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Evaluation of lignite combustion residues as cement additives☆

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Abstract

In this study the physical and chemical properties of lignite fly ashes obtained from electrostatic precipitator and cyclone, lignite bottom ash, cement + lignite ash mixtures, and their effects on mechanical properties of concrete were investigated. The ashes were classified into two general types based on total silica, alumina, and iron-III oxide: class A and class B. When 25% of the cement was replaced by class A lignite bottom ash (the combined three oxide contents were 30.2%), the 28-day compressive strength increased by 18.9% compared to the control mix, and when 25% of the cement was replaced by class B lignite ash (the combined three oxide contents were 78.1%), the compressive strength decreased by 3.5% compared to the control mix. The results obtained were compared with the Turkish Standards and, in general, were found to be within the limits. As a result, the lignite fly ash and bottom ash samples may be used as cementitious materials.

Keywords: Hydration; Bending strength; Compressive strength; Expansion; Physical properties

In recent years various fly ashes, coal bottom ashes, slags, phosphogypsum, borgypsum, ground biomass, and others have been investigated as additives in production of cement mixtures and in concrete [1–18]. Evaluation of industrial by-products has been an interesting subject of research for economical, environmental, and technical reasons. The solid wastes produced in coal-fired power plants create problems for both power-generating industries and environmentalists [19,20]. Power plant ash may be used as admixture in cement industry [21]. The construction industry is considerably interested in replacing a large part of cement with beneficiated fly ash in concrete because of the economy that can be achieved. Other advantages of using fly ash include improved workability, decreased rate and total amount of the heat of hydration, and improved permeability. Other combustion by-products besides fly ash may also be used as a cementitious material or as a mineral admixture in portland cement concrete in the same way as classic pozzolanic materials. Pozzolanic materials such as fly ash, silica fume, and natural pozzolans that were initially used to protect the environment and conserve energy have proved to be very useful in improving the durability of concrete. However, some disadvantages of using fly ash include the reduction in the development of early strength with some fly ashes [22]. Also, class C fly ash is not effective in mitigating alkali-silica reaction. Addition of blending agents, each different in composition, introduces a great diversity into cementitious systems.

In our previous study the effects of 11 lignite bottom ashes as mineral admixture in concrete were investigated [15]. The bottom ashes were classified into two types based on the amount of total silica, alumina, and iron oxide: Total content of these three major oxides must be more than 50% for class A and more than 70% for class B. It was found that the 28-day compressive strength was increased by 24% compared to that of control mix when 25% for the class A-type lignite bottom ash was added as replacement into the cement, based on 300 kg/m^3 cementitious material. The cementing properties of bottom ashes have increased with a decrease in the percent of their three major oxides. The bottom ashes with the major oxides more than 70% in total may be rejected as cementitious material.

Class A-type lignite bottom ashes vary in their degree of reactivity with cement despite similar chemical composition compared to similar concretes such as fly ash concrete [23].

In this work, physical properties of lignite fly ashes obtained from electrostatic precipitator (FAESP) and cyclone

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Table 1
Oxide compositions of cement, lignite ashes, and cement + lignite ash mixture, weight percent

Material	SiO_2	R_2O_3[a]	CaO	MgO	$Na_2O + K_2O$	SO_3	Loss on ignition
Cement	20.8	10.8	62.8	1.7	0.3	1.8	1.8
FAESP-1	50.5	27.6	13.3	3.5	1.1	2.0	2.0
FAESP-2	48.1	28.5	16.3	1.5	0.7	2.1	2.8
FAC-1	22.5	13.9	53.1	1.4	0.9	6.7	1.5
FAC-2	48.3	27.1	14.4	2.9	0.9	2.1	4.3
BA-1[b]	26.8	19.4	43.5	1.2	1.1	2.2	5.8
BA-2[c]	52.5	23.3	11.2	3.0	1.1	0.9	8.0
CFAESP-1	23.1	10.9	59.4	2.4	0.5	1.9	2.0
CFAESP-2	25.4	11.9	56.9	1.6	0.4	1.9	1.9
CFAC-1	22.0	10.6	62.0	1.5	0.4	2.4	1.7
CFAC-2	23.5	11.0	58.8	1.8	0.4	2.0	2.3
CBA-1	21.0	10.6	61.1	1.4	0.5	1.9	3.6
CBA-2	25.2	11.6	56.6	1.9	0.5	1.6	2.8

[a] $R_2O_3 = Al_2O_3 + Fe_2O_3$.
[b] Class A lignite ash.
[c] Class B lignite ash. Ash-to-cement ratio: 1/3 (w/w).

(FAC), lignite bottom ash (BA), cement + lignite ash mixtures (CFAESP, CFAC, and CBA) and their effects on mechanical properties of concrete were studied. The objective of this study is to compare the chemical and physical properties of lignite fly ashes (ESP and FAC) with those of lignite bottom ashes.

1. Materials and methods

Lignite ash samples used in this work were obtained from Soma Thermic Centrale, in Manisa, Turkey, and different Turkish lignite sources.

Approximate analyses of the samples were performed according to ASTM Standards D 3173-74 and D 3175-77 [24]. Ash content of the lignites were determined according to ASTM Standards D 3174-75 [24], and the mineral matter contents of the ashes were determined by the ASTM Standards D 2795-69 [24].

Crushed stone as coarse aggregate (1260 kg/m^3) (sieve size 4.8–12.7 mm) and local natural sand as fine aggregate (610 kg/m^3) (sieve size 0.1–2.36 mm) were used in cement mixtures. In the cement mixes, 25% of the cement was replaced by each lignite combustion by-product.

Cement test mixes were prepared according to Turkish Standards (TS) as described in the earlier studies [25]. The physical tests were carried out according to TS 24. The solution and hydration heats were determined according to TS 687.

2. Results and discussion

Table 1 shows the oxide compositions of portland cement, lignite ashes, and the mixtures of cement and the lignite ashes. The results of physical analyses of the control mix and the cementitious mixes are given in Table 2. The test results from the determination of water percent, volume expansion, and setting time for cement mixes are presented in Table 3. The compressive and bending strengths (N/mm^2) for cement mixes are summarized in Table 4. The dissolution heat (cal/g) and the hydration heat (cal/g) test results for cement mixes are shown in Table 5.

Fly ash for use as a mineral admixture in portland cement concrete has been classified in ASTM specification into two general types: class C and class F. The three major oxides must be in total more than 50% for class C fly ash and more than 70% for class F fly ash. Data for the chemical analyses of the ash samples from the present work as summarized in

Table 2
Physical characteristics of cementitious mixes

	Fineness (wt%)				
Mixture	+0.09 mm	+0.20 mm	Specific surface (cm^2/g)	Weight per volume (g/L)	Specific gravity (g/cm^3)
Control mix	8.2	0.2	2800	1120	3.20
CFAESP-1	4.3	0.2	3897	990	3.03
CFAESP-2	7.2	0.6	3510	960	2.94
CFAC-1	6.0	0.4	3570	1100	3.14
CFAC-2	6.0	0.4	3566	970	3.00
CBA-1	7.3	0.6	3076	1060	2.98
CBA-2	7.1	0.5	3507	980	2.95

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

		Setting time (h:min)		Volume expansion		
Mixture	Water (%)	Initial	Final	Cold	Hot	Total
TS 19	—	minimum 1:0	maximum 10:0	—	—	maximum 10
CFAESP-1	28.7	2:45	4:25	6	1	7
CFAESP-2	29.0	2:30	4:20	8	1	9
CFAC-1	28.2	2:35	3:15	4	0	4
CFAC-2	29.9	2:50	4:35	6	2	8
CBA-1	28.5	2:05	3:00	5	1	6
CBA-2	28.8	2:20	4:25	8	1	9

Table 4
Strength test results for cement mixes

	Compressive strength (N/mm^2)				Bending strength (N/mm^2)			
Mixture	2 days	7 days	21 days	28 days	2 days	7 days	21 days	28 days
TS 19	mimimum 10	mimimum 21	—	mimimum 32.5	—	mimimum 4.0	—	mimimum 5.5
Control mix	13.9	23.2	—	33.8	2.5	4.0	—	6.0
CFAESP-1	10.7	21.5	29.7	32.7	3.2	4.5	5.3	5.5
CFAESP-2	13.2	24.1	32.7	34.6	3.6	5.0	6.6	6.9
CFAC-1	13.0	21.7	35.8	37.9	3.6	4.1	5.8	6.1
CFAC-2	11.4	21.2	30.3	33.4	3.2	4.2	5.5	5.7
CBA-1	20.5	33.4	38.5	40.4	4.3	6.0	7.4	7.6
CBA-2	15.2	27.7	36.3	38.2	3.9	5.6	6.7	7.0

Table 1 shows that the lignite bottom ashes are classified into two general types: class A and class B. The total of $Al_2O_3 + Fe_2O_3$ was designated as R_2O_3.

The term "alkali" used in connection with the alkali-silica reaction is itself the subject of some confusion and misinterpretation [26]. Alkalies in clinker originate from the raw materials (i.e. clay, limestone, shale, and chalk) used for the manufacture of portland cement and their alkali contents are 3.56% in clay, 0.42% in limestone, 5.68% in shale, 0.21% in chalk, and 0.72% in a typical raw mix. Alkalies can also come from coal ash if coal is used as the primary fuel [27]. Cements containing less than 0.6% alkali as equivalent Na_2O have been considered low-alkali cements [28]. Earlier work by Bhatty showed that pastes made with both cement and pozzolan can retain more alkali-moist conditions compared to paste made from cement alone [29]. Increase in silica content represents the increase in the amount of pozzolan added. The amount of alkali ($>$0.9%) retained increased with increasing additions of pozzolans. In other work, low C/S (C = CaO, S = SiO_2) mole ratio calcium silicate hydrates can retain more alkali than high C/S mole ratio calcium silicate hydrates [30]. Kalousek found the same relationship in the pure Na_2O-CaO-SiO_2-H_2O system at 298 K [31]. Addition of pozzolan can reduce the C/S mole ratio of C-S-H (calcium silica hydrate), thereby reducing the amount of alkali available for deleterious expansion. C-S-H having a C/S mole ratio of 1.0 retained more alkali than a 1.3 C/S mole ratio C-S-H. The alkali was retained in these hydrates by virtue of a reaction that forms sodium calcium silica hydrate. However, in the C-S-H having a C/S mole ratio of 1.3, the alkali was taken up by the substitution of sodium for calcium, and calcium hydroxide appeared.

The mechanism is reinforced by Rayment, who studied cement and cement fly ash pastes that were cured for 8 days [30,32]. Her experiments showed that the presence of fly ash in a cement paste resulted in lowering of the C/S mole

Table 5
Hydration heat test results for cement mixes

	Cement dissolution heat (cal/g)				Cement hydration heat (cal/g)			
Mixture	Dry mixture	2 days	7 days	28 days	2 days	7 days	21 days	28 days
CFAESP-1	549.7	494.5	482.2	482.1	55.2	67.4	67.5	69.9
CFAESP-2	529.0	483.9	466.9	462.2	44.9	62.0	64.8	66.7
CFAC-1	560.5	513.3	500.0	493.5	46.3	60.6	63.7	66.8
CFAC-2	524.9	480.4	462.9	460.0	44.0	62.1	63.1	64.4
CBA-1	564.4	516.6	502.5	495.7	48.8	61.8	65.6	68.6
CBA-2	553.5	499.0	486.6	484.5	54.5	66.9	67.8	69.0

Table 6
Comparison of lignite ashes and standards

Constituent, weight percent	Results from analyses Minimum	Maximum	TS 639	ASTM C-350, 65T
$SiO_2 + R_2O_3$	30.2	78.2	minimum 70.0	minimum 70.0
CaO	11.2	53.1	maximum 6.0	—
MgO	1.2	3.5	maximum 5.0	maximum 5.0
SO_3	0.9	6.7	maximum 5.0	maximum 5.0
Loss on ignition	1.5	21.8	maximum 10.0	maximum 12.0
Specific surface (cm^2/g)	2800	3897	—	minimum 2800

ratio of inner hydrates around the alite from clinker grains. The C/S ratio was lowered from 1.7 to 1.5. It is important to note that the C/S ratio was reduced by an increase in the amount of silica present in the hydrate in the cement fly ash paste, and not by a reduction in the calcium oxide content. It was found that use of low-alkali cement may not necessarily prevent damage if alkali levels much greater than those present in low-alkali cements can be leached from nonreactive as well as reactive aggregate materials to cause deleterious expansion [28].

Comparison of the lignite ashes and the standard values are given in Table 6. From Tables 1 and 6, $SiO_2 + R_2O_3$, MgO, and SO_3 contents of all the ash samples are very reasonable with the TS and ASTM standards. Percentages of CaO of all the ash samples are higher than those given in TS 639 and ASTM C-350, 65T standards. Therefore, the lignite fly ash and bottom ash samples may be used as cementitious materials. However, the increased fineness and free CaO content of the cement necessitated an increase in the water demand of the concrete [2,33].

From the data in Table 4, when 25% of the cement was replaced by class A lignite bottom ash (sample code of mix: CBA-1), the 28-day compressive strength was increased by 19% compared to the control mix, and when 25% the cement was replaced by another lignite ash (sample code of mix: CFAESP-1), the compressive strength decreased by 3.5% compared to the control mix.

From these results, it can be suggested that the cementing properties of lignite ashes has increased with decreased the percent of their three major oxides. It was suggested that pozzolans reduce or eliminate alkali-aggregate expansion by producing by additional calcium silicate hydrate and low-lime calcium silicate hydrate [29]. In order to control alkali-aggregate expansion by the addition of pozzolan such as fly ash, results indicate that about 30% low-lime fly ash is required. In an earlier study, the hydration and setting time of MgO-type expensive cement were investigated and suggested that the setting time (the initial and final) of the cement mix increased with increasing of MgO contents [34]. It shows that the addition of MgO retards the initial hydration of cements and increases the setting time [34]. In Tables 1 and 5, the initial hydration heat increased with increasing of MgO contents of the cement mixes CFAESP-1, CFAC-2, and CBA-2.

3. Conclusion

This study and the earlier studies indicate that the optimal class A lignite ashes replacement to achieve optimal 28-day compressive strengths and class B lignite ashes could be used as lightweight aggregates in manufacturing of masonry products of cement [6,15]. Lignite combustion by-products vary in their degree of reactivity with cement despite similar chemical composition, compared to similar concretes such as fly ash and blast furnace slag concrete. The construction industry is keenly interested in replacing a large part of cement with beneficial lignite ash in concrete because of the economy that can be achieved.

It was established that a low C/S mole ratio C-S-H does retain more alkali than a high C/S mole ratio C-S-H [30,31]. The greater the amount of alkali retained by C-S-H, the smaller the amount left for deleterious expansion. Therefore, the generation of low lime calcium silicate hydrates by pozzolans can play an important role in controlling the extent or rate of the deleterious alkali-aggregate reaction.

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