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Effect of material characteristics on the properties of blended cements containing high volumes of natural pozzolans

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Abstract

The effect of three different natural pozzolans from Turkish deposits on the properties of blended cements produced by intergrinding cement clinker with a high volume of natural pozzolan (55 wt.% of the cementitious material) was investigated. The particle size distribution of blended cements, setting time, heat of hydration, and compressive strength of blended cement mortars were determined. Experimental results showed that the hardness of the pozzolanic material strongly influenced the particle size distribution and the related properties of the blended cements by affecting the fineness of the components of the blended product. The early strength of the mortars was strongly affected by the particle size distribution of blended cements, whereas the strength development performance of the mortars was more related to the pozzolanic activity of the natural pozzolan present in the blended cement.

Keywords: Blended cement; Grinding; Particle size distribution; Pozzolan

1. Introduction

Natural pozzolans are defined as either raw or calcined natural materials that have pozzolanic properties (e.g., volcanic ash or pumicite, opaline chert and shales, tuffs, and some diatomaceous earths). Historically, they are among the oldest materials used in combination with lime for construction purposes. For example, a volcanic eruption around 1500 BC on Santorin Island, Greece, left a large deposit of natural pozzolans there. In modern construction technology, natural pozzolans are still used in various applications. They are used either as an admixture for concrete or as a blended component in the production of portland–pozzolan cements.

It is generally accepted that the use of natural pozzolans in cement or concrete systems results in many beneficial properties such as low heat of hydration, high ultimate strength, low permeability, high sulfate resistance, and low alkali–silica activity [1]. In addition, it is known that the use of pozzolanic and cementitious materials in large quantities is very important regarding the sustainability of the cement and concrete industry. This importance is not only related to the energy efficiency and environmental aspects of cement industry but also with the durability and life cycle cost of concrete structures [2].

Turkey is rich in volcanic tuff deposits. Some of them are currently used as pozzolans by local cement factories in blended portland cement production. High water requirement for a given consistency and resulting low strength characteristics of blended cements are the major limiting factors against the use of natural pozzolans in proportions larger than 30%. Moreover, large variations in physical, chemical, and mineralogical characteristics of natural pozzolans make it difficult to produce blended cements with satisfactory properties consistently. However, there is potential to produce high-volume, natural pozzolan blended cements having adequate properties [3].

The objective of this study was to determine the effect of natural pozzolan characteristics on the properties of laboratory-produced blended cements containing large amount of a pozzolan (55 wt.%). Three different sets of raw materials, each consisting of a clinker and a natural pozzolan, were used to produce three different blended portland cements by intergrinding the clinker, natural pozzolan, and gypsum in the proportion of 42:55:3 by mass in a laboratory grinding mill. High-volume natural pozzolan blended cements produced in the experimental program were tested for particle

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size distribution, heat of hydration, water demand, setting time, and compressive strength.

2. Experimental

2.1. Materials

Three sets of raw materials, each consisting of a different portland cement clinker and a volcanic tuff, which are currently used in commercial portland–pozzolan cement production in Turkey, were obtained from different cement manufacturers. The chemical composition of the portland cement clinkers and natural pozzolans are given in Table 1.

Volcanic tuffs were received in a bulk form and were crushed to obtain particles less than 16 mm before intergrinding. During crushing, it was observed that the pozzolan P1 was significantly more resistant to the impact action of the crusher compared with pozzolans P2 and P3. This indicated that pozzolan P1 is considerably harder to grind than P2 and P3. The X-ray diffraction (XRD) pattern and identified phases of the pozzolans P1, P2, and P3 are shown in Fig. 1. According to XRD data, all three natural pozzolans contain some crystalline minerals and a glassy phase, indicated by the raised background of the diffraction pattern. The major crystalline mineral in all pozzolan samples was albite (plagioclase-group mineral). XRD patterns indicated that pozzolan P2 has higher glass content compared with the others. The glass content of pozzolan P3 seems also to be slightly higher than that of P1. From a comparison of the XRD peak intensities, it seems that the proportion of crystalline phases in pozzolan P2 is relatively lower when compared with that of the others.

Portland cement clinker, natural pozzolan, and gypsum were ground together in proportions 42:55:3 by weight, respectively, for each of the laboratory-produced blended cements. Before intergrinding, clinker and gypsum were crushed to particle size below ASTM No. 12 sieve (1.70 mm). A laboratory grinding mill, 450 mm in length and 420 mm in diameter, was used to produce blended cements. A combination of 50 and 20 kg cylindrical steel balls, 30×30 mm and 20×20 mm in size, respectively, were used as grinding media. For each batch, 10 kg of raw material was fed into the mill so that the raw-materials-to-grinding-media ratio was 1:7. This ratio was selected from the study reported by Bouzoubaa et al. [4].

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 in the range of 450–500 m^2/kg was found to be satisfactory with regard to the strength of the cement and grinding energy consumption. Therefore, blended cements were produced by intergrinding the materials to a Blaine fineness of approximately 470 ± 15 m^2/kg, while the reference portland cements were ground to a Blaine fineness of about 300 ± 5 m^2/kg, which is a customary value for ordinary portland cements.

Blended and portland cements were designated according to the type of raw materials used. For instance, BC1 and PC1 refer to the blended cement and portland cement, respectively, produced by using the portland cement clinker (C1) and natural pozzolan (P1), presented as Set-1 in Table 1.

2.2. Methods

Blended cements were tested for Blaine fineness, percent material retained on 45-μm sieve, water demand, setting time, heat of hydration, and compressive strength of mortars by using the respective ASTM methods. Particle size distributions of the cements were determined by the Mastersizer/E Malvern Laser Particle Size Analyzer, with particles suspended in isopropanol. For compressive strength tests (at 3, 7, 28, and 91 days of age), the mortar mixtures were prepared by using 0.45 water-to-cement ratio and 2.75 sand-to-cement ratio. A sulfonated naphthalene formaldehyde

Table 1
Chemical composition of clinkers and pozzolans used in the study

	Set 1		Set 2		Set 3	
	Clinker-1 (C1)	Pozzolan-1 (P1)	Clinker-2 (C2)	Pozzolan-2 (P2)	Clinker-3 (C3)	Pozzolan-3 (P3)
SiO_2	20.40	61.48	21.11	54.16	21.12	62.23
Al_2O_3	4.72	18.22	5.34	15.18	5.38	15.16
Fe_2O_3	3.44	3.78	3.29	6.44	2.81	3.27
CaO	65.78	4.62	64.52	8.78	65.7	4.93
MgO	2.81	0.91	2.92	2.44	1.52	1.51
Na_2O	0.60	3.90	0.5	1.50	0.60	3.50
K_2O	0.70	4.10	0.6	2.10	0.50	2.40
SO_3	0.40	0.10	0.61	0.5	0.50	0.5
C_3S	75.0	–	59.9	–	65.4	–
C_2S	1.9	–	15.3	–	11.2	–
C_3A	6.7	–	8.6	–	9.5	–
C_4AF	10.5	–	10.0	–	8.6	–
Loss on ignition	1.01	2.70	0.98	11.58	1.00	6.12
Insoluble residue	0.11	92.20	0.41	61.73	0.44	86.18

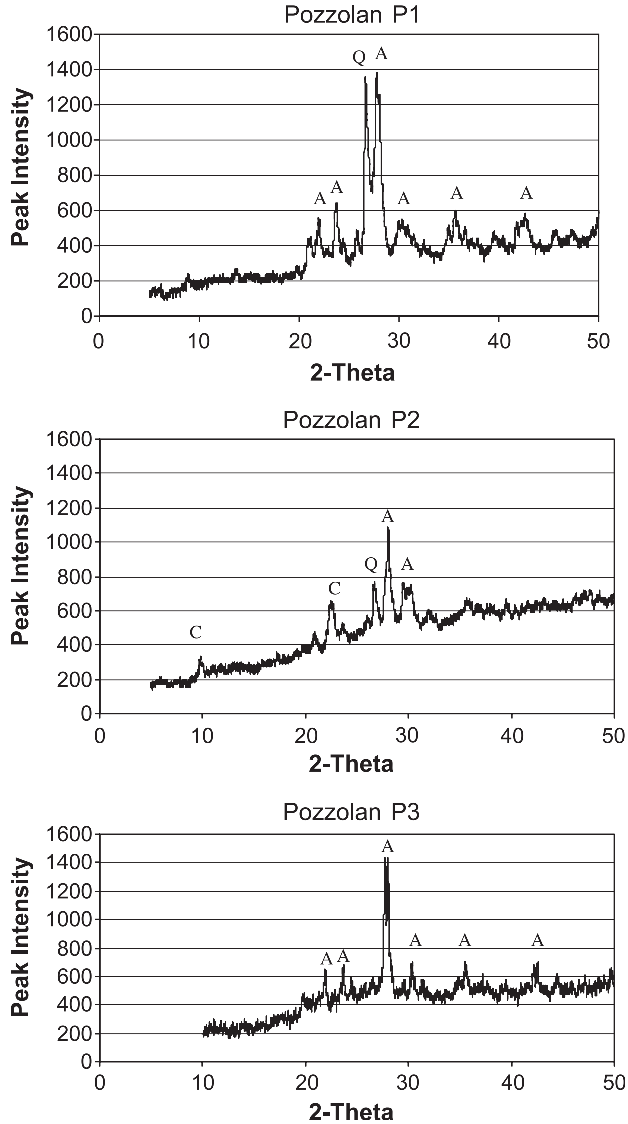

Fig. 1. XRD pattern of natural pozzolans P1, P2, and P3 (A: albite, Q: quartz, C: clinoptilolite).

condensate type superplasticizer, in dry powder form, was used to obtain adequate workability in mortar mixtures.

3. Results and discussion

3.1. Particle size distribution

The fineness parameters and required grinding time to obtain a specific Blaine fineness of cement are given in Table 2. The blended cements (BC1, BC2, and BC3) had higher Blaine fineness value compared with corresponding reference portland cements (PC1, PC2, and PC3) for equal or less grinding time. According to grinding time and corresponding Blaine fineness values, it seems that blended cements were easier to grind than portland cements. However, this is not true according to the percent material coarser than 45 μm, another fineness parameter. Blended cements were generally coarser than portland cements were, according to percent value of 45-μm sieve residue. This confirmed that Blaine fineness is not a reliable measure for materials other than portland cements. Particle size distribution curves obtained by laser diffraction are shown in Figs. 2–4 for the cements produced by using the raw materials of Set 1, Set 2, and Set 3, respectively. Particle size distribution curves showed that BC1 has a particle size distribution similar to the corresponding portland cement PC1 (Fig. 2), whereas BC2 was coarser than PC2 (Fig. 3). In addition, BC3 was coarser than PC3 for the particle size range bigger than 10 μm and was finer for the range of smaller than 10 μm (Fig. 4). The coarse phase in BC2 and BC3 was attributed to the clinker component, which was harder to grind compared with the pozzolans. On the other hand, the presence of relatively hard pozzolan particles in BC1 improved the grinding of clinker particles; thus, the quantity of coarse phase was reduced. According to the discussions above, it can be concluded that the relative hardness of starting natural pozzolan significantly influenced the particle size distribution of large-volume, natural pozzolan blended cements as a result of interactions between blended components during intergrinding.

Table 2
Fineness parameters and required grinding time of the cements

Cement	Blaine fineness (m^2/kg)	Retained on 45 μm (%)	Required grinding time (min)	Median particle size (μm)
PC1	295	25	120	20.6
PC2	298	21	125	14.0
PC3	297	22	90	19.8
BC1	459	18	108	17.4
BC2	456	29	100	22.0
BC3	482	25	90	23.4

3.2. Water demand, setting time, and heat of hydration

The water-to-cement ratio required for normal consistency and the initial–final setting times of the cements

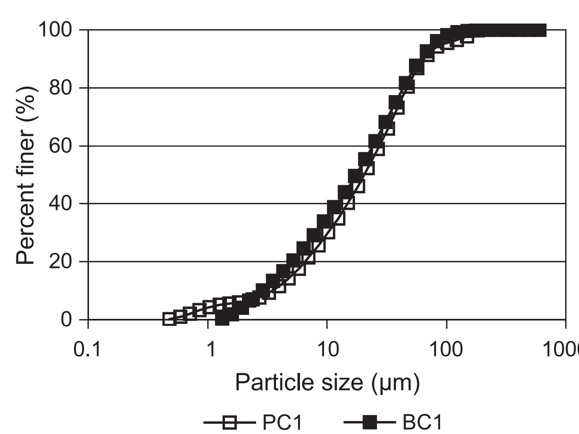

Fig. 2. Particle size distribution curves of BC1 and PC1.

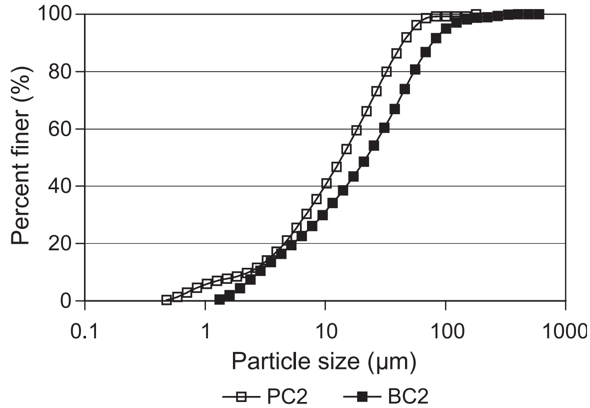

Fig. 3. Particle size distribution curves of BC2 and PC2.

are shown in Table 3. A large amount of natural pozzolan addition significantly increased the water demand of the cement pastes. Although the water-to-cement ratio values required to obtain normal consistency were similar for portland cements, they ranged from 0.29 to 0.36 for blended cements, depending on the type of natural pozzolan. This is due to the microporous nature and angular shape of the natural pozzolan particles. Although BC1 was slightly finer than BC2 and BC3, with respect to particles coarser than 45-µm sieve, the water requirement was lower. From the setting time data in Table 2, it is clear that the blended cement BC1 showed a prolonged initial and final setting time with respect to corresponding portland cement, whereas blended cements BC2 and BC3 exhibited a shorter setting time compared with that of the corresponding portland cements. The authors could not explain the reason for this anomalous behaviour. Therefore, additional tests were carried out to understand the effect of P2 natural pozzolan addition on the setting time of blended cements.

The blended cements containing 55% pozzolan P2 and the reference portland cement were produced again in addition to blended cements containing 35% and 45% pozzolan P2. These cements were then tested for setting time by standard Vicat apparatus to determine the effect of pozzolan content on setting times. The results are given in Table 4. The initial and final setting times of blended cements decreased as the pozzolan content increases. Blended cement containing 45% pozzolan showed a similar initial setting time to the portland cement. Blended cement containing 55% pozzolan exhibited initial and final setting times shorter than that of the portland cement.

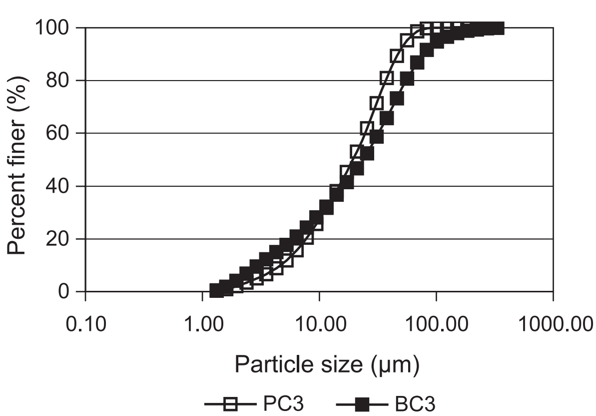

Fig. 4. Particle size distribution curves of BC3 and PC3.

Table 3
Heat of hydration, w/c for normal consistency, and setting time of the cements

Cements	Heat of hydration (cal/g)		w/c required for normal consistency	Setting time (min)	
	7 days	28 days		Initial	Final
PC1	74	102	0.22	150	188
PC2	82	117	0.22	175	215
PC3	69	105	0.24	160	189
BC1	35	46	0.29	197	295
BC2	51	68	0.32	103	157
BC3	48	63	0.36	115	144

A second series of tests were carried out to determine the effect of pozzolan P2 addition on setting times. In this series, pozzolan P2 was introduced as cement mass replacement instead of intergrinding. The results are given in Table 5. Initial setting time of the system decreased slightly as the pozzolan content increased. It is worth to note that the reductions were not significant compared with interground-blended systems. Final setting time increased with the increasing pozzolan content, as expected.

The reduction in setting times with the increasing pozzolan content contradicts the findings in the literature. A similar set-accelerating effect of natural pozzolan addition (especially for high volume content) has been reported by Targan et. al [5]. The authors of the paper expressed the acceleration in setting as follows: “This may be attributed to the increasing natural pozzolan content of the paste that results in greater interparticle contact due to its high surface area, and thus, speeds up setting”.

The heat of hydration of the cements was determined by the standard heat of solution method at 7 and 28 days, and the results are given in Table 3. Blended cements containing large amounts of natural pozzolan showed a significantly low heat of hydration with respect to the corresponding

Table 4
Setting time of blended cement containing different amounts of pozzolan P2

Cement	Blaine (m^2/kg)	w/cm	Setting time (min)	
			Initial	Final
PC-control	300	0.22	173	214
BC-35% pozzolan	450	0.28	190	315
BC-45% pozzolan	450	0.30	172	276
BC-55% pozzolan	450	0.33	122	197

portland cements for the testing ages, which were in agreement with the published literature [1].

For BC1, the heat of hydration, both at 7 and 28 days, was approximately proportional to the amount of clinker present in the blended system. For BC2 and BC3, however, the heat of hydration of the blended cements was found to be higher than the proportional value of the corresponding portland cement. This can be attributed to the higher contribution of pozzolanic reaction to the heat of solution due to more pozzolanic activity of pozzolan P2 and P3 present in BC2 and BC3, respectively. Based on the glass contents of the pozzolans discussed in Section 2.1 and on the contribution of pozzolanic reaction to the hydration heat of the blended cements, pozzolans can be arranged in terms of pozzolanic activity as P2>P3>P1.

3.3. Compressive strength

The compressive strength of the mortars made with blended cements and reference portland cements were determined, and the results are shown in Table 6. The compressive strength of the mortars made with blended cements containing large amount of natural pozzolans was lower than that of the corresponding reference portland cements at all ages of testing. The percent strengths of blended cements to the corresponding portland cements were 67%, 54%, and 77% for BC1, BC2, and BC3, respectively, even at 91 days of age. At longer ages, the differences in strength between portland cement and corresponding high-volume natural pozzolan cement are expected to be reduced.

Compared with the strength development of blended cements with age, different characteristics were observed. The percentage ratio of 3- to 91-day strength of blended cements, an indication of strength development performance, was 50, 23, and 34 for BC1, BC2, and BC3, respectively. The lowest strength development of BC1 (strength at 3 days divided by that at 91 days is 23%), despite the lowest value of percent material retained on 45-μm sieve and the smallest median particle size, was attributed to the weak pozzolanic activity of P1 present in BC1. BC2 had the highest, and BC1 had the lowest strength development. The result is in well agreement with the heat of hydration findings in terms of pozzolanic reactivity. Moreover, PC2 had the highest ultimate strength with the best performance of strength development (Table 6), probably due to relatively high C_2S content (Table 1). The highest strength development of BC2 was attributed to the combined effect of high pozzolanic activity of pozzolan P2 and high C_2S content of clinker C2. A further examination of the results exhibits that although pozzolan P2 was very reactive, the early strength value of BC2 was low. This was attributed to the grinding treatment: Because BC2 was not ground enough, probably, the clinker phase of BC2 remained coarse in the blended system (45-μm sieve residue of BC2 is 29%). BC3 exhibited a strength development characteristic that was between BC1 and BC2, conforming the pozzolanic activity order.

Table 5
Effect of pozzolan P2 replacement on the setting time of an ordinary portland cement

Cement	w/cm	Setting time (min)	
		Initial	Final
PC-control	0.24	125	170
30% Replacement	0.29	173	209
40% Replacement	0.30	170	214
55% Replacement	0.32	166	225

Table 6
Compressive strength of mortars

Cement	Superplasticizer[a] (%)	w/c	Flow %	Compressive strength of mortars (Mpa)			
				3 days	7 days	28 days	91 days
PC1	1	0.45	105	28.7	32.2	37.7	40.0
PC2	1	0.45	115	31.3	38.8	46.7	60.0
PC3	1.5	0.45	110	28.1	33.9	42.7	46.6
BC1	1	0.45	110	13.3	18.6	21.9	26.7
BC2	1	0.45	79	7.6	11.0	22.5	32.5
BC3	1.5	0.45	72	12.4	19.2	26.3	36.1

[a] Dry powder form of superplasticizer.

4. Conclusions

Based on the test results, the following conclusions are drawn on blended cements made with 55% natural pozzolans from three different Turkish deposits:

1. The pozzolanic reactivity of the materials was in the order of P2, P1, and P3.
2. The relative hardness of starting natural pozzolan compared with clinker significantly affected the particle size distribution of high-volume natural pozzolan blended cements. A harder natural pozzolan than clinker contributed to the finer grinding of the clinker phase in the blended system, whereas a softer pozzolan resulted in a relatively coarser grinding of the clinker phase.
3. Hydration heat of blended cements was influenced by the natural pozzolan present in the blended system, depending on the contribution of pozzolanic reaction to the heat of hydration.
4. Two of the blended cements produced and tested in the study exhibited a shorter initial and final setting time than the corresponding reference portland cements.
5. The strength development characteristic of blended cements was affected not only by the pozzolanic activity of natural pozzolans and the compound composition of the clinker, but also by the particle size distribution resulting from the interaction between the components of blended cement during intergrinding.

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