



## Effects of supplementary cementing materials on the properties of cement and concrete

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### Abstract

The effect of bentonite, colemanite ore waste (CW), coal fly ash (FA) and coal bottom ash (BA) on the properties of cement and concrete has been investigated through a number of tests. The properties examined include setting time, bending strength, volume expansion, compressive strength and water consistency of the mortar. The result showed that setting time of the cements was generally accelerated when bentonite replaced a part of the cement. Bentonite exhibited a significant retarding effect when used in combination with CW in Portland cement at lower replacement level and showed an accelerating effect at higher replacement level. Although the inclusion of bentonite at replacement levels of 5–10% resulted in an increase in compressive strength at early ages, it decreased the compressive strength when used in combination with other materials. The results obtained were compared with Turkish standards and, in general, were found to be acceptable. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Compressive strength; Expansion; Setting time; Colemanite ore waste; Bentonite

### 1. Introduction

In recent years, various types of materials, such as silica fume, fly ash (FA), bottom ash (BA) and others, have found extensive use in cement and concrete [1–5]. Their utilization has been an interesting subject of research for economical, environmental and technical reasons. Since the different replacement materials possess different chemical and mineralogical compositions as well as different particle characteristics, they could have different effects on the properties of cement and concrete. Appropriate use of FA prevents expansion due to alkali–silica reaction, reduces heat generation and gives better durability in concrete [6,7]. BA with the pozzolanic nature can be used as a replacement material in Portland cement [5]. It is also often used as a low-cost replacement for more expensive sand for concrete production, as a fine aggregate in high-performance lightweight concrete [8].

Chemical wastes containing boron possess environmental problems and have been suggested for use as a replacement material in Portland cement [9]. Kula et al. [5] reported that the total amount of colemanite ore waste (CW) could reach up to 7% in composite Portland cement, and that the strength of the concrete containing CW is greater than that of control concrete at 28 days of curing and increases with the incorporation of FA and BA. They attributed it to the pozzolanic activity of FA and BA. CW is typically cementitious, due possibly to formation of ettringite. Although ettringite forms in coal by-product that contains a high level of calcium and sulfate, these conditions may be met by CW that contains a high level of calcium and B<sub>2</sub>O<sub>3</sub>. According to Csetenyi [10], soluble borates can be insolubilized via their incorporation into ettringite structure. Ettringite is an important secondary hydration product commonly found in concrete. Bothe and Brown [11] pointed out that the hydration product, ettringite, sequesters borate during its formation as high boro-ettringite with the formula C<sub>3</sub>A·2Ca(B[OH]<sub>4</sub>)<sub>2</sub>·Ca(OH)<sub>2</sub>·30H<sub>2</sub>O and the low boro-ettringite with the formula C<sub>3</sub>A·Ca(B[OH]<sub>4</sub>)<sub>2</sub>·2Ca(OH)<sub>2</sub>·36H<sub>2</sub>O.

The present study was based on our previous studies on the utilization of chemical waste containing boron [5,12], and

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Table 1  
Chemical characteristics of used material

|                                | Chemical analysis (wt.%) |                  |         |            |           |        |
|--------------------------------|--------------------------|------------------|---------|------------|-----------|--------|
|                                | Clinker                  | Colemanite waste | Fly ash | Bottom ash | Bentonite | Gypsum |
| SiO <sub>2</sub>               | 21.34                    | 34.47            | 42.4    | 42.39      | 57.83     | –      |
| Al <sub>2</sub> O <sub>3</sub> | 5.96                     | 9.72             | 19.90   | 21.35      | 13.55     | 0.04   |
| Fe <sub>2</sub> O <sub>3</sub> | 3.81                     | 5.06             | 8.60    | 6.41       | 5.94      | –      |
| CaO                            | 64.96                    | 12.57            | 19.50   | 17.57      | 3.97      | 33.04  |
| MgO                            | 1.03                     | 9.82             | 1.30    | 1.52       | 2.44      | 0.03   |
| SO <sub>3</sub>                | 1.23                     | 1.72             | 4.9     | 2.34       | 0.08      | 46.18  |
| Na <sub>2</sub> O              | 0.28                     | –                | –       | –          | –         | –      |
| K <sub>2</sub> O               | 0.81                     | 3.03             | 1.40    | 1.11       | 1.59      | 0.02   |
| B <sub>2</sub> O <sub>3</sub>  | –                        | 18.71            | –       | –          | –         | –      |
| Loss on ignition               | 0.31                     | 12.55            | 1.00    | 10.17      | 10.17     | 20.15  |
| CaO free                       | 0.77                     | –                | 1.90    | –          | –         | –      |
| Water                          | –                        | –                | –       | –          | –         | 19.46  |

aimed to determine the effect of bentonite on the cementing properties. The present work has systematically studied the effect of increasing bentonite addition (5–30 wt.%) with the constant FA (10 wt.%), BA (10 wt.%) and CW (4 wt.%) content on the properties of Portland cement and concrete.

## 2. Experimental details

### 2.1. Materials

FA and BA were supplied from the Soma SEAS Thermal Plant (Manisa, Turkey); clinker and gypsum from the

Cimentas Cement Plant (İzmir, Turkey); colemanite waste from Etibank Boron Plant (Kütahya-Emet, Turkey); and bentonite from EMKO Mining Industry (Ayvacık-Çanakkale, Turkey). The chemical compositions and physical properties of cement and the other materials used in all the experiments are given in Table 1.

### 2.2. Cement mixtures

Four series of mixtures—noted as B (bentonite+PC), F (bentonite+FA+PC), C (bentonite+CW+PC), P (bentonite+BA+PC)—and one reference mix, R, were prepared according to TS 24 [13]. The mixing proportions are summarized in Table 2. The raw materials mixed in the required proportion were ground in a ceramic-lined ball to a fineness of 26% mass residue on a 32- $\mu$ m-size mesh. Physical characteristics of cementitious mixes are given in Table 2.

### 2.3. Setting time

The setting times of cement mixes were determined according to TS 24 [13] 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  $5 \pm 1$  mm from the bottom of the mould. Final setting time is defined as that at which the 5-mm cap ring leaves no visible mark when placed on the surface of the sample.

Table 2  
Physical characteristics of cementitious mixes

| Symbol         | Cement mixes        | Fineness (wt.%) |              | Specific surface<br>(cm <sup>2</sup> /g) | Specific gravity<br>(g/cm <sup>3</sup> ) | Grinding time<br>(min) |
|----------------|---------------------|-----------------|--------------|--|--|------------------------|
|                |                     | + 32 $\mu$ m    | + 90 $\mu$ m |  |  |                        |
| R              | Reference mix       | 26.0            | 2.0          | 2850                                     | 3.15                                     | 30                     |
| B <sub>1</sub> | 5% B+95% PC         | 26.1            | 1.9          | 3090                                     | 3.12                                     | 26                     |
| B <sub>2</sub> | 10% B+90% PC        | 25.9            | 2.0          | 3430                                     | 3.06                                     | 25                     |
| B <sub>3</sub> | 15% B+85% PC        | 25.7            | 1.8          | 3490                                     | 3.05                                     | 23                     |
| B <sub>4</sub> | 20% B+80% PC        | 26.2            | 1.7          | 3910                                     | 3.04                                     | 22                     |
| B <sub>5</sub> | 25% B+75% PC        | 25.8            | 2.0          | 5170                                     | 3.01                                     | 17                     |
| B <sub>6</sub> | 30% B+70% PC        | 26.0            | 2.1          | 5180                                     | 2.98                                     | 16                     |
| F <sub>1</sub> | 5% B+10% FA+85% PC  | 25.8            | 1.8          | 3730                                     | 3.13                                     | 22                     |
| F <sub>2</sub> | 10% B+10% FA+80% PC | 26.1            | 2.0          | 4060                                     | 3.09                                     | 21                     |
| F <sub>3</sub> | 15% B+10% FA+75% PC | 25.9            | 2.1          | 4220                                     | 3.05                                     | 20                     |
| F <sub>4</sub> | 20% B+10% FA+70% PC | 26.2            | 1.9          | 4480                                     | 3.00                                     | 18                     |
| F <sub>5</sub> | 25% B+10% FA+65% PC | 25.7            | 2.1          | 4720                                     | 2.97                                     | 17                     |
| F <sub>6</sub> | 30% B+10% FA+60% PC | 26.0            | 2.0          | 4930                                     | 2.95                                     | 16                     |
| C <sub>1</sub> | 5% B+4% CW+91% PC   | 26.0            | 2.1          | 3620                                     | 3.18                                     | 23                     |
| C <sub>2</sub> | 10% B+4% CW+84% PC  | 26.2            | 1.8          | 3870                                     | 3.17                                     | 22                     |
| C <sub>3</sub> | 15% B+4% CW+81% PC  | 25.9            | 1.9          | 4140                                     | 3.15                                     | 21                     |
| C <sub>4</sub> | 20% B+4% CW+76% PC  | 25.8            | 1.7          | 4390                                     | 3.13                                     | 20                     |
| C <sub>5</sub> | 25% B+4% CW+71% PC  | 25.9            | 2.0          | 4400                                     | 3.09                                     | 18                     |
| C <sub>6</sub> | 30% B+4% CW+66% PC  | 26.1            | 2.2          | 4710                                     | 3.07                                     | 17                     |
| P <sub>1</sub> | 5% B+10% BA+85% PC  | 25.8            | 2.2          | 3540                                     | 3.15                                     | 23                     |
| P <sub>2</sub> | 10% B+10% BA+80% PC | 26.0            | 1.9          | 4050                                     | 3.13                                     | 21                     |
| P <sub>3</sub> | 15% B+10% BA+75% PC | 25.9            | 2.0          | 4160                                     | 3.11                                     | 20                     |
| P <sub>4</sub> | 20% B+10% BA+70% PC | 26.1            | 1.8          | 4400                                     | 3.09                                     | 18                     |

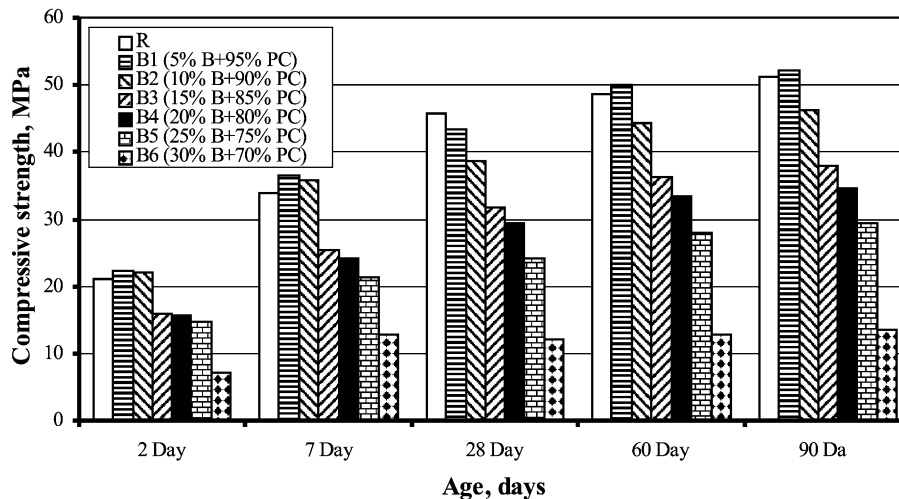


Fig. 1. Compressive strength of the concrete containing bentonite and PC.

#### 2.4. Strength tests

The specimen preparation for strength tests was performed at room temperature. The mix proportion of the specimens corresponded to 450 g of cement content, 1350 g of fine aggregate (standard Rilem Cebureau sand) and 0.5 water-to-cement (W/C) ratio. A typical batch weighed 2 kg. The cement–water mixtures were stirred at low speed for 30 s, then, with the addition of sand, the mixtures were stirred for 5 min. Twenty-one batches were prepared and cast into  $40 \times 40 \times 160$ -mm moulds for strength tests. After 24 h of curing at 20 °C with 95% humidity, the samples were demolded and immersed in a tap water and cured up to 90 days. Compressive strength and bending strength measurements were tested with a Tony technique compression machine at the loading rate of 20–40 N/mm<sup>2</sup>/s according to TS 24 [13]. The strength value was the average of three specimens. Some of the prismatic speci-

mens were not perfectly regular due to difficulty encountered in demolding ( $C_2$ ,  $C_3$  and  $C_6$  samples); hence, the compressive strength and bending strength values of these samples were not tested.

### 3. Results and discussion

#### 3.1. Strength results of concretes

The compressive strength of the concrete is a property that provides a good indicator of its quality. The compressive strength data observed at various ages are given in Figs. 1–4. It is observed that the replacement of 5–10% bentonite by Portland cement notably increases the compressive strength of concrete compared to control concrete up to 7 days. This can be attributed to the large pozzolanic contribution of bentonite at these early ages. However, as curing time ex-

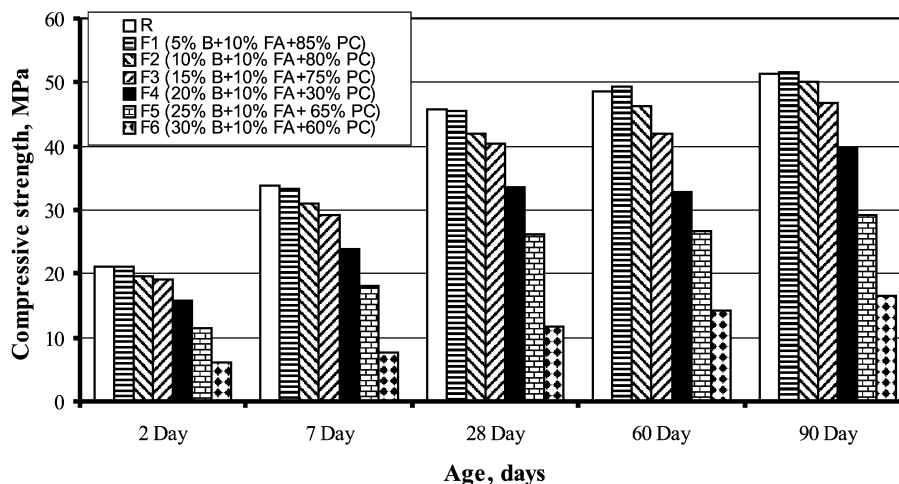


Fig. 2. Compressive strength of the concrete containing bentonite, FA and PC.

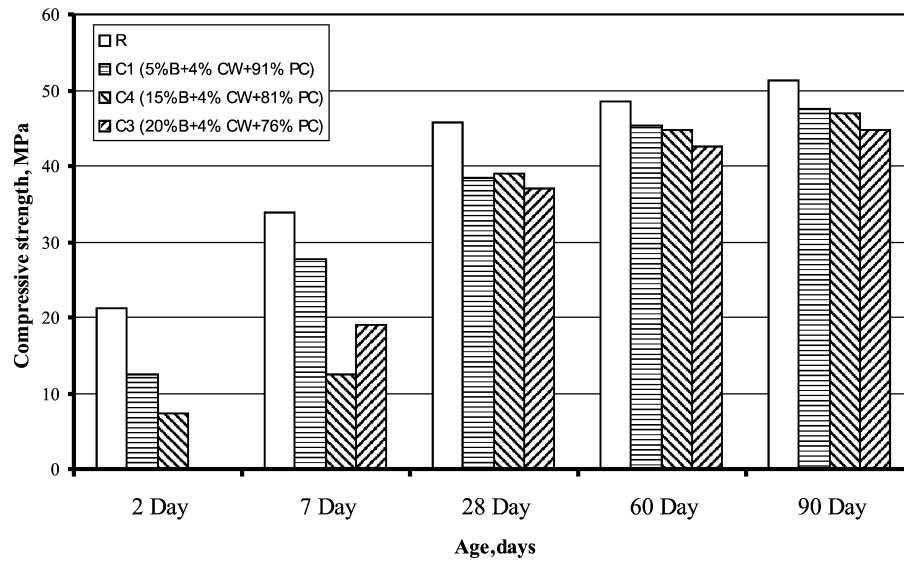


Fig. 3. Compressive strength of the concrete containing bentonite, CW and PC.

panded, bentonite shows a decreasing effect on the compressive strength of the concrete compared to that of control concrete. This is because the replacement of bentonite by Portland cement results in an increase in porosity that decreases strength resulting from pozzolanic contribution of bentonite.

All batches of concretes (except  $F_1$ ) prepared from bentonite + FA + PC and bentonite + BA + PC have lower strengths than the control at the ages of 2, 7, 28, 60 and 90 days. It seems that there exists a competition in strength development among FA, BA in concrete and the same amount of Portland cement in control concrete. At early ages, FA and BA substitutions decrease compressive strength due to small pozzolanic contribution while benton-

ite increases it. These observations are consistent with our previous results comparing the effect of supplementary materials on the properties of cement and concrete [5,12]. However, as curing time expanded, the compressive strength of the samples increased gradually. As suggested by Berry et al. [14], pozzolanic reaction in the FA/cement systems becomes dominant at ages after 28 days and results in a significant increase in the compressive strength compared to early strength.

Incorporation of CW and bentonite together with Portland cement results in a dramatic reduction in the compressive strength of the samples tested at the age of 2 days. This may be due to small pozzolanic contribution of CW at this age and may also be related to boron content of the

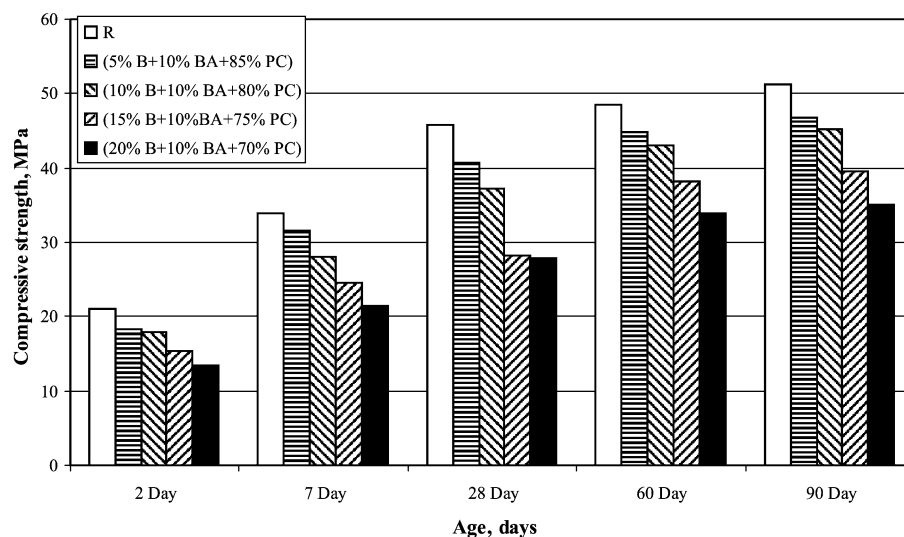


Fig. 4. Compressive strength of the concrete containing bentonite, BA and PC.

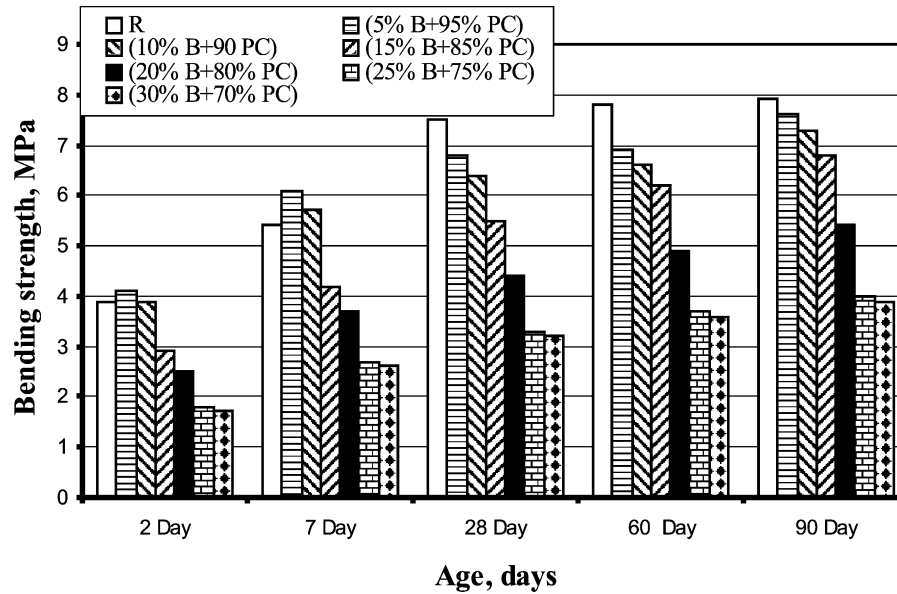


Fig. 5. Bending strength of the concrete containing bentonite and PC.

CW that interferes with the hardening of the cement. However, compressive strength of the samples gradually improved after 2 days of age. From these results, we can conclude that the presence of the boron in the sample develops greater bridging between particles. This seems to be in agreement with previous findings of other investigators [11,15,16].

Figs. 5–8 show the influence of different replacement materials on the bending strength of the concrete at various ages. As seen from the figures, the bending strength increased generally for all samples throughout the entire 90 days of experiment and a similar trend for compressive strength was observed. The results shows that most of the

bending strength values of the samples are within the acceptable range of TS 19 [13].

### 3.2. Volume expansion of cement mixes

The influence of replacement materials on the volume expansion of cement paste is shown in Table 3.

The results indicate that the effect of replacement materials on the expansion varies widely. This fact is best explained by comparing these results with our earlier results [5]. It was found that the replacement of the FA, BA and CW by Portland cement had no remarkable effect on the expansion of cement paste. Therefore, it can be suggested

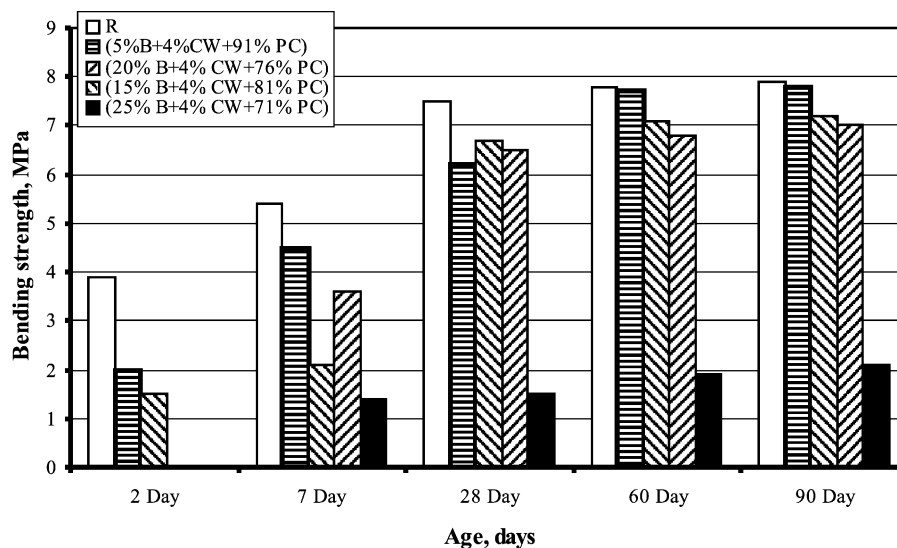


Fig. 6. Bending strength of the concrete containing bentonite, FA and PC.

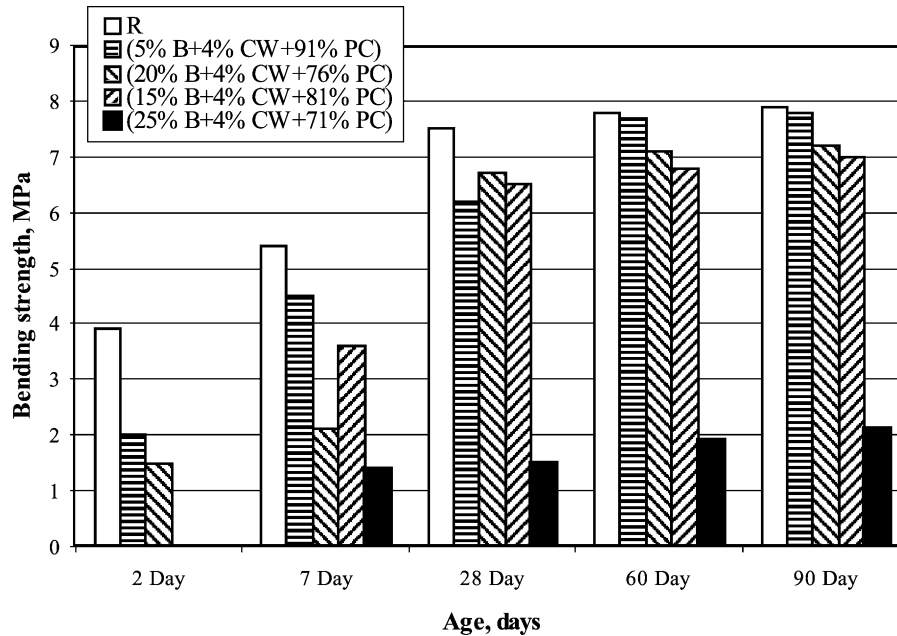


Fig. 7. Bending strength of the concrete containing bentonite, CW and PC.

that expansion in cement pastes arises from the bentonite content of the cement. However, increasing the bentonite content of cement paste does not show a similar trend for paste prepared from bentonite + CW + PC. The explanation of this matter is beyond our understanding.

### 3.3. Setting characteristics

The setting time of the cement paste containing different replacement materials is given in Table 3. From the results,

it can be seen that the effect of replacement of 5–10% bentonite is an increase in initial setting time and a negligible effect on final setting time. However, when the replacement level is further increased by 20%, there is a significant reduction in setting time particularly in the initial set when compared with the control mixture. The observed acceleration in setting time may be mainly attributed to the rate of pozzolanic reaction. Increasing the replacement of bentonite results in greater interparticle contact due to its high surface area, and thus speeds up the setting.

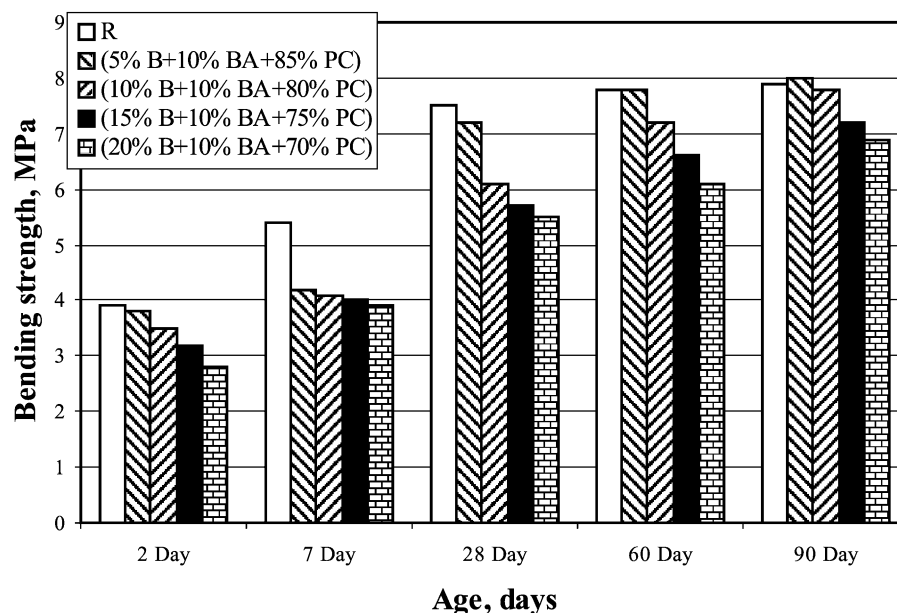


Fig. 8. Bending strength of the concrete containing bentonite, BA and PC.



Table 3

Water percent, volume expansion and setting time test result for cement mixes

| Cement mixes   | Water (%) | Setting time (h:min) |         | Volume expansion (mm) |
|----------------|-----------|----------------------|---------|-----------------------|
|                |           | Initial              | Final   |                       |
| TS24           | –         | minimum              | maximum | maximum               |
|                |           | 1:0                  | 10:0    | 10:0                  |
| R              | 29.4      | 2:05                 | 4:00    | 0                     |
| B <sub>1</sub> | 25.7      | 2:35                 | 3:55    | 1                     |
| B <sub>2</sub> | 26.6      | 2:30                 | 4:00    | 1                     |
| B <sub>3</sub> | 29.3      | 2:00                 | 3:35    | 3                     |
| B <sub>4</sub> | 32.6      | 1:30                 | 4:00    | 3                     |
| B <sub>5</sub> | 37.1      | 1:25                 | 3:00    | 3                     |
| B <sub>6</sub> | 37.3      | 1:05                 | 3:20    | 5                     |
| F <sub>1</sub> | 28.0      | 2:45                 | 4:15    | 2                     |
| F <sub>2</sub> | 29.7      | 2:45                 | 3:50    | 1                     |
| F <sub>3</sub> | 29.7      | 2:10                 | 3:50    | 2                     |
| F <sub>4</sub> | 31.7      | 2:45                 | 4:05    | 4                     |
| F <sub>5</sub> | 34.7      | 2:45                 | 3:35    | 4                     |
| F <sub>6</sub> | 38.0      | 1:20                 | 3:10    | 8                     |
| C <sub>1</sub> | 27.4      | 5:50                 | 9:10    | 4                     |
| C <sub>2</sub> | 28.2      | –                    | –       | –                     |
| C <sub>3</sub> | 29.0      | –                    | –       | –                     |
| C <sub>4</sub> | 30.3      | 8:00                 | 14:15   | 3                     |
| C <sub>5</sub> | 34.3      | 5:00                 | 12:30   | 6                     |
| C <sub>6</sub> | 37.1      | 2:55                 | 6:0     | 2                     |
| P <sub>1</sub> | 23.3      | 2:45                 | 4:00    | 2                     |
| P <sub>2</sub> | 25.7      | 2:40                 | 4:00    | 2                     |
| P <sub>3</sub> | 26.9      | 2:25                 | 4:10    | 4                     |
| P <sub>4</sub> | 26.9      | 2:25                 | 4:00    | 4                     |

In the case of Portland cement paste containing FA + bentonite, the effect of increasing the replacement level of bentonite up to 25% is an extended initial setting time of the paste compared to that of control paste. As the replacement level was increased to 30%, initial and final setting times decreased by factors of 2.04 and 1.08, respectively. One of the reasons of this difference could be the use of bentonite in the present investigation. The results of Kula et al. [5] showed that the initial and final setting times tend to increase with increasing FA content of the paste. It seems that the use of bentonite offsets the retardation that resulted from FA at higher replacement level. The results also show that incorporation of BA with bentonite extends initial setting time and has negligible effect on the final setting time.

In the case of cement paste containing up to 20% replacement of bentonite together with 4% CW, there is a clear trend that both initial and final setting times are extended as the replacement level increased. However, when the replacement level of bentonite is further increased to 25%, there is a marginal reduction in setting time particularly the initial set when compared with those of the C<sub>4</sub> (20% bentonite + 4% CW + 76% PC) mixture. This could be due to the greater pozzolanic contribution at the higher bentonite content. In this case, the effect of higher bentonite content would be to offset the effect of lower CW content. From these results, the retardation and acceleration of setting time can be attributed to the CW and bentonite content of cement mixture, respectively.

#### 4. Conclusions

This study was conducted to assess the effects of incorporation of bentonite with FA, BA and CW on the properties of cement and concrete. From the experimental results presented in this paper, the conclusions are as follows,

(1) The general effect of FA, BA and CW is to retard the setting time of the cement.

(2) Bentonite has a negligible effect on the final setting time of cement containing BA, but it has a significant accelerating effect when used alone or in combination with FA and CW at the higher replacement level.

(3) With the replacement of bentonite up to 15%, the compressive strength of the concrete was significantly increased compared with control concrete at 7 days. The replacement of Portland cement beyond 15 wt.% of bentonite caused a reduction in the compressive strength.

(4) When bentonite was added to BA, CW or FA, the compressive strength of the concrete decreased with increasing bentonite content.

Based on the findings of this study, the production of Portland cement—with up to 10% bentonite, 5% bentonite + 4% CW, 20% bentonite + 10% FA and 10% bentonite + 10% substitution by Portland cement, and with strength comparable to ordinary Portland cement and Turkish standards—seems possible.

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