Utilization of Boron Waste as an Additive for Cement Production

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Abstract

Turkey has 955,297 thousand tonnes of B_2O_3 reserves which correspond to 72.1% of the world. Colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$), ulexite ($NaCaB_5O_9\cdot 8H_2O$) and borax (tincal) ($Na_2B_4O_7\cdot 10H_2O$) are the most important boron minerals that are used in production of boric acid and different kinds of borates. During these production processes, boron including wastes form and these wastes pollute the environment. To minimize the pollution caused by these wastes, they are evaluated in different kinds of processes such as cement and concrete production. Borogypsum is one of the boron wastes that is used in cement mortar production.

In this study the aim was to compare the calcined and non-calcined borogypsum addition to clinker and also investigate its effects on cement mortar. Moreover, to see how borogypsum addition affected the cement properties, different ratios of borogypsum between 1% and 7% were used. Also setting time and consistency analyses were applied to fresh mortar; compressive strength and splitting tensile strength of 3, 7, and 28 days were investigated according to the Turkish Standard (TS EN 196-1). X-ray diffraction (XRD) analysis was realized for characterization of the chemical structure of 28-days mortars. 3% was the ratio at which the optimum results were obtained for both calcined and non-calcined borogypsum.

Keywords- cement mortar; borogypsum; calcination; XRD.

1 Introduction

Borogypsum is the waste that forms during boric acid production from the reaction between colemanite ore and sulphuric acid (1). Although borogypsum is used in many processes because of its B_2O_3 content it pollutes the soil and water. One of the processes in which the borogypsum can be used is cement production [1-8].

$$Ca_2[B_3O_4(OH)_3]_2\cdot 2H_2O + 2H_2SO_4 + 4H_2O \rightarrow 6H_3BO_3 + 2[CaSO_4\cdot 2H_2O] \quad (1)$$

There are lots of studies to investigate and improve the addition of the boron wastes to cement and concrete production. In the study of Sevim and Tümen [5], they used different ratios of borogypsum as concrete additive and they concluded that borogypsum retarded the initial and final setting times of concrete mixtures. Moreover, they reported that 3% and 5% borogypsum containing mixtures had higher compressive strength. Abalı, Bayca, and Targan [6], studied the addition of tincal waste with other wastes such as fly ash, bentonite and volcanic tuff to cement and they revealed that compressive strength decreased with increasing tincal waste ratio. Kavas, Olgun and Erdoğan [7], studied effects of borogypsum on the setting time of cement and strength of the mortar. Elbeyli [8], studied effects of the borax wastes addition on the mechanical and physical properties of cement and it was concluded that compressive strength, expansion and setting time properties of cement decreased with the increase in B_2O_3 content of waste.

In this study calcined and non-calcined borogypsum in different ratios were added to cement mortar and effects of waste ratios on cement mortar properties were compared.

2 Experimental Studies

2.1 Raw material preparation and characterization

Borogypsum, which was used in the experiments, was provided from Etibank Bandırma Boron and Acid Factory, Turkey. The waste was in the form of filter cake so that it was placed to the furnace at 105°C for 4 hours to remove its water content. The dried borogypsum was crushed, grinded and sieved. Specific surface area of borogypsum was calculated as 3205.61 cm^2/g according to Blaine Method and density was measured as 2.41 g/ml according to Le-Chatelier Method. Borogypsum was in its dihydrate form ($CaSO_4 \cdot 2H_2O$). To investigate the effects of borogypsum, which was both in the forms of dihydrate and hemihydrate, on strength of cement mortar, borogypsum was calcined at 185°C for 8 hours.

Clinker was provided from Akçansa Cement Factory. Specific surface area of clinker was calculated as 3020 cm^2/g according to Blaine Method and density was calculated 3.18 g/ml according to Le-Chatelier Method. In experiments clinker was used without any pretreatment.

Standard sand (according to TS EN 196-1 standard) was provided from Jeotest Construction Materials. Density of sand was 3.24 g/ml according to Le-Chatelier Method. Any pretreatment was not applied to sand before the experiments.

Distilled water was used for preparation of cement mixtures.

Borogypsum was characterized by Philips PANalytical X-ray diffraction (XRD) (Fig. 1) with Cu-Kα radiation at 45 kV and 40 mA. Elemental analysis of borogypsum was carried out by Philips PANalytical Minipal 4 brand X-ray fluorescence (XRF) (Fig. 2). Analyses were applied between 4 kV-30 kV and silicon detector was used.

Figure 1. Philips PANalytical XRD

Figure 2. Philips PANalytical Minipal 4 XRF

2.2 Preperation of Cement Mortars

In the studies, four samples which have ratios of 1%, 3%, 5% and 7% were prepared with both calcined and non-calcined borogypsum. Also there was a reference sample in which no borogypsum was included. Amounts of the raw materials and water/binder ratios in the samples were shown in Table I. "CB" represented calcined borogypsum and "B" represented non-calcined borogypsum samples.

During the studies, methods of TS EN 196-1 [9] cement experiment were applied but clinker and different ratios of borogypsum were used instead of cement.

Table 1. Amounts of raw materials for cement mortar

Sample	Clinker (g)	Borogypsum (g)	Sand (g)	Water (g)	Water/binder ratio	% Borogypsum
Reference	600	0	1800	300	0.5	0
CB1	594	6	1800	300	0.5	1
CB2	582	18	1800	300	0.5	3
CB3	570	30	1800	300	0.5	5
CB4	558	42	1800	300	0.5	7
B1	594	6	1800	300	0.5	1
B2	582	18	1800	300	0.5	3
B3	570	30	1800	300	0.5	5
B4	558	42	1800	300	0.5	7

According to the standard TS EN 196-1, amounts of raw materials shown in Table I were weighed. To mix materials, UTEST brand cement mixer (Fig. 3) was used and mixing realized mechanically. For the reference sample, first water and clinker were added to the mixer. Then mixer was turned to low speed and after 30 seconds sand was added within 30 seconds. After the addition of sand, mixing was continued for 30 seconds with high speed. Mixer was stopped after 1 minute and 30 seconds. After 15 seconds of waiting time, mixing was continued with high speed for 60 seconds.

Figure 3. Cement mixer

In order to test the workability of the samples, flow table experiments were applied to fresh mortar according to TS EN 12350-5 standard [10] with UTEST brand flow table (Fig. 4).

Figure 4. Flow table

After flow table experiments, mortars were filled to the prismatic moulds which had the dimensions of 40x40x160 mm. Moulds were covered with glass and they were placed to test cabinets at 20°C and relative humidity of 90% for 24 hours. The demoulded specimens were cured in water at 20±1°C for 3, 7 and 28 days for compressive and splitting tensile strength experiments.

To analyze the setting times, samples were poured to the vicat moulds and moulds were placed to the curing pool again. Setting time measurements were done in certain time intervals. Vicat apparatus was shown in Fig. 5.

Figure 5. Vicat apparatus

Unit volumes of samples were obtained from weight of the samples and volume of the vicat mould.

2.3 Cement composite experiments

Compressive and splitting tensile strengths of the samples at the ages of 3, 7 and 28 days (shown in Fig. 6) were measured with UTEST compressive and splitting tensile strength equipment which is shown in Fig. 7.

Experiments were repeated three times for each sample and results were averaged. XRD analysis was performed for samples of 28 days with the same parameters aforementioned for borogypsum.

Figure 6. Samples after 28 days

Figure 7. Compressive and splitting tensile strength equipment

3 Results and Discussion

3.1 Raw material characterization results

XRD pattern of borogypsum was shown in Fig. 8. According to the XRD results of borogypsum, gypsum ($CaSO_4 \cdot 2H_2O$) was found with powder diffraction file (pdf) number "00-006-0046".

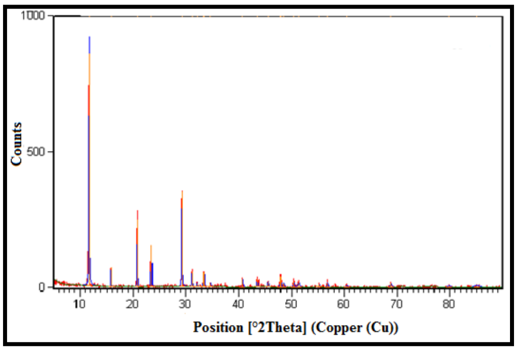

Figure 8. XRD pattern of borogypsum

XRF analysis results of borogypsum was given in Table I.

Table 2. XRF Analysis results of borogypsum

Compounds	%
SO_3	45.9
K_2O	0.55
CaO	46
Sc_2O_3	0.64
Fe_2O_3	1.1
CuO	0.07
As_2O_3	0.22
SrO	5.48
ZrO_2	0.01
PbO	0.03

3.2 Cement Mortars Experiments Results

Results of the experiments that were realized with addition of borogypsum were shown in Table III. Flowing value is a measure of workability. According to the flowability classifications specified in standards, all of the mortars including reference had flowing diameter smaller than 34 mm, therefore they were classified as F1.

Table 3. Flow table experiments results

Sample	Flowing Value (cm)
Reference	9.50
CB1	13.30
CB2	15.35
CB3	15.65
CB4	14.60
B1	13.00
B2	13.63
B3	11.63
B4	12.70

Table IV shows the unit volume of samples. Initial and final setting times of samples are represented in Table V.

Table 4. Unit volume of samples

Sample	Unit Volume (kg/m^3)
Reference	2134.75
CB1	2201.43
CB2	2302.57
CB3	2321.78
CB4	2322.91
B1	2277.71
B2	2315.57
B3	2300.88
B4	2047.16

Table 5. Setting times

Sample	Initial Setting Time (min.)	Final Setting Time (min.)
Reference	155	315
CB1	430	560
CB2	520	1770
CB3	1350	1830
CB4	1280	1945
B1	205	365
B2	335	500
B3	1295	1575
B4	1330	1720

3.3 Cement composite experiments results

Results of the compressive and splitting tensile strengths of the samples were given in Table VI. When these results were examined, it is obvious that addition of calcined borogypsum to mortars affects cement strength positively. If compressive and splitting tensile strengths of 3, 7, 28 days obtained from calcined and non-calcined mortars were compared, non-calcined mortars had lower strength.

Examination of 28 days strengths showed that increase of calcined borogypsum from 0% to 1%, increased compressive strengths by 47%, increased splitting tensile strength by 92%. Moreover with the increase of calcined borogypsum from 1% to 3%, compressive strength increased by 8.1% and splitting tensile strength decreased by 8.2%. Also increase in calcined borogypsum from 3% to 5% resulted in decrease of compressive strength by 6.7% and splitting tensile strength by 6.2%. Lastly, increase in calcined borogypsum from 5% to 7% resulted in decrease of compressive strength by 8.6% and increase of splitting tensile strength by 8.8%. Comparison of the 28 days strength results obtained from calcined and reference samples showed that strengths of calcined samples higher than reference sample.

Examination of 28 days strengths showed that the increase of non-calcined borogypsum in cement mortar from 0% to 1%, increased compressive strengths by 39.1%, increased splitting tensile strength by 69.5%. When the ratio of non-calcined borogypsum in mortar changed from 1% to 3%, compressive strength increased by 8.9% and splitting tensile strength increased by 7.8%. Moreover, the increase in non-calcined borogypsum from 3% to 5% resulted in decrease of compressive strength by 13% and splitting tensile strength increased by 8.7%. When the ratio of non-calcined borogypsum reached to 7% from 5% resulted in increase of compressive strength by 14.7% and decrease of splitting tensile strength by 25.16%. Comparison of the 28 days strength results obtained from non-calcined and reference samples showed that strengths of non-calcined samples higher than reference sample.

Investigation of the compressive and splitting tensile strength results of non-calcined borogypsum samples indicated that addition of non-calcined borogypsum affected strengths negatively if they were compared with calcined borogypsum samples. However their strengths were higher than the reference sample. Samples of 28 days including 3% and 5% non-calcined borogypsum had the best splitting tensile strength.

XRD pattern of CB2 sample which had the best compressive strength was shown in Fig. 9. According to the XRD results of the sample; silica (SiO_2) with powder diffraction file (pdf) number "00-033-1161", ettringite, ($Ca_6Al_2(SO4)_3(OH)_{12}\cdot 26H_2O$) with pdf number "00-041-1451" and portlandite, syn ($Ca(OH)_2$) with pdf number "00-044-1481" were found.

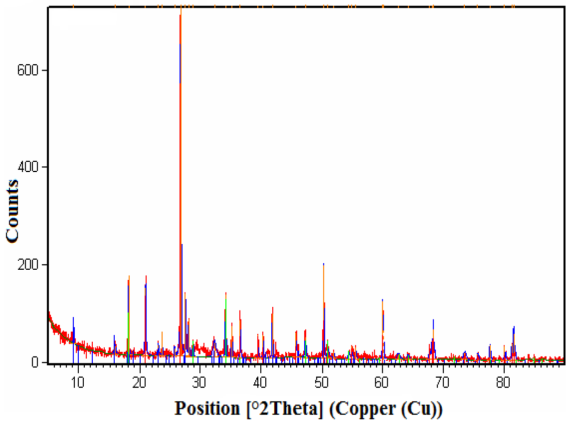

Figure 9. XRD pattern of CB2 sample

Table 6. Compressive and splitting tensile strengths of samples

Sample	Day	Splitting Tensile Strength (MPa)	Compressive Strength (MPa)
Reference	3	2.71	15.38
	7	2.99	18.18
	28	3.84	30.18
CB1	3	4.30	23.14
	7	5.76	36.05
	28	7.40	44.42
CB2	3	4.35	24.07
	7	6.13	35.88
	28	6.79	48.00
CB3	3	0.00	4.47
	7	5.43	31.47
	28	6.37	44.79
CB4	3	0.00	0.00
	7	5.01	28.22
	28	6.93	40.92
B1	3	3.84	24.35
	7	5.01	29.40
	28	6.51	41.98
B2	3	4.59	23.45
	7	6.04	36.27
	28	7.02	45.70
B3	3	5.43	29.66
	7	5.90	35.84
	28	7.63	39.74
B4	3	3.93	23.67
	7	4.40	33.13
	28	5.71	45.59

4 Conclusions

In this study, the aim was to specify the ratios of added borogypsum to the cement mortars and therefore the waste that forms in the production of boric acid would be evaluated. To realize this aim, samples including borogypsum waste with constant water/binder ratio and reference sample were prepared according to standard. Also borogypsum was used in the forms of both calcined and non-calcined. Samples were analyzed both before and after hardening of cement mortars. Flow table and setting time analyses were applied to the fresh mortar when after hardening, compressive and splitting tensile strength analyses were conducted to the samples. After all these analyses, it was concluded that mortars including borogypsum waste had higher compressive and splitting tensile strengths and higher setting time with respect to reference sample which was borogypsum-free.

From the studies realized with calcined borogypsum, it was seen that sample including 1% waste had the best splitting tensile strength (7.40 MPa) and sample including 3% waste had the best compressive strength (48.00MPa). According to results of non-calcined borogypsum experiments showed that sample including 5% waste had the best splitting tensile strength (7.63 MPa) and sample including 3% waste had the best compressive strength (45.70 MPa).

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