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THE EFFECT OF BORIC ACID SLUDGES CONTAINING BOROGYPSUM ON PROPERTIES OF CEMENT

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ABSTRACT

The effects on the compressive strength of Portland cement directly mixed with boric acid wastes such as reactor waste, borogypsum and sludges were studied. It was found that as the percent of the sludges increase in the cement mixture the compressive strength decreased.

Introduction

Türkiye has the largest boron sources in the world. Approximately one million four thousand tons of boron ore per year is produced in Türkiye and its approximate reserve is six thousand seventy million tons as given Table 1[1].

TABLE 1
Reserves of Known Boron Ores in the World

Country	Total Reserve (million Ton)	B_2O_3 %	Distribution %
Türkiye	666	29.48	53.12
USA	320	25.00	25.51
CCCP	136	20.00	10.84
Argentina	40	20.00	3.18
China	36	20.00	2.87
Chili	28	-	2.23
Peru	28	-	2.23
Total	1254		99.97

Sludge recovered from a boric acid factory includes mainly borogypsum (BG). BG consists of approximately 75 % $CaSO_4.2H_20$ and 11% B_2O_3 and it can used as a admixture in Portland cement concrete.

Previous studies have investigated the utilization of BG[2] and partly refined chemical by-product gypsums as cement additives[3,4,5,6]. Also borate containing waste waters have been investigated for incorporation in cement matrices[7]. The effects of the chemical additives such as the initial hydration and setting time, bending and compressive strengths, etc. on the properties of cement were discussed in detail in these studies.

In the earlier articles[2,3], ortho boric acid and lithium contents of BG and partly refining of these from BG, the bending and compressive strengths of concretes from various Portland cement and BG mixes were reported. It was shown that refined or partly refined BG can be used for Portland cement. However, because of the very long setting time and thus long workability period, BG, as currently produced and refined, would be unlikely to serve as a general replacement for natural gypsum in cement applications that can take advantage of the long workability period, but not in situations where rapid set or high early strength, within the first 24 hours especially, are required. Therefore, BG is a material where further research needs to be done to optimize its performance in cement for particular uses[8].

In this work, properties of concrete obtained from different BG replacement and the other cementing admixtures were studied. The objective of this study is to investigate the effect of boronic sludges on properties of cement and the optimal BG replaced by natural gypsum.

Materials and Methods

Sludges and samples used in this work were selected from two boric acid factories of Etibank Foundation, Bandırma in Türkiye. Chemical composition of Portland cement, natural gypsum, BG, reactor waste and sludge samples are shown in Table 2.

TABLE 2
Chemical Compositions of Samples by Weight Percent

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	B_2O_3	H_2O
Cement	20.8	5.9	4.5	62.9	1.5	1.0	--	0.6
Natural gypsum	11.2	0.8	0.8	28.7	0.7	36.8	-	1.0
BG	22.3	0.8	0.7	43.2	1.1	1.7	5.3	24.9
Reactor waste	10.9	1.2	0.7	28.5	0.8	44.5	1.6	11.8
Sludge-1	4.8	1.4	0.8	26.7	1.2	37.6	3.7	22.4
Sludge-2	5.2	1.8	1.0	23.5	0.8	34.1	7.2	24.2
Sludge-3	7.1	2.4	1.6	25.0	0.9	39.8	12.4	10.8
Sludge-4	6.3	1.8	1.2	21.2	0.7	28.5	15.4	17.6

Cement test mixtures prepared according to the earlier studies[9-10]. The physical tests were carried out according to TS 24[11].

Results and Discussion

The aggregate data and compressive strength test results for BG, reactor waste and sludges and Portland cement mixes compared to the control mix are given in tables 3,4 and 5.

From the results in Table 3, compressive strength values generally decrease with increasing ratio of reactor waste in the cement mixes.

As seen in Table 4, BG improves the compressive strength of concrete by 12 % and then the strength decreases with the increasing percent of BG in the mixtures. In the earlier work, refined BG, containing 6-8 % B_2O_3 was used[3]. B_2O_3 content of the BG used in this work was 1.6 %.

Unrefined boronic sludges were used without pretreatment in all the experiments. All the compressive strength values of concretes obtained from the sludge mixtures are considerably lower than that of the control mix. As seen from the

TABLE 3
Compressive Strength Test Results for Reactor Waste and Portland Cement Mixture

Portland Cement (g)	Reactor Waste (g)	Natural Sand (g)	Crush Stone (g)	Water	Compressive Strength, N/mm^2				
					1 Day	7 Day	28 Day	56 Day	90 Day
410	0	1215	1540	260	11.0	27.1	34.3	36.8	39.6
390	25	1200	1500	255	8.9	23.5	30.8	33.2	35.1
370	40	1210	1520	260	9.2	19.6	28.4	30.4	31.8
350	60	1215	1510	263	10.3	20.0	23.6	24.8	28.6
330	80	1210	1500	245	8.5	16.6	20.7	22.6	25.3
300	100	1200	1505	255	8.1	14.8	18.1	20.4	23.0
200	205	1210	1510	258	6.7	13.7	18.4	18.9	20.1

TABLE 4
Compressive Strength test results for BG and Portland Cement Mixture

Portland Cement (g)	BG (g)	Natural Sand (g)	Crush Stone (g)	Water (g)	Compressive Strength, N/mm^2				
					1 Day	7 Day	28 Day	56 Day	90 Day
410	0	1215	1520	260	11.0	27.1	34.3	36.8	39.6
385	25	1215	1518	254	17.6	30.8	43.0	43.8	45.3
360	45	1213	1520	251	14.5	25.0	32.1	38.6	39.6
350	60	1220	1510	260	13.6	22.6	28.8	30.4	36.7
330	80	1204	1502	250	13.8	20.8	24.4	27.7	33.4
300	100	1212	1516	256	11.0	18.7	25.2	28.0	32.8
200	210	1210	1520	260	9.6	15.6	18.6	19.3	21.0

Table 2 and 5, in general as the percent of B_2O_3 in the sludges increase with decreasing compressive strength of concrete obtained from the mixtures of cement and sludges. The compressive strength decrease as the amount of sludge and B_2O_3 increases, especially for sludge 4. These results are in agreement with the previous study[10].

TABLE 5
Compressive Strength Test Results for Sludge Samples and Portland Cement Mixture

Sample	Portland Cement	Sludge (g)	Natural Sand (g)	Crush Stone (g)	Water (g)	Compressive Strength, N/mm^2			
						1 Day	7 Day	28 Day	90 day
Control Mix	410	0	1215	1520	260	11.0	27.1	34.3	39.6
Sludge-1	304	102	1210	1515	253	6.2	8.8	10.4	14.2
Sludge-2	300	105	1205	1508	255	5.0	7.6	9.7	13.7
Sludge-3	305	100	1212	1510	251	4.3	7.5	7.2	12.0
Sludge-4	307	97	1207	1512	256	3.8	6.8	8.3	12.6

As a result, it might be suggested that boronic sludges maybe used as cement additives up to 4 %. However refined BG can be added to cement up to 12 % (Table 2 and 4).

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