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Effect of Elevated Temperatures on Properties of Blended Cements with Clinoptilolite

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We have investigated the effect of elevated temperature on properties of clinoptilolite blended cements. Clinoptilolite was used at 5 %, 10 %, 15 % and 20 % replacement by weight for Portland cement while sand and water quantities were kept constant in all mix designs. Dry weights, flexural strengths, and compressive strengths of specimens were determined as a function of time. The same properties were again evaluated after specimens, having reached the age of 90 days, were exposed to 300 °C, 400 °C and 500 °C temperatures for 3 h. Initial setting times for all cements prepared were ≥ 60 minutes, the limiting time according to TS EN 197-1. The mortars with 5 % or 10 % cliniptilolite substitution have compressive strength exceeding 42.5 MPa after being subjected to 400 °C and 500 °C.

Keywords: blended cement, clinoptilolite, cement compressive strength, elevated temperatures.

1. INTRODUCTION

Owing to its good performance to cost ratio, concrete is one of the most widely used traditional materials in construction [1 – 6]. Concrete is a heterogeneous material consisting of cement, water, sand and aggregates [7]. The properties of concrete are strongly dependent on the cement used [8]. While cement production originally focused on Portland cement, subsequent methods of production have replaced parts of the clinker content with supplementary cementitious materials. As a consequence, fly ash from coal power plants, granulated slag from iron production, and natural pozzolans are being used in increasing amounts [9]. The term pozzolan is associated with all siliceous/aluminous materials, which, in finely divided form and in presence of water, react chemically with $Ca(OH)_2$ in order to form compounds that possess cementitious properties [10].

Cement replacements include also volcanic ash, pumice, rice husk ash, silica fumes, and more [11]. It is well known that the incorporation of pozzolans into cement or concrete systems provides many benefits to properties of both fresh and hardened concrete such as improvement in workability, reduction in the heat of hydration, low permeability, high ultimate strength, and control of alkali–silica expansion. However, most pozzolanic materials, especially natural pozzolans, tend to increase the mixing water requirement for concrete and lower the rate of strength development. Therefore, for structural applications their proportion in blended Portland cements is generally limited to 30 % or less [12]. Zeolitic tuffs have been widely used, as mixtures with lime, in construction since Roman times. There is much discussion on the pozzolanic activity of natural zeolites and their incorporation in blended cements [13]. Most cement plants consume much energy and produce a large amount of undesirable products which affect the environment. In order to reduce energy consumption and CO_2 emission and also to increase production, cement manufacturers are blending or intergrinding mineral additions such as slag, natural pozzolan, sand and limestone [14]. Natural, zeolite-rich volcanic tuffs have been proposed and frequently are used as pozzolans in several countries such as Bulgaria, China, Cuba, Germany, Greece, Italy, Jordania, Russia, Turkey and United States [15].

Natural zeolite contains large quantities of reactive SiO_2 and Al_2O_3. Similar to other pozzolanic materials such as silica fume and fly ash, zeolite substitution can improve the strength of concrete by the pozzolanic reaction with $Ca(OH)_2$, an effect that is reportedly generally greater in concrete than in cement alone [16]. Zeolite tuff + lime mixtures have been also used in construction since ancient times. Today, more than 50 natural and 150 synthetic zeolite minerals are in use. In China the total quantity of zeolite consumed is as much as 30 million tons per year [17]. Concrete is more durable against elevated temperature and fire effects than many other construction materials [18]. Although ordinary concrete is considered to have a satisfactory fire resistance [19], it can lose 40 – 60 % of its original strength upon exposure to 500 °C [20].

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Concrete surfaces exposed to heat are significantly affected [21]. The most important effects of elevated temperatures on concrete are: dehydration of cement paste, porosity increase, modification in moisture content, thermal expansion, alteration of pore pressure, strength loss, thermal cracking due to incompatibility, thermal creep, and thermal spalling due to excessive pore pressure [22].

We have studied the effects of elevated temperatures on physico-mechanical properties of blended cements containing clinoptilolite. Clinoptilolite is a natural zeolite comprised of a microporous arrangement of silica and alumina tetrahedra. It has the complex formula: $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O.12H_2O$. It forms white to reddish tabular monoclinic tectosilicate crystals with a Mohs hardness of 3.5 to 4 and a specific gravity of 2.1 to 2.2.

2. MATERIALS AND METHODS

The materials used for this study consisted of clinoptilolite and ordinary Portland cement (OPC) CEM I 42.5 R. Natural zeolite in clinoptilolite form used in this study was obtained from the Gördes Mining Company, Gordes region, Turkey. The chemical, physical and mechanical properties of Portland cement and clinoptilolite used in the study are given in Table 1. Clinoptilolite is characterized as a natural pozzolan according to the Turkish standard TS EN 197-1. This standard specifies that the reactive SiO_2 content shall be not less than 25 % by mass; clinoptilolite samples used in this research satisfy this requirement, as seen in Table 1. The Portland cement (CEM-I 42.5 R) used in the experimental study was obtained from OYAK Bolu Cement and conforms to TS EN 197-1.

Mineralogical and microscopic analysis of clinoptilolite were provided by the manufacturer, Gördes Mining Company. As seen in an XRD pattern in Fig. 1, the zeolite used by us consists of a high concentration of the clinoptilolite phase with very low quartz and opal cristobalite (opal CT) content. The crystal structure of the clinoptilolite is presented as a scanning electron micrograph in Fig. 2.

The mortar mixtures were prepared with 450 g of cement, 1350 g of CEN standard sand, and 225 mL of water and mixed in accordance with TS EN 196-1. Clinoptilolite was used at 0 %, 5 %, 10 %, 15 % and 20 % replacement by weight for cement – while sand and water quantities were kept constant. Water demand and setting time analysis of mortars were performed with an automatic Vicat machine while soundness tests were carried out using a Le Chatelier tool. These measurements were conducted according to TS EN 196-3. For the mixture preparation, the mortars were placed in 40 × 40 × 160 mm prismatic molds. After removal from the molds at 24 h of age, mortar specimens were immersed in water saturated with lime at 20 °C until the time of testing. Compression and three points bending tests were conducted at 7, 28 and 90 days of age. The results reported are the averages for three flexural specimens and six compression tests. The elevated temperature resistance tests of the mortars were conducted on specimens aged to 90 days. At that time, dry weights, flexural strengths and compressive strengths were determined. Then each specimen type was exposed to 300 °C, 400 °C, and 500 °C temperatures for 3 h in a furnace. After the 3-hour-exposures at the specified temperatures, the hot mortar specimens were cooled in laboratory conditions. Upon reaching room temperature, the dry weights and flexural strengths were determined, taking the averages of three test results while the compressive strengths were determined by taking the average of six test results.

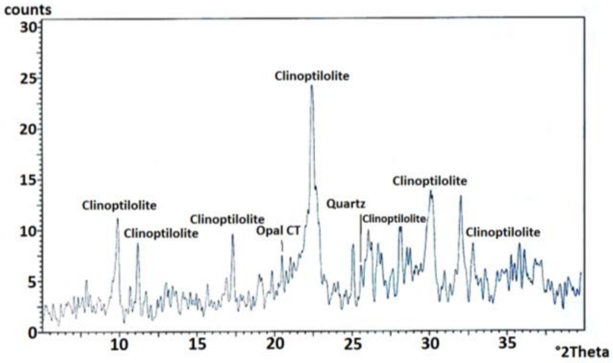

Fig. 1. XRD analysis of zeolite

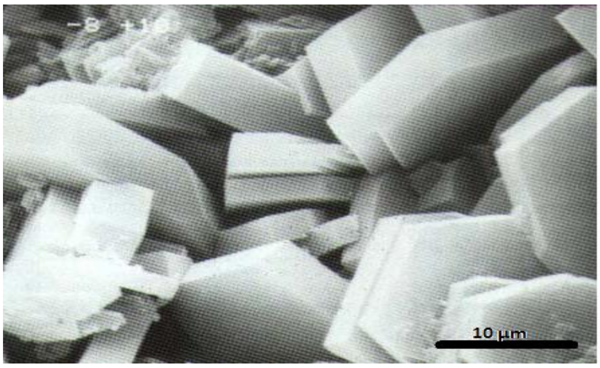

Fig. 2. SEM view of zeolite

3. PHYSICAL PROPERTIES

The physical properties of the reference Portland cement (RF) and Portland cement blended with clinoptilolite (CL5, CL10, CL15, CL20) are given in Table 2. As seen in that Table, the water content of mortars increased from 29.8 % to 36.8 % with increasing clinoptilolite concentration in the cement. Simultaneously the specific gravity decreases with increasing clinoptilolite concentration, owing to the porous structure of clinoptilolite. Actually, a reduction of specific gravity can be useful for the reduction of the dead weight of the structure. Volume expansion values of all specimens are acceptable within the limit of ≤ 10 mm given by TS EN 197-1. The initial and final setting times of mortars are listed in Fig. 3. Compared to the reference cement (RF), the initial setting time was lowered from 140 min to 130 min by the addition of 5 % clinoptilolite.

Further addition of clinoptilolite lengthened the initial setting time up to 230 min. Similarly, the final setting time of clinoptilolite cements was shorter for 5 % substitution and longer for specimens with higher concentration of clinoptilolite. Clearly all values of initial setting time are above the standard lower limit requiring a time ≥60 min.

Table 1. Physical, chemical and mechanical properties of cement and clinoptilolite used

Chemical composition, %	Cement	Clinoptilolite	Physical Properties of cement	
SiO_2	18.9	67.1	Initial setting time, min	140
Al_2O_3	5.3	11.8	Final setting time, min	160
Fe_2O_3	4.1	1.5	Volume expansion, mm	1
CaO	64.7	2.2	Specific gravity	3.18
MgO	1.3	1.2	Specific surface (Blaine, cm^2/g)	4663
SO_3	2.9	-	Mechanical properties of cement	
Na_2O	0.2	0.4		
K_2O	0.5	3.4	Compressive strength, MPa	
Loss of ignition	3.8	12.5	7 days	45
Insoluble residue	0.6		28 days	55
Free CaO	1.52		90 days	62

Table 2. Physical properties of the blended cement mortars

	RF	CL5	CL10	CL15	CL20
Water demand, %	29.8	30.8	32.8	34.8	36.8
Specific gravity, g/cm^3	3.18	3.09	3.02	2.92	2.86
Volume expansion, mm	1	1	1	1	1

Furthermore, it is seen from Fig. 3 that clinoptilolite substitution is obviously a factor in determining the setting times of cement mortars.

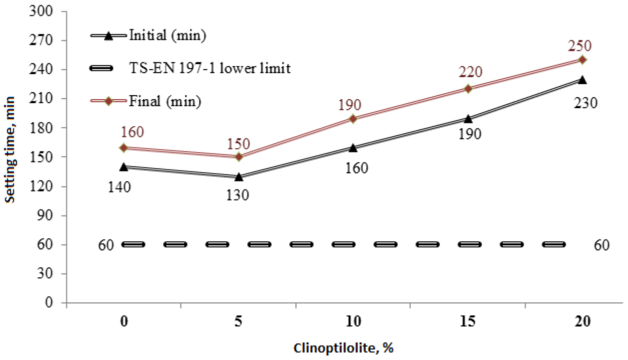

Fig. 3. Setting time variations for cements

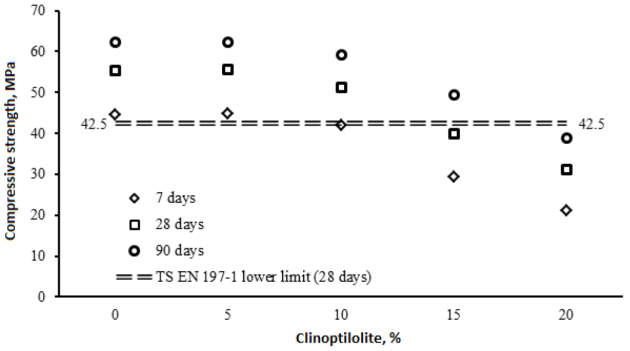

Fig. 4. Compressive strengths values for cements

4. MECHANICAL PROPERTIES

The compressive strengths of the mortars were determined at 7, 28 and 90 days, with the results shown in Fig. 4. As expected, the compressive strength values increase with age. Compared to the compressive strength of the plain cement reference, that of the specimen with 5 % clinoptilolite substitution was essentially unchanged.

The specimen with 10 % clinoptilolite had slightly lower values but still suitable given the minimum value of 42.5 MPa for the appropriate Turkish Standard. Further substitution up to 15 %, and 20 % reduces the compressive strength even to values below the lower limit of acceptability (according to the standard TS EN 197-1).

The flexural strength of concrete or mortar is important for pavements. There is no lower limit value for the flexural strength in EN 197-1. The behavior of both RF and clinoptilolite blended cements under flexural force – as seen in Fig. 5 – are similar to their behavior under compression.

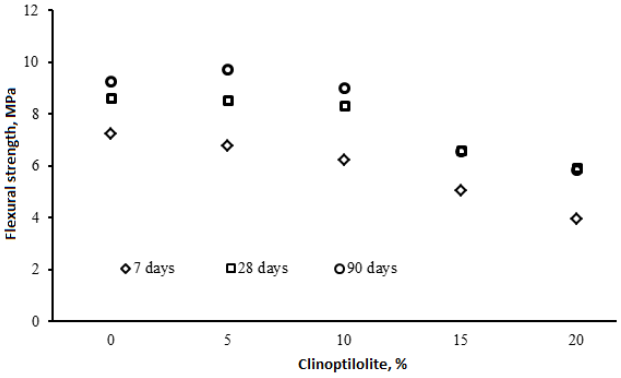

Fig. 5. Flexural strength results for the cements

5. WEIGHT LOSSES, COMPRESSIVE STRENGTHS AND FLEXURAL STRENGTHS OF CLINOPTILOLITE BLENDED CEMENTS AFTER HIGH TEMPERATURE EXPOSURE

Table 3 lists the weight loss of the mortars resulting from exposure to elevated temperatures (100 ºC oven-dried, 300, 400 and 500 °C), each time for 3 hours. As mentioned in the Methods, all data is taken at the age of 90 days. The unit weights decrease with increasing temperature. Compressive strength test results of blended cements after high temperature conditions are presented in Fig. 6.

Table 3. Dry weights of specimens

	Oven-dried	300 °C		400 °C		500 °C	
	Weight	Weight	Weight loss, %	Weight	Weight loss, %	Weight	Weight loss, %
RF	546	522	4.53	518	5.22	514	5.95
CL5	543	519	4.35	516	5.00	510	6.06
CL10	539	519	3.72	515	4.56	508	5.89
CL15	523	501	4.38	504	3.77	482	7.93
CL20	505	487	3.53	484	4.03	481	4.76

For every specimen type, the compressive strength decreases as the temperature of exposure increases. The values after exposure to the highest temperature, 500 °C, are slightly lower than the values for the same specimen at the age of 7 days. The trend in values as a function of clinoptilolite content is the same for high-temperature exposed specimens as for the specimens dried at 100 °C.

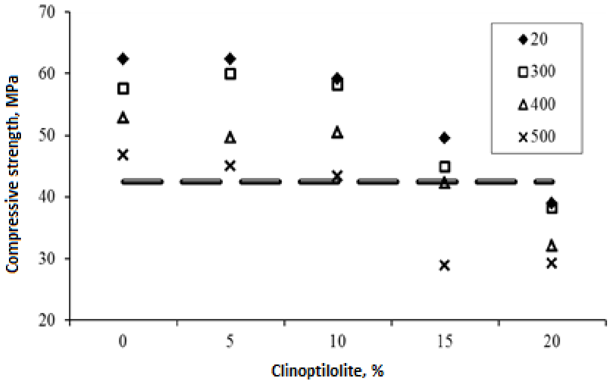

Fig. 6. Compressive strength of mortars subjected to elevated temperatures

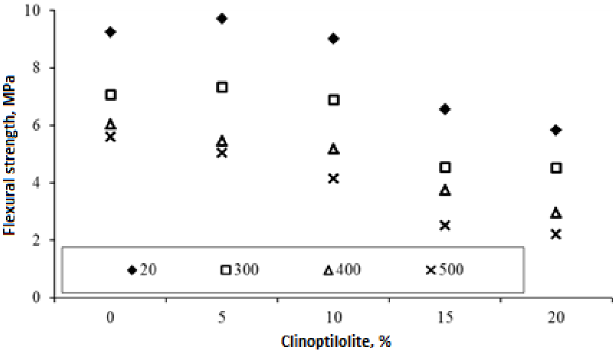

Fig. 7. Flexural strength results for blended cement mortars after high temperatures

There are only slight differences between properties of the reference cement and of cements substituted with 5 % or 10 % clinoptilolite. The further substitution of 15 % or 20 % substantially lowers the compressive strength for all temperatures. In reference to the standard lower limit, all specimens except CL20 are suitable for use after exposure to 300 °C while CL5 and CL10 perform above the limit even after exposure to 500 °C. Relative changes of compressive strengths of blended cements subjected to different temperatures are presented in Fig. 7. As seen from that figure, all mortars have a residual strength over 60 % which is important in terms of structural performance.

Flexural strengths of blended cement mortars are presented in Fig. 7. Knowledge of flexural strength is important in applications such as the design of highways, airfield slabs, and dams. The behavior of both RF and clinoptilolite blended cements under flexural force application are similar to their behavior under compressive forces. As expected, flexural strength decreases with exposure to increasingly higher temperatures, while the effect of clinoptilolite substitution is the same as before.

6. CONCLUSIONS

We have demonstrated the feasibility of using clinoptilolite as a substitute for cement to produce mortars that meet the requirements of existing standards. There is some increase in water demand with clinoptilolite substitution, but setting times exceed the standard lower limit.

Cements with higher levels of clinoptilolite substitution do not perform as well, especially after high temperature exposure, but up to 15 % substitution can provide suitable properties after 90 days aging and after exposure to 300 °C.

However, the substitution of cement with 5 % or 10 % clinoptilitolite yields specimens with properties nearly identical to those of unsubstituted concrete.

Moreover, at these levels of substitution, specimens perform well even after 3 hours exposure at temperatures up to 500 °C. Therefore, it is clearly possible to produce clinoptilolite substituted cement up to 10 % with adequate compressive strength after 90 days curing.

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