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Influence of natural pozzolan, colemanite ore waste, bottom ash, and fly ash on the properties of Portland cement

Ş. Targan[a], A. Olgun[b,*], Y. Erdogan[b], V. Sevinc[c]

[a]*Department of Chemistry, Celal Bayar University, Manisa, Turkey*
[b]*Department of Chemistry, Dumlupinar University, Kutahya, Turkey*
[c]*Department of Chemistry, Sakarya University, Sakarya, Turkey*

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Abstract

This study has examined the effect of natural pozzolan (NP), colemanite ore waste (CW), coal fly ash (FA), and coal bottom ash (BA) on the properties of cement and concrete. The parameters studied included compressive strength, bending strength, volume expansion, and setting time. A number of cements were prepared (in the presence of fixed quantity of 10% FA, 10% BA, and 4% CW) by the replacement of Portland cement (PC) with NP in range of 5–30%. The results showed that the final setting time of cement pastes were generally accelerated when the NP replaced part of the cement. However, NP exhibited a significant retarding effect when used in combination with CW. The results also showed that the inclusion of NP at replacement levels of 5% resulted in an increase in compressive strength of the specimens compared with that of the control concrete. The replacement of PC by 10–15% of NP in the presence of fixed quantity of CW improves the bending strength of the specimens compared with control specimens after 60 days of curing age.

Keywords: Setting time; Compressive strength; Bending strength; Colemanite ore waste; Natural pozzolan

1. Introduction

Many published literatures [1–6] have reported studies on the use of supplementary cementing materials such as fly ash (FA), bottom ash (BA), and natural pozzolan (NP) in cement and concrete. It is generally accepted that appropriate use of FA in concrete can prevent expansion due to alkali–silica reaction [7], can reduce heat generation, and gives better durability properties. Relatively few detailed studies have been conducted using BA as a replacement material in the production of cement and concrete. It can be used as a low-cost replacement material for the more expensive sand in concrete [8] and as a construction fill and landfill bottom liner [9]. A study by Cheriaf et al. [10] pointed out that pozzolanic activity of BA can be improved with adequate grinding and be used in PC and concrete. The use of NP in PC offers many advantageous properties that include cost reduction, reduction in heat evolution, decreased permeability, increased chemical resistance, and the improvement of the properties of high-strength concrete [5,6,11,12]. However, it results in a prolonged setting time and cause reduction in workability of pastes, mortar, and concrete beyond 35% replacement [6].

Wastes containing boron present an important economical resource. Various studies of FA leaching behavior [13,14] show that class F FA treated with lime accommodates borates into its interlayer region resulting in greater bridging between particles in the boron-spiked specimen. According to Erdogan et al. [15–17], Kula et al. [18], and Targan et al. [19], boron waste can be used as a cement replacement material in the production of PC. Incorporation of colemanite ore waste (CW) up to 7% with FA and BA generally results in a better performance of the PC pastes at 28 days of curing [18]. The use of tincal ore waste also gives rise to an improvement in the properties of Portland cement (PC) 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 [20].

The purposes of this study were to examine the effect of volcanic deposits on the cementing properties. The present

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* Corresponding author. Tel.: +90-274-265-2051; fax: +90-274-265-2056.

E-mail address: aolgun@dumlupinar.edu.tr (A. Olgun).

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Table 1
Chemical composition and physical properties of cementitious materials

Item	Clinker	CW	FA	BA	NP	Gypsum
SiO_2	21.34	34.47	42.4	42.39	50.79	–
Al_2O_3	5.96	9.72	19.90	21.35	20.53	0.04
Fe_2O_3	3.81	5.06	8.60	6.41	7.45	–
CaO	64.96	12.57	19.50	17.57	6.56	33.04
MgO	1.03	9.82	1.30	1.52	3.74	0.03
SO_3	1.23	1.72	4.9	2.34	0.08	46.18
Na_2O	0.28	–	–	–	–	–
K_2O	0.81	3.03	1.40	1.11	2.74	0.02
B_2O_3	–	18.71	–	–	–	–
Loss on ignition	0.31	12.55	1.00	10.17	10.17	20.15
CaO-free	0.77	–	1.90	–	–	–
Compounds						
C_3S	53.26	–	–	–	–	–
C_2S	21.19	–	–	–	–	–
C_3A	9.4	–	–	–	–	–
C_4AF	11.6	–	–	–	–	–
Physical analysis						
Fineness (wt.%)						
>32 μm	26	25.5	22.31	–	–	–
>90 μm	2.28	12.6	1.70	–	–	–
Specific surface (cm^2/g)	2650	3561	4632	–	–	–
Specific gravity	3.15	2.16	2.35	–	–	–

work systematically studied the effect of increasing volcanic deposit addition (5–30 wt.%) with constant FA (10 wt.%), BA (10 wt.%), and CW (4 wt.%) content on the properties of PC and concrete. The results were compared with work using ordinary PC and Turkish Standards (TS).

2. Experimental procedures

2.1. Materials

The cementitious materials used in this study were PC clinker, coal FA, coal BA, CW, and volcanic deposits. Physical and chemical properties of these materials are shown in Table 1. The FA and BA come from SOMA SEA[a] Thermal Plant (Soma, Manisa, Turkey). FA meets general requirements of ASTM class C and has a relatively high CaO content of 19.50%, whereas BA belongs to ASTM Type F with CaO content of 17.57%. The NP was a blend of volcanic deposits from Kula (Manisa, Turkey) and CW from Etibor Plant (Emet, Kütahya, Turkey).

2.2. Cement mixtures

Four series of mixtures and one reference mixture were prepared according to TS 24 [21]. Before mixing, gypsum optimization was done for the clinker used and was found to be 5 wt.% of the clinker. Reference mixture was prepared out of PC and designated as R(PC). The other series of mixtures were designated as V(PC + NP), F(NP + FA + PC), C(VT + CW + PC), and P(NP + BA + PC). The details of the mixtures are given in Table 2. The raw materials mixed in

Table 2
Physical characteristics of cementitious mixes

Symbol	Cement mixes	Fineness (wt.%)		Specific surface (cm^2/g)	Specific gravity	Grinding time (min)
		+ 32 μm	+ 90 μm			
R	Reference mix	26.0	2.0	2850	3.15	30
NP_1	5% NP + 95% PC	25.9	1.9	2880	3.13	28
NP_2	10% NP + 90% PC	26.0	2.0	3110	3.11	26
NP_3	15% NP + 85% PC	26.1	1.8	3200	3.10	25
NP_4	20% NP + 80% PC	25.8	1.7	3221	3.08	24
NP_5	25% NP + 75% PC	25.7	2.0	3300	3.07	22
NP_6	30% NP + 70% PC	26.1	2.1	3480	3.05	21
F_1	5% NP + 10% FA + 85% PC	25.8	2.1	3320	3.04	24
F_2	10% NP + 10% FA + 80% PC	26.1	1.9	3440	3.02	23
F_3	15% NP + 10% FA + 75% PC	25.9	2.0	3510	3.00	21
F_4	20% NP + 10% FA + 70% PC	26.0	1.8	3680	2.99	20
F_5	25% NP + 10% FA + 65% PC	25.7	2.2	3770	2.97	18
F_6	30% NP + 10% FA + 60% PC	26.0	2.1	4370	2.96	17
C_1	5% NP + 4% CW + 91% PC	25.8	2.0	3380	3.13	24
C_2	10% NP + 4% CW + 84% PC	26.0	2.2	3430	3.11	22
C_3	15% NP + 4% CW + 81% PC	26.1	1.9	3530	3.10	21
C_4	20% NP + 4% CW + 76% PC	25.9	2.1	3550	3.05	20
C_5	25% NP + 4% CW + 71% PC	25.7	1.8	3560	2.98	19
C_6	30% NP + 4% CW + 66% PC	25.6	2.1	3570	2.94	18
P_1	5% NP + 10% BA + 85% PC	25.8	2.0	3580	3.09	23
P_2	10% NP + 10% BA + 80% PC	26.1	1.8	3710	3.05	22
P_3	15% NP + 10% BA + 75% PC	25.9	1.9	3720	3.00	21
P_4	20% NP + 10% BA + 70% PC	26.0	2.1	3820	2.97	20
P_5	25% NP + 10% BA + 65% PC	26.2	2.1	3850	2.96	18
P_6	30% NP + 10% BA + 60% PC	28.8	2.0	4090	2.94	17

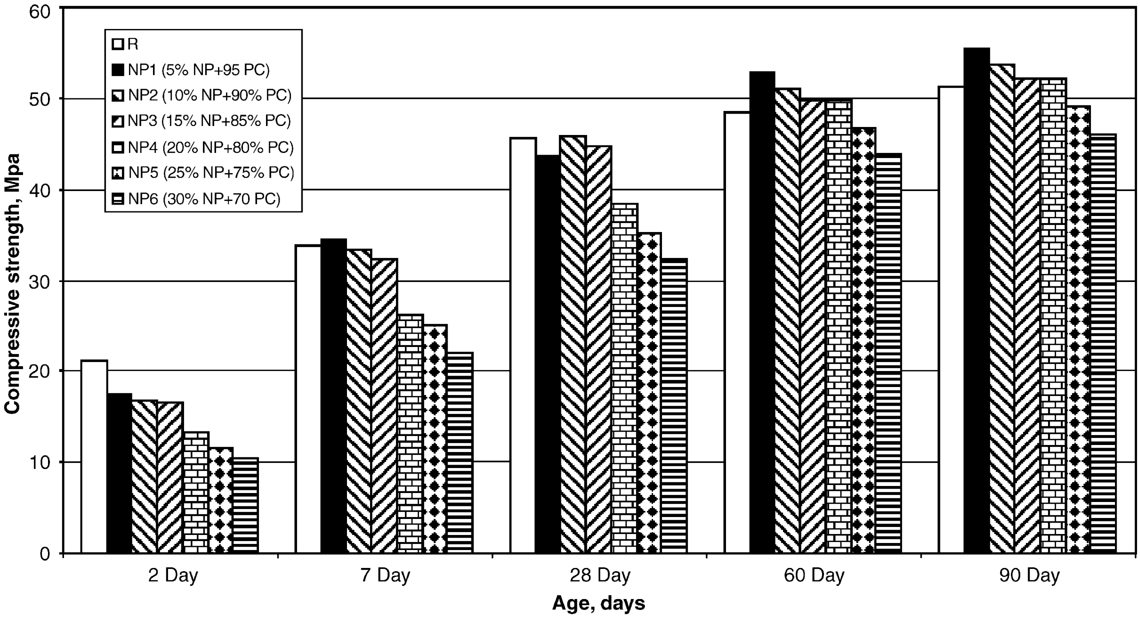

Fig. 1. Compressive strength of the concrete containing NP and PC.

the required proportion were ground to a fineness of 26 mass% residue on a 32-μm size mesh. The physical tests of the cement mixes were done according to TS 24.

2.3. Testing procedure

Water requirement and setting times of the cement mixes were determined in accordance to TS 24. The water requirement of cement was done by mixing water with cement and measuring the time for a vicat needle to penetrate 5–7 mm of the paste. The setting time was performed on cement paste, which was obtained by mixing cement with water and measuring the time required for a needle to penetrate 3–5 and 1 mm of the paste for initial and final setting times, respectively.

Specimen preparation for strength tests was performed at room temperature. The mixed proportion of the specimen corresponds to 450 g of cement content, 1350 g of standard sand, and 0.5 water-to-cement (w/c) ratio. Twenty-six batches were prepared and cast into 40 × 40 × 160-mm molds for strength tests. After casting, the specimens were stored in the laboratory at 20 °C with 90% relative humidity for 24 h and then demolded and placed under water. Each specimen was labeled with the date of casting, mix used,

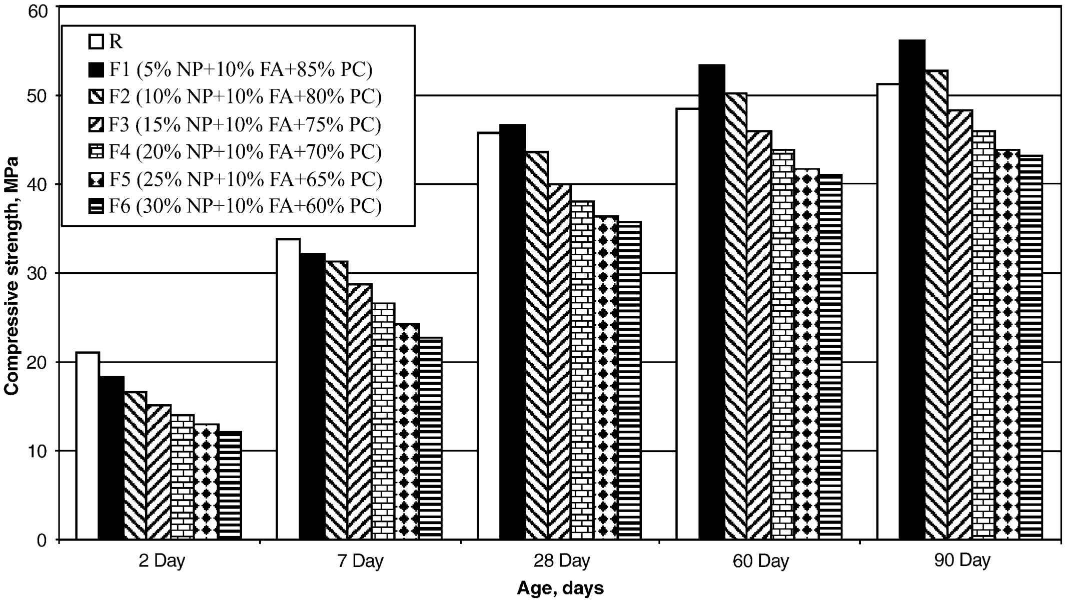

Fig. 2. Compressive strength of the concrete containing NP, FA, and PC.

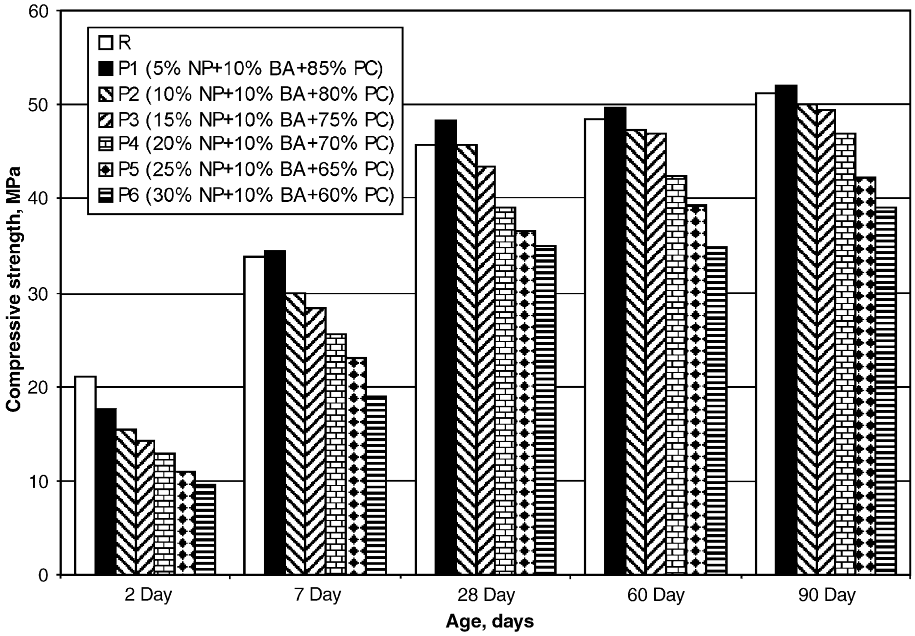

Fig. 3. Compressive strength of the concrete containing NP, BA, and PC.

and serial number. The specimens were then taken out of water 15 min before testing and dried with cloth. Compressive strength and bending strength measurements were determined with Tony Technique compression machine at a loading rate of 10–20 and of 5 N/mm^2/s, respectively. The strength value was the average of three specimens.

3. Results and discussion

3.1. Compressive strength

The compressive strength of different batches at different ages is shown in Figs. 1–4. The results of the control specimens without any supplementary material are also shown. At 2 days of curing time, the compressive strength of the specimens containing supplementary materials was less than that of control for all batches. Many researchers have reported that the appearance of the strength was slowed in the early curing period by adding pozzolanic material, such as FA and NP [5,6], because the overall pozzolanic reaction was slow. However, the strength was increased, exceeding the reaction by a large amount within a few weeks.

In Fig. 1, it is observed that the replacement of PC up to 15% by NP resulted in an increase (except sample NP1 containing 5% NP) in 28-, 60-, and 90-day strength relative to the strength of specimen containing no supplementary

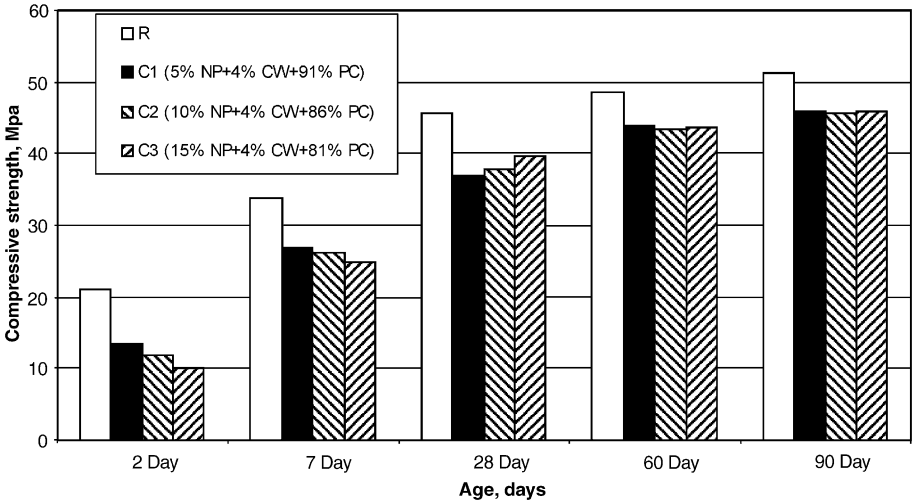

Fig. 4. Compressive strength of the concrete containing NP, CW, and PC.

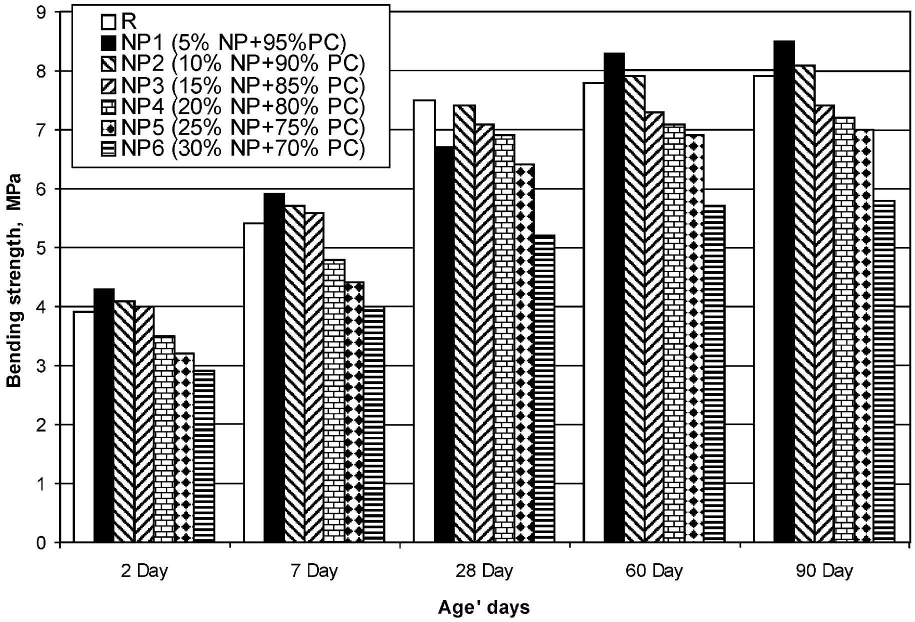

Fig. 5. Bending strength of the specimens containing NP and PC.

material. Further replacement of NP beyond 15% replacement resulted in a slight decrease in the compressive strength. It is interesting to see that among all the mixes made, the one containing 5% NP achieved the highest strength after 7 days (except 28 days). The increase in the strength of specimens due to replacement of NP can be attributed to the improved bridging between particles. On the other hand, the observed decrease in the strength of the specimens due to the replacement of PC by NP can be explained by the fact that larger replacement (more than 15%) leads to a surplus of the small-sized fraction, which begins to move apart PC grains, causing unpacking of the system and thus leading to a considerable decrease in the strength of the system [5].

It is known that pozzolanic reaction at room temperature is slow and therefore a long curing period is needed to observe its positive effects. Studies have found that if a low-reactive pozzolan, such as FA, was used together with bentonite, the pozzolanic activity of the low-reactive pozzolan could be improved [19]. This phenomenon was also investigated in this study. The batches with constant FA, BA, and CW and increasing replacement of NP by PC were prepared and tested. Consequently, the substitution of NP was competing with the same amount of cement in the reference batch in the presence of 10% FA and BA. The results of the compressive strength tests are shown in Figs. 2 and 3. As indicated above, at 2 days of age, all specimens had lower strength than the reference batch. As curing time

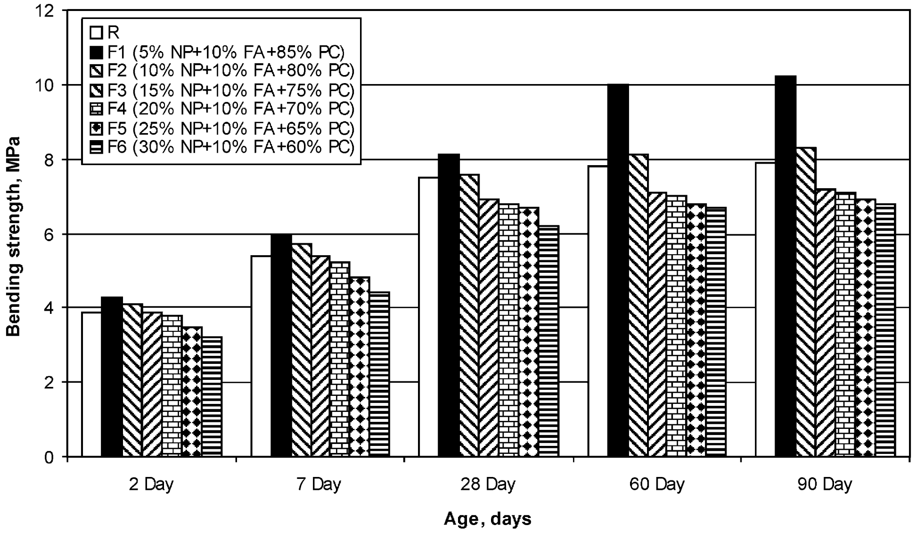

Fig. 6. Bending strength of the specimens containing NP, FA, and PC.

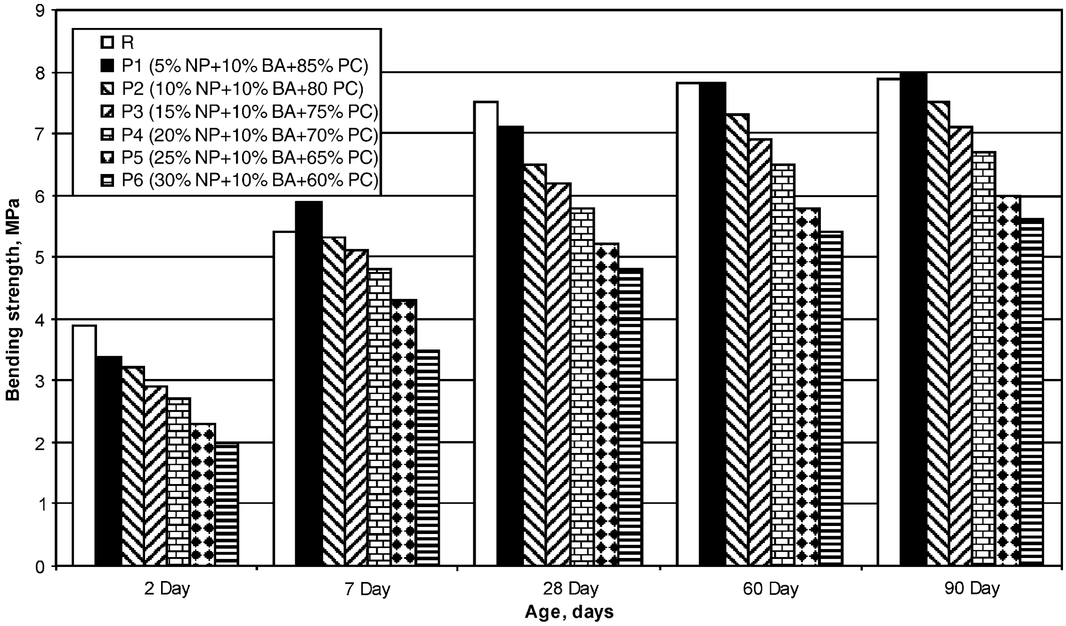

Fig. 7. Bending strength of the specimens containing NP, BA, and PC.

expanded, the strength of the specimens approached that of the reference and even exceeded that value. This result implies that the activities of BA and FA have been enhanced substantially by the NP and the strength gain in specimens is mainly attributed to NP.

Fig. 4 shows the compressive strength of the specimens containing NP, CW, and PC. From Fig. 4, it can be seen that the strength of the samples are lower than that of the control specimens and are gradually improved at three replacement levels after 28 days of curing age. It is very interesting to see that increasing the replacement of NP has no remarkable effect on strength development in the presence of 4% CW. This result indicates that the improvement in the strength is possibly due to CW containing boron. Boron can be incorporated into the ettringite structure, which result in an improvement in the strength of the sample [12].

3.2. Bending strength

The bending strength for the specimens with various kinds of pozzolanic materials is shown in Figs. 5–8. The result of the control specimens without any additives is also shown. It is observed that the replacement of PC up to 15% by NP and incorporation of 5–10% NP with 10% FA

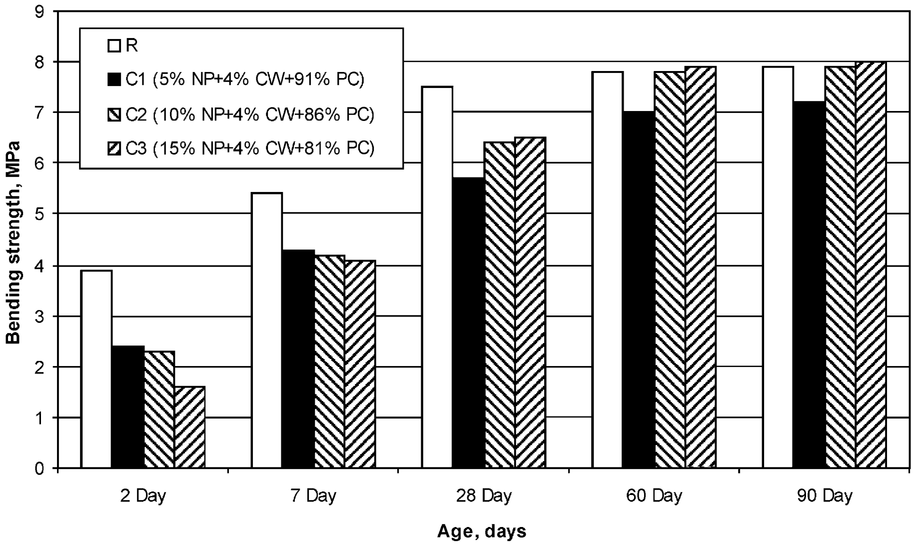

Fig. 8. Bending strength of the specimens containing NP, CW, and PC.

resulted in an increase in 2-day bending strength compared to the strength of the control mix. This may be attributed to the higher fineness of the FA and pozzolanic activity of NP. However, incorporation of NP with NP + CW resulted in a significant decrease in 2-day strength. As curing time expanded, the bending strength of the all specimens was gradually increased. However, it is interesting to note that although the replacement of NP by PC (beyond 10%) in the presence of constant FA and BA generally resulted to a decrease in strength, it improved bending strength of the sample containing NP + CW + PC after 28 days of curing. The increase in the strength of the specimens containing NP and CW can be explained in a way similar to the compressive strength increase in the concrete mixes. Furthermore, the reaction of potassium with borates and calcium hydroxide liberated during the hydration of PC helps in the formation of bonds between particles in the transition zone, which lead to further increase in strength [22].

3.3. Setting characteristic and volume expansion

The setting time of the cement paste containing different replacement material are given in Table 1. The results indicate that the effects of supplementary materials on the setting time of the paste vary widely. For NP paste, it is clear that the general effect of the NP is to increase initial setting time up to 20% replacement level. This seems to be in agreement with previous findings of other investigators. Shannag and Yeginobalı [6] showed that the use of NP as partial ordinary PC replacement extends the setting time of the paste. However, the final setting time of the paste is generally decreased as the replacement level is increased. This may be attributed to the increasing NP content of the paste that results in greater interparticle contact due to its high surface area, and thus, speeds up setting.

In the case of paste containing NP + FA and NP + BA, there is a clear trend that both initial and final setting times are decreased as the replacement level is increased (except the pastes, F1, F2). The acceleration in setting time of the pastes can be explained in a way similar to the final setting time decrease in cement paste containing NP and PC. Furthermore, NP with larger pozzolanic contributions at higher replacement level is responsible for early stiffening of the paste.

For the CW + NP paste, greater retardation was observed at higher replacement levels. As replacement level of NP was increased to 30%, the initial and final setting times increased by factors of 2.1 and 10.3, respectively. One of the reasons for this difference could be the use of CW in the present investigation. Recent studies [18,19,20] showed that the initial and final setting times of cement paste increased with the use of cementitious material containing boron.

The effects of replacement materials on the volume expansion of cement paste are shown in Table 3. The results indicate that the replacement of NP by PC has no remarkable effect on the expansion of cement paste. However, incorporation of NP with CW results in a volume expansion at higher replacement level. Explanation of this matter is beyond our understanding at the moment.

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	
TS 19	–	minimum 1:0	maximum 10:0	maximum 10:0
TS 640	–	minimum 1:0	maximum 10:0	maximum 10:0
R	29.4	2:05	4:00	0
NP$_1$	24.6	2:35	4:05	0
NP$_2$	24.8	2:55	3:45	0
NP$_3$	25.7	2:35	3:45	0
NP$_4$	26.2	2:25	4:10	0
NP$_5$	26.8	2:20	3:20	0
NP$_6$	27.1	1:55	3:15	0
F$_1$	26.8	2:45	4:05	0
F$_2$	27.7	2:55	4:15	0
F$_3$	28.0	2:45	3:45	1
F$_4$	28.3	2:45	3:50	0
F$_5$	29.4	2:25	3:35	1
F$_6$	30.0	2:10	3:25	0
P$_1$	29.1	2:30	3:45	1
P$_2$	28.9	2:15	3:35	1
P$_3$	28.6	2:15	3:20	1
P$_4$	28.3	2:15	3:20	0
P$_5$	29.7	1:35	3:05	1
P$_6$	29.1	1:45	2:55	1
C$_1$	26.9	5:00	8:30	1
C$_2$	26.9	5:35	10:15	2
C$_3$	26.0	4:15	8:15	1
C$_4$	27.7	–	–	–
C$_5$	28.0	–	–	–
C$_6$	26.0	7:30	14:30	3

4. Conclusions

This study was conducted to assess the effects of four supplementary materials on the properties of cement and concrete. These specific conclusions can be drawn from the results of this study:

1. The general effect of NP is to retard the initial setting time up to 20% replacement level. However, increasing replacement of PC by NP results in a decrease in the final setting time compared to control cement.
2. Increasing replacement of NP in the presence of a fixed quantity of FA and BA accelerates final setting.
3. The influence of increasing the level of NP in the presence of 4% CW is to provide greater retardation in the setting time of the cement.
4. As compared to control concrete, substitution of NP up to 15% by PC increases compressive strength of the specimens after 28 days of curing.
5. Although early compressive strength of the specimens containing NP + FA and NP + BA is lower, it increased

gradually for all samples throughout the entire 90 days of experiment.

6. Incorporation of NP with CW results in a significant increase in the compressive strength after 28 days of curing age.
7. At late curing ages, the NP and CW combinations can improve strength of the concrete.

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