Utilization of Boron Industry Wastes, Fly Ash, Bottom Ash and Alunite Mineral in Cement Production as an Additive Material

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ABSTRACT: In this work, colemanite concentrator wastes from Kütahya-Emet-Hisarcık, tincal concentrator wastes from Eskişehİr-Kırka, Seyitömer thermal power plant wastes and alunite from Kütahya-Şaphane were aimed to utilize in cement production as an additive material. Thus energy saving in cement production and elimination of environmental problems caused by these wastes were investigated. In this study, different ratios of colemanite concentrator waste-bottom ash, colemanite concentrator waste-fly ash, tincal concentrator waste- bottom ash, tincal concentrator waste- fly ash variations were added to a constant ratio of alunite mineral and they were used as a cement additive material. The effects of the additives on setting time, volume expansion, compressive strength of cement were studied and their chemical analysis were performed by XRF method. The obtained results were examined if they are suitable in accordance with the related Turkish standards or not and also it was investigated that the additives used in this study can be utilized or not as an additive material in cement production.

1. INTRODUCTION

Turkey has the 64% of the total world boron reserves (Eti Holding A.Ş. 2000) and known as the second producer following the United States with 1.72 million tons boron minerals and compounds production (Özdemir & Öztürk, 2003). The most important boron minerals in Turkey are colemanite, ulexite and tincal.

In our country there are four boron plants in which we can enrich the raw ores in the concentrators. We know that during the production, millions tons of boron disposed form in the plants. These wastes contain significant amount of boron oxide which results to an environmental pollution as well as an economical loss . The eight oxides (SİO2, Aİ2O3, Fe_20_3, CaO, MgO, $S0_3$, Na_20, K_20) found in the colemanite and tincal concentrator wastes are the same with the oxides found in the cement and other cement additive materials (Kula, 2000). Thus, their use as additives in the production of cement has been the subject of many investigations in recent years.

Also, thermal power plant wastes such as coal fly ash (FA) and coal bottom ash (BA) are the wastes that can be utilized in the cement industry (Kula, 2000). It is generally accepted that appropriate use of FA in concrete can prevent expansion due to alkali silica reaction (Shehata&Thomas, 2000), can reduce heat generation and gives better durability properties . Instead of using more expensive sand in concrete,(Ghgafoori &Cai,1998)BA can be used as a low-cost replacement material and is also used as a construction fill and land fill bottom iiner(Kayabaiı&Buluş,2000). A study by Cheriaf et al. pointed out that puzzolanic activity of B A can be improved with adequate grinding and it can be used in portland cement (PC) and concrete.

In this study a constant ratio of alunite is investigated in cement with boron wastes and thermal power plant wastes. Alunite additive cements are known as rapidly hardening cements and have high-strength properties (Özacar, 2003).

2. MATERIALS AND METHOD

In this study clinker, gypsum, colemanite waste (CW), tincal waste (TW), coal fly ash (FA), coal bottom ash (BA) and alunite (A) were used as cementitious materials. Their chemical compositions are given in Table 1. The chemical analyses were performed by ARL X-Ray fluorescence spectrometer. The amount of B2O1 m the tincal ore waste was determined according to the MTA titration method (Institute of Technical Mine Searching, Ankara), and m colemanite waste was studied by ICP-OES.

Table 1. Chemical analysis of materials.

Chemical analysis (wt%)	*Clinker*	*Gypsum*	*Colemanite waste*	*Tincal waste*	*Alunite*	*Fly ash*	*Bottom ash*
$Si0_2$	20,86	0,93	19,00	15,26	42,05	53,23	51,51
BÎO,	-	-	18,97	10,95	-	-	-
$Al_20,$	5,48	0,30	3,73	1,60	20,92	19,34	18,76
$Fe_20,$	4,06	0,21	1,80	0,42	0,19	10,21	9,57
P_20_5	-	0,01	0,09	-	0,14	0,08	0,07
CaO	66,01	32,29	16,38	14,55	0,13	4,42	5,08
MgO	1,29	0,24	5,35	10,95	0,057	0,88	0,93
SCh	0,68	45,84	1,39	0,66	18,43	0,13	0,007
CI	0,006	0,001	0,0008	0,07	0,0003	0,005	0,005
Na_30	0,11	0,02	0,12	5,33	0,35	0,55	0,52
K_20	0,55	0,03	!,98	1,05	4,546	2,85	2,56
Free CaO	1,28	-	-	-	-	-	-
Loss on ignition	-	-	26,10 '	34,56	13,18	8,3	10,85
Water	-	20,17	-	-	-	-	-

Gypsum optimization was done for the clinker used and found to be 3,5 wt % of clinker. Four series of mixtures and one reference mixture were prepared according to Turkish Standards (TS 24). (Turkish National Standards, TSE, TS 19 (1985), TS 24 (1985), TS 26 (1963), TS 639 (1975), Turkish Standard Institute, Ankara, Turkey).

Reference mixture was prepared out of Portland Cement and designated as R. The other series of mixtures were designated as A, B, C and D. The weight percent of each material used for each mixture are shown in the Table 2. For the grinding process a laboratory squared ball-mill was used and physical tests were carried out after this process according to TS 24. Particle size analysis was done by using Alpine Air Sieves with 45um, 90um and 200pm size sieves.

Specimen preparation for strength tests was performed at room temperature. The mixed proportion of the specimen corresponds to 450g of cement content, 1350 g of standard sand and 0,5 water to cement (W/C) ratio. The cement-water mixtures were stirred at low speed for 30 s. After the addition of sand the mixtures were stirred for more 5 minutes. For each mixture three 40 x 60 x 160 mm prismatic moulds were prepared and these mixtures were cast into them for strength tests. After casting, the specimens were stored İn the laboratory at 20 C°with 90 % relative humidity for 24 h and then demolded and placed under water and cured up to 28 days. Then they were tested in accordance with TS 24.

Table 2. Physical properties of cementitious mixtures.

Symbol	*Cement mixes*	*Fineness (wt %)*			*Specific*	*Specific*
		45 urn	90 urn	200 um	f^f* (cmVg) .	^ (g/cm*)
A,	1%CW+ 4% FA+1% A+94% PC	14,4	2,2	-	3670	3,01
A_2	3%CW+ 7% FA+1% A+89% PC	14,0	1,9	-	3820	3,00
A_3	5%CW+ 10% FA+1% A+84% PC	12,9	1,6	-	4140	2,96
A4	7%CW+ 13% FA+1% A+79% PC	11,0	1,3	-	4470	2,94
A_3	9%CW+ 16% FA+1% A+74% PC	10,6	1,6	0,4	4860	2,94
Bi	1%CW+ 4%BA+1%A+94%PC	14,0	1,9	0,4	3730	3,05
B_2	3%CW+7%BA+1%A+89%PC	12,0	1,5	-	3900	3,02
B_3	5%CW+ 10%BA+1%A+84%PC	11,5	1,2	-	4240	2,97
B_4	7%CW+ 13%BA+1%A+79%PC	10,6	1,2	-	4540	2,94
B_5	9%CW+ 16%BA+1%A+74%PC	-	-	-	4750	2,89
C,	1%TW+ 4% FA+1% A+94% PC	10,9	1,3	-	3670	3,07
C_2	3% TW+ 7% FA+ 1% A+89% PC	11,8	1,4	-	3760	3,01
C_3	5% TW+ 10% FA+ 1% A+84% PC	11,1	2,0	0,1	4040	2,97
C_4	7%TW+ 13% FA+ 1% A+79% PC	12,8	2,5	0,2	4240	2,93
C_5	9%TW+ 16% FA+1% A+74% PC	17,0	2,9	0,3	4210	2,89
D,	1%TW+ 4%BA+1%A+94%PC	10,7	1,2	-	3640	3,05
D_2	3%TW+ 7%BA+1%A+89%PC	13,3	1,3	-	3810	2,99
D_3	5%TW+ 10%BA+1%A+84%PC	13,2	1,8	-	3940	2,96
D_4	7%TW+ 13%BA+1%A+79%PC	13,4	1,8	-	4060	2,90
D_s	9%TW+ 16%BA+1%A+74%PC	12,9	1,4	-	4400	2,87
R	PC	16,9	2,2	0,3	3294	3,16

Table 3. Volume expansion and setting time test result for cement mixtures.

Cement	Setting time (hour : min.)		Volume expansion (mm)		
mixes	Initial	Final	Cold	Hot	Total
A!	03:00	04:15	1	1	2
A_2	04:00	05:30	1	1	2
A_3	04:00	13:00			
A,	00:00	09;45			
A_5					
B,	02:10	03:35	1	1	2
B_2	04:30	05:40	2	3	5
B_3	08:00	12:20	1	1	2
B_4	17:50	26:50	0	14	14
B_5					
Ci	03:05	05:00	1	1	2
C_2	00:00	00:10	1	0	1
C_3	00:00	02:00	1	10	11
C_4	00:00	01:50	0	3	3
C_5	00:40	01:50	2	0	2
Di	03:10	04.35	2	1	3
D_2	00:40	02:05	3	3	6
D_3	00:00	01:10	1	1	2
D_4	01:00	02:05	1	2	3
D_5			2	0	2
R	2:30	3:50	-	-	6
TS 12143	Min. 1:00	Max. 10:00	-	-	Max. 10:00

3. RESULTS AND DISCUSSION

Volume expansion and the setting time of the cement paste containing different replacement materials are given in Table 3. The compressive strength of different batches at different ages is shown in Figure 1-4. The results of the control specimens without any supplementary material are also shown. At 2 days of curing time, the compressive strength of the specimens containing supplementary materials was less than that of control for all batches. In addition, the mixture A_5, B_5, C_4, C_5, D_3, D4, D5 have no compressive strength values at this age due to difficulties of demolding. Although we can see a stability in the performance of mixtures containing colemanite at the age of 7 days, the mixtures with tincal do not show the same performance. Especially the values obtained for the cement containing coal bottom ash is rather bad. When curing extended to 28 days, the strength values obtained are with in the acceptable range of TS 639, TS 12143 except C_4 and D_3.

The compressive strength values of the mixtures including colemanite waste are very close to the values of control batch. But it isn't possible to say the same thing for the mixtures with tincal waste The obtained values of tincal are not in correct order. While Ci, $C_{2>}$ Di and D_5 (at 28 days)are similar with the control batch, the others are quite different.

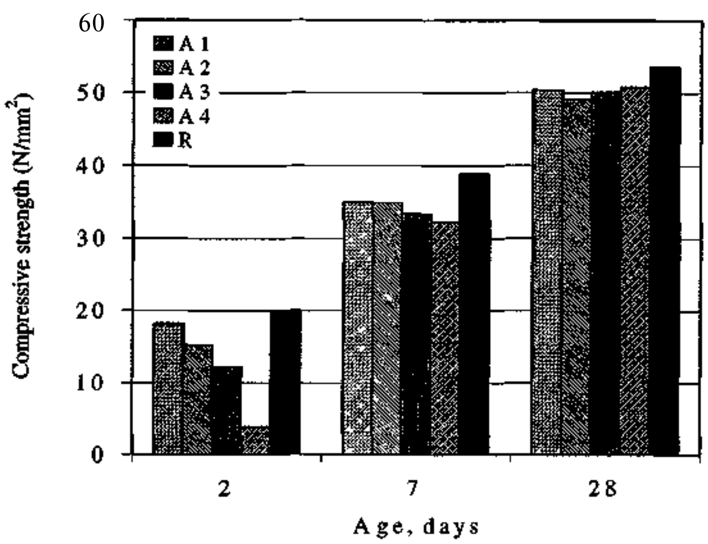

Figure 1. Compressive strength ofthe concrete containing CW, FA, A and PC.

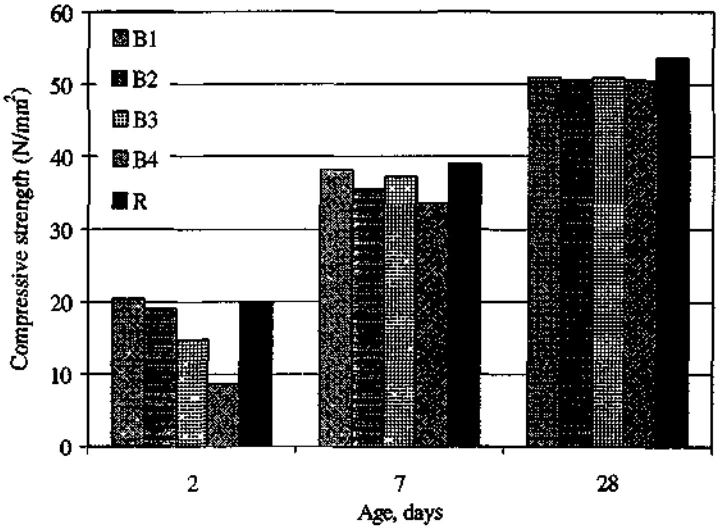

Figure 2. Compressive strength of the concrete containing CW, BA, A and PC.

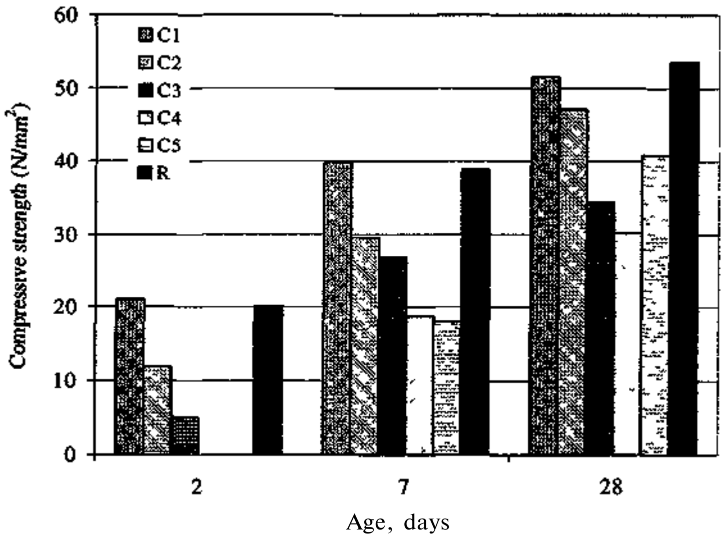

Figure 3. Compressive strength of the concrete containing TW, FA, A and PC.

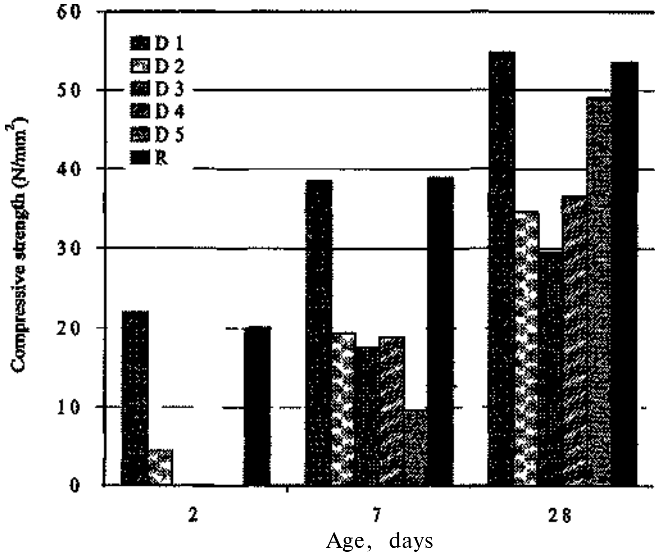

Figure 4. Compressive strength of the concrete containing TW, BA, A and PC.

4. CONCLUSIONS

By the results above, the following conclusion can be made:

1. The mixtures containing cement additive materials showed less specific gravity than the mixture containing no additive material. The specific gravity of the cements decrease with increasing amount of additives due to fineness of clinker. At the same time, specific surface values show a continuing improvement with the rising amounts of additives.

2. The initial and final setting time values obtained by the replacement of PC under 5 wt % (I wt %, 3 wt %) of CW exhibited fitting results with the TS. But the TW showed the suitable results only when it is used 1 wt %. There is no obtained initial setting time values in a number of samples with tincal.

3. In this study the aim of using alunite mineral was to accelerate the setting time of the pastes according to the values obtained by İ. Kula in recent years. However, it couldn't be possible to see the expected effects of alunite.

4. Considering compressive strength values, the combined action of both fly ash + colemanite ore waste + alunite and bottom ash + colemanite ore waste + alunite as cement replacement material is within the acceptable range of TS for wt 6%, wt 11 %, wt 16 %, at the age of 2 days. The results obtained after 7 days curing age comply with TS.

5. The replacement of PC with the mixture of tincal ore waste + fly ash + alunite mineral beyond the 11 wt % caused a significant reduction m the compressive strength. When tincal waste was replaced together with BA and alunite, the mixtures containing up to 6 wt % of this mixture showed considerable decrease in all ages.

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