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An investigation on the use of tincal ore waste, fly ash, and coal bottom ash as Portland cement replacement materials

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Abstract

The possibility of using tincal ore waste (TW), coal bottom ash (BA), and fly ash (FA) as partial replacement in concrete was examined through a number of tests. The properties examined include setting time, compressive strength, mortar expansion, water consistency of mortar, and microstructure. The results showed that compressive strength of all specimens containing 1 wt.% of TW was higher than that of the control at the 28th day of curing. At 90 days, the contribution to strength by BA + TW and FA + TW was higher than in the concrete-prepared equivalent TW beyond 3 wt.% of Portland cement (PC) replacement. With the replacement of 3–5 wt.% of PC by TW, the compressive strength of the concrete decreased compared to control concrete. However, the values obtained are within the limit of Turkish Standards (TS). Adding BA or FA with TW improved the performance relative to TW replacement only. Increasing replacement of TW gives rise to a higher setting time. As a result, TW, BA, and FA samples may be used as cementitious materials. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Compressive strength; Expansion; Setting time; Microstructure; Tincal ore waste

1. Introduction

Utilization of various types of waste materials such as coal fly ash (FA), coal bottom ash (BA), silica fume, municipal solid waste, and others for their use in the production of cement and concrete has been the subject of several investigations in recent years [1–5]. The research has confirmed that the addition of silica fume to blended Portland cement (PC) offers potential improvements in mechanical properties and sulfate resistance of cement mortars and that water pretreatment of municipal solid waste FA with water improves the setting characteristics of ash–cement mixtures [6]. Djuric et al. [7] studied sulfate corrosion of Portland cement — pure and blended with 30 wt.% FA. They suggested that there is a correlation among corrosion resistance factor, exposure time, and concentration of SO_4^{2-} ions. Mixes prepared from low-quality FA (which does not contain C_3A but contains free CaO) proved to be more resistant than the pure cement samples. They attributed it to the C_3A content of the mixture. Ash contributes to the lowering of the C_3A content and adds certain quantities of mullite and gehlenite. A short initial curing time offers potential improvement in the flexural strength of glass fiber-reinforced cement containing high amount of FA under accelerating ageing [8]. Addition of alkali-activated FA to cement mixes notably influences the development of the mechanical strength of the product [9]. Compressive strength of concrete decreases as the total silica, alumina, and iron III oxide contents are increased [10]. Naik et al. [11] found that the replacement Class F FA by Class C (up to 50%) for the preparation of ash mixture for use in concrete gives opportunity to control the rate of hydration reaction and to improve its microstructure. Hill et al. [12] pointed out that the carbon content of FA requires consideration because of its adverse effect on air entrainment in concrete. The presence of disordered carbon in FA gives a greater "active surface area" for air-entraining agents. Paya et al. [13] studied particle morphology in ground FA (GFA) and workability of GFA–cement mortars. They found a

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good correlation between workability of standard mortar with several substitution percentage of GFA.

It has been well established that the utilization potential of BA is mainly determined by its physical characteristic such as grain size distribution, staining potential, and color [14]. It is often used as a low-cost replacement for more expensive sand for concrete production and as a fine aggregate in high-performance lightweight concrete [15]. However, a recent study reported that pozzolanic activity of BA also needs consideration [16].

Chemical wastes containing soluble borates can be insolubilized via their incorporation into ettringite structure [17,18]. Ettringite formation is important to engineering and solidification/stabilization [17,19]. According to Bothe and Brown [20], the hydration product ettringite sequesters borates during its formation as high-boro-ettringite with the formula $C_3A \cdot 2Ca(B[OH]_4)_2 \cdot Ca(OH)_2 \cdot 30H_2O$ and the low-boro-ettringite with the formula $C_3A \cdot Ca(B[OH]_4)_2 \cdot 2Ca(OH)_2 \cdot 36H_2O$. Over the last few years, considerable experimental progress has been made on the utilization of chemical waste containing boron minerals as cement admixture. Erdogan et al. [21] studied the effects of the replacement of PC and trass cement (TC) by refined borogypsum (BG) on the mechanical properties of cement pastes. They found that the bending strength of PC pastes increases when 4% of the cement is replaced by refined BG. However, the replacement of TC by refined BG decreases the compressive strength of the paste. These results were confirmed by the another study of Erdogan et al. [22]. Their results show that the improvement in bending strength of paste is due to purities of BG. The strength values increase with decreasing ratio of impurities such as B_2O_3 and Li in the paste. These studies have shown that industrial wastes containing boron mineral could be used as cement additive material. Erdogan et al. [23] reported that colomanite ore waste (CW) can be used as cement additive up to 5% by weight of PC. Kula et al. [24] found that the replacement of PC by CW, BA, and FA generally results to better performance in the compressive strength of the PC paste.

This paper examines the influence of combined action of cement + tincal ore waste (TW), cement + FA + TW, and cement + BA + TW on the properties of PC. The present work has systematically studied the influence of increasing TW addition (1–9%), FA (4–16%), and BA (4–16%) on the mechanical strength and microstructure development of PC.

2. Materials and methods

BA and FA were supplied from Seyitömer Thermal Plant (Kütahya, Turkey), clinker and gypsum from Set Cement Plant (Balikesir, Turkey), TW from Etibank Borax Plant (Kirka, Eskisehir, Turkey). BA and concentrator waste containing tincal ore were dried at 105 °C. Chemical analyses of these materials were done by using X-ray fluorescence spectrometer (XRF). B203 in the TW was determined according to MTA titration method [25]. Table 1 shows chemical and physical properties of used materials.

Gypsum optimization was done for the clinker used and found to be 2.78 wt.% of clinker. Three series of mixtures and one reference mixture were prepared according to Turkish Standards (TS) [26]. Reference mixture was prepared out of PC and designated as R(PC). The other series of mixtures were designated as T(PC + TW), G(PC + BA + TW), and S(PC + FA + TW). Details of the mixtures are given in Table 2. A laboratory ball-mill was used for the grinding process. The physical tests were carried out following grinding according to TS 24 [26]. Particle size analysis was done by using alpine air sieves with 40-, 90-, and 120-μm size sieves. The fineness of the mixtures were between 2965 and 4204 of blain's specific surface.

Compressive strength test was conducted to study strength development of concrete containing additive materials at early and late ages. The concrete containing additives was compared to the concrete without any mineral additives. The mix proportions of mortars correspond to 450 g cement content/1350 g fine aggregate (Rilem Cebureau standard sand) and 0.5 water-to-cement (w/c) ratio. A typical batch weighted 2 kg. The cement–water mixtures were stirred at low speed for 30 s then with the addition of sand, the mixtures were stirred for 5 min more. Twelve 40 × 40 × 160-mm prismatic specimens for compression strength testing were made from each batch. After 24 h of curing at 20 °C with 95% humidity, the samples were placed in tap water and cured up to 90 days. Compression strength measurements were carried out at the age of 2, 7, 28, and 90 days according to TS 19 (compressive strength values of 10, 21, and 32.5 MPa for 2, 7, and 28 days, respectively) [26]. The strength value was the average of three specimens. Some of the prismatic specimens were not perfectly regular

Table 1

Physical and chemical characteristics of used material

	Clinker	TW	FA	BA	Gypsum
Chemical analysis (wt.%)					
SiO_2	21.47	17.11	56.13	50.98	–
Al_2O_3	6.04	2.61	18.49	14.96	0.05
Fe_2O_3	3.78	0.41	11.38	9.63	–
CaO	65.49	16.94	2.52	2.63	32.93
MgO	1.44	15.40	3.79	4.01	0.04
SO_3	1.12	0.25	0.05	0.16	45.95
Na_2O	–	0.21	0.71	0.47	–
K_2O	0.93	1.05	2.17	1.30	0.01
B_2O_3	–	15.20	–	–	–
Loss on ignition	0.20	28.90	4.20	15.70	21.13
Free CaO	0.85	–	–	–	–
Water	–	–	–	–	19.35
Physical analysis					
Fineness (wt.%)					
+ 40 μm	25.8	24.8	25.7	24.2	–
+ 90 μm	2.3	10.2	5.9	5.6	–
+ 200 μm	0.30	0.1	0.5	0.3	–
Specific surface (cm^2/g)	2400	3487	6418	7200	–
Specific gravity (g/cm^3)	3.20	2.41	1.81	1.98	–

Table 2
Physical characteristics of cementitious mixes

Symbol	Cement mixes	Fineness (wt.%)		Specific surface	Specific gravity
		+40 μm	+90 μm	(cm^2/g)	(g/cm^3)
R	Reference mix	25.0	1.1	2965	3.23
T_1	1% TW + 99% PC	25.1	1.0	3120	3.16
T_2	3% TW + 97% PC	25.0	1.1	3188	3.12
T_3	5% TW + 95% PC	25.2	1.1	3210	3.08
T_4	7% TW + 93% PC	24.9	0.8	3230	3.02
T_5	9% TW + 91% PC	25.0	1.0	3555	2.94
S_1	1% TW + 4% FA + 95% PC	24.9	1.0	3142	3.21
S_2	3% TW + 7% FA + 90% PC	25.2	0.8	3348	3.11
S_3	5% TW + 10% FA + 85% PC	25.0	0.9	3856	3.05
S_4	7% TW + 13% FA + 80% PC	24.9	1.1	3851	2.99
S_5	9% TW + 16% FA + 75% PC	25.1	0.8	4098	2.85
G_1	1% TW + 4% BA + 95% PC	24.8	1.0	3079	3.11
G_2	3% TW + 7% BA + 90% PC	24.9	0.9	3221	3.03
G_3	5% TW + 10% BA + 85% PC	25.1	0.9	3498	2.98
G_4	7% TW + 13% BA + 80% PC	24.9	0.8	3679	2.91
G_5	9% TW + 16% BA + 75% PC	25.2	1.1	4204	2.89

due to difficulty encountered in demolding (T_5, G_5, and S_5 samples). The compressive strength values of these samples were not tested. Surface morphology was examined using scanning electron microscope (SEM, Model JSM-5200, Jeol), which was operated at 20 kW. Cement pastes were prepared for SEM by mixing cements (R, T_1, S_3, and G_1) with adequate water and cured for 28 days. The samples were then coated with gold.

3. Result and discussion

Figs. 1–3 show the compressive strength of the concrete at various ages. As seen in the figures, compared to control concrete mixture, the overall effects of TW admixture on the compressive strength of the concrete is negative, except that the strength of the concrete prepared from T_1, S_1, and G_1 cements (which have 1% TW) exceeded that of the control concrete after 28 days of curing. It seemed that there existed a competition in strength development between TW in concrete and the same amount of PC cement in control concrete at this age. With the replacement of TW beyond 5%, the compressive strength of the concrete was significantly decreased regardless of curing time. The decrease in strength measurement of the concrete containing only TW as admixture is relatively higher than those of other admixtures. This might be due to small pozzolanic contribution of TW. Figs. 2 and 3 show the compressive strength of samples with different FA + TW and BA + TW replacements. The samples prepared with BA + TW show higher strength than the sample containing TW + FA. It is difficult to interpret which of the additive materials, TW or BA, had more pronounced effect on the compressive strength of the samples. Results show that combined action of TW and BA has more pronounced positive effect on the compressive strength compared to the sample containing FA and TW. Cheriaf et al. [16] pointed out that the pozzolanic activity of BA proceeds slowly at early ages and accelerates after 28 days resulting to a gradual increase in compressive strength. This gradual increase in strength may be related to the pozzolanic activity of BA.

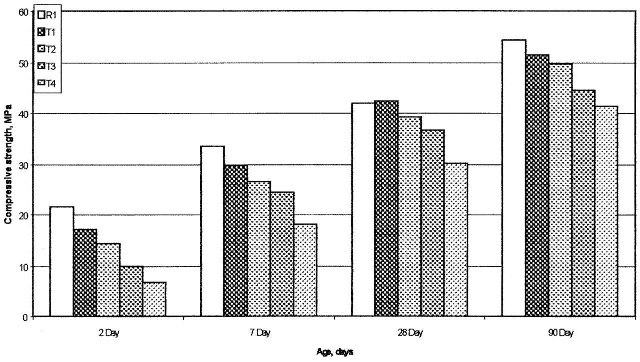

Fig. 1. Compressive strength of the concrete containing TW and PC.

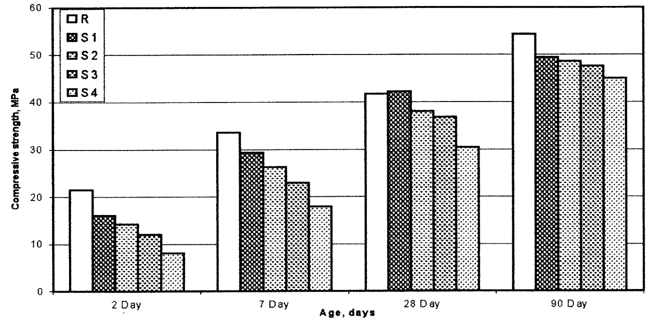

Fig. 2. Compressive strength of the concrete containing FA, TW, and PC.

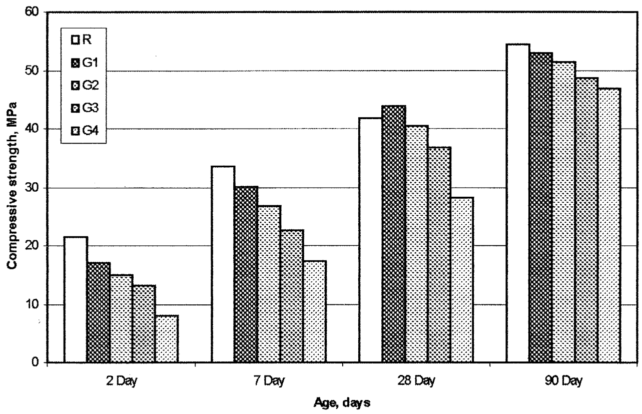

Fig. 3. Compressive strength of the concrete containing TW, BA, and PC.

SEM micrographs of the surface of the mortar specimens cured for 28 days are shown in Fig. 4. As seen in the figure, the samples studied have quite a different microstructure. Compared to control mortars containing no additive material, when TW is used as admixture, the resulting material shows a dense structure composed of large and irregular grains (Fig. 4b). The structure of mortar prepared from G_1 is about the same as that of the control mortar. However, the deposition of $Ca(OH)_2$ around the aggregate is remarkably reduced by the replacement of TW (Fig. 4c). As the TW content of mortar increased (Fig. 4d), the grain size decreased and the interconnection between neighboring particles is lost. The reduced size of the grain is considered to be mainly caused by the increase in MgO content and partly caused by the production of smaller C-S-H in the pozzolanic reaction than the C-S-H directly produced by the hydration of clinker.

The physical characteristics of the used materials are summarized in Table 2. The results obtained show that the additions of BA and FA into system increase specific surface that results to an increase in the water demand. The TW + PC mixtures do not follow this trend; in fact, adding TW alone reduces the water demand relative to the reference PC.

Table 3 shows the test results from the determination of water — percent, volume expansion, and setting time for cement mixes. As seen from the table, similar loading of FA and BA to the PC + TW shows the final set time to lag for FA relative to BA, despite a somewhat lesser MgO content, slightly contradicting the stated major trend. The observed lag in setting times may be mainly attributed to K_2O content of FA. This seems to be in agreement with our previous study [24]. Increasing replacement of TW with PC results to a higher setting time. There is a correlation between the setting time and TW ratio of cement. This is certainly due to high MgO content of TW. These results comply with an earlier study of Zheng et al. [27]. They found that the setting time (initial and final) of the cement mix increased with increasing MgO content. It should be noted that the setting characteristics of cement are influenced by a number of other factors such as source of mineral admixtures, chemical admixture, etc. [28,29]. Although this study does not include the effect of ettringite formation on the setting time, its formation may be related to the retardation of setting time

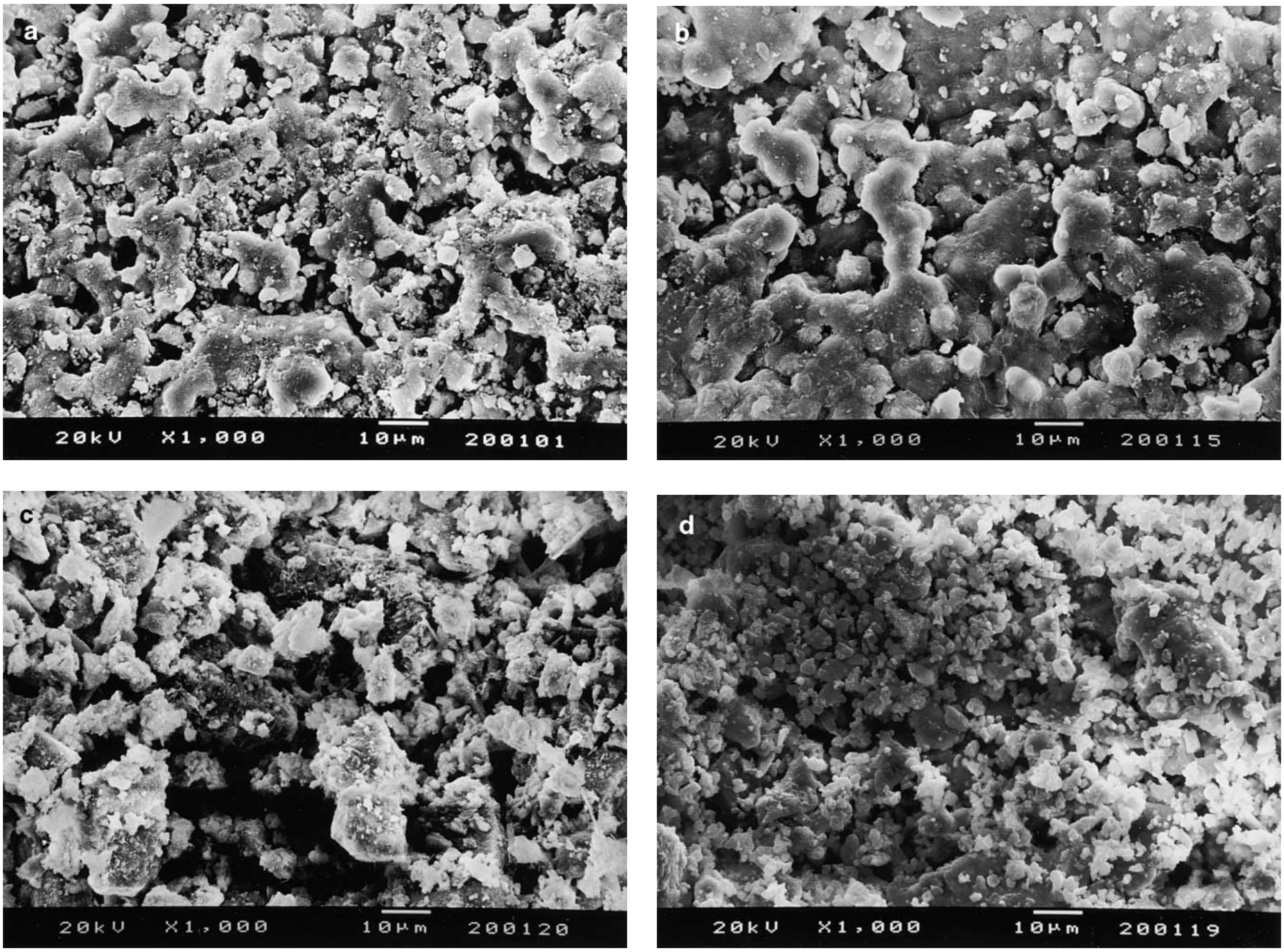

Fig. 4. SEM micrographs of fracture surface of mortars after 28 days of hydration: (a) control mortar, (b) Sample T_1, (c) Sample G_1, and (d) Sample S_3.

Table 3
Water percent, volume expansion, and setting time test result for cement mixes

Cement mixes	Water (%)	Setting time (h:min)		Volume expansion (mm)		
		Initial	Final	Cold	Hot	Total
TS 24	–	minimum 1:0	maximum 10:0	–	–	maximum 10
R	27.6	2:40	3:30	1	1	2
T_1	23.1	2:40	3:35	1	1	2
T_2	24.8	2:55	4:10	1	0	1
T_3	25.6	3:30	5:50	1	1	2
T_4	27.2	4:25	12:15	1	0	1
T_5	27.6	6:45	23:30	2	1	3
S_1	25.4	3:35	4:45	1	0	1
S_2	27.1	4:25	5:40	1	0	1
S_3	27.3	5:30	6:25	1	1	2
S_4	29.6	7:05	14:10	1	0	1
S_5	35.8	8:20	24:40	1	1	2
G_1	27.3	3:05	3:50	1	0	1
G_2	28.8	3:45	4:55	1	1	2
G_3	28.6	4:30	6:05	1	1	2
G_4	30.2	6:10	13:55	1	0	1
G_5	33.5	7:40	24:20	1	0	1

via soluble borate incorporation into ettringite structure. According to Bothe and Brown [20], the hydration product ettringite sequesters borates during its formation as high-boro-ettringite and low-boro-ettringite. These two phases are found together in the system. However, as indicated by Csetenyi [30], high carbonate concentration in solution decomposes low-boro-ettringite phase during the hydration, which may affect the setting characteristics.

The results show that long-term performance of the concrete with coal ash begins to recover the strength decrease caused by TW (relative to the reference PC), although higher loading of coal ash is hindered in this study by the negative effect of coupled higher loading of TW. Perhaps, a study of fixed TW additions could be performed with variable FA or BA additions to determine the effect of coal ash addition in the presence of a fixed quantity of TW. This may help promote increased utilization of the waste materials used.

The cementitious nature of TW, BA, and FA suggest that they could be used in concrete and construction materials. However, it should be noted that the long-term environmental stability of ettringite formation involving borates needs careful investigations.

4. Conclusions

This study has investigated the possibility of using BA, TW, and FA as cement replacements materials. Based on the above results and discussion, the following conclusions can be drawn:

1. The replacement of PC beyond 5 wt.% of TW caused a significant reduction in the compressive strength. When TW was replaced together with BA, the mixtures containing up to 1 wt.% of TW showed a considerable increase in the 28th day compressive strength. The strength performance for TW + PC only increases relative to R(PC) for 1% addition. By 90 days, the 5% addition is nearly as "poor" as the 7% addition.

2. At the 2-day age, all mixtures showed lower compressive strength than control mixture. The compressive strength increased gradually for all samples throughout the entire 90-day experiment. The compressive strength values of the mixtures containing more than 5 wt.% of TW are out of the limit of TS 19 [26].

3. At 28 days, all concrete containing 1 wt.% TW showed higher strength than the control concrete. As curing was extended to 90 days, control mixture showed the best result but mixtures containing up to 5 wt.% of TW exhibited comparable results with the TS 1 values.

4. Finally, the use of TW, FA, and BA as a high-volume cement replacement in the production of concrete is possible.

Research is in progress to further evaluate the influence of chemical wastes containing boron mineral on the properties of cement. Studies along these lines are crucial to properly handle boron wastes' potential to protect the environment.

References

[1] R.M. Majko, M.F. Pistilli, Optimizing the amount of class C fly ash in concrete mixture, Cem. Concr. Aggregates 6 (1984) 105–109.

[2] L. Wei, T.R. Naik, D.M. Golden, Construction materials made with coal combustion by-products, Cem. Concr. Aggregates 16 (1994) 36–42.

[3] A. Demirbas, S. Karslioglu, The effect of boric acid sludges containing borogypsum on properties of cement, Cem. Concr. Res. 25 (1995) 1381–1395.

[4] M. Conceand, C.M. George, F.D. Sorrenrio, A new steel slag for cement manufacture: Mineralogy and hydraulicity, Cem. Concr. Res. 11 (1981) 85–102.

[5] H.A. Toutanji, Z. Bayasi, Effect of curing procedures on properties of silica fume concrete, Cem. Concr. Res. 29 (1999) 497–501.

[6] T. Mangialardi, A.E. Paolini, A. Polettini, P. Sirini, Optimization of the solidification/stabilization process of MSW fly ash in cementitious matrices, J. Hazard. Mater. B70 (1999) 53–70.

[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] 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.

[9] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes, a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.

[10] A. Demirbas, A. Aslan, Evaluation of lignite combustion residues as cement additives, Cem. Concr. Res. 29 (1999) 983–987.

[11] T.R. Naik, S.S. Singh, M.M. Hossain, Enhancement in mechanical properties of concrete due to blended ash, Cem. Concr. Res. 26 (1996) 49–54.

[12] R.L. Hill, S.L. Sarkar, R.F. Rathbone, J.C. Hower, An examination of fly ash carbon and its interactions with air entraining agents, Cem. Concr. Res. 27 (1997) 193–204.

[13] J. Paya, J. Monzo, M.V. Borrachero, E. Peris-Mora, E. Gonzales-Lopez, Mechanical treatment of fly ashes: Part II. Particle morphologies in ground fly ash (GFA) and workability of GFA–cement mortars, Cem. Concr. Res. 26 (1996) 225–235.

[14] B.W. Ramme, J.W. Lingle, T.R. Naik, Coal combustion products

utilization in Wisconsin — an environmental approach, in: Proc. Three-Day CANMET/ACI Int. Symp. Sustainable Dev. Cem. Concr. Ind., Ottawa, Canada, 1998, pp. 349–383 (October 21–23).

[15] H. Afshin, Y. Matsufuji, High-performance lightweight concrete containing large quantities of coal combustion by-products, in: Proc. Three-Day CANMET/ACI Int. Symp. Sustainable Dev. Cem. Concr. Ind., Ottawa, Canada, 1998, pp. 511–521 (October 21–23).

[16] M. Cheriaf, J.C. Rocha, J. Pera, Pozzolanic properties of pulverized combustion bottom ash, Cem. Concr. Res. 29 (1999) 1387–1391.

[17] J.K. Solem-Tishmack, G.J. McCarthy, B. Docktor, K.E. Eylands, J.S. Thompson, D.J. Hassett, High-calcium coal combustion by-products: Engineering properties, ettringite formation, and potential application in solidification and stabilization of selenium and boron, Cem. Concr. Res. 25 (1995) 658–670.

[18] J. Duchesne, E.J. Reardon, Lime treatment of fly ash: Characterization of leachate composition and solid/water reaction, Waste Manage. 19 (1999) 221–231.

[19] H.F.W. Taylor, Cement Chemistry, Academic Press, San Diego, 1990.

[20] J.V. Bothe Jr., P.W. Brown, Phase formation in the system $CaO-Al_2O_3-B_2O_3-H_2O$ at 23 ± 1 °C, J. Hazard. Mater. B63 (1998) 199–210.

[21] Y. Erdogan, H. Genç, A. Demirbas, Utilization of borogypsum for cement, Cem. Concr. Res. 22 (1992) 841–844.

[22] Y. Erdogan, H. Genç, A. Demirbas, Partially-refined chemical by product gypsums as cement additives, Cem. Concr. Res. 24 (1994) 601–604.

[23] Y. Erdogan, M.S. Zeybek, A. Demirbas, Cement mixes containing colemanite from concentrator wastes, Cem. Concr. Res. 28 (1998) 605–609.

[24] I. Kula, A. Olgun, Y. Erdogan, V. Sevinc, Effects of colemanite waste, coal bottom ash and fly ash on the properties of cement, Cem. Concr. Res. 31 (2001) 491–494.

[25] Institute of Maden Teknik Arama (MTA), Ankara, Turkey.

[26] Turkish National Standards, TSE, TS 24 (1985), TS 19, Turkish Standard Institute, Ankara, Turkey, 1985.

[27] L. Zheng, C. Xuehua, T. Mingshu, Hydration and setting time of MgO-type expansive cement, Cem. Concr. Res. 22 (1992) 1–5.

[28] J.J. Brooks, M.A. Megat Johari, M. Mazloom, Effect of admixture on the setting times of high-strength concrete, Cem. Concr. Compos. 22 (2000) 293–301.

[29] A.M. Alshamsi, A.R. Sabouni, A.H. Bushlaibi, Influence of set retarding superplasticizer and microsilica on setting times of pastes at various temperatures, Cem. Concr. Res. 23 (1993) 592–598.

[30] L.J. Csetenyi, Boron-Containing Wastes Encapsulated in Cement, PhD Thesis, University of Aberdeen, Aberdeen, UK, 1993.