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Effect of large amounts of natural pozzolan addition on properties of blended cements

L. Turanli*, B. Uzal, F. Bektas

Department of Civil Engineering, Middle East Technical University, 06531 Ankara, Turkey

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Abstract

In this study, the effects of 35, 45, and 55 wt.% natural pozzolan addition on the properties of blended cement pastes and mortars were investigated. Blended cements with 450 m^2/kg Blaine fineness were produced from a Turkish volcanic tuff in a laboratory mill by intergrinding portland cement clinker, natural pozzolan, and gypsum. The cements were tested for particle size distribution, setting time, heat of hydration, compressive strength, alkali–silica activity, and sulfate resistance. Cement pastes were tested by TGA for $Ca(OH)_2$ content and by XRD for the crystalline hydration products. The compressive strength of the mortars made with blended cements containing large amounts of natural pozzolan was lower than that of the portland cement at all tested ages up to 91 days. Blended cements containing large amounts of pozzolan exhibited much less expansion with respect to portland cement in accelerated alkali–silica test and in a 36-week sulfate immersion test.

Keywords: Alkali–aggregate reaction; Blended cement; Compressive strength; Pozzolan; Sulfate attack

1. Introduction

Portland cement is the principal hydraulic binder used in modern concrete practice. Portland cement manufacturing is an energy-intensive process that approximately 4 GJ of energy/tonne, mostly obtained from burning of fossil fuels, is consumed. The production of every tonne of portland cement releases approximately 1 tonne of carbon dioxide—a major contributor to the greenhouse gas emissions that is responsible for global warming. Considering the yearly portland cement production of 1.6 billion tonnes, the cement industry itself is responsible for 7% of the total carbon emissions [1,2].

Pozzolanic or cementitious materials, both natural pozzolans and industrial by-products, have been used for decades, either as an additive in cement production or as mineral admixture in concrete production. Quantity may vary according to the needs and the type of the material; however, there are successful applications in which mineral admixtures, i.e., slag and fly ash, were utilized up to 60% of cement by weight [2]. Saving in economy or, at least, in ecology is the inevitable outcome of high-volume pozzolan application due to the reduction in portland cement clinker.

Mehta [3] has reported that blended portland cements containing 10–30% Santorin earth, a natural pozzolan from

Table 1
Chemical composition of the clinker and the natural pozzolan as percent by weight

	Clinker	Pozzolan
SiO_2	21.11	54.16
Al_2O_3	5.34	15.18
Fe_2O_3	3.29	6.44
CaO	64.52	8.78
MgO	2.92	2.44
Na_2O	0.50	1.50
K_2O	0.60	2.10
SO_3	0.61	0.50
C_3S	59.90	–
C_2S	15.30	–
C_3A	8.60	–
C_4AF	10.00	–
Loss on ignition	0.98	11.58
Insoluble residue	0.41	61.73

* Corresponding author. Tel.: +90 312 210 2429; fax: +90 312 210 1262.
E-mail address: turanli@metu.edu.tr (L. Turanli).

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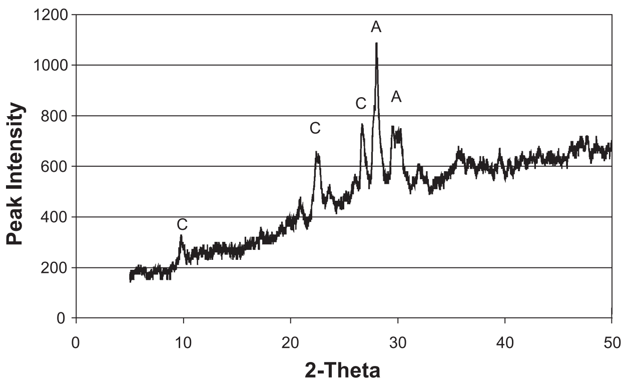

Fig. 1. X-ray diffraction pattern of the natural pozzolan and identified mineral phases (A: albite, C: clinoptilolite, Q: quartz).

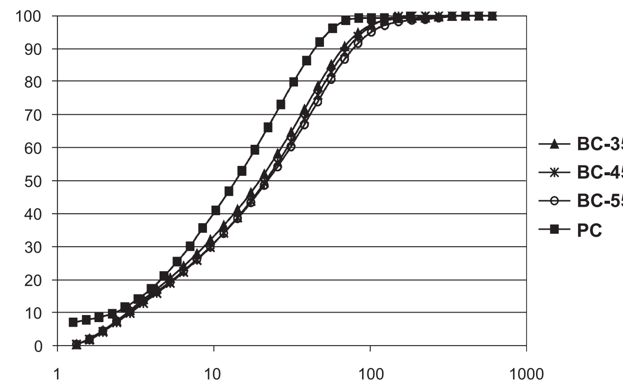

Fig. 2. Particle size distribution curves of the cements.

Greece, produced similar or higher compressive strength than the reference Portland cement did; also, it possessed much better durability to alkali–silica expansion and sulfate attack. Due to recent interest in high-volume pozzolanic cements to reduce greenhouse gas emissions, data are needed of blended cements containing high volumes of natural pozzolan. In a recent study carried out by Uzal and Turanli [4], natural pozzolan has the potential to be used at higher volumes in blended cements for structural concrete application.

In this study, the effects of 35, 45, and 55 wt.% natural pozzolan addition on the properties of blended cement pastes and mortars were investigated. Blended cements with 450 m^2/kg Blaine fineness were produced from a Turkish volcanic tuff in a laboratory mill by intergrinding portland cement clinker, natural pozzolan, and gypsum. The cements were tested for particle size distribution, setting time, heat of hydration, compressive strength, alkali–silica activity, and sulfate resistance. Cement pastes were tested by TGA for $Ca(OH)_2$ content and by XRD for the crystalline hydration products.

2. Experimental

2.1. Materials

The chemical compositions of the portland-cement clinker and gypsum obtained from a commercial source are shown in Table 1. Volcanic tuff from a Turkish deposit was used as a natural pozzolan in this study. The natural pozzolan was received in a bulk form and crushed to obtain particles less than 16 mm before intergrinding with the clinker and gypsum. The chemical composition of the natural pozzolan is shown in Table 1. According to X-ray diffraction patterns shown in Fig. 1, the material contains some crystalline minerals and a glassy phase.

Before intergrinding the clinker and gypsum to produce blended cements with different pozzolan contents, the component materials were crushed to pass through No. 12 sieve (1.70 mm). A laboratory grinding mill, 450 mm in length and 420 mm in diameter, was used for producing blended cements. A combination of 50- and 20-kg cylindrical steel balls, 30×30 and 20×20 mm size, respectively, was used as grinding media. For each test, a 10-kg batch of raw materials was fed into the mill, thus, the raw-materials-to-grinding-media ratio was 1:7. This ratio was selected according to studies reported by Bouzoubaa et al. [5].

Preliminary tests showed that a Blaine fineness less than 400 m^2/kg was not sufficient to obtain satisfactory early strength values; however, a Blaine fineness of about 450 m^2/kg was found to be satisfactory in regard to the strength of the cement mortar and grinding energy consumption. Therefore, blended cements were produced by intergrinding the components to a Blaine fineness of approximately 450 ± 15 m^2/kg, while the reference portland cement was ground to a Blaine fineness of about 300 ± 5 m^2/kg, which is a customary value for ordinary portland cements.

The blended cements were designated according to the pozzolan content present. BC35, BC45, and BC55 indicate the blended cements containing 35, 45, and 55 wt.%

Table 2
Physical properties of the cements

Cement	Specific gravity	Blaine fineness (m^2/kg)	Passing 45 μm (%)	Median particle size (μm)
PC	3.10	305	73.3	13.8
BC-35	2.84	455	72.8	19.5
BC-45	2.77	450	71.2	21.4
BC-55	2.71	455	69.5	22.0

Table 3
Water-to-cement ratio for normal consistency, and setting time

	w/c for normal consistency	Setting time (min)	
		Initial	Final
PC	0.22	175	215
BC35	0.28	190	315
BC45	0.30	172	276
BC55	0.32	105	157

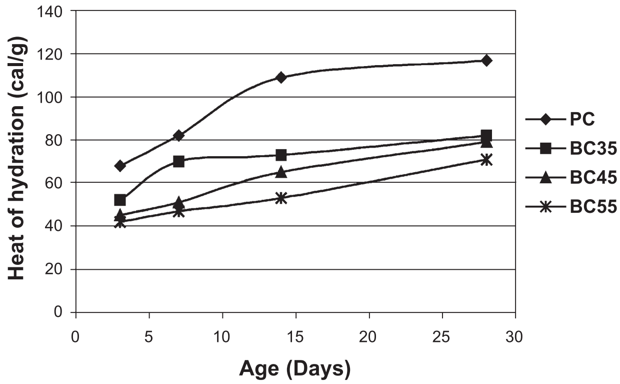

Fig. 3. Heat of hydration of the cements.

pozzolan, respectively. Therefore, a laboratory-produced portland cement with a Blaine fineness of about 300 m^2/kg was designated as PC.

2.2. Methods

The cements were tested for percent material finer than 45 μm, normal consistency, and setting time in accordance with ASTM standard test methods. The particle-size distributions of the cements were determined by the Mastersizer/E Malvern Laser Particle Size Analyzer, with particles suspended in isopropanol. The free $Ca(OH)_2$ content of the hardened cement pastes at various ages was determined by the TGA method. In addition, the XRD method was utilized to observe the crystal hydration products of hardened cement pastes at various ages. For compressive strength tests at 3, 7, 28, and 91 days of age, mortar mixtures were prepared using a water-to-cement ratio required for a standard flow of 110±5% and 2.75 sand–cement ratio. A sulfonated naphthalene formaldehyde condensate type superplasticizer in a dry powder form, 2 wt.% of cement for BC55 and 1% for the other cements, was used to obtain the standard flow without increasing the water content.

The potential expansion due to alkali–silica reaction was evaluated with an accelerated test method (ASTM C 1260), which involves the measurement of the expansion of mortar bars exposed to 1 N NaOH solution at 80 °C. A local aggregate that is known to be reactive in alkali–silica reaction was used to prepare the test mortars. The expansion of the mortar bars due to alkali–silica reaction was determined up to 30 days.

The sulfate resistance of the blended cements was evaluated by the ASTM C 1012 test method. The expansion of standard mortar bars was measured up to 36 weeks of exposure to 5 wt.% $MgSO_4$ solution.

3. Results and discussion

3.1. Particle size distribution

The physical properties of the cements are summarised in Table 2. According to the particle size distribution curves of the cements shown in Fig. 2, blended cements are coarser than the portland cement, especially for relatively bigger particle size range, although they have much higher Blaine fineness value. The higher Blaine fineness of the blended cements may be caused by the higher carbon content of natural pozzolan, which is indicated by the high loss on ignition value. In addition, coarse phase in blended cements may be attributed to the coarser clinker phase, which is harder to grind when compared with the pozzolan phase. The particle size distribution of the blended cements ground to 450 m^2/kg Blaine fineness was not affected significantly by increasing the pozzolan content from 35% to 55%.

3.2. Normal consistency, setting time, and heat of hydration

The experimental results of normal consistency and setting time of the cement pastes are shown in Table 3. The water-to-cement ratio required for standard consistency of the cement pastes increased with increased pozzolan content in the blended system. Increasing the pozzolan content from 35% to 55% resulted in an approximately 14% increase in water demand.

The blended cements showed quite different setting times according to pozzolan content. The blended cement containing 55% natural pozzolan exhibited shorter initial and final setting times when compared with reference portland cement, while for the blended cement containing 35% pozzolan, the reverse is true. The blended cement containing 45% pozzolan showed similar initial setting time and prolonged final setting time when compared with the portland cement. The mechanism that governs the effect of pozzolan content on setting time could not be explained by the authors.

Table 4
$Ca(OH)_2$ contents in cement pastes

Cement	Percent $Ca(OH)_2$				Percent $Ca(OH)_2$ (normalized to portland cement content)			
	3 days	7 days	28 days	90 days	3 days	7 days	28 days	90 days
PC	15.8	16.3	17.1	20.3	15.8	16.3	17.1	20.3
BC35	11.1	10.6	9.7	9.1	17.0	16.4	14.9	14.0
BC45	8.0	7.7	6.8	6.1	14.6	14.3	12.4	11.1
BC55	6.5	6.2	3.6	2.4	13.7	14.5	8.1	5.3

The heat of hydration curves for various ages are shown in Fig. 3. Blended cements showed lower heat of hydration for all pozzolan contents when compared with the portland cement tested, and, as expected, hydration heat decreased with increased pozzolan content for a given age.

3.3. The $Ca(OH)_2$ content and XRD analysis of the hardened cement pastes

The $Ca(OH)_2$ content in hardened cement pastes was determined by TGA at various ages, and the results are given in Table 4. The $Ca(OH)_2$ contents normalized with respect to the proportion of portland cement present in a blended cement is also shown in Table 4. As expected, the data show that the $Ca(OH)_2$ content of the pure portland cement paste increased with an increase in the hydration age, whereas in the blended cements, it decreased with the hydration age as a result of the pozzolanic reaction of the natural pozzolan present in blended system. The higher the pozzolan content in the blended cement, the lower $Ca(OH)_2$ content in the hardened cement paste at a given age due to less $Ca(OH)_2$ produced and the higher amount of $Ca(OH)_2$ consumed by the pozzolanic reaction.

According to the values of the $Ca(OH)_2$ contents normalized to cement content, 31%, 45%, and 74% of $Ca(OH)_2$ produced in BC35, BC45, and BC55, respectively, were consumed by pozzolanic reaction in blended systems at the end of 90 days of hydration.

The XRD patterns of the hardened cement pastes at 90 days are shown in Fig. 4. The patterns confirmed the decreasing $Ca(OH)_2$ content by increasing pozzolan content in the blended cements. The peaks in the patterns, indicated by ×, could not be identified. Especially, it is interesting that these peaks exist in BC35 and BC55 blended cements but not in BC45.

3.4. Compressive strength of mortars

The compressive strength data for 3, 7, 28, and 91 days of age for blended cements and reference portland cement, as determined according to ASTM C 109, are shown in Table 5. The strength values of the mortars were normalized with respect to portland cement content in each cement and are also given in Table 5.

The compressive strength of the mortars made with blended cements decreased with the increased pozzolan content for all tested ages. The normalized strength values of blended cement mortars were lower than that of the reference portland cement at 3 days of age, and the difference between the normalized strength values of blended and portland cements increased as the pozzolan content in the blended system increased. This was attributed to the increasing water-to-portland-cement ratio by increasing pozzolan content, which is 0.73, 0.91, and 1.0 for the mortars made with BC35, BC45, and BC55, respectively, whereas the w/c was 0.44 for portland cement.

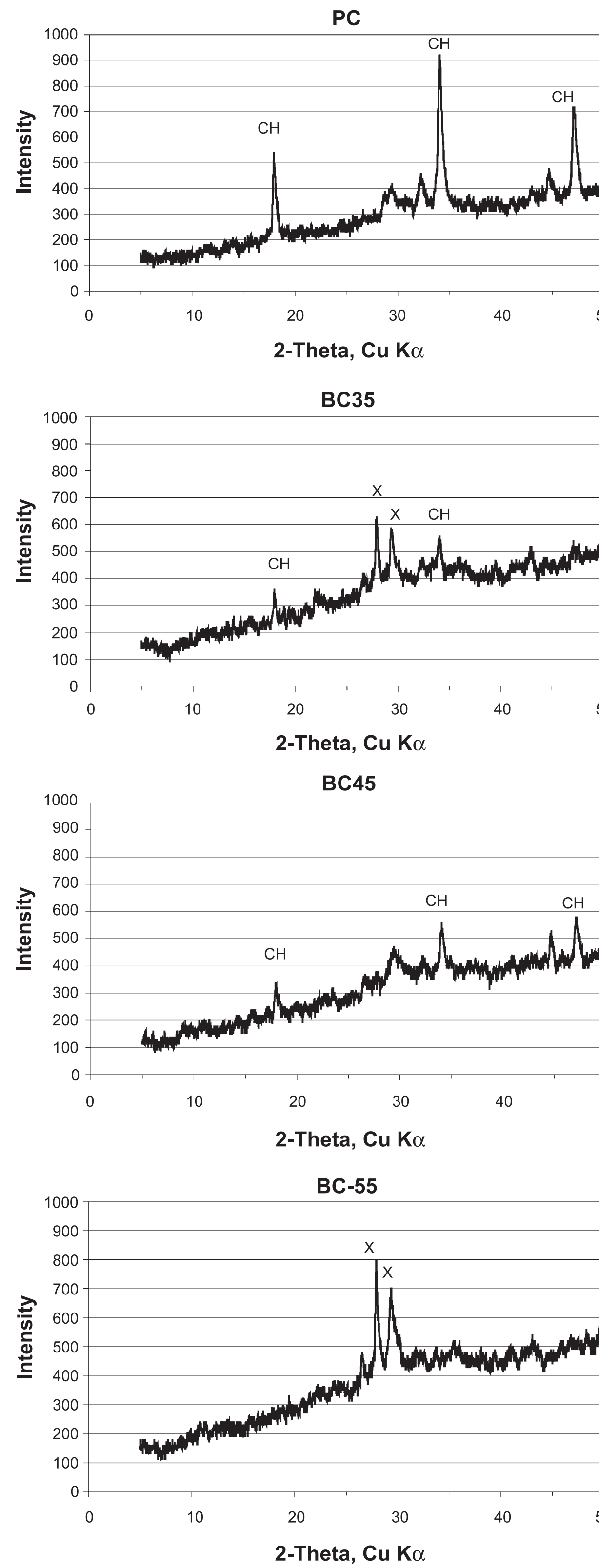

Fig. 4. X-ray diffraction pattern of the hardened pastes at 90 days of age [CH: $Ca(OH)_2$; the peaks marked with × is an unidentified phase].

Table 5
Compressive strength of mortars

Cement	w/c	SP %	Flow %	Compressive strength (MPa)				Compressive strength, (MPa; normalized to PC content)			
				3 days	7 days	28 days	90 days	3 days	7 days	28 days	90 days
PC	0.44	1	115	31.3	38.8	46.7	60.8	31.3	38.8	46.7	60.8
BC35	0.48	1	110	18.3	27.8	34.1	45.3	28.2	42.8	52.4	69.7
BC45	0.50	1	110	11.5	16.7	30.1	35.0	20.9	30.4	54.7	63.6
BC55	0.45	2	105	8.3	14.7	24.5	32.3	18.4	32.6	54.4	71.7

SP: superplasticizer (wt.% of the cement).

3.5. Alkali–silica activity

The expansion of mortar bars due to alkali–silica reaction was measured as a percent of the original length, and the results are shown in Fig. 5. Evidently, the blended cements containing large amount of natural pozzolans showed much reduced expansions when compared with the reference portland cement. However, no significant effect of increase in pozzolan content, from 35% to 55%, was found on the alkali–silica expansion.

3.6. Sulfate resistance

The expansion of mortar bars in the accelerated test for sulfate attack in accordance with ASTM C 1012 was measured, and the results are shown in Fig. 6. Again, the reference portland cement showed much higher expansion in 36 weeks of sulfate immersion than did the blended cements; cements BC35 and BC45 exhibited somewhat higher expansion than BC55 did.

4. Conclusions

Based on the test results, the following conclusions can be drawn on the properties of blended cements containing large amounts of the Turkish pozzolan used in the study:

1. In terms of particle size distribution, the blended cements containing large amount of the pozzolan, produced by using a laboratory-type grinding mill, were coarser than the reference portland cement.
2. The final setting time of the blended cements containing 35% and 45% pozzolan increased substantially when compared with the reference portland cement, which may be attributed to the difference in normal consistency. However, 55% pozzolan showed a decrease in the setting times with respect to the reference portland cement. This behaviour could not be explained.
3. The $Ca(OH)_2$ content of the hardened blended cement pastes decreased as the pozzolan content was increased, for a given age of hydration. A significant amount of available $Ca(OH)_2$ (approximately 74%) was consumed by the pozzolanic reaction in the blended cement containing 55% natural pozzolan at the end of 90 days of hydration. XRD analysis confirms that there was no detectable amount of $Ca(OH)_2$ in BC55 (blended cements containing 55% pozzolan) at the end of 90 days.
4. The compressive strength of the mortars made with blended cements containing large amounts of natural pozzolan was lower than that of the portland cement at all tested ages up to 90 days. Especially, the early strengths of blended cements decrease significantly as a result of combined effects of low portland cement content and relatively high water-to-portland-cement ratio in blended cement mortars.
5. The blended cements containing 35%, 45%, and 55% pozzolan showed excellent performance for suppressing the expansions caused by alkali–silica reaction.

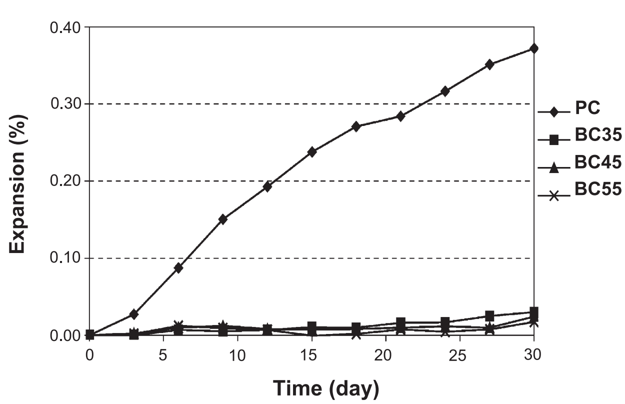

Fig. 5. Expansion of mortar bars due to alkali–silica reaction.

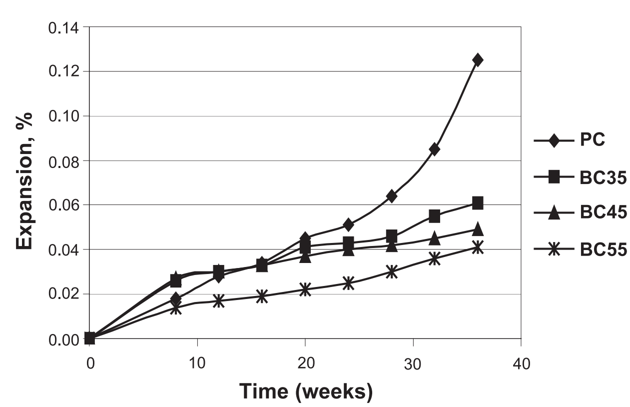

Fig. 6. Expansion of the mortar bars due to sulfate attack.

6. In terms of sulfate resistance, blended cements containing large amounts of pozzolan exhibited much less expansion with respect to portland cement in a 36-week sulfate immersion test (ASTM C 1202).

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