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Setting and hardening of borogypsum–Portland cement clinker–fly ash blends. Studies on effects of molasses on properties of mortar containing borogypsum

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Abstract

The present work describes a study of setting and hardening of blends of borogypsum, fly ash, and Portland cement clinker (PC). The possibility of using borogypsum instead of natural gypsum in fly ash–cement matrix has been investigated through several tests. In addition, the effects of molasses on the setting times of cement and strength of the mortar were also studied. The setting times of the cement were retarded when the natural gypsum was replaced by borogypsum. Molasses exhibited a rather significant retarding effect when used in combination with borogypsum in cement. The inclusion of molasses to the system at a level of 0.1% resulted in a reduction in early strength of the mortar. However, it significantly enhanced the strength of the mortar after 7 days of curing age. In general, the cement prepared with borogypsum was found to have similar strength properties to those obtained with natural gypsum, and inclusion of molasses into the system significantly increased the strength of the sample after 7 days of curing age.

Keywords: Borogypsum; Cement; Fly ash; Strength; Setting time

1. Introduction

The developing of world economy consumes a large amount of resources and energy and produces a huge quantity of wastes, causing environmental pollution that results in the destruction of the ecological balance. In recent years, the use of waste materials in the production of cement and concrete has become commonplace because it offers cost reduction, energy savings, and arguably superior products. Two major by-products are fly ash and borogypsum, which are produced in an annual magnitude of a hundred million tons in Turkey. Of the two wastes, only a small amount of fly ash is properly used in Turkey presently. Therefore, there is a continuing interest in establishing different processes in which these waste materials can be valuably reused.

It is well known that natural gypsum is added to clinker to delay rapid reaction between tricalcium aluminate (C_3A) and water. However, in some countries, because of scarcity of gypsum resources and environmental concern, a new source of gypsum, i.e., by-product gypsum, is utilized in cement production. The addition of phosphogypsum directly into the raw mix of cement before clinkering lowers the temperature for clinker formation and delays setting [1]. In a number of studies [2–4], attempts were made to produce gypsum–cement–pozzolona binder. In these studies, the gypsum binder made of natural gypsum was used for producing gypsum–cement–pozzolona blends as well. A binder containing high-quality fly ash, florogypsum and Portland cement results in high strength and good volume stability and enhances water resistance [5,6]. Yan and Yang have suggested that a binder containing low-quality fly ash, florogypsum and Portland cement could be used tin the manufacture of wall elements [7]. Desulphogypsum, from desulphurisation process in coal-burning plants, and citrogypsum, a by-product of citric acid production, are other important sources of chemical gypsum. Ozkul [8] has showed that the use of citrogypsum and desulphogypsum instead of natural gypsum in cement results in a decrease in early strength of the mortar. However, agglomeration pro-

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cess increased the strength at all ages, suggesting the formation of a new crystal structure after compacting [8]. Borogypsum, a waste material formed during the production of boric acid from colemanite, is another important source of chemical gypsum. Several studies were made on the possible use of borogypsum instead of natural gypsum in cement production. Boncukoğlu et al. [9] showed that borogypsum up to 10% of the cement could be used as a set retarder. However, increasing the borogypsum level in Portland cement from 5% to 20% causes a decrease in compressive strength and tensile strength. Elbeyli et al. [10] suggested that calcined borogypsum in cement application decreases soundness and markedly increases the setting time and 28-day compressive strength of the mortar compared to that of untreated borogypsum.

One obvious disadvantage of using wastes containing boron in cement production is their long setting time and slow early-strength development [11–14]. For these reasons, the use of high proportions of these kinds of waste materials in cement production is limited. Therefore, there is a strong need for finding a suitable admixture that would enable an increase in utilized ratio of wastes. The object of this study was to reveal specific peculiarities of the setting and hardening of Portland–fly ash cement in order to find out the optimum structure possessing both advantages of using borogypsum and molasses. The behavior of borogypsum in Portland–fly ash cement was compared with that of pure gypsum. The strength and microstructure characteristics of mortars admixed with molasses were also given.

2. Materials and methods

2.1. Materials

Borogypsum was obtained from the Etibor Bandirma Boric Acid Plant in Turkey. Borogypsum is the solid part on the filter press in boric acid production, which forms in the reaction of colemanite with H_2SO_4. Molasses is a by-product of the sugar industry. It is the mother liquor remaining after removal of sucrose from the juice of sugar beet. Fly ash was obtained from Seyitömer Thermal Plant (Kütahya, Turkey). The chemical composition and physical properties of materials used are given in Table 1.

Table 1
Chemical characteristics of materials used

	Chemical analysis (wt.%)			
	Clinker	Fly ash	Gypsum	Borogypsum
SiO_2	21.36	51.75	1.84	4.57
Al_2O_3	5.40	22.10	0.43	1.28
Fe_2O_3	3.26	11.08	0.18	0.38
CaO	65.00	3.68	32.50	27.75
MgO	2.24	5.74	0.44	1.45
SO_3	1.15	1.28	43.12	37.79
Na_2O	0.20	0.25	–	–
K_2O	0.99	2.87	0.10	0.73
B_2O_3	–	–	–	4.30
Loss on ignition	0.38	1.00	21.32	20.62
CaO free	2	–	–	–

2.2. Cement mixtures

Gypsum optimization was done for the clinker used and was 4.5 wt.% of the clinker. Three series of cements were prepared and designated as P, B and C. The first series of cement was prepared with natural gypsum, clinker and varying levels of fly ash replacement. In the second series, borogypsum was used instead of natural gypsum. In the third series, borogypsum levels ranged from 2% to 10% in the presence of a fixed quantity of fly ash. The raw materials mixed in the required proportion were ground in a ceramic-lined ball mill. Details of the mixtures are given in Table 2.

2.3. Specimen preparation, curing and testing

The preparation of specimens for strength tests was performed at room temperature. The mix proportion of the specimens corresponds to 450 g of cement and 1350 g of sand; water-to-cement ratio was 0.5. Molasses was added to water before the beginning of the preparation of the B and C series of batches. The cement–water mixtures were stirred at low speed for 30 s, then, with the addition of sand, the mixtures were stirred for 4 min. Twenty-five batches were prepared and cast into $40 \times 40 \times 160$-mm moulds for strength tests. After 24 h of curing at 20 °C, the samples were demolded and immediately immersed in a water-curing tank. The temperature of the water was maintained at 20 ± 1 °C during the curing period. Compressive strength and bending strength tests were performed at the ages of 2, 7 and 28 days according to TS EN 196-1[15]. The strength value was the average of three specimens.

Setting time of the cement was done according to TS EN 196-3 [15] using a Vicat apparatus at room temperature. The initial set time occurs when a Vicat needle 1 mm in diameter penetrates the sample to a point 4 ± 1 mm from the bottom of the mould. Final setting time was defined as that at which the needle penetrates to the sample 0.05 mm from the top of the mould. Particle size analysis was done by using sieves with a diameter of 40, 90 and 120 μm. The phases present in the samples were characterized by X-ray difractometer (Shimadzu XRD-6000). The microstructure of the fractured surface of specimens was examined by scanning electron microscopy (SEM, Jeol JXA 840A).

3. Results and discussion

3.1. Compressive strength

The compressive strength of the mortar at different ages is shown in Figs. 1–3. Fig. 1 shows the comparison of the

Table 2
Percent water, setting time, and physical characteristics of cementitious mixes

Symbol	Cement mixes	Water (%)	Setting time (h:min)		Fineness (wt.%) + 40 μm	Specific surface (m^2/kg)	Density (kg/m^3)
			Initial	Final			
P_1	4.5%G + 5%FA + 90.5%PC	27.0	2:54	4:36	20.4	312	2900
P_2	4.5%G + 10%FA + 85.5%PC	27.2	3:12	4:42	18.8	339	2800
P_3	4.5%G + 15%FA + 80.5%PC	27.0	3:06	4:30	19.5	361	2820
P_4	4.5%G + 20%FA + 75.5%PC	27.2	3:18	5:30	20.2	405	2840
P_5	4.5%G + 25%FA + 70.5%PC	27.6	3:54	5:54	20.4	435	2750
B_1	4.5%BG + 5%FA + 90.5%PC	27.4	3:06	4:36	20.5	293	2950
B_2	4.5%BG + 10%FA + 85.5%PC	27.4	3:12	5:12	19.6	313	2930
B_3	4.5%BG + 15%FA + 80.5%PC	27.6	3:18	5:24	18.0	342	2800
B_4	4.5%BG + 20%FA + 75.5%PC	29.8	3:30	5:06	19.8	372	2800
B_5	4.5%BG + 25%FA + 70.5%PC	30.6	6:00	8:24	19.6	399	2700
D_1	4.5%BG + 5%FA + 90.5%PC + 0.1% M	27.4	5:03	7:42	–	–	–
D_2	4.5%BG + 10%FA + 85.5%PC + 0.1% M	27.4	5:26	9:08	–	–	–
D_3	4.5%BG + 15%FA + 80.5%PC + 0.1% M	27.8	5:58	11:14	–	–	–
D_4	4.5%BG + 20%FA + 75.5%PC + 0.1% M	30.0	6:26	13:12	–	–	–
D_5	4.5%BG + 25%FA + 70.5%PC + 0.1% M	30.5	7:05	15:02	–	–	–
C_1	2%BG + 20%FA + 78%PC	28.6	4:12	6:00	20.5	369	2900
C_2	3%BG + 20%FA + 77%PC	29.0	3:18	6:18	19.0	395	2890
C_3	4%BG + 20%FA + 76%PC	29.2	4:36	6:12	20.9	384	2820
C_4	5%BG + 20%FA + 75%PC	29.2	3:30	5:54	19.4	393	2820
C_5	6%BG + 20%FA + 74%PC	29.4	4:12	6:06	20.0	411	2820
E_1	2%BG + 20%FA + 78%PC + 0.1% M	26.4	6:03	11:00	–	–	–
E_2	3%BG + 20%FA + 77%PC + 0.1% M	26.8	6:25	12:28	–	–	–
E_3	4%BG + 20%FA + 76%PC + 0.1% M	27.0	6:36	13:01	–	–	–
E_4	5%BG + 20%FA + 75%PC + 0.1% M	27.4	6:14	13:12	–	–	–
E_5	6%BG + 20%FA + 74%PC + 0.1% M	27.0	6:58	14:40	–	–	–

G, gypsum; FA, fly ash; PC, clinker; BG, borogypsum; M, molasses.

compressive strength of the mortar prepared from Portland cement clinker (PC) (clinker + gypsum and clinker + borogypsum). Regardless of curing age, the compressive strength of the borogypsum-added mixes was a little lower than that of the gypsum-added mixes. These observations indicate that the presence of boron in gypsum interferes in the hardening of cement that results in compressive strength reduction particularly at early ages. However, the results obtained are within the acceptable range of TS EN 196-1 [15]. These observations may be explained by previous findings of other researchers [16]. In these studies, it was found that mechanical strengths developed by the activated fly ashes were higher than those reached by Portland cement. The authors suggested that the interaction

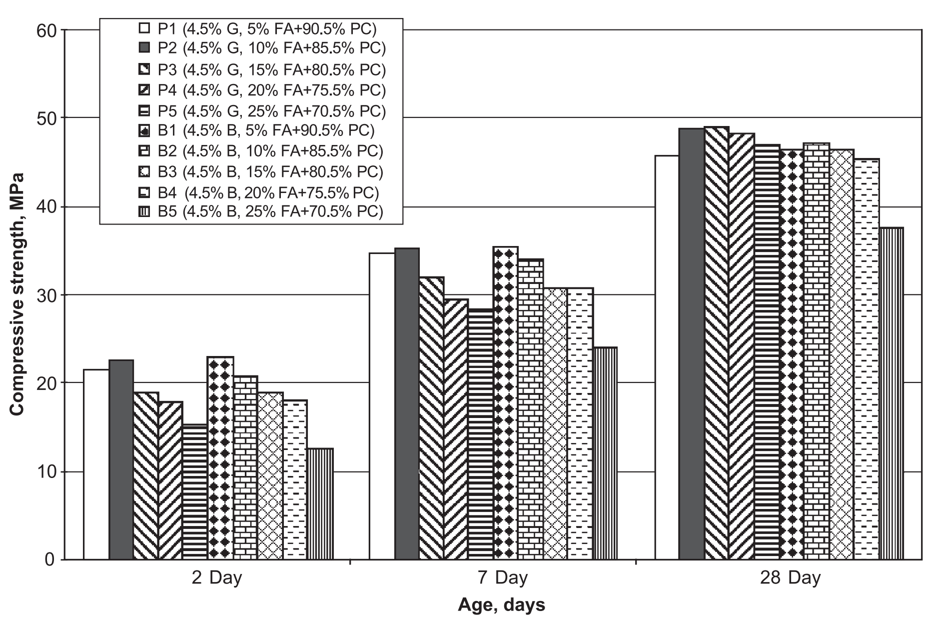

Fig. 1. Comparison of compressive strength of the mortar containing natural gypsum (G) and borogypsum (B).

of the caustic solution with the vitreous silica aluminates of the initial materials leads to the formation of a pseudozeolitic, three-dimensional structure that results in a compact structure.

The influence of molasses on the compressive strength of the mortar prepared from cement (borogypsum + clinker) is shown in Fig. 2. From these results, it can be seen that the effect of adding 0.1% molasses to the mix reduces compressive strength at 2 days' curing age. The reduction in compressive strength is mainly attributed to the hydration rate of the tricalcium silicate phase, which is mainly responsible for the early-strength development of cement. The addition of molasses to the mix retards the hydration of the tricalcium silicate phase due to its sugar content [17]. It is interesting that as curing time expanded to 7 days, the mortar prepared with borogypsum–cement containing molasses gave better compressive strength than that of borogypsum–cement at all replacement levels. This improvement in strength was more pronounced at 28 days. These results may be explained with a mechanism suggested by Juenger and Jennings [17]. According to the authors, the addition of sugar to the mix increases initial dissolution of ions and causes formation of a protective coat around the cement grains that prevents their contact with water. The ions in the pore solutions nucleate independently rather attaching to the existing poisoned sites during the retardation period. When the poisoning effects of sugar are overcome by the excess of ions in solution, these ions immediately react with each other to increase hydration products. In view of this proposed mechanism, it may be suggested that once the retardation barrier is broken some sugar molecules act as bridging forces between more than one cementitious particle at the same time, thereby forming a link that holds the particles with hydrogen/chemical bonding. These interactions may lead to an improvement in the compressive strength of mortar after 7 days of curing.

Fig. 3 shows the compressive strength of the mortar prepared with borogypsum–fly ash–cement containing different amounts of borogypsum. As expected, the presence of molasses and boron together in the mortar resulted in a reduction in early strength. However, the compressive strength values obtained after 7 days of curing are within the acceptable range of Turkish standards. This result shows that considering compressive strength values, borogypsum can replace natural gypsum up to 6 wt.% of the cement in cement production.

3.2. Bending strength

The results of the bending strength test are shown in Table 3. Regardless of curing age, bending strength of the mortar prepared from borogypsum–fly ash–cement was almost the same as that of PC mortar. The addition of molasses to the mixture resulted in the reduction of bending strength at 2 days' age. As curing time extended, the bending strength of all specimens gradually increased and even exceeded that of the specimens containing no molasses. The increase in strength can be explained in a way similar to the compressive strength increase in mortar mixes as indicated above.

3.3. Effects of addition of molasses and type of gypsum on setting time

The effects of type of gypsum and addition of molasses on setting time were assessed by comparing the initial and final setting times measured for each paste, as given in Table 2. From the results, it can be seen that the use of borogypsum instead of natural gypsum retards both initial and final setting times. The observed retardation in setting time may be mainly attributed to the presence of boron in the paste that interferes with hardening of the cement [11,13]. Al-

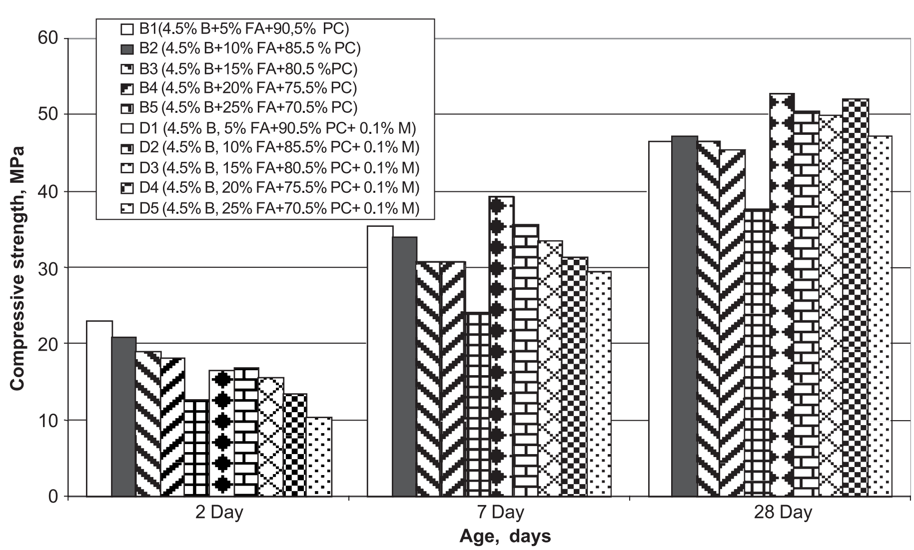

Fig. 2. Effects of molasses on the compressive strength of the mortar containing borogypsum (B).

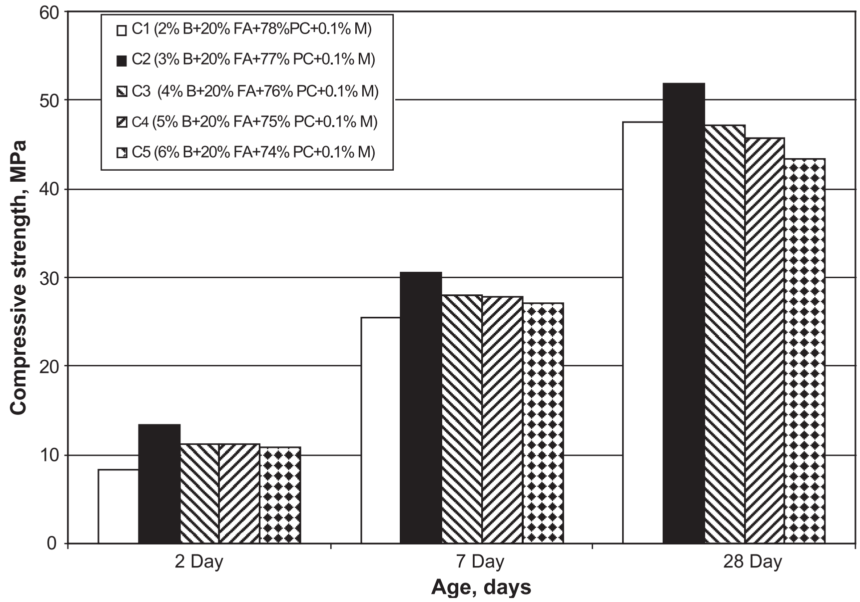

Fig. 3. Compressive strength of the mortar containing increasing amount of borogypsum (B) with 0.1% molasses (M).

though the use of borogypsum retards setting time, the values of final setting time obtained are within the acceptable range of standards [15].

The addition of molasses to the paste containing borogypsum significantly retards both the initial and final setting times. This increase is more pronounced for final setting time. These results indicate that the hydration mechanism of cement containing boron is different from that of cement containing molasses. The underlying chemistry is complex because more than one mechanism is probably involved. In the case of borogypsum, retardation would be caused by the presence of boron, which accelerates portlandite solubility [18]. The retarding effects of molasses may be due to its sugar content. This result seems to be in agreement with the previous finding reported by other researchers [19]. Thomas and Birchall [20] have shown that sugar solutions solubilise ordinary Portland cement and retardation occurs through the complexation of sugar onto phases containing calcium. Juenger and Jennings [17] have recently proposed that because of the poisoning effects of sugar, ions in the pore solutions nucleate independently, resulting in a large number of poisoned sites. Retardation proceeds until the poisoning effects of sugar are overcome.

Table 3
Bending strength of the specimens

Mixture	Bending strength (MPa)		
	2 Days	7 Days	28 Days
P_1	4.6	6.6	8.6
P_2	4.7	7.1	8.5
P_3	4.3	6.4	8.1
P_4	4.3	6.0	8.2
P_5	3.5	5.9	8.1
B_1	4.9	6.8	8.4
B_2	4.5	6.4	8.8
B_3	4.4	6.4	8.4
B_4	4.0	6.0	7.7
B_5	2.9	5.0	7.3
D_1	3.7	7.3	9.1
D_2	3.8	7.0	8.4
D_3	3.5	6.8	8.1
D_4	3.2	6.3	8.5
D_5	2.4	6.0	8.0
C_1	2.1	5.6	7.9
C_2	3.1	6.1	8.7
C_3	2.8	5.8	7.6
C_4	2.7	5.3	8.2
C_5	2.5	5.3	8.0

3.4. SEM observation of microstructure

SEM micrographs of the surface of the mortar specimens cured for 28 days are shown in Figs. 4–8. It can be

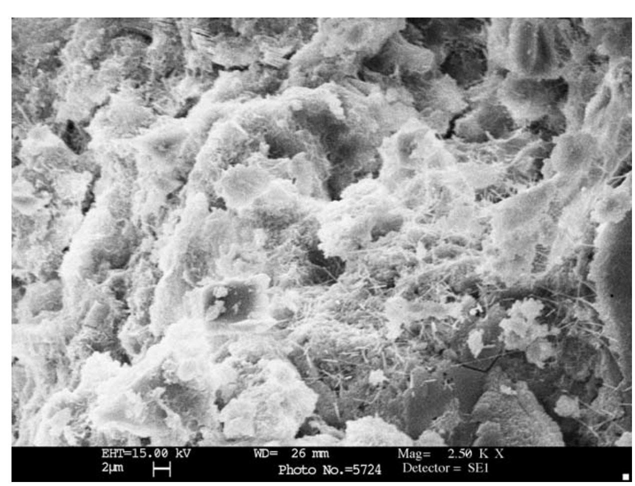

Fig. 4. SEM micrographs of fracture surface of mortar after 28 days of hydration (the cement used contains 4.5% G + 20% FA + 75.5% clinker).

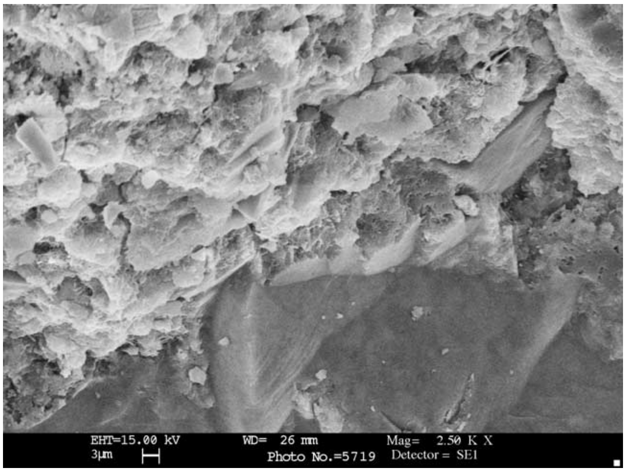

Fig. 5. SEM micrographs of fracture surface of mortar after 28 days of hydration (the cement used contains 4.5% BG + 20% FA + 75.5% clinker).

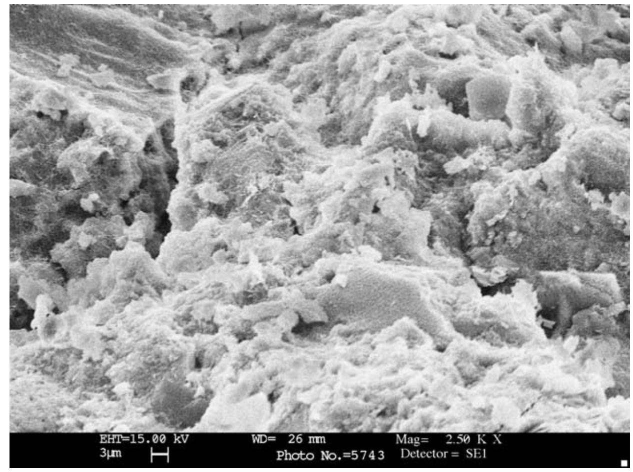

Fig. 7. SEM micrographs of fracture surface of mortar with 0.1% molasses after 28 days of hydration (the cement used contains 2% BG + 20% FA + 78% clinker).

seen that the morphology and deposition of portlandite around the aggregate is significantly affected by molasses and borogypsum. In the PC mortars, the interface is mainly composed of CH and ettringite (Fig. 4). The mortar prepared from borogypsum–cement appears to contain much less ettringite than PC mortar. It is clear that the presence of borogypsum in mortar results in the formation of a denser microstructure compared to natural gypsum (Fig. 5). As molasses is added to the mix, the crystallite size of the portlandite phase significantly changes, indicating the increased deposition of CH around the aggregate (Fig. 6). Figs. 7 and 8 show the effects of borogypsum content on the microstructure of the mortar treated with molasses. Although the SEM micrograph of the mortar did not show the presence of ettringite at the interface, this was indicated by XRD patterns of the mortar. As the borogypsum content increased, the mortar appeared to contain much ettringite, and interconnection between neighboring particles seemed to be slightly lost (Fig. 8). Compared to the addition of borogypsum to mortar, the addition of molasses to the mix enhanced the formation of ettringite crystals.

3.5. X-ray diffraction

X-ray diffraction analysis was performed to see the effects of the addition of molasses on the amount of phases occurring in the systems that contained different ratios of borogypsum. The results for 28-day-old, molasses-containing samples cured at room temperature are shown in Fig. 9. The three systems had very similar hydration products, as expected. The largest peak corresponded to quartz (Q) and other peaks identified were portlandite (P), larnite (L) and calcium carbonate (C). The major differences shown in Fig. 9 are the amounts of calcium hydroxide and ettringite. Fig.

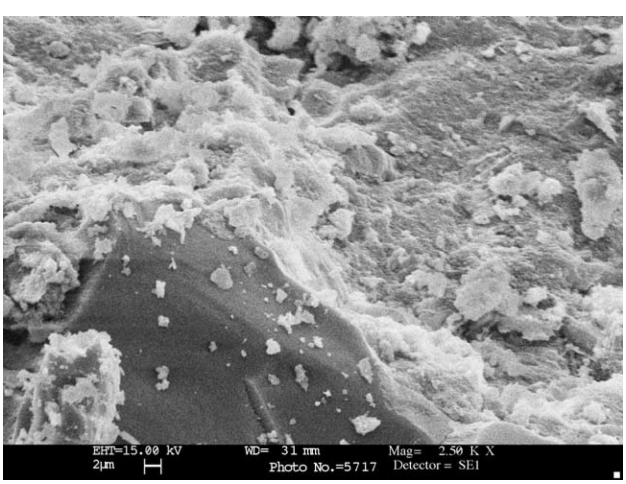

Fig. 6. SEM micrographs of fracture surface of mortar with 0.1% molasses after 28 days of hydration (the cement used contains 4.5% BG + 20% FA + 75.5% clinker).

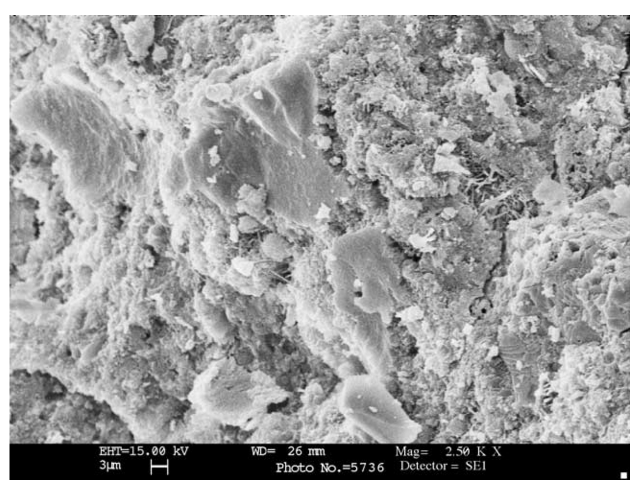

Fig. 8. SEM micrographs of fracture surface of mortar with 0.1% molasses after 28 days of hydration (the cement used contains 6% BG + 20% FA + 74% clinker).

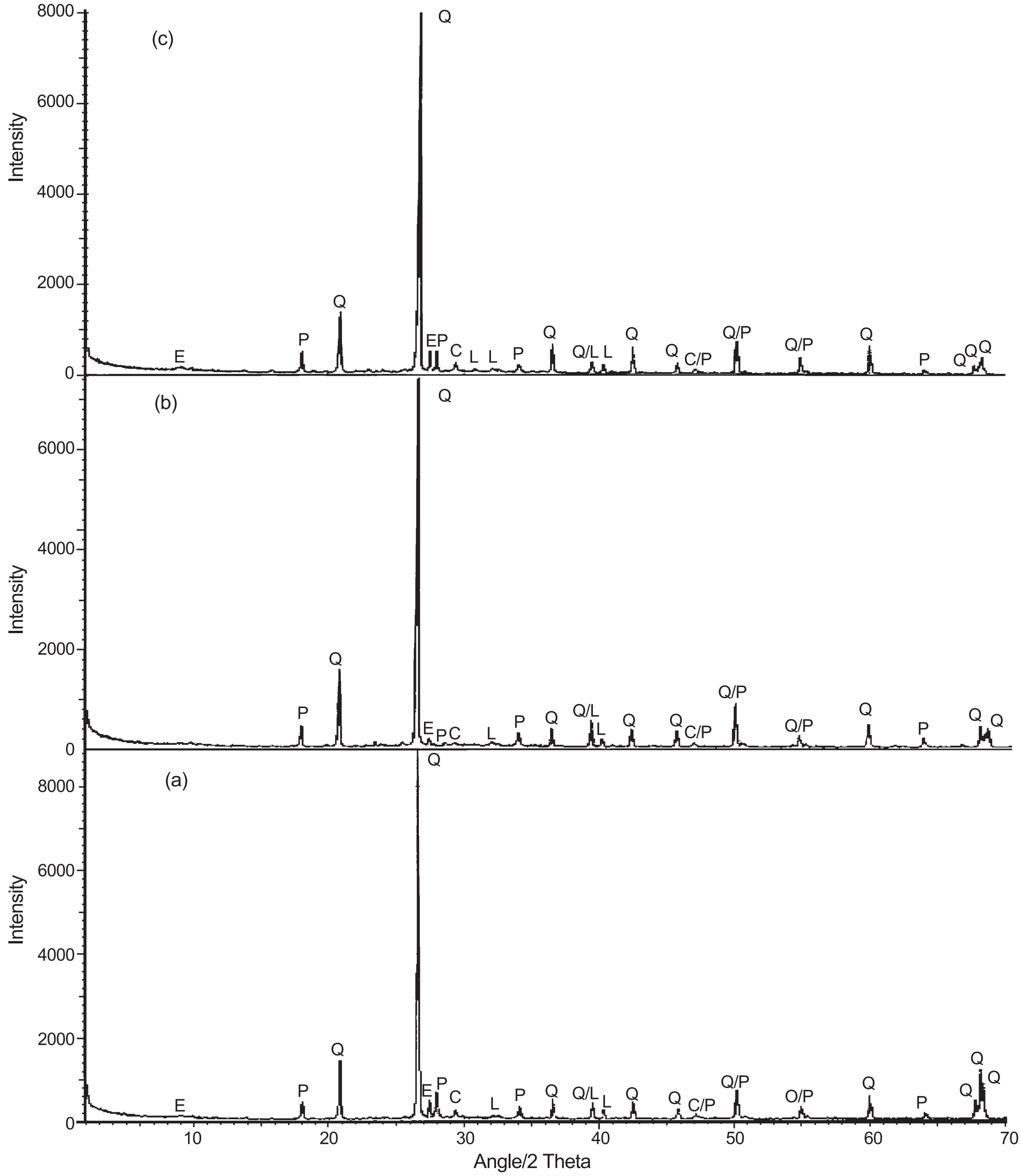

Fig. 9. XRD pattern of the mortar with 0.1% molasses after 28 days of hydration. P, calcium hydroxide; C, calcium carbonate; Q, quartz; L, larnite; E, ettringite. The cement used contains (a) 2% BG + 20% FA + 78% clinker, (b) 4.5% BG + 20% FA + 75.5% clinker, (c) 6% BG + 20% FA + 74% clinker.

9b shows that compared to other samples, the hydration is clearly associated with consumption of calcium hydroxide and reduction in the relative intensity of ettringite peaks. Experimental results in Fig. 3 show that the compressive strength of the mortar gradually increases with the use of borogypsum up to 3% and decreases as the replacement level increases beyond this value. One of our goals in this study was to investigate the possibility of using borogypsum instead of natural gypsum in the preparation of cement. Therefore, considering the strength of the mortar and setting characteristics of the cement, the optimum borogypsum content in the matrix was taken to be 4.5%. This observation suggests that the formation of ettringite and the consumption of calcium hydroxide depend sensitively on the optimum borogypsum content in the matrix. Deviation from the optimum borogypsum content enhances the formation of ettringite.

4. Conclusions

From the results presented in this paper, the conclusions are as follows:

1. The general effect of borogypsum is to retard the setting time of the cement.

2. Addition of molasses to the cement at a level of 0.1% causes excessive retardation in both initial and final setting times.
3. Replacement of natural gypsum by borogypsum caused a slight reduction in the strength of the mortar. However, the strength values obtained were within the acceptable range of standards.
4. Addition of molasses to the system at a level of 0.1% resulted in a reduction in early strength of the mortar. The strength of the mortar containing molasses gradually increased after 7 days of curing age.
5. The influence of increasing the levels of borogypsum resulted in a reduction in the strength of the mortars.

Based on the findings of this study, the use of borogypsum instead of natural gypsum in Portland cement production seems possible. Although the inclusion of the molasses into the system retards the setting time and causes a reduction in early strength, it has positive contributions to the strength after 7 days.

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