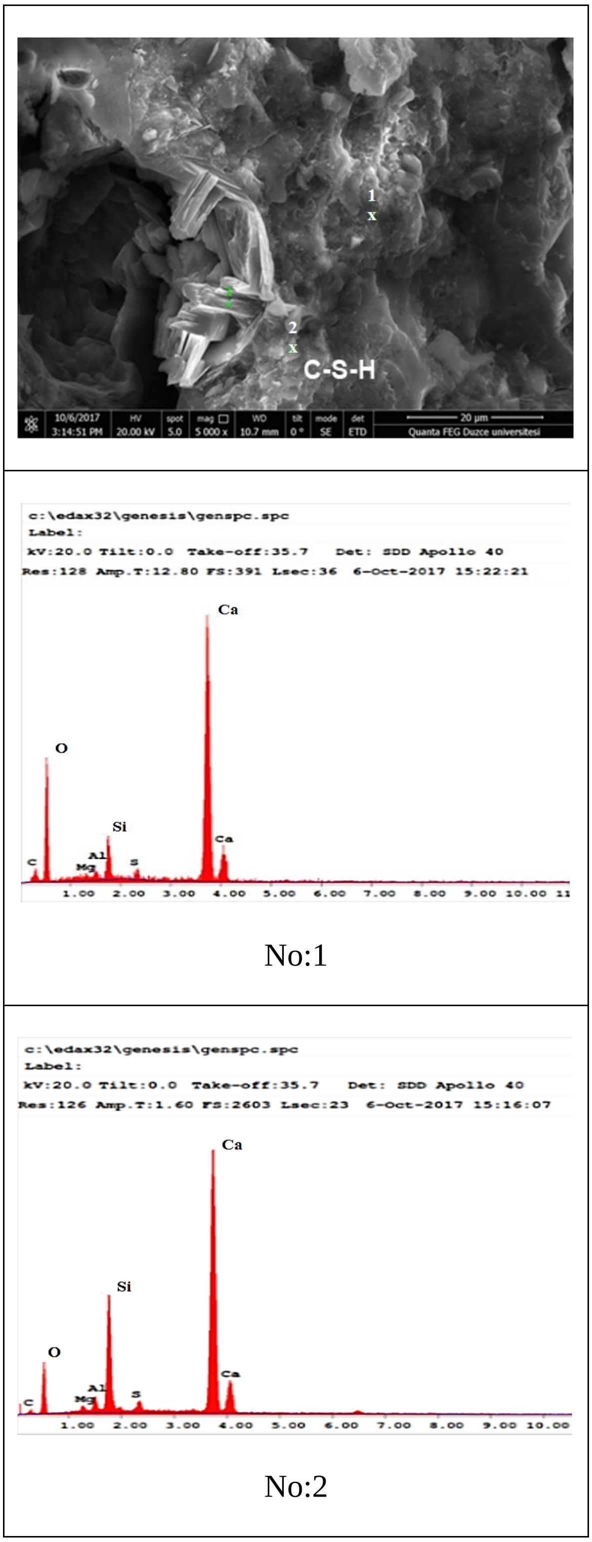

Figure 8. EDS analysis and SEM image of the control sample with 0% substitution

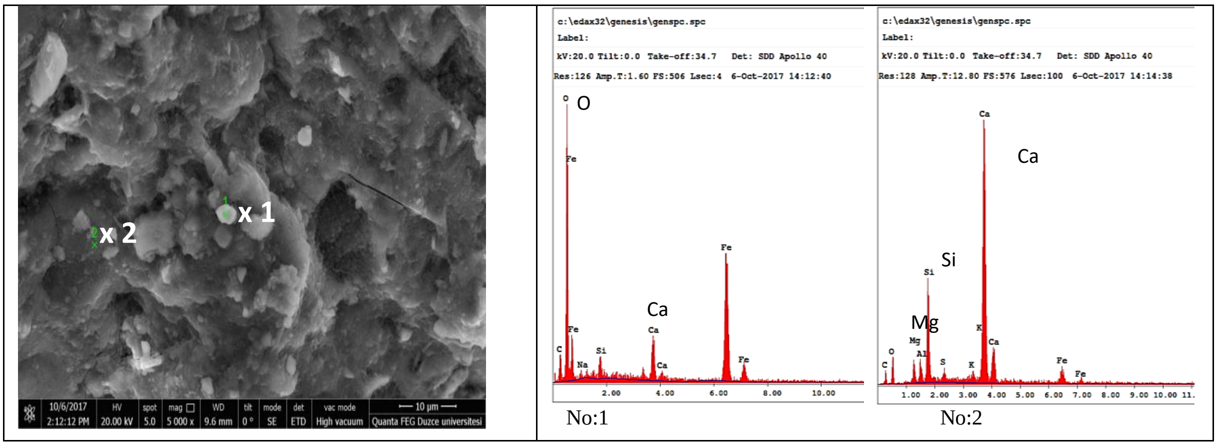

Figure 9. EDS analysis and SEM image of 20% crude sepiolite substituted sample

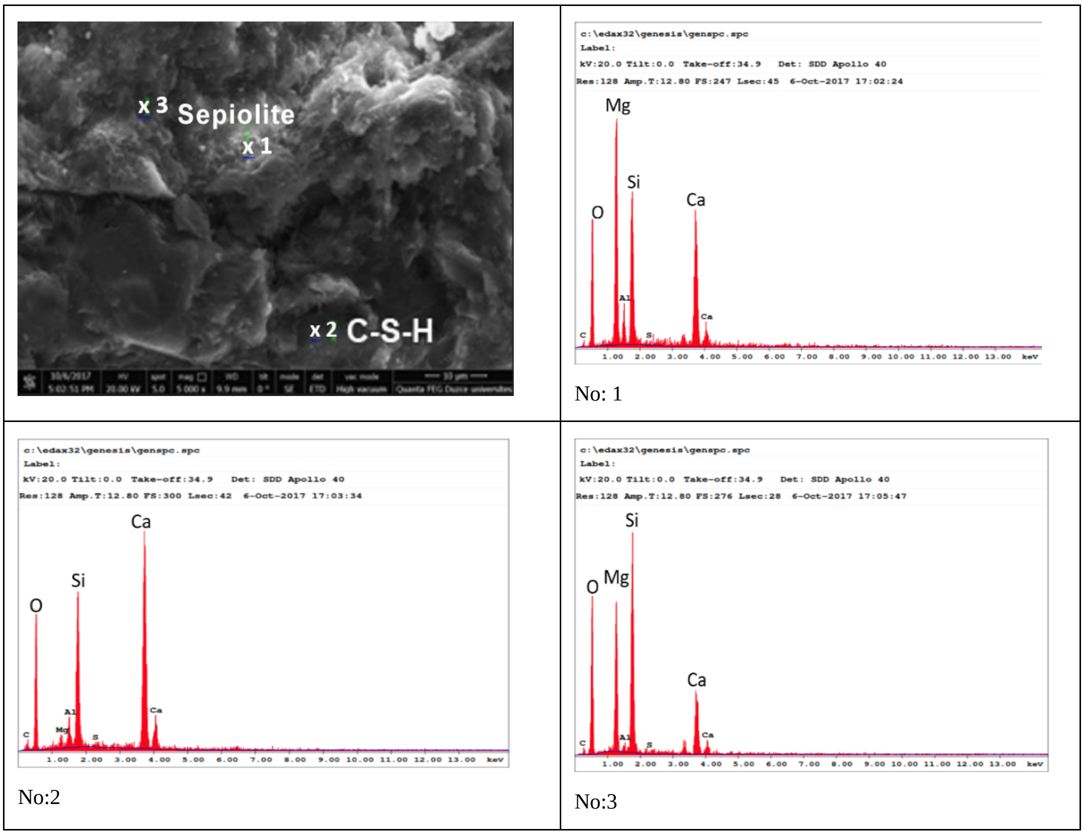

Figure 10. EDS analysis and SEM image of 20% calcined sepiolite substituted sample

When the SEM results were examined, hydrated phases such as CSH, CH and ettringite were determined in the structure. It has been observed that the adherence between the cement matrix and the sepiolite is weak, and as a result of this weakness, cracks are formed at the interface between the matrix and the sepiolite, thus adversely affecting the strength of the concrete. It is understood from the crack formation observed between the cement products and the crude sepiolite that the bond is weaker in crude sepiolite compared to calcined sepiolite.

When the EDS results are examined, Si, Ca, O, Al, Mg, S elements in the paste show similarity in all sepiolite substituted samples. In addition, it is seen that the Mg ratio in the sepiolite samples is high.

3.3. Experiments on mortar samples

3.3.1. Flow diameter results

The flow diameter of the sepiolite-free control mortar was determined in accordance with the standard, and water content determinations were made to reach similar spreading diameters in the samples with different ratios of calcined and crude sepiolite substituted. The graphical representation of the W/B ratios depending on the sepiolite substitution ratio is given in Figure 11. When the results were evaluated, the increase in the sepiolite ratio in connection with the consistency test performed on the paste mixtures increased the water requirement of the mortar samples. When calcined and crude sepiolite were compared, it was observed that calcination of sepiolite resulted in a decrease in the water absorption of the samples.

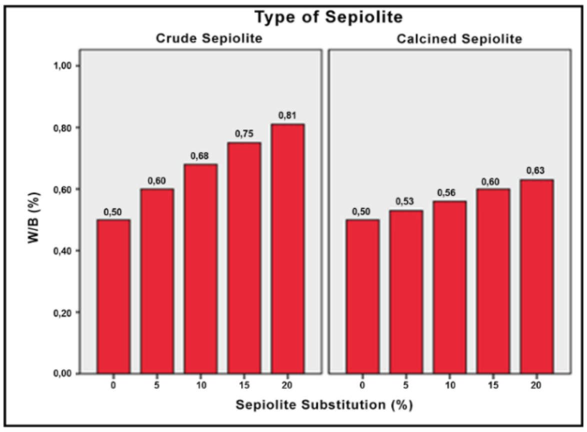

Figure 11. W/B values based on sepiolite substitution ratio

The highest water demand was observed in samples with 20% crude sepiolite replacement, an increase of 62% compared to the control. In samples with 20% calcined sepiolite replacement, the increase value was determined as 26%.

3.3.2. Alkali silica reactivity results by accelerated experiment method

Mortar samples containing different amounts of sepiolite were subjected to expansion test using the alkali silica method with accelerated mortar stick. The changes in sample lengths are given graphically in Figure 12.

Sepiolite substitution did not cause significant expansion on the mortar samples. This shows that although calcined and crude sepiolite have a high MgO ratio, there is no expansion feature in cementitious composite materials. While some more expansion was observed in mortar samples replaced with calcined sepiolite compared to samples replaced with crude sepiolite, the highest expansion value was observed in the sample with 20% calcined sepiolite substituted at the rate of 0.16%. While there was no significant change in the expansion values of the samples on the 3rd and 7th days, nearly 4 times of expansion value was observed in the 14th day expansion values compared to the 3rd and 7th days.

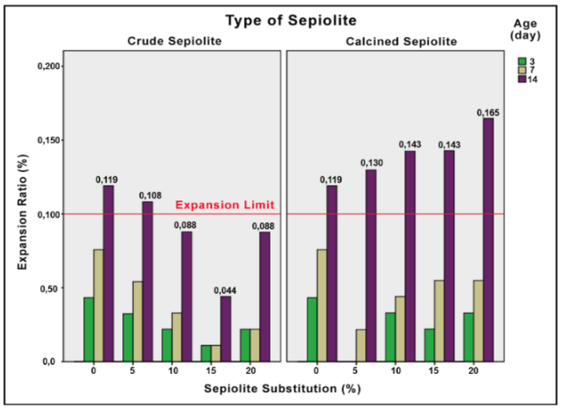

Figure 12. Expansion values depending on the sepiolite substitution ratio

It was observed that the expansion value caused by alkali silica reaction in samples was below 0.2% and it was determined that sepiolite was suspicious (harmful-harmless) in terms of alkali silica reactivity, except 10%-15%-20% crude sepiolite substitutions.

3.3.3. Compressive strength test results

According to TS EN 196-1, the graph of 7, 28, 56 and 90-day compressive strength tests based on the sepiolite replacement rate performed on the mortar samples produced is given in Figure 13.

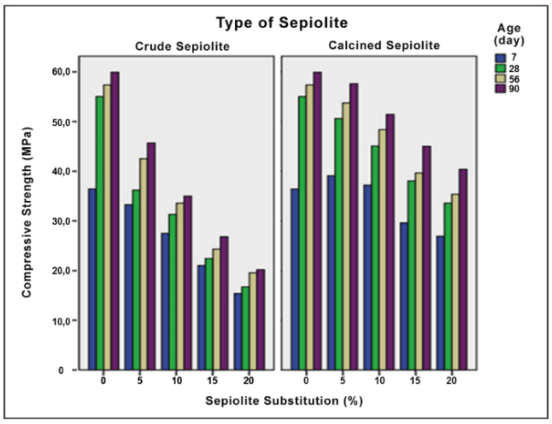

Figure 13. Compressive strength results of mortar samples

When compressive strength results were examined, it was seen that the compressive strength results decreased as the sepiolite substitution increased. It was observed that compressive strength results of samples containing calcined sepiolite were higher than samples containing crude sepiolite. In addition, with 5% and 10% calcined sepiolite replacement, it is understood that the compressive strength value at early ages is higher than the compressive strength value of the control sample.

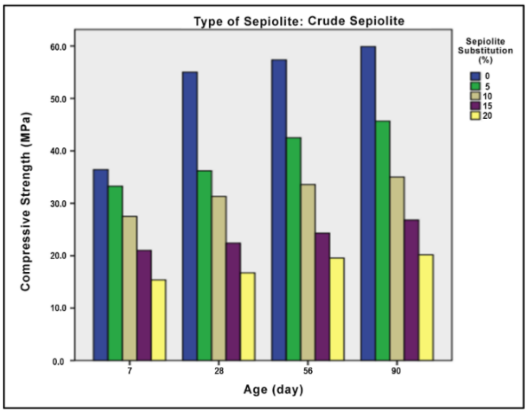

Figure 14. Results of compressive strength values of crude sepiolite substituted mortar samples at 0%,5%, 10%, 15% and 20% depending on the curing age of the sample

In addition, the graphical representation of the results of the compressive strength of the crude sepiolite substituted mortars at 0%, 5%, 10%, 15% and 20% depending on the sample age is given in Figure 14. The test results of the compressive strength values of the calcined sepiolite-replaced mortar samples are given graphically in Figure 15.

According to results, as the sample curing time increases, the compressive strength values of all mixtures increase. The samples reached their highest compressive strength after 90 curing days. In addition, as the crude sepiolite substitution rate is increased, the compressive strength values of the samples decrease, while the lowest compressive strength was observed in the samples with 20% crude sepiolite substitute, and the highest compressive strength value was observed in the control samples without sepiolite. After 28 days of curing, the highest increase in strength is in the control samples with 51%.

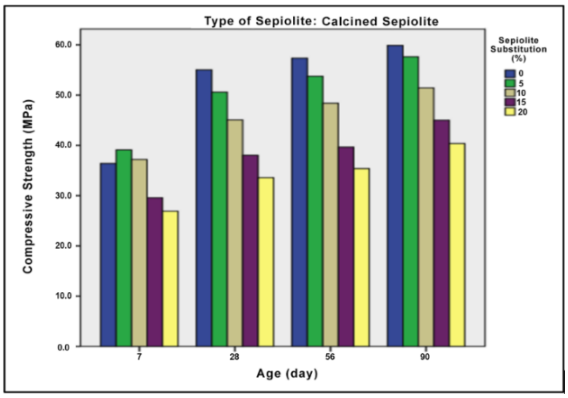

Figure 15. Test results of compressive strength values of samples with 0%, 5%, 10%, 15% and 20% crude sepiolite replacement depending on the sample curing time

When the early compressive strength results at the end of 7 days of curing of 5% and 10% calcined sepiolite-replaced samples were examined, it was observed that the strength values were higher than the control sample, and the compressive strength was lower at later ages than the control sample.

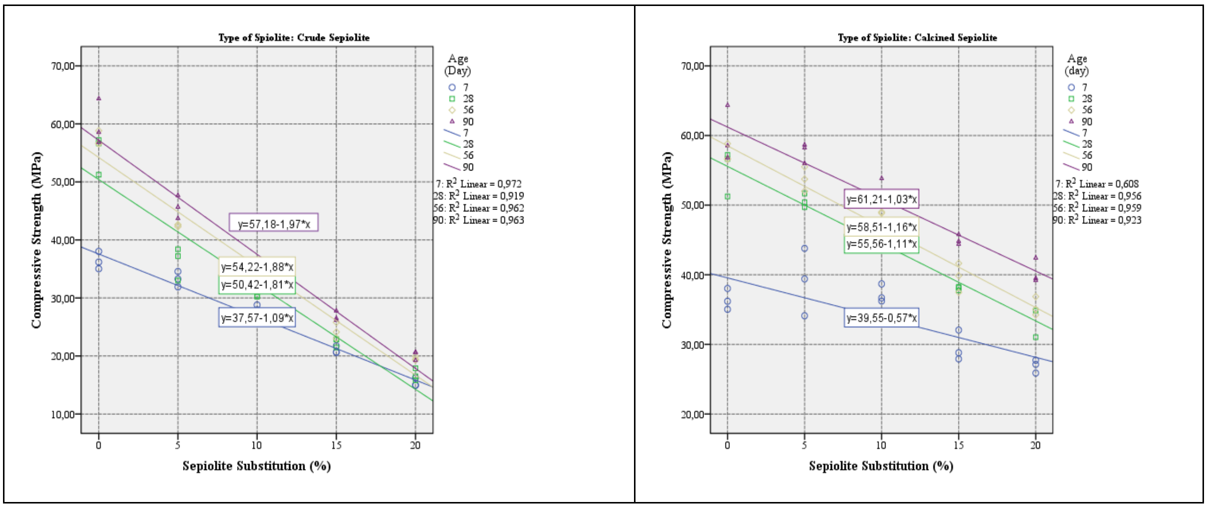

Figure 16. Graph of the relationship between sepiolite substitution rates and compressive strength results

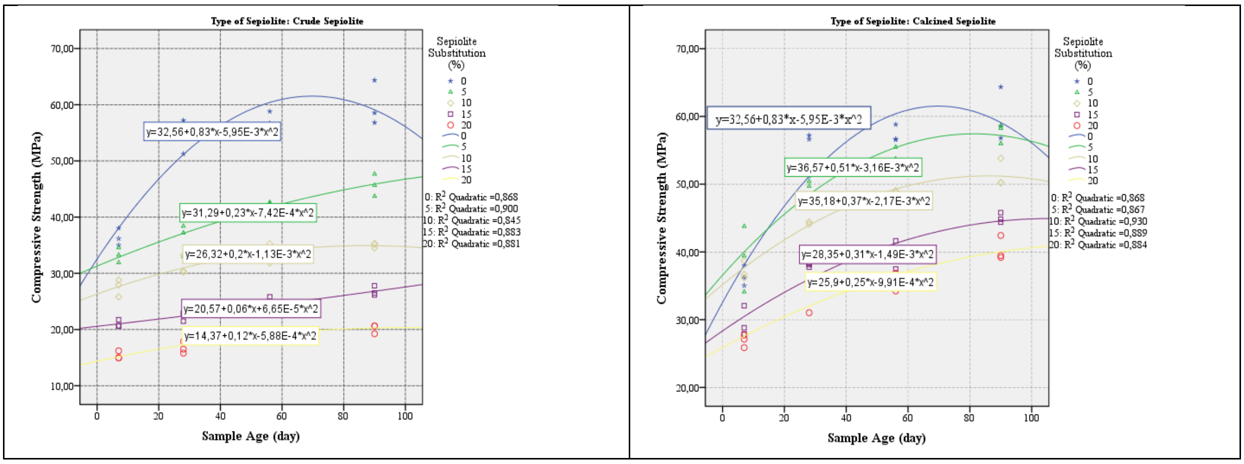

Figure 17. Graph of the relationship between sample curing age and compressive strength results

Regression analysis was performed to model the relationship between the substitution sepiolite ratio and the compressive strength results. It has been observed that there is a relationship between the amount of sepiolite substitution and the compressive strength, which can be explained by the first-order equation Y=a+bX. The relationship graph between the values and the explanatory model equations are shown in Figure 16, and the relationship graph between the compressive strength results and the sample age, which can be explained by the second-order equation $Y=a+bX+cX^2$, is shown in Figure 17.

3.3.4. Pozzolanic activity experiment results

The pozzolanic activity index was calculated based on the strength of the 20% calcined and crude sepiolite-substituted samples after 28 days of curing, according to the ASTM C-311 standard, and is given in Table 6. According to the table, it was observed that the pozzolanic activity index value of calcined and crude sepiolite was below 75% according to ASTM C-311 and did not show adequate pozzolanic properties.

Table 6. Pozzolanic activity index strength results.

	0% Sepiolite Control Sample	**20% Crude Sepiolite Samples**	**Samples with 20% Calcined Sepiolite**
28 G. Compressive Strength (Mpa)	55.03	16.73	33.57
Pozzolanic Activity Index	-	30.40	61.00

4. Conclusion

Density, chemical analysis, laser particle size analysis, FTIR analysis, thermal analysis, calcination process and SEM-EDS analyzes were performed on calcined and crude sepiolite samples to investigate the usability of ground sepiolite obtained from Eskisehir region in cement production. SEM-EDS analyzes and consistency test were performed on paste samples, and compressive strength, flow diameter determination, pozzolanic activity and alkali-silica reactivity tests were performed on mortar samples.

As a result of the data obtained from the test results and the statistical evaluations;

In powder samples;

- The density value increases with the calcination of the crude sepiolite, and the highest density is reached with the calcination applied at 900°C,

- crude sepiolite also has a fibrous structure, and after calcining, its fibrous structure deteriorates and turns into an oval shape [18].

In paste samples;

- Compared to the control mixture, 20% crude sepiolite substitute increased the water demand by 59%, while 20% calcined sepiolite by 28%. Crude sepiolite retains more water than calcined sepiolite. Studies in the literature confirm that the water demand of the mixture increases with the increase in sepiolite content [29],

- The bond between the sepiolite and the matrix is weak, and as a result, cracks occur at the sepiolite interface, thus negatively affecting the strength properties of the concrete, the bond is weaker in crude sepiolite compared to calcined sepiolite,

In mortar samples;

- The water absorption values of the samples decreased by calcining the sepiolite, 20% of the crude sepiolite replacement increased the water requirement by 62% compared to the control mixture, and this increase was 26% in the samples with 20% calsined sepiolite replacement. Since the workability of the control mixture decreased with sepiolite substitution, the water content was increased [30].

- The expansion value of the samples can be considered suspicious (harmful-harmless) in terms of reactivity, as it remains between 0.2% and 0.1% after 14 days, except 10%-15%-20% crude sepiolite substitutions,

- Due to the increase in the sepiolite replacement ratio, the compressive strength values of the samples decrease in the early and advanced ages compared to control samples [31]. The increase in water demand with the increase in the substitution rate were effective in this decrease. The crude sepiolite substitution causes lower compressive strength compared to the calcined sepiolite substitute, and at the end of 90 curing days, a 62% decrease in the lowest compressive strength value is realized in the samples with 20% crude sepiolite replacement. The addition of more water to reach similar spreading diameters reduced the strength of mortar [32],

It has been determined that crude and calcined sepiolite substitutions in different proportions to cement do not show sufficient pozzolanic properties in cementitious composites. The study conducted by Wu et al. confirmed that the pozzolanic activity increased by calcining sepiolite [31].

Article Information Form

Funding

This article was supported by Düzce University Scientific Research Project numbered 2016.07.05.466.

Authors' Contribution

The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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