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The Effects of Accelerating Admixture on the Mechanical Properties of Boric Acid Added Mortars

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Use of boron compounds has not become widespread because of the hardening and the other related problems in cementitious composites. The boron compounds as an additive material can be used widely in the production of cement and concrete in case of the elimination of these negative conditions. Thus the control of workability and hydration process of fresh concrete and mortar, some technological properties such as fire resistance, the radiation impermeability of hardened concrete and mortars can be enhanced. In this study, the effects of accelerating admixtures to the mechanical properties of boric acid added mortars were investigated. In order to determine of these effects and the results obtained to compare with those of control mortars, prismatic mortar samples were prepared in accordance with TS 196-1. Boric acid was added to mortar samples by up to 1% from 0.25% by weight of cement. Boric acid was not added to control mortar samples. Portland cement, boron modified active belite cement and calcium aluminate cement as binding material were used in mortar samples. 2, 7, 28 day compressive strengths and 28 day flexural strengths of 315 prismatic samples which were prepared in accordance with the design of 35 different mixes were determined. Results of boric acid added mortar samples were compared with control samples produced by using Portland cement, BAB cement and CAC cement. 2, 7, and 28 day compressive/flexural strength of mortar samples which were added 1% boric acid was determined as 0/0, 12.8/2.90, 40/6 MPa, respectively. Other hand, 2, 7, and 28 day compressive/flexural strength of mortar samples which were added 1% boric acid and 2% sodium aluminate was determined as 14.2/3.07, 27.2/5.57, 34.2/5.97 MPa, respectively. As a result, the retarding effect of the boric acid in terms of early strength of concrete was suppressed using sodium aluminate.

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1. Introduction

Boron-containing wastes of nuclear power plants have been solidified using cement and stored underground for many years. However, the compressive strengths of these concretes are limited with 8–10 MPa, and it can take 90 days reaching to this strength value. In the other word, the negative effect of boron compounds on cement hydration is well-known phenomenon. These effects can be described as the increase of hydration time, a much reduction of early strength, weakening of cement–aggregate bond strength, solidification-hardening problems and strength-durability problems.

Phenomena which are caused by these effects can be explained as follows: calcium borate ($CaOB_2O_3$) occur with reacting of boron oxide (B_2O_3) and calcium hydrate (CaOH) which are formed during interaction of cement with mixing water. This compound is cover to surface of cement particles partially or completely. As a result, the hydration reaction of cement is interrupted.

In recent years, many studies have been carried out for the usability of boron wastes at the cement production. Kula et al. (2002) have mentioned that the use of tincal ore waste also gives rise to an improvement in the properties of Portland cement (OPC) at 1% replacement level. Although it retards setting time, it gives an opportunity for use as a cement replacement material up to 5 wt% of the cement [1]. According to Targan et al. (2003), the compressive strength of concrete samples is made by cement with grinding the 81–96% Portland clinker, 4% colemanite waste, and 5–15% natural pozzolan materials at 90 days of curing performs 90% of control concrete samples. They also stated that the 28 days strengths of concrete made by high pozzolan cements including colemanite waste are higher than that of the concrete samples by low pozzolan cements [2].

In 2006 year, the boron modified active belite cement (BAB) with using colemanite ore was produced at Goltaş Cement Factory in Isparta, Turkey. According to researches based on this cement type, this cement with no alite (C_3S) phase could be successfully used specially in dam concretes due to its very low hydration temperature. In addition, the final compressive strength of concrete made by BAB cement is much higher than concrete's made by OPC [3].

In addition, properties such as shrinkage and fire resistibility of concrete and cementitious other composites including boron compounds in appropriate concentrations may be improved. Furthermore, these products may also gain new features such as radiation impermeability and antibacteriality. In some research, Volkman and Bussolini (1992) have stated that the boron compounds adding to concrete absorbs the neutrons and low energy gamma rays spreads. Therefore, it could be supplied as an effective radiation protection. However, adding boron seriously retards the setting time and decreases the concrete strength [4].

TABLE II

Physical and chemical properties of cements used as a binder [9, 10].

Chemical properties of clinkers				Physical properties of cements			
Components [%]	OPC	BAB	CAC		OPC	BAB	CAC
SiO_2	20.52	20.37	2.20	volumetric expansion [mm]	1	0	0
Al_2O_3	4.00	4.45	40.70	fineness [90μ]	0.1	0.1	6.5
Fe_2O_3	3.45	3.27	17.00	slightness [200μ]	1.1	1.8	1.2
CaO	64.28	58.19	38.20	specific surface area [cm^2/g]	3340	3560	3540
MgO	1.63	4.70	0.80	initial setting time [min]	185	220	245
SO_3	2.53	3.08	0.02	final setting time [min]	240	265	265
Na_2O+K_2O	1.35	1.50	0.07	specific gravity [g/cm^3]	3.12	2.98	3.29
B_2O_3	0.00	1.12	0.00	flexural strength (MPa, at 2 days)	4.5	2.5	6.0^a
CaO (free)	1.81	0.63	–	flexural strength (MPa, at 7 days)	5.8	4.1	7.5^b
L.O.I.	2.72	4.02	0.30	flexural strength (MPa, at 28 days)	7.2	6.0	9.5^c
Clinker phases [%]				compressive strength (MPa, at 2 days)	11.7	11.7	55.2^d
C_3S	–	56.66		compressive strength (MPa, at 7 days)	39.3	23.2	81.6
C_2S	66.23	17.65		compressive strength (MPa, at 28 days)	51.0	38.6	–
C_3A	7.86	6.33		Other properties of cements			
C_4AF	14.01	12.03		Cl^-	0.000	0.006	0.000

[a] 6 hours; [b] 24 hours; [c] 6 hours; [d] 24 hours

On the other hand, Demir and Keleş (2006) have prepared the concrete samples including borogypsum and colemanite concentrator wastes. They tested the differences in gamma rays passing energies for normal and boron waste added concretes samples. They observed that concrete samples including boron wastes supply an effective protection against radioactive radiations [5]. National Boron Research Institution (BOREN) stated that BAB cement has more than 20% of a neutron absorbing capacity compared to OPC [6]. Çelik (2008) also has stated that cellulose insulation materials including approximately 20% $B(OH)_3$ or borax are more resistant up to 57% against fire. They have also killing capacity up to 99.8% against micro-organisms and insects [7].

The improvements and additional features which are provided by boron compounds to concrete and cementitious composites are very closely relevant to B_2O_3 concentrations of using boron compounds. Furthermore, it is intensively researched a phenomenon, when the cement hydration slows down and even stops with the increase of B_2O_3 concentration and the setting time of mortar increases related to the situation [8].

In this study, there was investigated the effect of anhydrous boric acid as additive material on the compressive and flexure strengths of mortar samples which are produced with different cements. In addition, we tried to suppress the effect of the boron compound on the especially early strength of some mortar samples by using accelerator additives.

2. Material and methods

Boric acid (BA) obtained from Eti Mine Works as a source of B_2O_3, OPC, and BAB cement obtained from Göltaş Cement Factory and calcium aluminate cement (CAC) obtained from CİMSA were used in this study. Also accelerator additive materials such as calcium chloride (CC), sodium aluminate (SA) were added in the mortar mixtures in order to suppress the retarding effect of boric acid to cement hydration. The dosages of cement (PC, BAB, or CAC) used in all mortar samples are equal. The grain size distribution of CEN standard sand were used as aggregate, and physical and chemical properties of PC, BAB, and CAC cements using as a binder were given in Tables I and II, respectively.

TABLE I

The grain size distribution of CEN standard sand.

Sieve mesh size [mm]	Cumulative percent retained sieve [%]
2.00	0
1.60	6
1.00	35
0.50	68
0.16	89
0.08	99

TABLE III

The amounts of materials used in the mortar mixes (for three pieces).

Components	Amount [g]
cement	450 ± 2
standard sand	1350 ± 5
water	450 ± 1

Mortar mixtures were prepared in accordance with TS EN 196-1 standard. Mortar mixture designs for 3 pcs prisms (one set) were given in Table III.

Except for the control mortar samples, boric acid was added to mortar mixtures at 0.25%, 0.5%, 0.75% and 1%

by weight of cement

$$2B[OH]_3 + \text{heat} \rightarrow B_2O_3 + 3H_2O. \quad (1)$$

If 2 mol of $B[OH]_3$ is heated up to 600 °C approximately, 1 mol of B_2O_3 and 3 mol of water occurs. As 1 g of $B[OH]_3$ is heated, approximately 0.577 g of B_2O_3 is obtained. For mortar samples which were added boric acid, B_2O_3 amount was calculated according to Eq. (2):

$$M_{B_2O_3} = c \times 0.02 \times 0.577, \quad (2)$$

where M_{B2O3} — amount of B_2O_3 included in boric acid added mortar samples (g), c — cement dosage (g).

After determination of B_2O_3 amount, W_{B2O3}/c ratios for each set of samples were calculated as 0.144, 0.288, 0.434, and 0.577, respectively. In addition, the accelerator additives (sodium aluminate, calcium chloride) were added at rates of 1.0%, 1.5%, 2% by weight of cement in order to suppress of retarding effect of boric acid (Table IV).

TABLE IV

Amount of cement type, boric acid and chemical admixture used in mortar samples.

Sample No.	Cement type	W_{BA}/c [%]	W_{B2O3}/c	AA type	W_{AA}/c [%]
P	Portland	0	0.00	–	–
B	boron modified active belite	0	1.112	–	–
C	calcium aluminate	0	0.00	–	–
Pb1	Portland	0.25	0.144	–	–
Pb2	Portland	0.50	0.288	–	–
Pb3	Portland	0.75	0.434	–	–
Pb4	Portland	1.00	0.577	–	–
Cb1	calcium aluminate	0.25	0.144	–	–
Cb2	calcium aluminate	0.50	0.288	–	–
Cb3	calcium aluminate	0.75	0.434	–	–
Cb4	calcium aluminate	1.00	0.577	–	–
Pb1c1	Portland	0.25	0.144	calcium chloride	1.0
Pb2c1	Portland	0.50	0.288	calcium chloride	1.0
Pb3c1	Portland	0.75	0.434	calcium chloride	1.0
Pb4c1	Portland	1.00	0.577	calcium chloride	1.0
Pb1c2	Portland	0.25	0.144	calcium chloride	1.5
Pb2c2	Portland	0.50	0.288	calcium chloride	1.5
Pb3c2	Portland	0.75	0.434	calcium chloride	1.5
Pb4c2	Portland	1.00	0.577	calcium chloride	1.5
Pb1c3	Portland	0.25	0.144	calcium chloride	2.0
Pb2c3	Portland	0.50	0.288	calcium chloride	2.0
Pb3c3	Portland	0.75	0.434	calcium chloride	2.0
Pb4c3	Portland	1.00	0.577	calcium chloride	2.0
Pb1s1	Portland	0.25	0.144	sodium aluminate	1.0
Pb2s1	Portland	0.50	0.288	sodium aluminate	1.0
Pb3s1	Portland	0.75	0.434	sodium aluminate	1.0
Pb4s1	Portland	1.00	0.577	sodium aluminate	1.0
Pb1s2	Portland	0.25	0.144	sodium aluminate	1.5
Pb2c2	Portland	0.50	0.288	sodium aluminate	1.5
Pb3s2	Portland	0.75	0.434	sodium aluminate	1.5
Pb4s2	Portland	1.00	0.577	sodium aluminate	1.5
Pb1s3	Portland	0.25	0.144	sodium aluminate	2.0
Pb2s3	Portland	0.50	0.288	sodium aluminate	2.0
Pb3s3	Portland	0.75	0.434	sodium aluminate	2.0
Pb4s3	Portland	1.00	0.577	sodium aluminate	2.0

P: Portland cement	B: BAB cement	C: calcium aluminate cement	
b1: ($W_{B2O3}/c = 0.144$)	b2: ($W_{B2O3}/c = 0.288$)	b3: ($W_{B2O3}/c = 0.434$)	b4: ($W_{B2O3}/c = 0.577$)
c1: calcium chloride, 1%	c2: calcium chloride, 1.5%	c3: calcium chloride, 2.0%	
s1: sodium aluminate, 1%	s2: sodium aluminate, 1.5%	s3: sodium aluminate, 2.0%	

The prepared mortars were poured into the moulds having dimension of $40 \times 40 \times 160$ mm^3, compressed, and removed from the moulds after one day. The samples removed from the moulds were cured at 20 °C in water until the time of testing. The flexural and compressive strengths of mortar samples at 2, 7, and 28 days were determined in accordance with TS EN 196-1 standard [11]. The flexural and compressive strengths of these samples

were calculated using Eqs. (3) and (4), respectively

$$R_{\mathrm{f}} = 1.5F \times \frac{L}{b^3}, \tag{3}$$

where R_{f} — flexural strength, MPa, b — the side length of square cross-section of prism, mm, F — the force applied to center of the prism at breaking time, N, L — the distance between the support rollers, mm.

$$R_{\mathrm{c}} = \frac{F_{\mathrm{c}}}{1600}, \tag{4}$$

where R_{c} — compressive strength, MPa, F_{c} — the maximum load at the time of failure, N, 1600 — the area of plates used in the experiment (40×40 mm^2).

3. Results and discussion

The results of compressive strengths of mortar samples at 2, 7, and 28-d were given in Fig. 1. C sample has the highest 28-d compressive strength ($f_{\mathrm{c-28d}}$) between the control samples. However, $f_{\mathrm{c-2d}}$, $f_{\mathrm{c-7d}}$, and $f_{\mathrm{c-28d}}$ values of P control samples were higher than values of B control samples. The mortar samples of Cb1, Cb2 and Cb3 having $B_2O_3/c \leq 0.434$ ratios were not solidified at 2 and 7 days. Similarly, the mortar sample of Cb4 having $B_2O_3/c = 0.577$ ratio was not solidified at 28 days. While Pbc samples reached the highest 28-d compressive strengths ($f_{\mathrm{c-28d}}$), Pbs samples showed the highest flexural strengths ($f_{\mathrm{c-2d}}$ and $f_{\mathrm{c-7d}}$) at 2 and 7 days among the mortar samples used in the Portland cement and additives.

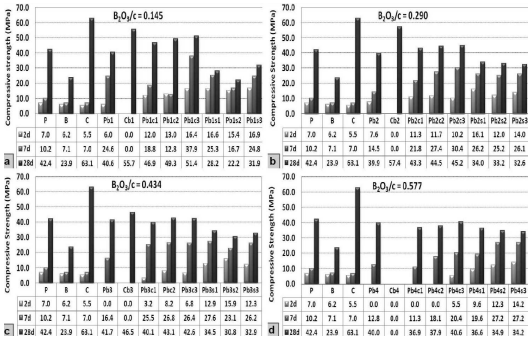

Fig. 1. 2, 7 and 28-d compressive strength of control (P, B, C) and mortar samples with additive.

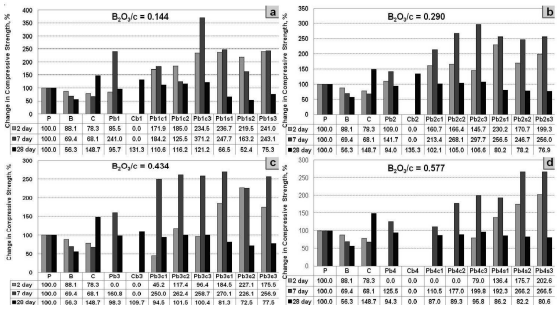

Fig. 2. The changes of compressive strengths of mortar samples with additive in comparison with P control sample.

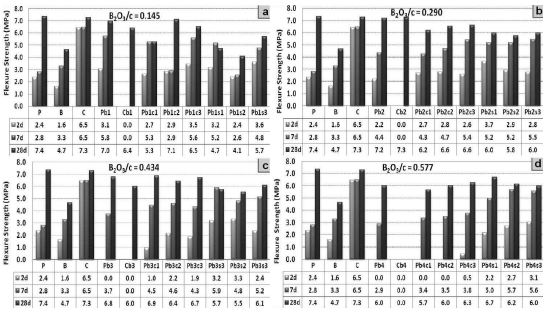

Fig. 3. 2, 7 and 28-d flexural strength of control (P, B, C) and mortar samples with additive.

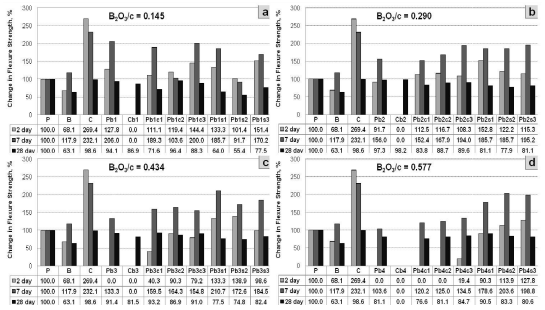

Fig. 4. The changes of flexural strengths of mortar samples with additive according to P control sample.

In addition, the changes (Δf_{c}) of compressive strengths of mortar samples with additive in comparison with P control sample at 2, 7 and 28-d were given in Fig. 2. $\Delta f_{\mathrm{c-28d}}$ ratio of Pbc samples is the highest between mortar samples with additive in comparison with P control sample. On the other hand, Pbs samples have the highest $\Delta f_{\mathrm{c-2d}}$ and $\Delta f_{\mathrm{c-7d}}$ ratios at $B_2O_3/c \geq 0.434$ ratios.

The results of flexural strengths of mortar samples at 2, 7 and 28-d were given in Fig. 3. P and C have the highest 28-d compressive strength ($f_{\mathrm{cf-28d}}$) between the control samples. The highest $f_{\mathrm{cf-28d}}$ value is belonged to $Pb3c1$ sample, the highest $f_{\mathrm{c-2d}}$ value belongs to $Pb3s2$ sample and the highest $f_{\mathrm{c-7d}}$ value also belongs to $Pb3s3$ sample between mortar samples with Portland cement.

The changes (Δf_{cf}) of flexural strengths of mortar samples with additive in comparison with P control sample at 2, 7 and 28-d were given in Fig. 4. Pbc samples have the highest $\Delta f_{\mathrm{cf-28d}}$ ratios between mortar samples with additive in comparison with P control samples (except for $B_2O_3/c \leq 0.577$ ratio). On the other hand, the highest $\Delta f_{\mathrm{cf-2d}}$ and $\Delta f_{\mathrm{cf-7d}}$ ratios belong to Pbs samples at $B_2O_3/c \geq 0.434$ ratios.

4. Conclusion

The negative effect of boron compounds on the early strength of cemented composites is well known. In this study, there was investigated the effect of boric acid compound to the compressive and flexural strengths of mortar samples at 2, 7 and 28-d. In addition, accelerator

additive materials in mortar samples were used for suppressing this effect.

For $B_2O_3/c \leq 0.290$ ratio, the compressive and flexural strengths of mortar samples in 2 and 7-d are reduced in comparison with P control sample. On the other hand, an important change is not established for 28-d strengths values. However, mortar samples are not solidified at 2 day and strengths values are quite reduced at 7 day for $B_2O_3/c \geq 0.434$ ratio. SA and CC additives were added to mixture at rates of 1.0%, 1.5%, 2% by weight of cement due to suppressing this negative effect. With SA additive, 2-d compressive strengths of mortar samples increased at a 202% ratio in comparison with the P control samples and 7-d compressive strengths of these samples also increased at a 266% ratio for $B_2O_3/c \geq 0.577$ ratio which is the highest ratio used in this study. Furthermore, 2 and 7-d the flexural strengths of the same samples increased at 128% and 200% ratios in comparison with the control samples. As a result, the negative effect of boron compounds on the early strength of cemented composites was suppressed with SA additive.

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