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OPTIMIZING THE PHYSICAL AND TECHNOLOGICAL PROPERTIES OF CEMENT ADDITIVES IN CONCRETE MIXTURES

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ABSTRACT

In this article, the physical and technological properties of phosphogypsum, borogypsum, sludges and reactor residue recovered from boric acid factory, lignite ashes, and steel making slags samples were investigated. Physical test results obtained from these cement additives were studied with comparing to the control mix. The optimal values of cementitious additives as replacement of cement and/or of replacement of natural aggregates were concluded.

Introduction

Recently in many countries, industrial by-products and wastes are widely used as cementitious components or as replacement of natural aggregates in cement concretes(1,2,3,4,5,6.) Detailed studies of using different sources of cement additives are an important part of understanding behavior of new low-cost construction materials made from industrial by-products and wastes.

By the treatment of by-products and wastes, production theory and practice of building materials has been developed very rapidly all over the world. Various fly ashes, coal bottom ashes, slogs, phosphogypsums, borogypsums, and the others have been investigated as additives in production of cements and concretes(7,8,9,10,11,12,13,14,15,16,17,18.)

There is an increasing tendency worldwide to use blended cements containing blast-furnace slag and pozzolanic materials such as fly ash, silica fume, and natural pozzolans in concrete. These materials, which were initially used to protect the environment and conserve energy, have proved to be very useful in improving the durability of concrete. Thus, incorporation of these materials in concrete leads to environmental, economic, and technological benefits. However, addition of blending agents, each different in composition, introduces a great diversity into cement systems. The relationship between the type of blending agent and the modification to the concrete properties, especially the long-term corrosion-resisting characteristics, is not yet fully quantified. Such data will not only help the concrete technologists in selecting the proper type of materials to produce dense and impermeable concrete but will also enhance the scope of the data base, which will be necessary to model and predict the long-term behavior of blended cements[19].

Refined or partly-refined boro- and phosphogypsums were mixed with portland and trass cements and their effects on the setting and mechanical properties of these mixes were studied in the earlier articles[9,10]. If all water-soluble impurities, especially B_2O_3, are removed from borogypsum by a simple water extraction process, the bending and compressive strengths properties portland cement and trass cement mixes are improved and strength values generally increase with decreasing ratio of B_2O_3 in borogypsum[9]. The untreated phosphogypsum retarded the setting time of portland cement mixes, and reduced strength, but did not significantly effect the setting time and the strength values of trass cement mixes. Phosphogypsum which will be used to control the setting of portland cement should be washed with lime milk, while phosphogypsum can be used with trass cement without any refinement process[10]. In the earlier work, the effects of boric acid sludges containing borogypsum on properties of cement was studied[10]. It was found that as the percent of the unrefined boronic sludges increase in the cement mixture the compressive strength decreased[11]. In the previous study[18], the effects of eleven lignite-bottom ashes as mineral admixture on concrete was investigated. The lignite-bottom ashes were classified into two types based on total of silica, alumina, and iron oxide: Total content of three major oxides must be more than 50% for Class A and those of more than 70% for Class B. It was found that the 28-day compressive strength increased 24.3% compared to control mix when 25.0% of the Class A type lignite-bottom ash was added into the cement, based on 300 kg/m^3 cementitious material. The cementing properties of lignite-bottom ashes have increased with the decreasing the percent of their three major oxides. Lignite-bottom ashes have the major oxides more than 70% can be rejected as cementitious material. However, they might be accepted as mineral admixtures in cement concrete. 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[20].

In the earlier studies[21,22,23,24,25], different methods were introduced for producing high-strength concrete. One of these methods was the effect of the ultrafine aggregate on concrete strength. An ultrafine portland cement with a specific surface of about 750 m^2/kg was used with several different types of aggregates: an expanded slate lightweight coarse and fine aggregate, a good quality crushed granite, gravel, basalt, and limestone coarse aggregates with natural sand. The granite aggregate consisted mainly of silica and alumina and had a specific gravity of 2.80 g/cm^3 and a crushing strength of 363 N/mm^2(26). With an ultrafine cement having a specific surface of the order of 750 m^2/kg, strengths of 60 to 70 N/mm^2 and 35 to 40 N/mm^2 were obtained in 24h with granite aggregate and expanded slate aggregates, respectively. With a portland cement containing about 75% tricalcium silicate, and lightweight aggregates, strengths of 10 to 25 N/mm^2 and 25 to 45 N/mm^2 were obtained in 12 and 24h, respectively[27].

Alkalies are unavoidably introduced in minor quantities into portland cement clinker. Alkalies in portland cement clinker occur as sulfates and, depending on the amount of SO_3 available, may also be present in calcium silicate and aluminate phases. Introduction of alkalies into clinker mineral modifies their crystal structure which, in turn, can change their hydraulic reactivity. Alkalies affect the clinkering process by modifying the physico-chemical properties of the melt formed in the kiln, and may have an adverse effect on the phase composition of clinker[28-30]. The mechanism of alkali-aggregate reactions was summarized by Diamond[31,32]. The effect of alkali sulfates and chlorides on clinker, especially on its physico-chemical properties such as the rate of formation of C_3S and decreasing the temperature of melt formation, were extensively investigated[32,33,34,35,36,37].

TABLE 1

Chemical Composition of Cement and Cement Additives, Weight Percent

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on Ignition
Cement	20.8	5.9	4.9	62.8	1.9	1.8	1.9
PG	2.8	0.4	0.3	31.4	0.6	42.9	21.6
BG	10.5	1.9	0.7	33.5	2.0	51.4	-
NG	11.2	0.8	0.8	28.7	0.7	36.8	1.0
BS-1	9.2	3.1	2.1	32.3	1.2	51.8	0.3
BS-2	9.9	2.9	2.0	34.7	1.2	49.0	0.3
BRW	13.9	1.8	1.3	31.6	1.0	49.9	0.5
LBA-A	15.6	23.7	19.1	26.1	12.5	1.9	0.1
LBA-B	55.8	22.5	12.4	5.0	2.1	2.0	0.2
SS	49.4	2.8	27.5	3.0	0.5	0.2	16.6

In this work, Physical properties of phosphogypsum (PG), borogypsum (BG), natural gypsum (NG), boronic sludge (BS), boronic reactor waste (BRW), lignite-bottom ash (LBA), steel making slag (SS), and dicalcium phosphate and their effects on mechanical properties of concrete were studied. The objectives of the study are to investigate optimum physical properties of these cement additives and their effect on mechanical properties of concrete.

Materials and Methods

Wastes of the boric acid factory (BG, BS, and BRW) were taken from Bandyrma, PG supplied from Samsun phosphoric acid factory in Türkiye. LBA samples were obtained from different Turkish lignite sources and SS samples were provided by Simkent production Industry in Kazakhstan. Chemical composition of cement and all cement additives are given in Table 1. Specific constituents of PG, BG, BS, BRW, and SS are given in Tables 2, 3, and 4. The physical properties of the cement mixes are shown in Table 5. Cement test mixes prepared according to Turkish Standards (TS) and the earlier studies[9-11,18]. The physical tests were carried out according to TS 24.

Results and Discussion

The compressive strength, volume expansion, and setting time test results for cement additives are summarized in Table 6. Effects of the impurities added to cement on setting times

TABLE 2

Chemical Composition of PG Samples, Weight Percent

Sample	R_2O_3	CaO	MgO	SO_3	Total phosphate	Total fluoride	Combined Water	SiO_2 and Water Insoluble
Dehydrate	0.27-0.96	31.10-32.10	0.07-0.32	43.04-45.13	0.55-1.08	0.41-1.19	19.41-20.49	1.22-2.95
Hemihydrate-Dihydrate	0.25-0.46	29.92-32.15	0.08-0.44	42.73-44.70	0.16-0.60	0.15-1.25	19.36-20.52	0.98-6.43

TABLE 3

Chemical Composition of Bg, BS, and BRW Samples, Weight Percent

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	B_2O_3	H_2O
BG	22.3	0.8	0.7	43.2	1.1	1.7	5.3	24.9
BS-1	7.1	2.4	1.6	25.0	0.9	39.8	12.4	10.8
BS-2	6.8	1.9	1.4	23.4	0.7	30.8	16.4	18.6
BRW	10.9	1.2	0.7	28.5	0.8	44.5	1.6	11.8

are given in Table 7. The influence of dicalcium phosphate on bending and compressive strengths of cement are shown in Table 8.

For the characterization of a cement or cementitious material as a binding agent for concrete it is not sufficient to determine bending and compressive strengths, setting time and soundness. Its physical properties such as specific gravity, specific surface, grain size distribution, aggregate to cementitious material ratio, fineness, water demand, and moisture content should be available. Moreover, for the introduction of a new material it is advisable to inform its origin, micro structure, chemical and phase composition. The total heat evolved by hydration of cement mix and its pozzolanic activity should be investigated.

This high CaO content of a cement additive contributes to higher early strength[8]. If no retarder is used, the large amount of BG, BS-1, BS-2, BRW, and LBA-Class A with high CaO would lead to rapid setting(Tables 1 and 6). Free or uncombined CaO occurs in clinker as aggregates or single grains, rounded in shape and frequently as large as the C_2S grains. It is not easily distinguished in thin section but is readily seen in the polished surface, being soft and easily stretched. It is readily etched by water or moist air and then appears dark, and when over-etched, pitted. In powdered clinker or cement free CaO is readily detected under the microscope by White test[38]. The calcium hydroxide content of various hydrated cement products has been determined by X-ray quantitative analyses[39].

The influence of fineness on strength varies with cement and the concrete mix. The particle size analysis data correlate with the Blaine specific surfaces of the slags and fly ashes[2], showing progressively finer distribution of particle sizes with increasing specific surface[40]. An increase in specific surface from 1800 to 2500 cm_2/g raises the compressive strength at 1 day by 50-100 percent, at 3 days by 30-60 percent, and at 7 days by 15-40 percent. The particle-size fraction below 3μm has been found to have the predominant effect on the strength at 1 day while the 3-25 μm fraction has a major influence on the 28-day strengths[38,39,40,41]. On of the most important properties of coal ash is the influence of fineness upon its pozzolanic activity in concrete. The finer fraction(those less than 45μm) allows the hydration and pozzolanic and hydration reactions from coal ash are similar to the hydration of cement, an effect should also be shown for water demand and loss on ignition[20]. The data

TABLE 4

Chemical Composition of SS Samples, Weight Percent

Material	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Lost on Ignition
Steel Slag	41.4	21.4	3.6	4.2	0.7	0.2	18.5
Steel Slag with Dust	57.5	33.8	2.2	1.5	0.5	0.1	2.4

TABLE 5

Physical Properties of Cement Mixes

Physical Test	TS 19	10%SS +90% C	25% LBA-A +75%C	25%LBA -B+75%C	4%PG+ 96%C	25%BRW +75%C	25%BS +75%C
Specific Gravity (g/cm^3)	3.20	3.19	3.13	2.98	3.15	2.84	2.98
Specific Surface (cm^2/g)	2800.0	2887.0	2864.0	2836.0	2795.0	2818.0	2826.0
Fineness, retained on 45 m(No.325) wet sieve, %	8.2	11.8	14.6	17.3	9.1	10.2	10.6
Water Demand (% of control)	100.0	94.2	95.0	108.7	98.8	_	_
Moisture Content (% by weight)	0.38	0.40	0.41	0.56	0.37	0.51	0.54

in Tables 5 and 6 show that the compressive strength decreased with the increase in water demand for the sample of LBA-Class B. The increased fineness and free CaO content of the cement necessitated an increase in the water demands of the concrete[21,8]. The higher water demand of LBA-Class B (Table 5) might result from its free CaO content.

TABLE 6

Compressive Strength, Volume Expansion, and Setting Time Test Results for Cement

Cement Mixes[a]	Compressive Strength(MPa)					Volume Expansion	Vicat Set Time Hour: Minute	
	1-day	7-day	28-day	56-day	90-day	Total(mm)	Initial	Final
Cont.Mix(C)	11.2	26.8	34.8	37.3	39.7	10(max.)	1:00	10:00
4%PG +96%C	_	27.2	36.7	40.2	45.6	9	2:40	5:00
10%SS +90%C	9.8	21.6	30.6	34.1	36.4	8	3:05	4:15
25%LBA-A +75%C	8.8	28.9	41.9	45.4	47.0	4	3:10	5:40
25%LBA-B +75%C	5.6	25.6	29.4	36.2	38.3	4	2:90	4:80
25%BRW +75%C	8.1	14.7	18.2	20.5	23.1	2	3:00	6:10
25%BS +75%C	5.2	7.8	9.8	11.3	12.1	4	2:85	5:25

[a] Cement Mix: 300 kg/m3, Natural Sand: 700 kg/m3, Crash Stone: 1000 kg/m3, Water: 170 kg/m3.

TABLE 7

Effects of the Impurities Added to Cement on Setting Time

Impurity	F^-	F^-	P_2O_5	P_2O_5	MCP[a]	MCP	DCP[b]
%by weight	0.50	1.50	0.50	1.00	0.75	1.50	1.50
Initial set time, hour:min	3.23	2.28	2.30	2.28	2.36	3.24	4.00
Final set time, hour:min	3.57	3.32	3.25	3.38	4.49	4.49	5.00

[a]MCP: Monocalcium Phosphate, [b]DCP: Dicalcium Phosphate

The compressive strength values generally increase with decreasing ratio of impurities[10]. From the test results in Table 6, the straight values decrease in the cement mixes with SS, LBA-Class B, and especially for BRW and BS in the mixture.

Borogypsum retards cement setting primarily because of the orthoboric acid impurity present, but setting time is not clearly related to the B_2O_3 content in BG[5,42]. The data in Table 7 shows the fluoride compounds contribute to rapid setting, but phosphates, especially dicalcium phosphate slacken the setting reactions.

As can be seen in Table 8, the strength values of concretes have increased with increasing of content of dicalcium phosphate in cement mixes.

From physical test results in Table 5, specific gravity, specific surface, and fineness values of cement mixes are very reasonable with the Turkish Standard, TS[43].

Conclusions

This study and the earlier study[18], indicated that the lignite-bottom ash-Class A samples could be used as a partial replacement of cement and the lignite-bottom ash-Class B samples as lightweight aggregate in manufacturing of masonry products. LBA-Class B may be used as a partial replacement of natural aggregates. Large size LBA-Class B can be used as coarse aggregates and finer LBA-Class B used as sand.

TABLE 8

Effect of Dicalcium Phosphate on Bending and Compressive Strengths of Cement

DCP[a], % of C	Bending Strength				Compressive Strength			
	3-day	7-day	28-day	91-day	3-day	7-day	28-day	91-day
0.000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.018	98.9	99.2	94.5	108.1	96.1	104.7	93.4	96.0
0.053	92.1	105.8	95.7	101.1	101.1	105.7	98.9	100.5
0.089	106.8	95.8	106.6	107.5	101.6	114.5	102.6	102.8
0.142	103.4	103.0	100.7	112.8	101.6	113.5	95.8	106.1
0.266	104.2	103.0	100.7	108.6	100.8	114.0	95.0	101.9
0.880	98.3	95.2	95.8	95.8	97.7	109.1	95.8	101.4

[a]DCP: dicalcium phosphate

The incorporation of additives with fluoride, SS, and LBA-Class B contribute an increased time of set of concrete especially at high fluoride contents, but phosphates retard the setting of concrete. The cement mixes containing PG, BG, and LBA-Class A types additives significantly improve the compressive strength of concrete.

The fineness of the ground-granulated additive and the Portland cement used in the mix have a significant effect on the performance of the concrete.

For product quality control, the physical/chemical parameters are found to be the best indicator of additive quality.

The results of the study indicate that 25% Portland cement replacement by the high-lime-content additives, such as BG, BS-1, BS-2, and LBA-Class A, used may provide an acceptable compromise to obtain a concrete with high compressive strength.

References

1. X. Wu, D.M. Roy and C.A. Langton, Cem.Concr.Res. 13, 227(1983).
2. M. Van Roode, E. Dougles, and R.T. Hemmings, Cem.Concr.Res. 17, 183(1987).
3. M.S.Y. Bhatty, Cement, Concrete, and Aggregates, 7, 69(1985).
4. J. Bensted, Cem.Concr.Res. 11, 219(1981).
5. J. Bensted, Cem.Concr.Res. 10, 165(1980).
6. A.V. Kisilev, T.Y. Gal'perina, A.A. Lukatskii, G.V. Kozhemyakin, and V.F. Sukhanov, Tsement (4), 15(1977).
7. R.M. Majko and M.F. Pistilli, Cement, Concrete, and Aggregates, 16, 105(1984).
8. L. Wei, T.R. Naik, and D.M. Golden, Cement, Concrete, and Aggregates, 16, 36(1994).
9. Y. Erdoğan, H. Genç, and A. Demirbaş, Cem.Concr.Res. 22, 841(1992).
10. Y. Erdoğan, A. Demirbaş, and H. Genç, Cem.Coyncr.Res. 24, 601(1994).
11. A. Demirbaş and S. Karslyoğlu, Cem.Concr.Res. 25, 1381(1995).
12. T.R. Naik, 'Production of Masonry Blocks for Developing Countries', Presented in the 7th ASCE Structure Congress, San Francisco, CA, May, 10 pages(1989).
13. D.M. Roy, G.R. Gouda, A. Bobrowsky, Cem.Concr.Res., 2, 349(1972).
14. J.W. Hamling and R.W. Krimer, Cement, Concrete, and Aggregates, 14, 13(1992).
15. M. Conjeand, C.M. George and F.D. Sorrenrio, Cem.Concr.Res., 11, 85(1981).
16. J. Bensted, World Cement Technology, 10, 404(1979).
17. F.J. Hogan and J.W.Meusel, Cement,Concrete, and Aggregates, 10, 3, 40(1981).
18. A. Demirbaş, S. Karslyoğlu, and A. Ayas, Cem.Conc.Res., 25, 1610(1995).
19. M. Masluhuddin, A.I. Al-Mana, H. Saricimen, and M. Shamim, Cement, Concrete, and Aggregates, 12, 24(1990).
20. H.A. Harris, J.L. Thompson, and T.E. Murphy, Cement, Concrete, and Aggregates, 9, 34(1987).
21. C.D. Jonston and V.M. Malhotra, Cement, Conrete, and Aggregates, 9, 101(1987).
22. B. Mother, 'Stronger Concrete', Symposium on Concrete Strength, Highway Research Record, No.210, pp.1-28(1967).
23. E.W. Bennett and B.C. Coyllings, Proceedings of the Institution of Civil Engineers, 43, 443(1969).
24. R.N. Swamy, A.B. Ibrahim, K.L. Anand, RILEM Materials and Structures, 8, 413(1975).
25. J.F. Young and H.S. Tong, Cem.Concr.Res., 7, 627(1977).
26. R.N. Swamy, Cemant, Concrete, and Aggregates, 8, 33(1986).
27. I. Jawed and J. Skalşny, Cem.Concr.Res., 7, 717(1977).
28. T.E. Stonton, Proc.Am.Soc.Civ.Eng., 66, 17811940.
29. G.M. Idorn, Proc.Symp.Effect of Alkalies on the Properties of Concrete, Sept.1976 C and CA. London, p.3(1977).
30. S. Diamond, Cem.Concr.Res., 5, 329(1973).

31. S. Diamond, ibid, 6, 549(1976).
32. V.M. Blonakaya and V.M. Stepanov, Tsement, (4), 12(1969).
33. W. Danowski and W. Strubel, Zement-Kalk-Gips, 29, 458(1976).
34. K. Fujii et all., Yogyo Kyokai Shi, 76, 50(1968).
35. F.W. Locher et al.,Zement-Kalk-Gips, 25(1), 1(1972).
36. W. Gutt and M.A. Smith, Cem.Tech., 2, 143(1971).
37. F.W. Locher, Zement-Kalk-Gips, 28, 265(1975).
38. F.M. Lea, The Chemistry of Cement and Concrete, Edward Arnold(Publ.)Ltd., Glasgopw(1970).
39. H. Lehmann, F.V. Locher, and D. Prusso0g, Tonind-Ztg.keram.Rdsh., 94,230(1970).
40. E. Douglas, A. Elelo, and V.M. Malhotra, Cement, Concrete, and Aggregates, 12, 38(1990).
41. F.W. Locher, J. Wohrer, and K. Schweden, Tonind-Ztg.keram.Rdsh. 90, 547(1966).
42. H. Uchikawa and S. Uchida, Semento Gijitsu Nempo, 31, 30(1977).
43. Turkish Standard, TS 19(1985), Turkish Standards Institute, Ankara.