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CEMENT MIXES CONTAINING COLEMANITE FROM CONCENTRATOR WASTES

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ABSTRACT

In this article, colemanite ore wastes of particle size <25 mm and sludge from concentrator were dried by hot air flow and then were mixed with Portland and trass cements. The effects on the setting and mechanical properties of the colemanite ore wastes mixed with Portland and trass cements were investigated. It was found that some colemanite wastes can be used as cement additives. © *1998 Elsevier Science Ltd*

Introduction

Türkiye has the largest boron reserve in the world and its approximate reserve is 90,002,000 tons (1). It is estimated that Türkiye has about 54% of the known reserves of the world. The estimated boron reserves of Türkiye is given in Table 1 (2).

Colemanite ($2CaO{\cdot}2B_2O_3{\cdot}5H_2O$) is a borate ore. Previous studies have investigated the utilization of borogypsum (3), boric acid sludge (4), and partly refined chemical by-product gypsums as cement additives (5,6). Also, wastewaters containing borate have been studied for incorporation in cement matrices (7).

Recoverable reserves of boron are in the form of the hydrated borate minerals pandermite ($CaB_6O_{19}{\cdot}7H_2O$), ulexide ($NaCaB_5O_9{\cdot}H_2O$), tincal ($Na_2B_4O_7{\cdot}10H_2O$), and colemanite. The boron is usually recovered as boric acid by acid leaching of the borate minerals. In situ, colemanite is leached by using sulphuric acid, but the disposal of its by-products, especialy borogypsum, can cause severe environmental problems (8).

Colemanite ore obtained from the mine of district Espey in Kütahya was subjected to crushing, cleaning, and sieving operations, and then 3 different concentrated colemanite fractions were obtained with particle sizes of +100 mm, 25–100 mm, and 3–25 mm. The concentrator wastes, after passing a screen of 25-mm aperture, were discharged into ditches in an unoccupied land and sludges obtained from the concentrator were dropped into a waste pool.

In this work, the concentrator waste passing a screen of 25-mm opening and the concentrator sludge were dried by heating with air, and then were added to Portland and trass cements to obtain cement mixes with different proportions.

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TABLE 1
Known boron reserves in Türkiyee.

Province	Known Ore Reserve, tons			Average, B_2O_3 Tenor	Total Tonnage	B_2O_3 Content Tons
	In Appearance	Probable	Possible			
Eskişehir1	39,525,112	13,489,278	486,541,278	27.00	514,553,549	139,015,487
Kütahya2	26,708,443	85,217,416	2,584,232	39.80	114,510,091	45,576,437
Balıkesir3	24,709,393	9,359,210	975,000	31.66	35,043,603	11,094,008
Bursa4	1,202,000	420,000	150,000	33.00	1,722,000	584,760
Totally	92,143,947	108,485,786	465,250,510	29.48	665,879,243	192,270,800

Districts: [1]Seyitgazi, Fethiye, Sarıkaya, Salihiye, Depçilkaya, Kırkka, and Sandıközü
[2]Emet, Alpanoz, Bahatlar, Espey, and Hisarcık
[3]Bigadiç, Yeniköy, Çamköy, Çamköy, Değirmenli, Faraş, Yolbaşı, and Osmancık
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Materials and Methods

Colemanite waste and sludge samples were supplied from the concentrator at Etibank Foundation, Kütahya-Emet, Espey in Türkiye.

Air-dried waste mud and coarse waste passing a screen of 25 mm aperture were analyzed by using XRF. B_2O_3 in the samples was determined according to MTA (9) titration method. The chemical analyses results of the colemanite wastes present in Table 2.

The colemanite wastes were added to Portland and trass cements in 1, 3, 5, and 7% proportions by weight. The cement mixes were ground to a certain fineness. In all tests, sample passing 45 μm (No: 325) sieve was used.

The physical tests such as setting time, volume expansion, and bending and compressive strenghts were carried out according to Turkish Standards (10). The obtained results were compared with the TS 19 and TS 26 standard requirements.

TABLE 2
Chemical analyses of colemanite wastes, weight percent.

Constituent	Waste Passing a Screen 25 mm Aperture (Coarse Waste)	Waste Mud (Sludge)
SiO_2	30.77	19.76
Al_2O_3	9.38	4.05
Fe_2O_3	3.51	1.47
CaO	11.99	19.44
MgO	5.40	2.40
SO_3	0.18	0.10
Na_2O	0.06	0.01
K_2O	3.18	1.45
B_2O_3	17.00	29.00
Loss Ignition	14.54	15.53
Water Insoluble Residue	3.99	8.60

TABLE 3
Symbols of cement mixes.

Symbol	Cement Mixes	Symbol	Cement Mixes	Symbol	Cement Mixes	Symbol	Cement Mixes
P1	1% CW + 99% PC	P5	1% S + 99% PC	T1	1% CW + 99% TC	T5	1% S + 99% TC
P2	3% CW + 97% PC	P6	3% S + 97% PC	T2	3% CW + 97% TC	T6	3% S + 97% TC
P3	5% CW + 95 PC	P7	5% S + 95% PC	T3	5% CW + 95% TC	T7	5% S + 95% TC
P4	7% CW + 93% PC	P8	7% S + 93% PC	T4	7% CW + 93% TC	T8	7% S + 93% TC

CW, Coarse Waste; PC, Portland Cement; S, Sludge; TC, Trass Cement.

TABLE 4
Setting time of cement mixes.

Symbol of Cement Mix.	Setting Time		Symbol of Cement Mix.	Setting Time	
	Initial h:min	Final h:min		Initial h:min	Final h:min
P1	2:10	3:15	T1	2:35	3:55
P2	2:35	3:35	T2	3:00	9.30
P3	2:15	4:50	T3	3:10	15.45
P4	4:45	10:00	T4	3:25	21:55
P5	2:20	3:30	T5	2:45	4:20
P6	2:25	3:25	T6	3:10	17:00
P7	2:40	9.55	T7	3:00	21.00
P8	4:40	12.00	T8	3:00	23:20
TS 19	1h (Min.)	10h (Max.)	TS 26	1h (Min.)	10h (Max.)

TABLE 5
Volume expansions of cement mixes.

Cement Mix.	Volume Expansion (mm)			Cement Mix.	Volume Expansion (mm)		
	Cold	Hot	Total		Cold	Hot	Total
TS 19	—	—	10.00 (Max.)	TS 26	—	—	10.00 (Max.)
P1	1	1	2	T1	1	1	2
P2	1	1	2	T2	1	0	1
P3	2	1	3	T3	1	0	1
P4	1	1	2	T4	1	0	1
P5	1	1	2	T5	1	1	2
P6	1	1	2	T6	1	0	1
P7	1	1	2	T7	1	0	1
P8	2	5	7	T8	1	0	1

TABLE 6
Bending strength of cement mixes.

	Bending Strength (N/mm^2)				Bending Strength (N/mm^2)		
Cement Mix.	2 Day	7 Day	28 Day	Cement Mix	2 Day	7 Day	28 Day
Cement Mix.	—	4.0	5.5	TS 26	—	4.0	5.5
P1	4.1	6.5	7.5	T1	2.8	4.9	6.1
P2	3.6	5.8	7.8	T2	2.0	3.9	5.2
P3	3.7	6.1	7.7	T3	—	—	—
P4	3.0	6.2	6.9	T4	—	—	—
P5	4.5	6.4	7.6	T5	2.5	4.0	5.2
P6	3.5	5.8	7.5	T6	—	—	—
P7	2.6	5.6	7.4	T7	—	—	—
P8	—	—	—	T8	—	—	—

Results and Discussion

The symbols of the cement mixes are given in Table 3. The setting times of the cement mixes are shown in Table 4. The volume expansion values of the cement mixes are given in Table 5.

From the data in Table 4, setting times for P1, P2, P3, P5, P6, and P7 are reasonable compared with the Turkish Standards (TS) requirements but setting time values for P4 and P8 are outside the limits. Data for volume expansions of all cement mixes are in accord with the values from TS mixes.

As can be seen in Table 6, the bending strength values of Portland cement mixes, apart from P8, resulted better than the values obtained from TS mixes. However results from trass cement mixes, except T1, are not good.

From physical test results in Table 7, the compressive strength values of all the cement mixes are generally in agreement with the values obtained from TS mixes. All the compres-

TABLE 7
Compressive strengths of cement mixes.

	Compressive Strength (N/mm^2)				Compressive Strength (N/mm^2)		
Cement Mix.	2 Day	7 Day	28 Day	Cement Mix.	2 Day	7 Day	28 Day
TS 19	10.0	21.0	32.5	TS 26	10.0	21.0	32.5
P1	20.3	37.1	40.3	T1	14.0	25.9	34.4
P2	18.0	32.0	41.3	T2	9.11	22.9	32.3
P3	17.4	34.4	39.9	T3	—	—	—
P4	14.8	34.8	44.7	T4	—	—	—
P5	20.3	35.6	40.7	T5	12.4	24.2	31.4
P6	17.3	32.7	43.2	T6	—	—	—
P7	11.6	33.3	42.7	T7	—	—	—
P8	—	—	—	T8	—	—	—

sive strength values of concretes obtained from the colemanite waste mixes are considerable near to the values given for TS mixes.

Conclusion

Unrefined borate wastes and sludges were used without pretreatment in all the experiments. The results are in agreement with the earlier study (4). As a result, it is suggested that colemanite wastes can be used as cement additives up to 5% by weight of cement.

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