EFFECT OF HIGH TEMPERATURE ON SEPIOLITE – HYDRAULIC LIME MORTAR

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ABSTRACT

Sepiolite is a natural clay mineral consisting of magnesium hydrosilicate. High surface area and micropores which form micro structure of sepiolite play an important role for the sepiolite to be used as a binder in the construction sector. The adsorbed water molecules, which are located in the chemical composition of sepiolite, move away from the structure while temperature goes up. When the temperature reaches 950°C chemical structure of sepiolite becomes impaired. This behavior under high temperature of sepiolite supports the use in the construction industry. Pozzolans such as sepiolite have little binding effect on their own. Therefore lime or cement is used together. The use of lime and sepiolite together in the repair mortars for restoration of historic buildings is one of the recent studies. However authors didn't encounter a study on high temperature resistance of mortars added with sepiolite. In this study to determine the behavior of mortars at high temperature, mixtures are designed at different rates of sand/binder and sepiolite/hydraulic lime. Specimens were exposed to 400°C and 700°C. The effect of high temperature on the lime mortar was determined, with respect to the loss in unit weight, ultrasonic pulse velocity, compressive strength and bending strength. At the end of the test results, there wasn't any significant change in physical and mechanical properties of mortars up to 400°C. However above 400°C, negative effects were observed.

KEYWORDS

Sepiolite, hydraulic lime, high temperature, physical and mechanical properties.

INTRODUCTION

Sepiolite is a natural clay mineral consisting of magnesium hidrosilicate, belonging to the group of phyllosilicates (layered silicates). Slick-looking, fine-grained, earthy and layered sepiolite may be usually in white, cream, gray or pink color. Depending on its organic content, it can also be dark brown or nearly black (Sabah & Celik, 1999). The chemical formula of sepiolite, according to the model of Nagy and Bradley is $Si_{12}Mg_9O_{30}(OH)_6(OH_2)_4 6H_2O$ according to the model of Brauner and Preisinger is $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4$-$8H_2O$ (Karakaş, 2006). Sepiolite has a crystalline structure, comprising the Si-O tetrahedron and octahedral layers. Si-O tetrahedron is arranged up or down from the base plane of oxygen. The crystal structure of sepiolite is given in Figure 1 (Galan, 1996).

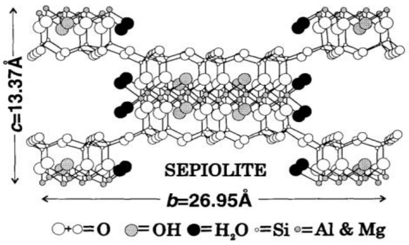

Figure 1 Structure of sepiolite (Galan, 1996)

Spain ranks first in the world in the production of sedimentary sepiolite. Sepiolite reserves of this country are between 15 and 20 million tones. Besides, in PRC economic sepiolite deposits are known to exist. Also in Turkey and in the United States sepiolite clay mining is done in small tonnages. Industrial or layered type sepiolite deposits which can be regarded as commercial product in Turkey are located in Eskisehir, Izmir, Bursa, Kütahya and Isparta. Layered sepiolite reserves in Eskisehir are around 57 million tons (Sabah & Celik, 1999; Tekin, 2004). High surface area and micropores and the zeolitic channels which form micro structure of sepiolite play an important role for the sepiolite to be used as supporting material in various sectors. The adsorbed and the zeolitic water molecules which are located in the chemical composition of sepiolite, move away from the structure while temperature increases. When the temperature reaches to 900-950°C destruction occurs in the chemical structure of sepiolite (Martinez-Ramirez, Puertas, & Blanco-Varela, 1995; Pinilla Melo, Sepulcre Aguilar, & Hernández Olivares, 2014). The chemical composition of sepiolite is given in Table 1.

Table 1 Chemical composition of sepiolite (Sabah & Celik, 1999)

Composition (%)	Turkey	Spain	Japan	Madagascar	Australia	USA
SiO_2	**55.97**	**60.60**	**52.05**	**52.50**	**52.43**	**50.80**
Al_2O_3	**1.56**	**1.73**	**1.03**	**0.60**	**7.05**	**0.66**
Fe_2O3	**0.77**	**0.62**	**0.04**	**2.99**	**2.24**	**1.05**
MgO	22.81	22.45	23.74	21.31	15.08	16.18
Na_2O	0.12	0.16		-	-	8.16
K_2O	0.27	0.58		-	-	-
FeO			0.01	0.70	2.40	1.51
MnO	0.02			-	-	-
TiO_2	0.12			-	-	-
CaO	0.57	0.40	0.51	0.47	-	0.12

Pozzolans such as sepiolite have little binding effect on their own. Therefore lime or cement are used together. Especially prior to the discovery of cement, lime is known to be a widely used construction material (Martinez-Ramirez et al., 1995). CaO is obtained by calcination of limestone. CaO reacts with the water and $Ca(OH)_2$ is transformed (Böke, Akkurt, & İpekoğlu, 2004). Lime can be classified into three groups; lime putty, hydrated lime and hydraulic lime. Characteristic that distinguish Hydraulic lime from other limes is that its structure comprises a high percentage of silica. Hydraulic lime can be classified into two groups; natural hydraulic lime and hydraulic lime. Natural hydraulic lime is produced from limestone that contains a high percentage of siliceous materials. This kind of limestone is composed of CaO, MgO and alumina, iron and silica and several other foreign matters. When the limestone, which contains a high percentage of silica and clay materials, used as raw material for the production of lime, these foreign matters are reacted with quicklime during the high temperature calcinations and calcium aluminates and silicates are produced. Pure hydraulic limes harden under water. Therefore, this type of lime is used as binders for mortar in the construction of bridges, drainage systems, water cisterns, foundations etc. Hydraulic lime is produced by the addition of the pure silicate into the powder limestone (clay minerals) and this mixture is heated at a temperature from 950°C to 1250°C. While non-hydraulic lime hardens only with CO_2, the hydraulic limes harden with water as well as CO_2 gas (Toprak, 2007). When hydraulic lime is quenched it turns into slaked lime $Ca(OH)_2$ and the main mixed oxide of cement $2CaO.SiO_2$ (Akman, 2003). The calcium aluminate silicates are formed calcium silicate hydrate and calcium aluminate hydrates with water and lime is converted to calcium carbonate. Therefore the strength of the hydraulic mortar is greater than the strength of the non-hydraulic mortar (Böke et al., 2004).

Table 2 Chemical analysis of hydraulic lime(Lanas, Pérez Bernal, Bello, & Alvarez Galindo, 2004)

Lime	I.L. (%)	SiO_2 (%)	CaO (%)	MgO (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SO_3 (%)	Na_2O (%)	K_2O (%)
Hidraulic Lime	15.00	12.57	54.26	7.65	5.42	1.16	2.13	0.34	1.35

There are a few, studies about the behavior of hydraulic lime based mortars and concretes in the literature. It has been proved that sepiolite slows down the rate of carbonation process in the lime mortars due to its capacity of water adsorption without affecting the mechanical behavior of the mortars. However, it has been observed that sepiolite influenced the development of the microstructure of mortar. On the other hand, the weak surface load of sepiolite, together with the absence of swelling and the needle shape of its particles, confers a singular rheological behavior on this material (Martinez-Ramirez et al., 1995).

Table 3 The chemical analysis of sand, lime and sepiolite (Martinez-Ramirez et al., 1995)

	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	SO_3	PF	IR
Sand	98.92	0.28	0.18	0.00	0.06	0.00	0.05	0.40
Lime	0.39	1.10	73.82	0.20	0.00	0.00	24.45	0.02
Sepiolite	55.10	19.43	5.91	5.13	1.96	0.00	12.02	0.10

The use of lime and sepiolite together in the repair mortars for restoration of historic buildings is one of the recent studies. Various researches has been done to determine the behavior of lime mortars containing sepiolite under various conditions and to determine the optimum mixture ratio. It has been observed that adding sepiolite 5% by weight of lime mortar did positive changes in the final properties (Martinez-Ramirez, Puertas, Blanco-Varela, & Thompson, 1998; Pinilla Melo et al., 2014).

In most of the studies the mechanical properties and physical characteristics were evaluated of sepiolite mortars and concrete, however the studies are limited for durability. When reinforced concrete elements exposed to high temperature, changes are seen in its physical and mechanical properties. Such as, decrease in the compressive strength and modulus of elasticity of concrete, formation of cracks, fragmentation and disintegration, decrease in yield strength, ductility and tensile strength of steel. It has been observed that when temperature reaches 600°C the concrete loses 50% of its strength when it reaches 800°C it loses approximately 80% of its compressive strength (Kızılkanat & Yüzer, 2008). Limestone's thermal conductivity depends upon the nature and status of its pores. As temperature increases, the thermal conductivity decreases. Specific heat is another feature which varies with temperature. The changes of specific heat of limestone with temperature are given below in Table 4. All types of limestone are converted to oxides before they melt. The melting point of CaO is 2800°C. Calcitic and dolomitic limestones are chemically the most stable substances. They certainly do not decompose at temperatures up to 600°C and they are not affected by water which does not contain CO_2. Limestone decomposes at higher temperatures is converted to calcium oxide (Parlakyıldız, 2008).

Table 4 The changes of specific heat of limestone with temperature (Parlakyıldız, 2008)

Temperature, °C	Specific heat (cal/g°C)
0	0.191
200	0.239
400	0.270
600	0.296
800	0.322

The objective of this work is to determine the features of the mortars which used sepiolite together with lime as a binder. Especially the mortar used in the external environment is open to various physical and chemical effects. For any reason, if the water reaches the sepiolite-lime mortar hydraulic lime was used to protect. Different sepiolite-lime mortar binder-sand ratios were produced and specimens were subjected to high temperature such as 20, 400, 700°C. With experiments such as the unit weight, ultrasonic pulse velocity, compressive strength loss was determined as a result of high temperatures.

EXPERIMENTAL STUDIES

Materials

Sepiolite: In this study, the sepiolite from Kaymaz region of Eskisehir was used. The surface area of sepiolite is 300 m^2 and its density is about 2.3 kg/m^3. Sepiolite has a porous structure and the average micro pore diameter is 1.5 nm. The chemical composition of sepiolite is given in Table 5.

Table 5 The chemical analysis of sepiolite and hydraulic lime

	Na2O	MgO	Al2O3	SiO2	SO3	K2O	CaO	Fe2O3
Sepiolite [2]	0.09	22.28	1.36	13.24	0.03	0.15	23.18	0.51
Hidraulic Lime [16]	0.34	7.65	5.42	12.57	2.13	1.35	54.26	1.16

Hydraulic lime: In this study, pure hydraulic lime produced by Tekno firm was used. Hydraulic lime properties are shown in Table 6. The chemical composition of hydraulic lime is given in Table 5.

Table 6 Properties of hydraulic lime

Bending Strength, MPa	Compressive Strength, MPa	Unit Weight, kg/dm3	Color
1	3.7	0.75	Ecru

Aggregate: The standard sand named RILEM Cembureau prepared by Trakya Cement Set Cement Industry and Trade Inc. suitable for TSE EN 196-1 was used.

Water: Eskisehir tap water was used as mixture water. The contents of water were 45 mg/l sulfate, 57 mg/l calcium, 83 mg/l magnesium, 49 mg/l chloride, 438 mg/l evaporation balance and pH was 6.75.

Method

Mortar series were created using Sand/Binder and Sepiolite/Hydraulic Lime at different rates. In Table 7 the different compositions of prepared hydraulic lime mortars are shown.

Table 7 Lime Mortar Compositions

Sand/Binder (S/B)		0			1/3			1	
Sepiolite/Hydraulic Lime (S/L)	1/3	1	3	1/3	1	3	1/3	1	3

The required ratio of water was determined as the consistency of each mixture will be the same. The Flow Test used for the determination of consistency is given in the Figure 2.

Figure 2 Flow test

From the produced mortar 4x4x16cm sized specimens were taken as shown in Figure 3. The specimens were kept 28 days in standard curing conditions. These mortars were exposed to 20, 400 and 700°C temperatures for 3 hours. Specimens were cooled down to room temperature in air. The unit weight and ultrasonic tests as nondestructive testing method were done on the specimens. Destructive test methods as the bending and compression experiments were made. The effect of high temperature on the lime mortar was determined, with respect to the loss in unit weight, ultrasonic pulse velocity (UPV), compressive strength and bending strength.

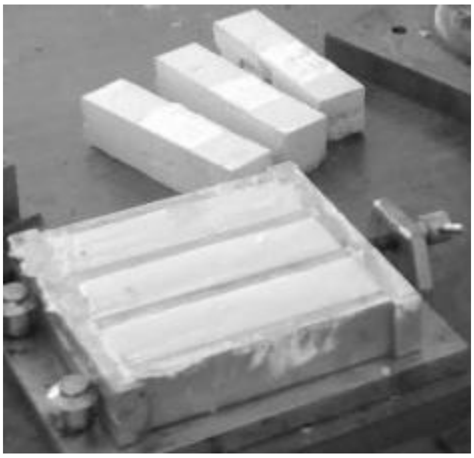

Figure 3 Produced Specimens

RESULTS AND DISCUSSIONS

In Figure 4, the change of the unit weight of the produced materials with respect to temperature is given. Unit weight values were changed in the range of 0.8-1.7 kg/dm^3. Generally the decrease of unit weight of the produced mortar series with increasing temperature reached at 20%. As the S/B ratio increases, the unit weights of the produced mortars increased at rates up to 30% at 20°C and 40% at 400°C, 50% at 700°C. The specific weight of the sand is greater than the specific weight of sepiolite. Therefore, as the S/B ratio increased, the unit weights of the specimens were increased. Especially, in sand-free specimens, after 400 degrees the cracks occur in the structure as a result of increase in the volume, therefore unit weight loss was found to be more than the other specimens.

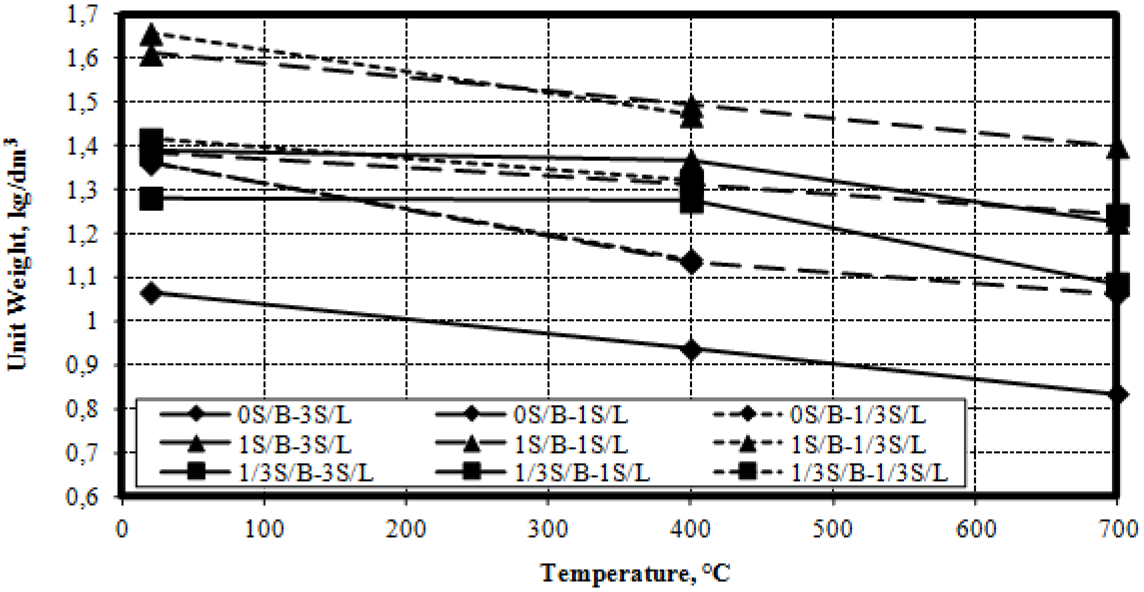

Figure 4 Unit weight versus temperature for different compositions of mortars

Mortar specimens including sand is prone to shrinkage due to water loss. On the contrary, aggregate resists this shrinkage. Therefore, in the micro structure the cracks are formed resulting from arising stress. Generally it has been seen that the unit weight loss was more significant in the 400°C and before. As the S/L ratio increases, unit weights of the control specimens have been decreasing at rates up to 20% at 400°C and 15% at 700°C. The specimens which have 1/3 S/L ratio disintegrated at 700 degrees. Therefore the measurements couldn't be made. When the sepiolite amount increases the unit weight of the specimens are decreased. The reduction in unit weights of the specimens which have the highest sepiolite ratio was less and more regular. This is because when the mortars are exposed to high temperatures the lime volume changes more than sepiolite. Even more the dissolution was observed in the mortar specimens which has more lime ratio, 1/3 S/L, at high temperatures.

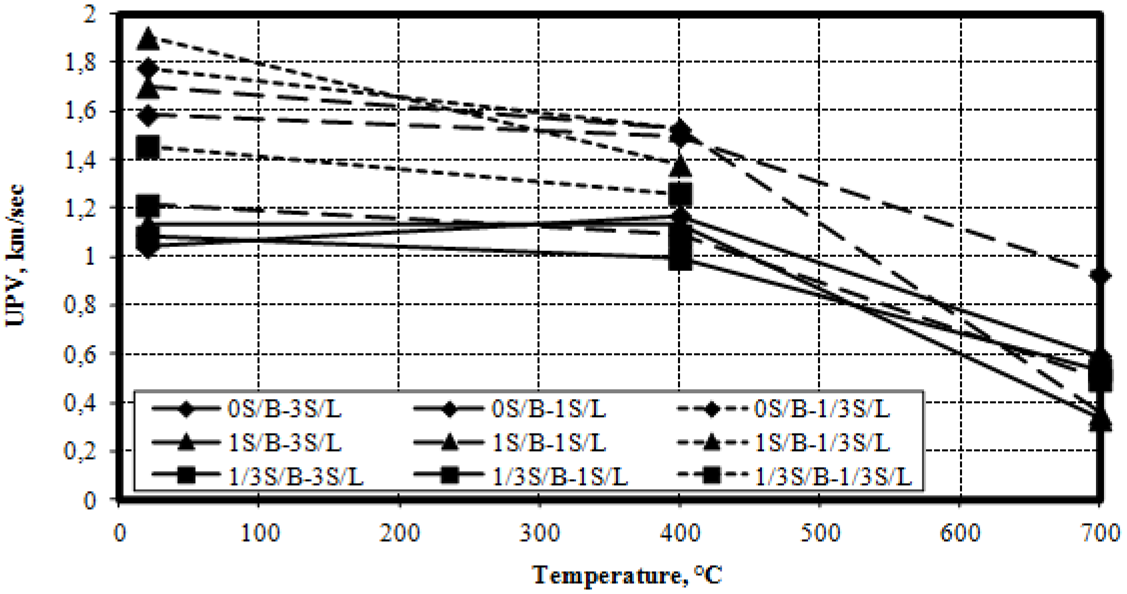

Figure 5 UPV versus temperature for different compositions of mortars

Ultrasonic pulse velocity (UPV) test is a practical non-destructive method which used to measure the quality of the specimens depending on the amount of cavity of the specimens. In Figure 5, the calculated ultrasonic pulse velocity for each specimen which has been exposed to 20, 400 and 700 degrees temperatures were shown. UPV values were changed in the range of 1.9-0.3. Generally, the calculated UPV values of the mortar series have decreased with the temperature increase. When the temperature increases, in the mortars the water loss and shrinkage occurs. The cracks, which have been as a result of this shrinkage, cause a reduction in the UPV values.

As S/B ratio increases, firstly UPV values of the produced mortars have been decreasing at rates up to 20%. When the S/B ratio is 1, generally UPV values have been increasing at rates up to 10%. It has been considered that the reason for this increase is due to the UPV of the binder dough is lower than the UPV of the sand. As the S/B ratio increases, unit weights of the produced mortars have been decreasing at rates up to 20% at 400°C and 65% at 700°C. At 570°C the cracks occur in the micro structure of the quartz sand due to polymorphic transformation. Thus, as the S/B ratio increases a significant decrease occurs at 700°C. If we look at the increase in S/L ratio, the reduction in the UPV's of the mortars can be seen as 40% at 20°C, 25% at 400°C, 40% at 700°C. As the sepiolite rate increases the UPV values are decreased. The volume change that occurs at high temperatures in the micro structure of sepiolite reduces UPV values. When the specimens which have maximum sepiolite ratio are exposed to higher temperatures, the UPV values increased when temperature reaches up to 400°C. After 400°C it has become a more regular decrease.

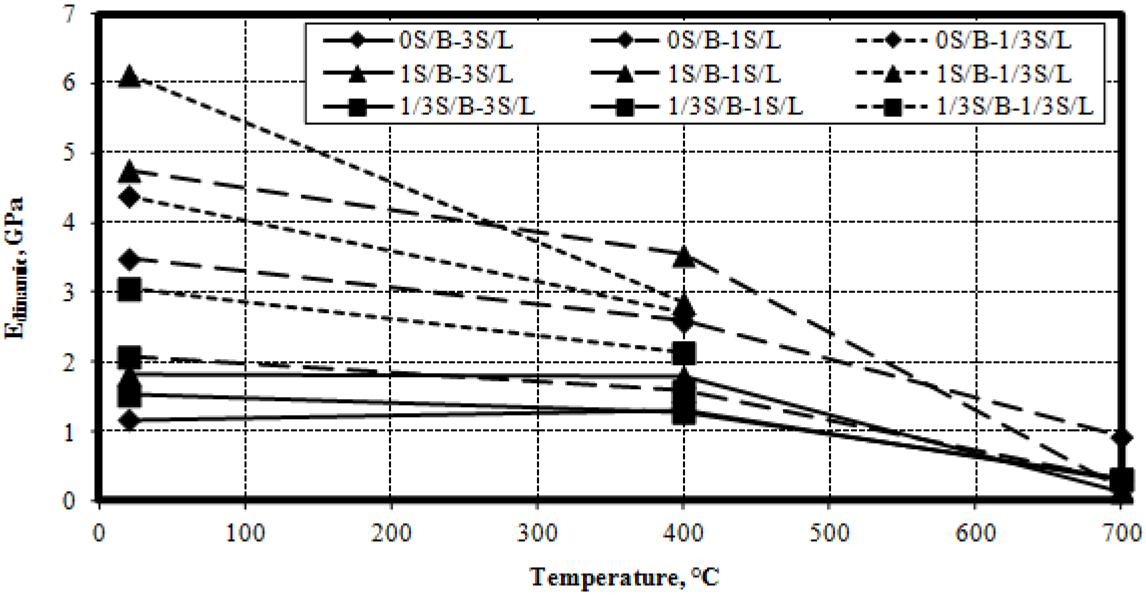

Figure 6 $E_{dinamic}$ versus temperature for different compositions of mortars

Dynamic modulus of elasticity is calculated depending on the square of the UPV and the unit weight. In Figure 6, the changes of the dynamic elasticity modulus of the produced materials with respect to temperature are given. Overall, the dynamic elasticity modulus decreased as the temperature increased. Dynamic modulus of elasticity has values between 0.1 and 6. As the S/B ratio increases, till it reaches 1, the values of the dynamic elasticity modulus are decreased. After that the values of the dynamic elasticity modulus were increased as the S/B ratio increases. Dynamic elasticity modulus have been increasing at rates up to 40% at 20°C and 35% at 400°C, while it has been decreasing up to 70% at 700°C. There are many factors those affect the elasticity modulus of mortars, such as properties of the used materials, porosity, moisture conditions of the specimens and loading conditions. Dynamic elasticity modulus is directly proportional to the square of UPV and the unit weight. Therefore, the change in dynamic elasticity modulus with S / B ratio is similar to the changes in UPV values. When considering the increase in S/L ratio it is observed that dynamic elasticity modulus has decreased at rates up to 80% at 20°C, 35% at 400°C, and 90% at 700°C. The increase in the sepiolite ratio has made decrease in the dynamic elasticity modulus values. This decrease has been faster after 400 degrees, and after 700 degrees the dynamic elasticity modulus has been decreased down to zero. This reduction is a result of crack propagation which occurs in the micro structure of the specimen under the influence of high temperatures.

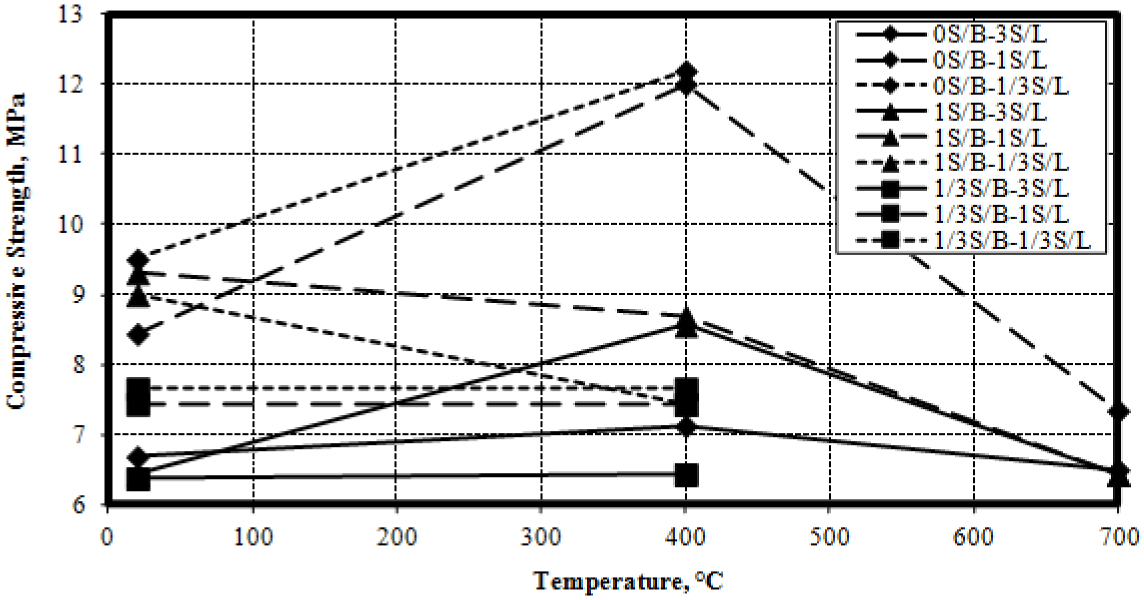

Figure 7 Compressive strength versus temperature for different compositions of mortars

The change of the compressive strength of the produced mortars with respect to temperature is given in Figure 7. The compressive strength of the mortar series ranged from 6 MPa to 12 MPa. In general, the compressive strength of the specimens remained stable up to 400 degrees. It can be clearly seen from the chart that, after 400 degrees, the compressive strength of the mortar series has decreased dramatically. The increase in the S/B ratio reduces the compressive strength in general. Reduction of binder ratio caused a decrease in compressive strength. This reduction in compressive strength of the mortar series reached up to 15% at 200°C, 25% at 400°C and 10% at 700°C. It is observed that the compressive strength of sand-free specimens increased up to 12 MPa. Different thermal expansion of the sand and binder phase caused a decrease in compressive strength of the specimen containing sand. In specimens containing a low content of sepiolite, the compressive strength was not obtained at 700°C. Increasing binder ratio used in the construction of mortar also increases compressive strength.

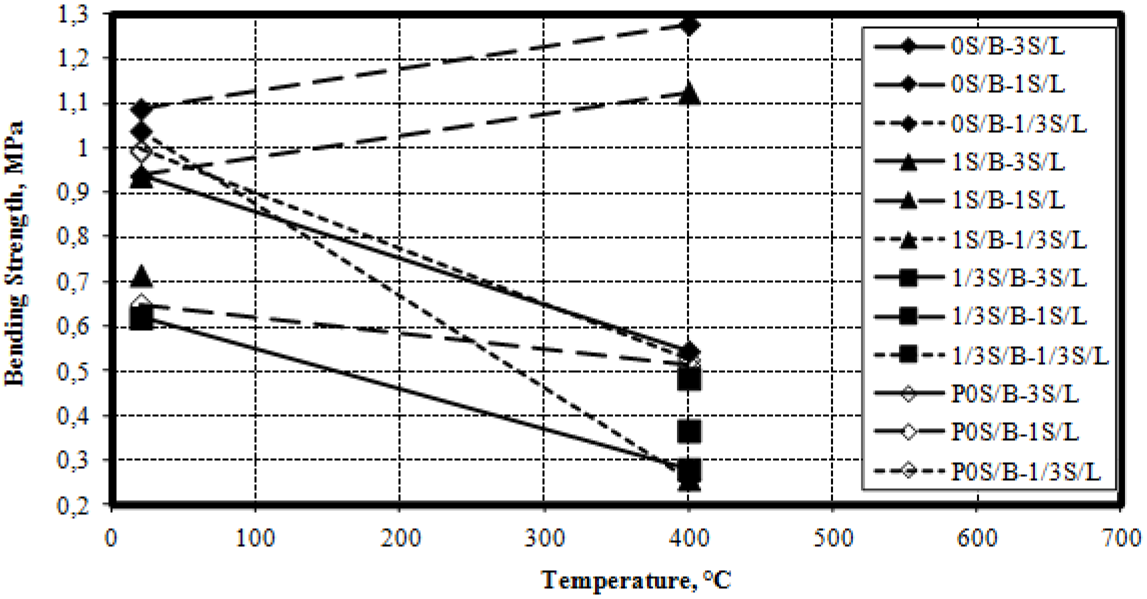

Figure 8 Bending strength versus temperature for different compositions of mortars

The results of the bending tests conducted on the specimens at 20°C, 400°C, and 700°C are shown in Figure 8. Bending strength of mortar series ranged from 0 to 1.3 MPa. Generally under high temperature the bending strength of the mortar series of S/L ratio of 1 has increased while others bending strength decreased. It was thought that the fibrous structure of sepiolite increased the strength of the clay binder and this increased the bending strength of the mortar. The reason for the reduction in the bending strength of the mortars of S/L ratio is greater than 1 could be shown as the loss of the hydraulic lime which is the actual binder. It is observed that as the S/B ratio increases the bending strength of the mortar series has increased until the S/B ratio is 1. As S/B ratio increases, firstly the bending strength of the mortars has been decreasing as well. When the S/B ratio is 1, although a slight increase is observed they did not reach the bending resistance possessed by the sand-free specimens. Depending on the temperature as the S / B ratio increased the bending strength decreased at rates up to 90% at 20°C, 70% at 400°C. The reason for the reduction of the bending strength under increasing sand ratio could be shown as the strength of the binder paste is higher than the sand strength. Overall, the amount of sepiolite in a certain ratio (S/L = 1) showed a positive effect on the bending strength of the mortar series exposed to high temperature. However, increased sepiolite ratio reduces the bending strength.

CONCLUSIONS

The conclusions of the study are summarized as follows:

1. With the increasing content of sepiolite in prepared mortars the unit weight decreased overall. As a result of less volume changes of sepiolite compared to lime, the reduction in unit weight at high temperatures in specimens with more sepiolite content was observed to be lower and more regular. As the S/B ratio increases the unit weight of mortar series are increased. With the increasing volume as a result of micro cracks the unit weight of specimens, without sand, decreased especially after 400°C.

2. Because of the volume changes in sepiolite at high temperatures, as the sepiolite ratio increases it has been observed that UPV values of the mortars were decreased. Even though increasing sand ratio has improved the UPV values around 10%, under high temperatures especially after 700°C decrease was observed up to 65% in those values. At about 570°C, sand loses its polymorphic structure, and volume expansions occur. Therefore the UPV values were decreased. There is also a similar behavior in the Dynamic elasticity modulus as in the UPV values.

3. As a result of being directly proportional to the mixture water requirement with sepiolite content, increasing sepiolite ratio reduces the compressive strength of specimens under high temperatures. Increased sand content decreased the compressive strength of the mortar specimens.

4. Under high temperature the flexural strength of mortar specimens with S/L ratio=1 showed a favorable behavior, but increasing sepiolite ratio has reduced the flexural strength of those specimens.

Consequently, it was determined that use of sepiolite as a binding material with hydraulic lime for mortars doesn't have adverse effect on the mechanical properties of mortar. Also it may be advisable that the addition of sepiolite with the rate of S/L=1 to reduce the unit weight of the mortars and for use in bending members. Considering the versatility of sepiolite, more research should be done on the mortars those contains sepiolite for the use in repair mortars in countries which have high reserves of sepiolite.

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