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Research Article

THE EFFECT OF SODIUM CARBONATE ON ELEVATED TEMPERATURE RESISTANCE OF CEMENT MORTARS CONTAINING NATURAL ZEOLITE

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ABSTRACT

In this paper, the effect of sodium carbonate (Na_2CO_3) on the flexural and compressive strength of cement mortars containing natural zeolite subjected to high temperatures were examined. The results obtained from the tests were compared with the reference mortars. In the mortar mixtures, sand and water quantities were kept constant. Water/binder and sand/binder ratios were 0.5 and 3.0, respectively. In the mixtures, the crushed sand was used and ordinary Portland cement (OPC) was replaced with 5, 10, 15 and 20% natural zeolite by weight. For activation of zeolite, sodium carbonate having 7% Na dosage was used as an activator. The findings showed that the resistance of mortars subjected to high temperatures were dependent on the temperature level, and that the fire resistance of zeolite mortars was higher than that of mortar made with OPC only. Additionally, it was seen from the test results that Na_2CO_3 used for activation in zeolite mortars led to a decrease in the flexural and compressive strength values after the high temperatures.

Keywords: *Fire Resistance, Mortar, Zeolite, Activator*

1. INTRODUCTION

Portland cement is an important building material that is incorporated into concrete and is widely used today in the world. However, remarkable energy requirements and significant emissions of carbon dioxide to atmospheres as well as the use of natural resources lead to serious environmental problems in the production of cement. High energy costs and environmental problems resulting from the production process make it necessary to develop sustainable binder systems that can be an alternative to cement in the construction industry. One of the alternative methods of reducing cement consumption is the use of pozzolans in concrete production. The use of pozzolans in the construction sector, where building elements in large volumes are produced, will not only save energy but will also contribute to the solution of environmental problems. One of the pozzolans that can be used in concrete is natural zeolites that have emerged as an important binder material in recent years. Zeolite tuffs contain alumina silicate just as pozzolans which are used as additives in cement (Lea, 1970; Poon *et al.*, 1999). Studies performing on pozzolanic activity have shown that zeolitic tuffs have excellent pozzolanic activity (Drzaj *et al.*, 1978), and they are more reactive than glassy materials in terms of lime fixation (Massazza, 1998; Sersale, 1995). Their some physical and chemical properties such as low specific gravity, pore structure and silica content enable zeolites to be used in many industrial areas like pollution management, energy, agriculture, stock farming and mine metallurgy (Kurudirek *et al.*, 2010; Bilim, 2014). They also possess special properties such as ion exchange, molecular sieves, a large surface area and catalytic activity (Breck, 1971). The investigations on concretes containing natural zeolite have shown that zeolite improves concrete properties and can be used in high performance concrete production due to its high pozzolanic activity (Feng *et al.*, 1990; Perraki *et al.*, 2003; Canpolat *et al.*, 2004). Natural zeolites have good pozzolanic activity and their use as partial replacement of OPC lead to an increase in durability of cement and concrete composites (Najimi *et al.*, 2012). The use of natural zeolite in concrete causes less strength loss in early ages and contributes to the development of strength by reducing the porosity of the binder material (Poon *et al.*, 1999). Due to the pores in the structure of natural zeolites, superplasticizing chemical admixture is needed in the mixture (Fragoulis *et al.*, 1997; Quanlin and Naiqian, 2005). Natural zeolite also prevents the undesirable expansions resulting from sulfate attack and alkali aggregate reaction (Janotka and Števula, 1998; Uzal *et al.*, 2003). Other hand, the studies carried out in recent years have showed that natural pozzolan as well as industrial wastes could be used as raw materials in geopolymer binders (Allahverdi *et al.*, 2008). In other study, Yousef *et al.* (2009) produced geopolymer concrete samples using Jordan zeolitic tuffs and compared them with kaolin incorporated geopolymers. According to the experimental data, the compressive strength of geopolymers containing zeolitic tuff was higher than that of kaolin added geopolymers. Furthermore, the samples containing zeolitic tuffs had lower densities and higher water absorption rates. As a result, they concluded that zeolitic tuffs could be utilized in geopolymer production. Additionally, Davidovits (2008) have noted that geopolymerization of alumina silicate-containing materials such as fly ash, coal slag, blast furnace slag, silica fume, volcanic tuff, depends on the applied temperature and duration.

As seen, various research results on this material have been reported. The findings have showed that it is possible to evaluate natural zeolites, which are present in great quantities in our country, as a cementitious material instead of industrial by-products such as silica fume, fly ash and blast furnace slag in case of some factors such as not being close to the industrial waste zone, expenditures in transporting the waste, harmful compounds in the waste. In addition to the limited data obtained from the tests, the lack of research on the use of natural zeolites as a cement / concrete mineral admixture is negatively affecting the widespread use of natural zeolites in the construction sector. In order to overcome this problem, more research findings need to be published in the literature and still, many properties related to zeolite wait to be explored. For example, fire resistance of mortars and concretes with zeolite has received almost no attention. Therefore, within the scope of this paper, the compressive and flexural strengths of zeolite incorporated mortars with and without Na_2CO_3 subjected to high temperatures were investigated.

2. EXPERIMENTAL PROGRAM

In the study, OPC conforming to the requirements of TS EN 197-1 (2012) class 42.5R was used as reference binder. Table 1 presents chemical compositions and physical properties for OPC and ground natural zeolite supplied by Manisa/Gördes region. On the other hand, Fig. 1 shows the mineralogical results investigated by using X-ray diffraction (XRD; Rigaku, Tokyo, Japan, Miniflex II with a nickel filtered Cu Kα) for natural zeolite which consists of clinoptilolite as the primary phase, and which contains small amounts of quartz.

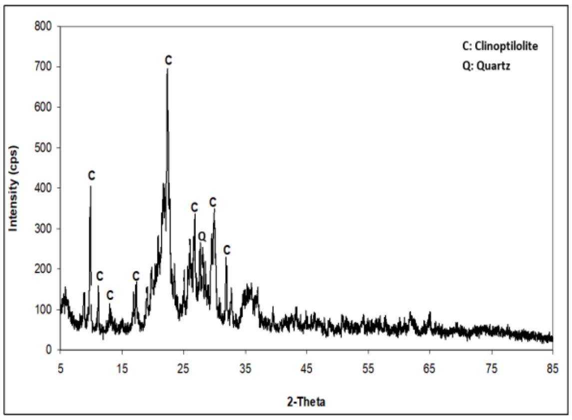

Fig. 1. XRD analysis of Gördes natural zeolite

In the mixtures, superplasticizer, drinkable tap water and crushed sand with a maximum size of 4 mm were used. While determining superplasticizer dosages, the flow values of zeolite incorporated mortars were maintained in the vicinity of ± 10% of the flow value obtained from OPC mortar. Cement was replaced with 5, 10, 15 and 20% zeolite by weight. A w/b ratio of 0.5 was used to prepare mortar samples. The sand to cementitious binder ratio was 3:1. In the mortars containing Na_2CO_3, the Na dosage was 7% according to mass of zeolite.

Table 1. Chemical compositions and physical properties of cement and zeolite

Oxides (%)	Cement	Zeolite	Physical properties of Portland cement	
SiO_2	20.65	63.01	Specific gravity	3.15
CaO	63.15	3.87	Initial setting time (min)	186
Al_2O_3	4.75	10.72	Final setting time (min)	230
Fe_2O_3	3.05	2.68	Volume expansion (mm)	1.0
MgO	3.55	1.07	Blaine specific surface (cm^2/g)	3250
SO_3	2.52	0.22	Compressive strength (MPa) of cement	
Na_2O	0.13	0.23	2 days	27.8
K_2O	0.74	3.80	7 days	42.1
LOI	1.10	14.00	28 days	52.3
IR	0.94	-	Physical properties of zeolite	
Free CaO	0.91	-	Specific gravity	2.17
			Specific surface (Blaine) (cm^2/g)	9660
			Pozzolanic activity index (%) of clinoptilolite	
			7 days	58
			28 days	81

A summary of the experimental program is presented in Table 2.

Table 2. The experimental program

Mix.	Cement	Zeolite	Superplasticizer	Na
Z0	100%	-	-	-
Z5	-	5%	1.25%	-
Z10	-	10%	2.30%	-
Z15	-	15%	3.50%	-
Z20	-	20%	4.50%	-
Z5N	-	5%	1.50%	7%
Z10N	-	10%	2.70%	7%
Z15N	-	15%	4.00%	7%
Z20N	-	20%	5.00%	7%

To produce the mortars, firstly, superplasticizer added water, Na_2CO_3 and zeolite were placed in the mortar mixer and blended in slow mode for 30 s and then, the crushed sand was poured for 30 s while continuing to mix in slow mode. Next, the mixture was blended in fast mode for 30 s and then stopped and held for 15 s, followed by further mixing for 60 s in fast mode (TS EN 196-1, 2009). Eventually, the fresh mortar mixtures were taken from the mixer and cast into sample moulds with 40 x 40 x 160 mm dimensions. Then, to obtain a good compaction, the samples were jolted 60 times in 1 min. Samples were demoulded 24 h after casting and were kept in water at a temperature of 20 °C for 27 days. After the curing period, the samples were removed from water and the test procedure was performed. For the elevated temperature resistance tests, three samples of each mortar mixture were exposed to 300, 600 and 900 °C temperatures for 1 h in furnace. The heating rate was set at 5 °C/min up to reach the target temperature. Then, the hot mortar samples were kept in furnace. After the cooling period to laboratory temperature, the compressive and flexural strength values of samples were determined according to TS EN 1015-11 (2000). The compressive strength test was carried out using six broken pieces of test prisms remained from the flexural strength tests performed on three samples. The test results were compared with those of unheated control mortar at 20 °C.

3. RESULTS AND DISCUSSION

3.1. Residual Compressive Strength after High Temperatures

The residual compressive strength results of mortars after exposure to 300, 600 and 900°C temperatures are presented in Table 3.

Table 3. Compressive strengths of mortars (MPa)

		Cooled in furnace		
	20°C	300°C	600°C	900°C
Z0	53.48	55.11	16.69	2.06
Z5	54.22	58.25	26.00	9.29
Z10	54.74	59.10	32.21	9.69
Z15	42.52	48.83	31.81	5.26
Z20	39.91	47.85	24.96	4.15
Z5N	33.00	34.52	24.14	3.94
Z10N	36.15	32.44	25.89	4.07
Z15N	27.30	29.78	20.08	1.78
Z20N	26.59	28.86	18.10	1.53

According to Table 3, at 20 °C, the OPC mortar (Z0) achieved a compressive strength of 53.48 MPa while the compressive strengths of the mortars containing zeolite ranged from 39.91 MPa to 54.74 MPa. The increment up to 10% in zeolite content of mixtures increased the compressive strength values for mortar specimens at this temperature (20 °C). For example, the increment in the compressive strength of mortar containing 10% zeolite (Z10) was approximately 3%, compared to the mixture containing 100% OPC (Z0). In zeolite mortars containing Na_2CO_3, the compressive strengths values ranged from 26.59 MPa to 36.15 MPa. The increase in zeolite amount of mixture for a constant Na dosage of 7% decreased the compressive strengths for mortar specimens at 20 °C.

At 300 °C, the compressive strengths of zeolite incorporated mortars ranged from 47.85 MPa to 59.10 MPa while the compressive strength of OPC mortar (Z0) was 55.11 MPa. The increase up to 10% in zeolite amount increased the compressive strength values for mortar specimens at this temperature (300 °C). For example, the increment in the compressive strength of mortar containing 10% zeolite (Z10) was approximately 7% in comparison with 100% OPC mortar (Z0). The compressive strengths values ranged from 28.86 MPa to 34.52 MPa for Na_2CO_3 added mortars containing zeolite. Namely, the use of Na_2CO_3 in zeolite mortars reduced the compressive strength values at 300 °C. Additionally, an increase was observed in the compressive strengths of all mortar samples exposed to 300 °C temperature in comparison with the mortar samples at 20 °C. This increase observed in strength may depend on the relief of pressures in the course of drying, which also leads to greater van der Waals forces resulting from a closer formation of capillary pores (Aydın *et al.*, 2008).

After 600 °C, although the compressive strength of all mortars began to decrease seriously, the performance of mortars containing zeolite was better than OPC mortar. For example, at 900 °C, the compressive strength of OPC mortar (Z0) was 2.06 MPa while the compressive strengths of zeolite added mortars were between 4.15 MPa and 9.69 MPa. At this temperature, the mortar with the highest strength was the Z10 mixture having 10% zeolite content. Other hand, the mortars containing Na_2CO_3 had the lowest compressive strengths among zeolite added mortars. The compressive strengths of these mortars varied between 1.53 MPa and 4.07 MPa. These significant losses occurring in the compressive strength values of mortars after 900°C temperature may be attributed to the disintegration of calcium silicate hydrate gel (Poon *et al.*, 2001; Xu *et al.*, 2001).

3.2. Residual Flexural Strength after High Temperatures

The residual flexural strength results of mortars after exposure to 300, 600 and 900°C temperatures are presented in Table 4.

Table 4. Flexural strengths of mortars (MPa)

		Cooled in furnace		
	20°C	300°C	600°C	900°C
Z0	10.31	7.70	2.39	1.27
Z5	10.97	9.72	3.60	2.13
Z10	10.69	9.07	4.66	1.75
Z15	9.68	8.51	4.71	1.36
Z20	8.84	8.10	3.37	1.00
Z5N	7.36	6.05	4.06	2.03
Z10N	7.50	6.45	4.08	2.41
Z15N	7.17	3.42	2.16	1.01
Z20N	7.52	2.69	1.05	0

As seen in Table 4, at 20 °C, the flexural strength of OPC mortar (Z0) was 10.31 MPa while the flexural strengths of the mortars containing zeolite varied from 8.84 MPa to 10.97 MPa. The zeolite substitution made after 10% in the mixtures began to decrease the flexural strength values for mortar specimens at this temperature (20 °C). Moreover, it was seen that the addition of Na_2CO_3 having a Na dosage of 7% into mixtures containing zeolite negatively affected the flexural strength. As a result of this, zeolite incorporated mortars containing Na_2CO_3 exhibited the flexural strengths ranging from 7.17 MPa to 7.52 MPa.

The harmful effects of high temperatures on the flexural strength were more evident than the case in the compressive strength. In this regard, although all mortars increased their compressive strength up to 300°C, they lost the flexural strengths as from 300 °C. On other hand, at 600 °C, the flexural strengths for all of mortars were between 1.05 MPa and 4.71 MPa while they showed the flexural strength values varying from 1.01 MPa to 2.41 MPa at 900 °C temperature. Also, the flexural strength of the mortar (Z20N) containing 7% Na and 20% zeolite could not be determined at 900 °C. The explanation for these low flexural strengths obtained from the tests is as follows: thermal cracks occur from the important temperature differences between the core and the surface of sample cross section (Kong and Sanjayan, 2010). The presence of these cracks decreases the valid area of cross sections and the existence of tensile stresses below the neutral axis in the samples exposed to the flexural test brings about the increase in size of cracks (Özturan and Cülfik, 2002; Xu *et al.*, 2003; Li *et al.*, 2004). Therefore, the effect of cracks on the flexural strength value is more evident than on the compressive strength value due to the drop in the valid area of cross section which resists the stresses (Bilim, 2014). Also, the mixtures containing Na_2CO_3 had the lowest flexural strengths among zeolite mortars for both 600 °C and 900 °C temperatures.

4. CONCLUSION

The following conclusions can be drawn from this study:

1. The replacement of zeolite up to 10% with OPC improved the mechanical strengths of mortars kept at room temperatures. Additionally, all mortars containing zeolite showed generally better performance to high temperatures such as 900 °C than OPC mortar.
2. The resistances of mortars subjected to elevated temperatures were determined to be dependent on the temperature level.
3. The detrimental effect of high temperatures on the flexural strength was more severe than the case in the compressive strength.
4. It was seen that the use of Na_2CO_3 as an activator in mortars containing zeolite reduced both the compressive strengths and the flexural strengths for all temperatures studied within the scope of this research. For this reason, it is considered that the researches on the mixtures containing zeolite activated by different alkaline activators such as water glass or sodium hydroxide should be carried out.

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