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Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production

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Abstract

In this research, the effects of zeolite, coal bottom ash and fly ash as Portland cement replacement materials on the properties of cement are investigated through three different combinations of tests. These materials are substituted for Portland cement in different proportions, and physical properties such as setting time, volume expansion, compressive strength and water consistency of the mortar are determined. Then, these physical properties are compared with those of PC 42.5. The results showed that replacement materials have some effects on the mechanical properties of the cement. The inclusion of zeolite up to the level of 15% resulted in an increase in compressive strength at early ages, but resulted in a decrease in compressive strength when used in combination with fly ash. Also, setting time was decreased when zeolite was substituted. The results obtained were compared with Turkish Standards (TS), and it was found that they are above the minimum requirements.

Keywords: Fly ash; Zeolite; Pozzolan; Compressive strength; Expansion

1. Introduction

In recent studies, various types of materials such as silica fumes, fly ash and coal bottom ash have been investigated as Portland cement replacement materials [1–3]. Their substitution in Portland cement has been an interesting subject for research due to environmental and technical reasons. Clearly, different substitution materials will have different effects on the properties of the cement due to their chemical, physical and mineralogical characteristics [4,5].

The previous research has concluded that fly ash lowers the early heat of hydration and gives better durability compared to plain Portland cement due to alkali–silica reaction [6]. Low-quality fly ash is adequate for cement mixes because it has sufficient resistance to sulfate corrosion [7]. Addition of alkali-activated fly ash to the blended cement mixes improves the mechanical strength of the concrete [8]. Compressive strength of the concrete decreases with increasing silica, alumina and iron(III) oxide content [9]. With adequate grinding, coal bottom ash with pozzolanic activity can be used as a replacement material in Portland cement production [10].

Natural zeolite contains large quantities of reactive SiO_2 and Al_2O_3 [11]. Similar to other pozzolanic materials such as silica fumes and fly ash, zeolite substitution can improve the strength of concrete by the pozzolanic reaction with $Ca(OH)_2$. In general, natural zeolite, like other pozzolanic materials, contributes to the strength of concrete better than the strength of cement [12]. Natural zeolite also prevents the undesirable expansion due to alkali–aggregate reaction. In this study, the physical properties of zeolite (Z), coal bottom ash (BA) and fly ash (FA) and their effects on the mechanical properties of cement were examined. The objective of this research is to compare the chemical and physical properties of the cement mixes.

2. Materials and methods

2.1. Materials

The zeolite used was obtained from natural deposits in Manisa while the fly ash and the coal bottom ash were

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obtained from the Soma and the Etibank Soma thermal plants in Manisa, Turkey, respectively. The chemical compositions of zeolite and fly ash were determined by an X-ray fluorescence spectrometer. The chemical compositions and physical characteristics of the materials are given in Table 1.

2.2. Cement mixtures

Three series of mixtures and reference mixtures were prepared according to Turkish Standards (TS) [13]. The reference mixture, designated as R, was composed of ordinary Portland cement (PC) type PC 42.5, which has a 28-day compressive strength of 42.5 MPa. The other series of mixtures were designated as follows: A for PC + Z, B for PC + Z + FA and C for PC + Z + BA. The details of the mixtures are given in Table 2.

2.3. Specific surface, grinding time and specific gravity

The specific surface, grinding time and specific gravity of the different combinations of cement mixtures are shown in Table 2. Zeolite, which is a softer material than the Portland clinker, increases the fineness of the ground material and reduces the grinding time. When the ratio of zeolite substitution was increased to 35%, grinding time was reduced to 30%. Therefore, using zeolite as a replacement material in cement reduces the production cost. In addition, when the ratio of substituted materials was increased, specific weight was also reduced. As seen from Table 1, the specific weights of zeolite and fly ash are less than that of the clinker.

2.4. Volume expansion, water percentage and setting time

The volume expansion, water percentage and setting time of the different combinations of cement mixtures are shown in Table 3. Volume expansions of zeolite-substituted cement mixtures were below the limits given by TS 10156. From the results of the experiments, it is observed that there is no trend between the ratio of substituted materials and the volume expansion of the mixtures.

Water percentage increased when the ratio of zeolite was increased. Zeolite-substituted cements needed lower water percentages than Z + FA- and Z + BA-substituted cements. This difference comes from the increase in spe-

Table 1
Physical and chemical characteristics of materials used

	Clinker	Natural zeolite	Fly ash	Coal bottom ash
Chemical analysis (wt.%)				
SiO_2	19.43	62.17	42.81	44.26
Al_2O_3	5.78	9.76	23.03	21.48
Fe_2O_3	3.69	2.02	5.33	6.40
CaO	63.34	1.43	21.60	17.57
MgO	0.66	0.75	1.81	1.29
SO_3	0.74	0.07	3.39	2.17
KK	0.20	14.06	1.28	14.10
Na_2O	0.29	0.46	0.34	0.29
K_2O	0.68	3.72	1.38	0.77
Free CaO	1.44	–	3.17	0.32
Physical analysis				
Specific gravity (g/cm^3)	3.18	2.19	2.43	2.39
Specific surface (cm^2/g)	1860	8150	3340	830
Fineness (wt.%)				
+ 32 μm	25.6	32.20	22.31	27.3
+ 90 μm	2.7	6.10	1.70	7.4

Table 2
Physical analysis of cement mixtures

Symbol	Cement mixtures	Fineness (wt.%)		Grinding time[a] (min)	Specific surface (cm^2/g)	Specific weight (g/cm^3)
		+ 32 μm	+ 90 μm			
R	Reference mix PC 42.5	27.4	2.2	20	2850	3.13
A_1	5% Z + 95% PC	26.7	1.9	35	5350	3.09
A_2	10% Z + 90% PC	25.4	2.1	33	5520	3.02
A_3	15% Z + 85% PC	24.5	2.2	29	5640	2.96
A_4	20% Z + 80% PC	24.8	2.2	26	5700	2.88
A_5	25% Z + 75% PC	25.0	2.4	22	5760	2.83
A_6	30% Z + 70% PC	24.9	2.3	19	5880	2.80
A_7	35% Z + 65% PC	25.1	2.3	17	6130	2.74
B_1	5% Z + 5% FA + 90% PC	22.6	2.0	30	4270	3.08
B_2	10% Z + 5% FA + 85% PC	22.5	1.9	28	4300	2.98
B_3	15% Z + 5% FA + 80% PC	22.3	2.1	26	4350	2.96
B_4	20% Z + 5% FA + 75% PC	23.1	2.2	25	4460	2.86
B_5	25% Z + 5% FA + 70% PC	23.4	2.2	22	4550	2.84
B_6	30% Z + 5% FA + 65% PC	26.1	2.0	20	4690	2.74
B_7	35% Z + 5% FA + 60% PC	27.7	2.0	18	4770	2.72
C_1	5% Z + 5% BA + 90% PC	25.2	2.3	32	4710	3.01
C_2	10% Z + 5% BA + 85% PC	25.5	2.1	30	4790	2.98
C_3	15% Z + 5% BA + 80% PC	25.3	2.1	27	4830	2.96
C_4	20% Z + 5% BA + 75% PC	26.5	2.2	25	4890	2.86
C_5	25% Z + 5% BA + 70% PC	26.2	2.3	23	4910	2.82
C_6	30% Z + 5% BA + 65% PC	28.3	2.2	21	4990	2.78
C_7	35% Z + 5% BA + 60% PC	28.9	2.0	19	5130	2.72
	TS 10156[b]	–	< 14.0	–	> 2800	–

[a] Time required to reach specified fineness by grinding a 2500-g sample.
[b] Standard of additive cement.

Table 3
Water percentage, setting time and volume expansion of the cement mixtures

Symbol	Cement mixtures	% of water	Setting time (h:min)		Volume expansion (mm)
			Beginning of setting	End of setting	
R	Reference mix PC 42.5	25.4	2:37	4:37	2
A_1	5% Z + 95% PC	29.2	3:17	4:42	2
A_2	10% Z + 90% PC	29.0	3:37	4:42	4
A_3	15% Z + 85% PC	30.5	2:41	3:31	3
A_4	20% Z + 80% PC	31.0	2:45	3:37	3
A_5	25% Z + 75% PC	32.5	2:36	3:41	4
A_6	30% Z + 70% PC	33.5	1:26	2:26	4
A_7	35% Z + 65% PC	34.5	1:41	2:52	6
B_1	5% Z + 5% FA + 90% PC	28.8	2:58	3:48	3
B_2	10% Z + 5% FA + 85% PC	29.8	3:16	4:32	2
B_3	15% Z + 5% FA + 80% PC	29.5	3:38	4:33	2
B_4	20% Z + 5% FA + 75% PC	32.5	2:42	3:47	6
B_5	25% Z + 5% FA + 70% PC	35.6	2:58	3:39	5
B_6	30% Z + 5% FA + 65% PC	35.7	2:06	3:01	3
B_7	35% Z + 5% FA + 60% PC	35.0	2:16	2:46	4
C_1	5% Z + 5% BA + 90% PC	29.0	3:17	4:22	3
C_2	10% Z + 5% BA + 85% PC	29.5	3:21	4:12	7
C_3	15% Z + 5% BA + 80% PC	30.0	3:34	3:56	5
C_4	20% Z + 5% BA + 75% PC	31.5	2:46	3:36	4
C_5	25% Z + 5% BA + 70% PC	33.0	2:47	3:22	5
C_6	30% Z + 5% BA + 65% PC	35.8	2:40	3:41	5
C_7	35% Z + 5% BA + 60% PC	36.5	2:47	3:32	4
	TS 12142[a]	–	At least 1:00	–	At most 10

[a] Standard of composite cement.

cific surface of the compositions. When the ratio of substituted materials increased, the specific surface of the mixtures also increased. Therefore, when the ratio of substituted materials increased for the same weight of mixtures, more water was needed. This increase in water volume reached up to 20% when the ratio of substituted materials was 35%.

Setting times are within the limits given in TS 10156. Setting times decreased when water percentage increased. The decrease in setting time was evident at the beginning of setting times of zeolite-substituted cements. When the ratio of substituted materials was increased, setting time decreased. This decrease in setting time due to fineness of the cement can be explained in this way: When zeolite is ground with clinker, the fineness of the cement increases; hence, the hydration process becomes faster, and that reduces setting time.

Table 4
Compressive strength of cement mixtures

Symbol	Cement mixtures	Compressive strength (N/mm^2)			
		2 days	7 days	28 days	90 days
R	Reference mix PC 42.5	21.2 (47)	34.4 (76)	45.1 (100)	57.6 (128)
A_1	5% Z + 95% PC	25.2 (56)	38.6 (86)	52.5 (116)	55.7 (124)
A_2	10% Z + 90% PC	23.5 (52)	36.8 (82)	51.3 (114)	53.6 (119)
A_3	15% Z + 85% PC	22.1 (49)	33.5 (74)	52.8 (117)	56.8 (126)
A_4	20% Z + 80% PC	17.8 (39)	30.7 (68)	54.2 (120)	58.5 (130)
A_5	25% Z + 75% PC	14.2 (31)	25.6 (57)	49.8 (110)	57.2 (127)
A_6	30% Z + 70% PC	13.4 (30)	26.8 (59)	47.8 (106)	58.5 (130)
A_7	35% Z + 65% PC	11.7 (26)	22.2 (49)	46.2 (102)	53.5 (119)
B_1	5% Z + 5% FA + 90% PC	20.8 (46)	29.6 (66)	49.5 (110)	56.2 (125)
B_2	10% Z + 5% FA + 85% PC	19.4 (43)	33.8 (75)	51.4 (114)	58.7 (130)
B_3	15% Z + 5% FA + 80% PC	17.8 (39)	28.4 (63)	51 (113)	59.4 (132)
B_4	20% Z + 5% FA + 75% PC	15.4 (34)	26.2 (58)	50.8 (113)	60.8 (135)
B_5	25% Z + 5% FA + 70% PC	14.4 (32)	27.3 (61)	50.8 (113)	58.3 (129)
B_6	30% Z + 5% FA + 65% PC	11.8 (26)	24.2 (54)	47.6 (106)	54.3 (120)
B_7	35% Z + 5% FA + 60% PC	9.6 (21)	23.1 (51)	43.3 (96)	50.4 (112)
C_1	5% Z + 5% BA + 90% PC	20.5 (45)	33.8 (75)	53.6 (119)	61.3 (136)
C_2	10% Z + 5% BA + 85% PC	18.5 (41)	33.4 (74)	54.1 (120)	58.4 (129)
C_3	15% Z + 5% BA + 80% PC	15.5 (34)	29.6 (66)	52.7 (117)	57.9 (128)
C_4	20% Z + 5% BA + 75% PC	13.9 (31)	26.8 (59)	48.9 (108)	56.7 (126)
C_5	25% Z + 5% BA + 70% PC	13.7 (30)	26.6 (59)	50.2 (111)	54.1 (120)
C_6	30% Z + 5% BA + 65% PC	11.6 (26)	24.1 (53)	46.8 (104)	51.3 (114)
C_7	35% Z + 5% BA + 60% PC	11.9 (26)	21.9 (49)	45.6 (101)	48.9 (108)
	TS 12142–TS 12144	≥ 10	–	42.5–62.5	–
	TS 26–TS 10156	≥ 10	>21.0	>32.5	–

Values inside parentheses show the percentages with respect to the 28-day compressive strength of PC 42.5.

2.5. Compressive strength

The compressive strengths of zeolite-substituted cement pastes and the reference sample (PC 42.5) are given in Table 4. Compressive strengths of the cement pastes were normalized by the compressive strength of the reference sample on the 28th day. As seen in Table 4, when the ratio of zeolite is 15%, compressive strength increases with respect to the reference mixture. At later times, the strengths of the mixtures get closer to each other. In this category, the optimum substitution ratio becomes 20% for all ages of cement pastes. In the first 7 days, the compressive strength of the zeolite-substituted cement paste decreased when the ratio of zeolite increased.

3. Results and discussion

This study was conducted to examine the effects of zeolite, zeolite + fly ash and zeolite + coal bottom ash on the properties of the cement. The properties of the materials used are given in Table 1. In this table, the SiO_2, Fe_2O_3, Al_2O_3, MgO and SO_3 contents of ash samples are reasonable with TS.

The results of the physical analysis of the cement mixtures, which are fineness, specific surface, specific weight and grinding time, are given in Table 2. As shown in Table 2, when fineness of the cement is increased, setting time decreases. The water percentage, setting time and volume expansion of the cement mixtures are given in Table 3. The setting time and water demand of cement mixtures are different. These differences may arise from the fineness and free CaO content of cement mixes. Also, setting time decreases when water percentage increases. The decrease in setting time was very clear at the beginning of setting times of zeolite-substituted cements. When the ratio of substituted materials is increased, the specific surface also increases and grinding time decreases, as seen in Table 3, thereby reducing the production cost. When the ratio of substituted materials is increased, specific weight decreases. The volume expansion of zeolite-substituted cement mixtures is within the limits given in TS 10156. However, there is no trend between the ratio of substituted materials and the volume expansion of the mixtures. Water percentage increased when the ratio of zeolite is increased. Zeolite-substituted cements need lower water percentages than Z + FA-substituted cements.

The compressive strength of the cement is directly related to the structure of the concrete. The compressive strengths of the cement mixtures at various ages (2, 7, 28 and 90 days) are given in Table 4. At the age of 2 days, the reference mixture shows a higher value of compressive strength than those of the B and C series of mixtures. In addition, the mixtures with fly ash (B_1, C_1) show results close to those of the reference mixture. The mixture B_5 has the lowest value of compressive strength at the age of 2 days. The poor performance of this mixture is due to its high content of bottom ash, which did not contribute sufficiently to the strength at this very early age because of its relatively low reactivity. At the age of 7 days, there was a continuing improvement in the performance of the mixtures, and all observed values comply with the TS 639 requirement [3]. When curing was extended to 28 days, a dramatic increase in the performance of the mixtures was noticed. Most of the compressive strength values of all the cement mixes are better than that obtained from the reference mixture. This is probably due to the large pozzolanic contribution of the fly ash and bottom ash [3]. As can be seen from Table 4, at 90 days, a similar general trend as in the 28-day strength data was observed. Most of the fly ash and bottom ash mixtures show compressive strength values better than that of the reference mixture.

4. Conclusion

Cement mixtures obtained in this study by the substitution of zeolite, fly ash and coal bottom ash require less amount of clinker, which results in increases in production and savings in energy, thereby reducing air pollution by decreasing the emission of CO_2 and other gases. Mineral-substituted cement mixtures can have a big market share in the future since the emission limits on CO_2 and other gases are being applied in the cement industry. This shows that an investment on mineral-substituted cement has economical and ecological advantages.

Examination of the chemical properties of the cement mixtures (see Table 1) showed that harmful materials such as CaO, MgO and SO_3 can damage the volume stability. The ratio of these materials in cement mixtures should be kept under the values given in the specifications. In this study, when the ratio of CaO was less than 2%, there was no such volume increase that may cause any problem. The ratio of MgO was less than 5% as specified in TS 19. Because the chemical properties of the cement mixtures obtained in this study are comparable with the specifications, these cement mixtures can successfully be produced as an alternative to Portland cement.

As seen in Table 4, when the ratio of zeolite is 15%, compressive strength increases with respect to the reference mixture. At later times, the strengths of the mixtures get closer to each other. In this category, the optimum substitution ratio becomes 20% for all ages of cement pastes. In the first 7 days, the compressive strength of the zeolite-substituted cement paste decreased when the ratio of zeolite increased.

Based on results of this study, the production of Portland cement with a substitution rate of up to 20% zeolite or 5% zeolite + 5% fly ash or 5% zeolite + 5% coal bottom ash seems possible, providing adequate strengths required by TS. Such a production would be an economical alternative to conventional Portland cement as well as an environmentally friendly solution.

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