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Effects of colemanite waste, cool bottom ash, and fly ash on the properties of cement

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Abstract

In this study, the physical and chemical properties of colemanite ore waste from concentrator, coal bottom ash, fly ash, cement + ash mixtures, cement + colemanite ore waste, and their effects on the mechanical properties of concrete were investigated. These materials with different proportion were substituted with Portland cement. Physical properties such as setting time, volume expansion, and compressive strength were determined and compared to reference mixture and Turkish standards (TS). The results showed that cement replacement materials had clear effects on the mechanical properties. The use of fly ash and bottom ash even at the concentration of 25% showed either comparable or better result compared to reference mixture. Although replacement of Portland cement by 9 wt.% of colemanite ore waste causes reduction in the compressive strength, the values obtained are within the limit of TS. As a result, colemanite ore waste, fly ash, and bottom ash may be used as cementitious materials. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of various types of waste materials as additives in the production of cement and concrete has received substantial attention during recent years. The research has confirmed that ground granulated blast furnace slag (GGBS) and fly ash addition to the cement has considerable effects on the heat of hydration. GGBS and fly ash lower early heat of hydration compared to a plain normal Portland cement [1–4]. The total amount of steel slag and fly ash could reach up to 50% in composite Portland cement [5]. Fly ash addition to the glass fiber-reinforced cement decreases the flexural strength of the samples under accelerated aging and prevents alkali-resistant fiber from a chemical attack originating from the matrix [6]. Lowquality fly ash is adequate for blending cement mixes because it has satisfactory resistance to sulfate corrosion

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[7]. Alkali-activated fly ash addition to cement mixes notably influence the development of the mechanical strength of the product [8]. Compressive strength of concrete decreases as the total silica, alumina, and iron-III oxide contents are increased [9].

Although, the utilization potential of fly ash is mainly controlled by its chemical composition and fineness, the utilization potential of bottom ash is determined by its physical characteristics such as grain size, staining potential, and color. With adequate grinding, the pozzolanic activity of bottom ash can be improved and be used as a low-cost replacement for more expensive sands in concrete [10].

In our previous study, the effects of colemanite ore waste as mineral admixture in Portland and trass cement were investigated [11]. Colemanite wastes were added to Portland and trass cements in 1, 3, 5, and 7 wt.% proportion. The result showed that colemanite waste could be used as cement additive up to 5 wt.% of cement.

In this study, the physical properties of the colemanite ore waste (CW) obtained from concentrator, fly ash (FA),

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Table 1 Physical and chemical characteristics of used material

	Clinker	Colemanite waste	Fly ash	Bottom ash	Gypsum
Chemical analysis (wt.%)					
SiO_2	21.47	18.02	56.13	50.98	_
Al_2O_3	6.04	3.73	18.49	14.96	0.05
Fe_2O_3	3.78	0.98	11.38	9.63	_
CaO	65.49	22.83	2.52	2.63	32.93
MgO	1.44	6.99	3.79	4.01	0.04
SO_3	1.12	0.54	0.05	0.16	45.95
Na ₂ O	_	2.02	0.71	0.47	_
K_2O	0.93	1.41 2.17		1.30	0.01
B_20_3	_	17.65	_	_	_
Loss on ignition	0.20	22.75	4.20	15.70	21.13
Free CaO	e CaO 0.85				_
Water	ter –		_	_	19.35
Physical analysis					
Fineness (wt.%)					
+40 μm	25.8	26.5	25.7	24.2	_
+ 90 μm	•		5.9	5.6	_
+ 200 μm	0.30	0.4	0.5	0.3	_
Specific surface (cm ² /g)	2400	3602	6418	7200	_
Specific gravity (g/cm ³)	3.20	2.13	1.81	1.98	_

bottom ash (BA), cement + FA, cement + BA, cement + CW, cement + CW + FA, cement + CW + BA, and their effects on the mechanical properties were studied. The objective of this study is to compare the chemical and physical properties of cement mixes.

2. Materials and methods

Clinker and gypsum were supplied from Set Cement Plant (Balıkesir, Turkey), Bottom ash and fly ash from Seyitömer thermal plant (Kütahya, Turkey), colemanite

Table 2
Physical characteristics of cementitious mixes

Symbol		Fineness (wt.%	b)	Specific surface	Specific gravity
	Cement mixes	+40 μm	+90 μm	(cm ² /g)	(g/cm^3)
R	Reference mix	25.0	1.1	2965	3.23
A_1	1% CW + 99% PC	25.0	1.0	3139	3.14
A_2	3% CW + 97% PC	25.1	1.1	3183	3.11
A_3	5% CW + 95% PC	24.9	0.8	3223	3.06
A_4	7% CW + 93% PC	24.8	0.8	3228	3.02
A_5	9% CW+91% PC	25.1	1.0	3445	2.96
F_1	5% FA+95% PC	24.9	0.9	3068	3.19
F_2	10% FA+90% PC	25.2	1.0	3225	3.05
F_3	15% FA+85% PC	25.0	0.8	3563	2.98
F_4	20% FA+80% PC	24.9	0.9	3842	2.95
F ₅	25% FA + 75% PC	25.1	0.8	4363	2.86
B_1	5% BA+95% PC	24.8	0.8	3439	3.16
B_2	10% BA+90% PC	24.9	1.0	3837	3.06
B_3	15% BA+85% PC	25.1	1.1	3956	2.98
B_4	20% BA+80% PC	24.9	0.9	4368	2.89
B_5	25% BA+75% PC	25.2	1.1	4656	2.75
P_1	1% CW + 4% FA + 95% PC	24.9	0.9	3326	3.12
P_2	3% CW + 7% FA + 90% PC	25.1	1.0	3402	3.05
P_3	5% CW + 10% FA + 85% PC	25.0	1.0	3588	3.00
P_4	7% CW + 13% FA + 80% PC	25.0	1.0	3882	2.94
P_5	9% CW + 16% FA + 75% PC	24.8	0.8	4099	2.88
C_1	1% CW + 4% BA + 95% PC	25.1	0.9	2891	2.98
C_2	3% CW + 7% BA + 90% PC	25.0	1.1	2928	2.95
C_3	5% CW + 10% BA + 85% PC	24.8	0.9	3052	2.93
C_4	7% CW + 13% BA + 80% PC	24.9	0.8	3192	2.80
C_5	9% CW+16% BA+75% PC	25.2	1.0	4257	2.87

Table 3
Compressive strength test result for cement mixes

Cement	Compressive strength (N/mm ²)								
mixes	2 days	7 days	28 days	90 days					
TS 639	minimum 10	minimum 21	minimum 32.5	_					
R	21.5	33.6	41.8	54.4					
A_1	17.2	32.0	45.5	52.4					
A_2	17.0	30.5	43.1	50.6					
A_3	16.8	27.6	41.5	49.4					
A_4	15.0	26.8	37.3	47.4					
A_5	13.8	24.5	34.5	46.3					
F_1	21.0	33.5	47.4	59.0					
F_2	17.6	30.0	45.2	58.1					
F_3	16.6	27.6	45.1	56.6					
F ₄	14.7	26.0	43.1	54.0					
F_5	13.4	23.8	40.6	52.3					
B_1	18.2	30.6	48.5	56.8					
B_2	17.8	30.3	47.8	56.0					
B_3	15.8	29.0	46.0	55.1					
B_4	15.8	27.8	44.7	54.8					
B_5	13.0	24.1	44.1	54.0					
P_1	20.0	32.9	46.5	53.5					
P_2	19.2	31.0	45.4	52.5					
P_3	18.5	28.6	44.6	51.6					
P_4	16.5	27.2	42.6	49.7					
P_5	14.4	25.0	41.8	48.4					
C_1	18.4	30.9	44.5	55.0					
C_2	17.5	29.2	43.6	53.2					
C_3	16.5	27.4	42.5	51.3					
C_4	15.2	25.6	40.4	48.9					
C ₅	14.0	24.3	39.0	47.0					

waste from Etibank Boron Plant (Kütahya-Emet, Turkey). The chemical compositions of cement, colemanite waste (waste passing a screen 25-mm aperture), bottom ash (dried at 105° C), and fly ash were done by using X-ray fluorescence spectrometer. B_2O_3 in the colemanite ore waste was determined according to the MTA titration method [12]. The chemical compositions and physical properties of materials are given in Table 1.

Five series of mixtures and one reference mixture were prepared according to Turkish standards (TS) as described in the earlier studies [13]. Reference mixture was prepared out of Portland cement (PC) and designated as R. The other series of mixtures were designated as A, F, B, P, and C. The weight percent of material used for each mixture are given in Table 2. The raw materials mixed in the required proportion were ground in a ceramic lined ball to a fineness of 25 mass% residue on a 40-µm size mesh. The physical tests of cement mixes were done according to TS 24 [13].

The specimen were prepared with cements (0.450 kg) + Rilem Cebureau standard sand (1.350 kg) + tap water (0.225 kg). The cement-water mixtures were stirred at low speed for 30 s, then, with the addition of sand, the mixture were stirred for 5 min. Three $40 \times 40 \times 160$ -mm prismatic specimens for compression testing were made from each mixture. The specimens were cured at 20°C with 95% humidity for 24 h after that, placed in tap water, and cured up to 90 days. Then they were tested in accordance with TS 24 [13].

3. Result and discussion

The compressive strength data observed at various ages (2, 7, 28, and 90 days) are shown in Table 3. At age of 2 days, reference mixture showed the highest value of compressive strength of the mixtures tested. In addition, the mixture with fly ash (F1, P1) showed close results to the reference mixture. The mixture B₅ has the lowest value of the compressive strength at the age of 2 days. The poorest 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 continuing improvement in the performance of the mixtures and all observed values comply with TS 639 requirement [13]. When curing extended to 28 days, a dramatic increase in he performance of the mixtures was noticed. Most of the compressive strength values of all the cement mixes are better than the value obtained from the reference mixture. This was probably due to large pozzolanic contribution of the fly ash and bottom ash [10,14]. As can be seen from Table 3, at 90 days, a similar general trend as the 28-day strength data was observed. Nevertheless, there was a marked difference between the reference mixture and the mixtures. The compressive strength of the mixture containing colemanite

Table 4
Water percent, volume expansion, and setting time test result for cement mixes

Cement	Water	Setting tim	Volume expansion (mm)			
mixes	(%)	Initial	Final	Cold	Hot	Total
TS 639	_	minimum	maximum	_	_	maximum
		1:0	10:0			10
R	27.6	2:40	3:30	1	1	2
A_1	26.7	2:30	3:10	1	1	2
A_2	27.2	2:36	3:25	1	1	2
A_3	28.5	2:40	2:40	1	0	1
A_4	30.1	2:45	3:55	1	1	2
A_5	30.4	2:55	4:15	1	0	1
F_1	28.0	2:45	3:35	1	1	2
F_2	29.7	2:55	3:45	1	1	2
F ₃	31.3	3:05	3:55	1	0	1
F_4	34.7	3:30	4:10	1	0	1
F ₅	35.1	3:50	4:25	0	0	0
B_1	29:1	2:20	3:10	1	0	1
B_2	30:8	2:25	3:10	1	0	1
B_3	31:4	2:35	3:30	1	1	2
B_4	34:2	2:40	3:40	1	1	2
B_5	35:6	2:50	3:50	1	0	1
P_1	27.3	2:30	3:05	0	1	1
P_2	28.5	3:10	4:50	1	1	2
P_3	29.2	3:50	5:40	1	1	2
P_4	31.7	4:20	6:25	1	0	1
P_5	32.0	5:00	7:40	1	1	2
C_1	27.6	3:00	3:55	1	0	1
C_2	28.4	3:50	4:30	1	0	1
C_3	29.8	4:35	5:35	1	1	2
C_4	33.1	5:20	6:55	2	1	3
C_5	34.2	6:05	7:55	2	1	3

Table 5
Comparison of cement mixes and standards

	PC+CW	I	PC+FA	<u>.</u>	PC+BA	1	PC+C	W+BA	PC+C	W+FA	ASTM C-35	
Constituent	Min.a	Max.b	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	TS 639	65 T
$SiO_2 + R_2O_3^c$	29.63	30.25	34.15	45.14	32.11	42.55	32.09	37.57	32.40	38.42	Min. 70.0	Min. 70
CaO	60.77	64.18	48.86	61.46	48.89	61.46	50.71	61.66	49.81	60.77	_	_
MgO	0.346	0.75	0.32	1.05	0.33	1.10	0.36	1.37	0.35	1.33	Max. 5.0	Max. 5.0
SO_3	2.32	3.06	2.12	2.35	2.14	2.52	2.13	2.35	0.88	1.11	Max. 5.0	Max. 5.0
B_2O_3	0.17	1.58	_	_	_	_	0.17	1.58	0.17	1.58	_	_
Loss on ignition	0.82	2.63	0.79	1.62	1.37	4.50	1.42	5.54	0.41	2.63	Max. 10.0	Max. 12.0

^a Minimum.

ore waste decreased to a very significant extent. This may be due to small pozzolanic contribution of colemanite ore waste at this age. Most of the fly ash and bottom ash mixtures showed compressive strength values better than the reference mixture.

Table 4 shows the test results from the determination of water percent, volume expansion, and setting time for cement mixes. As seen from Table 4, setting time and water demand of mixes are different. This difference may arise from fineness and free CaO content of cement mixes.

Comparisons of the mixes are given in Table 5. From Tables 1 and 5, $SiO_2 + R_2O_3$, MgO, and SO_3 content of ash samples are reasonable with TS and ASTM standards. However, there is no any written standard value for B_2O_3 in the cement. It must be pointed out that the presence of B_2O_3 in the colemanite ore waste has remarkable effect on the mechanical properties of cement apart from increased replacement of colemanite ore waste with Portland cement results higher setting time and specific surface.

4. Conclusion

Based on the above results an discussion, the following conclusion can be drawn:

- 1. The effect of colemanite ore waste was significant on the mechanical properties of concrete mixture tested. Up to a certain level of replacement of colemanite ore waste with Portland cement (3%), the compressive strength of mixture was significantly improved at the age of 28 days.
- 2. The mixtures containing either fly ash or bottom ash mixtures showed higher compressive strength than mixture containing no additive material at the age of 28 days, except mixtures F_5 and B_5 .
- 3. At early ages, reference mixture showed higher strength than mixture containing cement replacement material. The difference between the mixtures became significantly small as curing was extended beyond 7 days. At 90 days, both ash and fly ash mixtures showed the

best result, but all the other mixtures exhibited comparable results.

4. Combined action of both fly ash+colemanite ore waste and bottom ash+colemanite ore waste as cement replacement material resulted to better performance in the compressive strength compared to mixture containing colemanite ore waste.

References

- F. Massazza, M. Daiman, 9th Int. Congr. Chem. Cem., 1 (1992) 383-446.
- [2] A.M. Alhamsi, Microsilica and ground granulated blast furnace slag effects on hydration temperature, Cem. Concr. Res. 27 (1997) 1851–1859.
- [3] G. De Schutter, L. Taerwe, General hydration model for portland cement and blast furnace slag cement, Cem. Concr. Res. 25 (1995) 593-604.
- [4] A.M. Alhamsi, Temperature rise inside pastes during hydration in hot climates, Cem. Concr. Res. 24 (1994) 352–360.
- [5] W. Xuequan, Z. Hong, H. Xinkai, L. Husen, Study on steel slag and fly ash composite portland, Cem. Concr. Res. 29 (1999) 1103–1106.
- [6] Y. Zhang, W. Sun, L. Shang, G. Pan, The effect of high content of fly ash on the properties of glass fiber reinforced cementitious composites, Cem. Concr. Res. 27 (1997) 1885–1891.
- [7] M. Djuric, J. Ranogajec, R. Omorjan, S. Miletic, Sulfate corrosion of portland cement — pure and blended with 30% of fly ash, Cem. Concr. Res. 26 (1996) 1295–1300.
- [8] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes, a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.
- [9] A. Demirbas, A. Aslan, Evaluation of lignite combustion residues as cement additives, Cem. Concr. Res. 29 (1999) 983–987.
- [10] M. Cheriaf, J. Cavalcante Rocha, J. Pera, Pozzolanic properties of pulverized coal combustion bottom ash, Cem. Concr. Res. 29 (1999) 1387–1391.
- [11] Y. Erdogan, M.S. Zeybek, A. Demirbas, Cement mixes containing colemanite from concentrator wastes, Cem. Concr. Res. 28 (1998) 605–609.
- [12] Institute of Maden Teknik Arama (MTA), Ankara.
- [13] Turkish National Standards, TSE, TS 19 (1985), TS 24 (1985), TS 26 (1963), TS 639 (1975), Turkish Standard Institute, Ankara, Turkey.
- [14] E.J. Garboczi, D.P. Bentz, Digital simulation of the agrigatecement paste interfacial zone in concrete, J. Mater. Res. 6 (1991) 196–201.

^b Maximum.

 $^{^{}c}$ R₂O₃ = Fe₂O₃ + Al₂O₃.