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Characteristics of pastes from a Portland cement containing different amounts of natural pozzolan

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Abstract

This work is concerned with assessing the influence of natural pozzolan on the physical, mechanical and durability properties of blended Portland cement pastes. The results indicate that final setting times of natural pozzolan blended Portland cement pastes range from 4 to about 5 h. Naphthalene-type superplasticizer tends to retard the hydration process of plain and natural pozzolan blended Portland cement pastes. These blends show slightly higher setting times than those without superplasticizer. The use of superplasticizer is found to have a significant influence on the workability. At a lower level of Portland cement replacement by natural pozzolan, the addition of 1% superplasticizer by weight of blended Portland cement leads to a significant decrease in the water to Portland cement plus natural pozzolan ratio for a given workability. However, for the blended Portland cement with a high proportion of natural pozzolan, the increase in water content causes the porosity to increase with an accompanying decrease in compressive strengths. The variations in composition and cure time are found to provide significant changes in compressive strength. Depending on these parameters, the variation in compressive strength can be estimated by using the equation, $\sigma = \sigma_0/[1+\exp(a+bp+cp^2)]^n$, where σ is the compressive strength of natural pozzolan blended Portland cement paste at a given cure time and natural pozzolan replacement level (MPa); σ_0 is the compressive strength of plain Portland cement pastes with or without superplasticizer at a given cure time (MPa); *p* is the natural pozzolan replacement level (%); *a*, *b*, *c*, *n* are the empirical constants to be determined. The blend with a composition of 80% Portland cement and 20% natural pozzolan and 1% superplasticizer provides superior strength and durability characteristics in comparison to the counterparts without superplasticizer and to the blends with a high proportion of natural pozzolan. At high contents of natural pozzolan, the resistance to freezing and thawing is found to be impaired. Moreover, these blended cements do not provide high durability performance against sulfate attack.

Keywords: Natural pozzolan blended Portland cement pastes; Physical, mechanical and durability properties

1. Introduction

The major hydration product affecting the durability performance of Portland cement pastes, mortars and concretes is the easily soluble calcium hydroxide. However, this phase can be changed into relatively insoluble calcium silicate hydrate phases. This has been achieved by replacement of Portland cement with mineral admixtures such as slag [1,2], fly ash [3], silica fume [4,5] and natural pozzolan [6]. Studies [3] have shown that not only does the fly ash strongly improve the workability of the blended Portland cement pastes, but also it is capable of exerting a substantial influence on the strength and durability characteristics of the hardened composite. The effect of fly ash addition on the strength becomes remarkable at advanced stage of hydration. Whereas, with a highly reactive mineral admixture such as silica fume, substantial improvements in the strength of concrete at early ages up to 7 days have been obtained [2]. Silica fume due to its ultra fine particles leads to an acceleration of Portland cement hydration reactions and to a lowering of calcium hydroxide content. Therefore, blended Portland cement pastes with silica fume is highly resistant to sulfate solutions. As in the case of fly ash or slag replacements, silica fume also changes the pore size distribution of Portland cement pastes from larger to finer pores [2]. This modification of microstructure plays an important role in decreasing the permeability of Portland cement pastes. In conclusion, it can be said that the lower amounts of calcium

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hydroxide in blended Portland cement pastes with mineral admixtures such as slag, fly ash and silica fume and a reduction in permeability provide a considerable improvement in the durability characteristics of these composites.

The aim of this work is to evaluate the use of natural pozzolan as an admixture in Portland cement paste and to determine how to affect its physical, mechanical and durability properties. In addition, an equation is derived empirically to estimate the compressive strength of natural pozzolan blended Portland cement paste depending on its composition and cure time.

2. Materials and methods

Ordinary Portland cement and natural pozzolan were used in the production of blended Portland cement paste. The Blaine-specific surface areas of Portland cement and natural pozzolan are 4028 and 4564 cm^2/g, respectively. Their chemical compositions are given in Table 1. Natural pozzolan is a volcanic tuff that consists of glassy particles of variable silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) content. The $SiO_2+Al_2O_3+Fe_2O_3$ proportion affecting the pozzolanic activity within the material is 80.6% that goes beyond the limit of 70% determined in TS 25 (Turkish standard). Thus, the material differs between neutral and acid rocks and is classified in the group of dacite. In the pozzolanic activity test, a commercial hydrated high calcium lime was used. The lime–pozzolan pastes with a lime/pozzolan ratio of 35% and water content of 45% were cured at 20 ± 2 °C and 90% relative humidity (RH) for various periods of up to 90 days. The 28- and 90-day compressive strengths of these paste with dimensions of $4\times4\times4$ cm were found as 4.45 and 9.12 MPa, respectively. This test of strength development with lime can be a very good indication of the performance of volcanic tuff with respect to use in blended cements. Nevertheless, the pozzolanic reactivity of volcanic tuff was also evaluated with the changes of calcium hydroxide contents of plain and blended Portland cement pastes during 180 days of curing at 20 ± 2 °C in sealed plastic moulds (2 cm diameter $\times$ 4 cm). Blended Portland cement pastes were prepared by replacing Portland cement with 20% natural pozzolan. Calcium hydroxide contents of these pastes were determined by thermogravimetric analysis. For the plain Portland cement paste, the calcium hydroxide content increased from about 23.81% at 28 days to about 26.87% at 180 days. With the 20% substitution of Portland cement for natural pozzolan, the calcium hydroxide content decreased to about 19.03% in 28 days and to about 17.42% in 180 days. When these values are compared on the basis of constant Portland cement content, it is found that there is no reduction in the amount of calcium hydroxide of natural pozzolan blended Portland cement paste at 28 days of hydration. However, at 180 days of hydration, it appears that the pozzolanic reactions reduce the amount of calcium hydroxide in this blend. Natural pozzolan replacements of 20, 30 and 40 by weight of Portland cement were used. Mix designation was made according to the mixing proportions of the materials. For example, 80:20 identifies a mix with a composition of 80% Portland cement and 20% natural pozzolan. Similarly, 80:201 represents the same mix with superplasticizer at a dosage of 1% by weight of blended Portland cement. The consistency of all paste is plastic. The addition of 1% naphthalene-type superplasticizer to the plain and natural pozzolan blended Portland cement pastes decreases the water content required for obtaining the same consistency. Setting measurements were performed with the Vicat needle method. The pastes cast into $4\times4\times4$ cm moulds for physical and mechanical tests or $4\times4\times16$ cm moulds for durability tests and then compacted by jolting. The pastes were stored under 90% RH at 20 ± 2 °C for a period of 1 day. At the end of this period, they were demoulded and cured in lime-saturated water at 20 ± 2 °C over a curing period of 7–180 days. The samples were tested for compression and porosity after 7, 28, 56, 90 and 180 days, to see the effect of cure time on the strength development and porosity of plain and natural pozzolan blended Portland cement pastes. In compression, the samples were tested in both wet and dry conditions. Former condition is obtained by storing the samples in a laboratory environment of 20 ± 2 °C and 65% RH and the latter by drying the samples in an oven at 105 °C to constant weight and then by cooling to room temperature in a desiccator. Durability assessments were made by examining the behaviour of plain and blended Portland cement pastes in freezing and thawing or wetting and drying cycles with sodium sulfate solution. The samples with a curing period of 28 days were used in these tests. In the freezing and thawing test, a cycle consists of thawing the sample for 4 h in water at 20 °C followed by 4 h freezing at -20 °C in air. In the sulfate exposure test, the samples were subjected to wetting in sodium sulfate solution at 20 °C for 16 h and then drying in an oven at 65 °C for 6 h followed by cooling in laboratory conditions for 2 h. Each cycle takes about 1 day in the sulfate exposure test. The solution, made up of 440 g $Na_2SO_4\cdot10H_2O$ and 1000 g water, has the density of 1.128 g/cm^3 at 20 °C. These tests were continued until the samples were broken. The compressive tests were made on these broken parts to determine the loss in the strength. The effects of durability tests were also estimated by changes in the dynamic modulus of elasticity of the specimens. The ultrasonic velocity measurements made at various stages were used to determine the dynamic modulus of elasticity.

Table 1
Chemical compositions of Portland cement and natural pozzolan

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
Portland cement	20.56	5.38	3.08	63.39	1.31	2.45	0.45	0.67	2.59
Natural pozzolan	65.3	2.82	12.48	0.41	0.07	5.42	0.34	2.9	9.8

The reduction in the modulus after a number of cycles of freezing and thawing or wetting and drying with sulfate solution indicates the deterioration of the pastes.

3. Results and discussion

3.1. Setting times

The setting characteristic of the pastes is affected by the replacement of the Portland cement with natural pozzolan. As can be seen in Table 2, the setting times of these blends increase with an increase in natural pozzolan content. Small amounts of natural pozzolan has little effect on the setting times. This effect is more pronounced when the natural pozzolan is used at large percentage. For the blend with a natural pozzolan content of 40%, the initial setting time delays 35 min and the final setting time 50 min in comparison to the plain Portland cement paste. The increase in setting time is probably due to the increase in the water to Portland cement ratio [3]. The addition of naphthalene-type superplasticizer interferes with the hydration of Portland cement and causes some retardation. The observed increases in the initial and final setting times of plain Portland cement paste due to retardation are at least 10 and 15 min, respectively. The same principle is also valid for natural pozzolan blended Portland cement pastes containing 1% superplasticizer. As in the case of plain Portland cement paste, the initial and final setting times of these blends are slightly higher than those of the blends without superplasticizer. However, in this case, the precise mechanism for the observed improvements in setting times of these blends is somewhat different. The combine action of superplasticizer and the increase in the water to Portland cement ratio can be regarded as the main factors responsible for this increase.

3.2. Workability

The effect of natural pozzolan on the water requirement is shown in Table 3. The water to Portland cement plus natural pozzolan ratios vary from 35.5% to 38.33% for blended Portland cement pastes without superplasticizer. From these findings, it can be concluded that the water requirement for blended Portland cement pastes increases with an increase of natural pozzolan content in the mixture. Low natural pozzolan replacements of up to approximately 30% appear to have similar effect on workability. There is no significant change in the water contents of these blends having natural pozzolan replacements of 20% and 30%. Natural pozzolan replacement of 40% has the strongest effect on the workability of fresh blends. The water content required to achieve the same workability with this blend increase considerably. The increase of water requirement for a given consistency of the Portland cement paste containing natural pozzolan may be attributed to the flocculent structure of these type of blends [3]. On the other hand, this structure may be broken down by adding a suitable superplasticizer to the mixture. As can be seen in Table 3, the use of superplasticizer affects the rheology of fresh Portland cement and natural pozzolan blended Portland cement pastes. The water to Portland cement ratio for the paste without natural pozzolan decreases from 34% to 27.78%. This significant reduction in the water to Portland cement ratio by using superplasticizer may appear to offer a potential for producing better natural pozzolan blended cement pastes. However, the rate of reduction in water requirement depends on the composition of the paste. The results indicate that the rate of reduction is inversely proportional to the amount of natural pozzolan in the blended Portland cement. Since the increased proportion of finely ground natural pozzolan particles causes the workability of the mixture to decrease, the same amount of superplasticizer would not be expected to provide a much greater reduction in water requirement for blended Portland cement paste. Indeed, the test result obtained for the blend with a composition of 60% Portland cement, 40% natural pozzolan and 1% superplasticizer shows a clear evidence of the fact that the water to Portland cement plus natural pozzolan ratio can only be reduced up to 34%.

3.3. Strength development

One of the major factor affecting the strength and strength development rate is the natural pozzolan content

Table 2
Initial and final setting times of plain and blended Portland cement pastes

Composition of blend	Initial setting time (min)	Final setting time (min)
100:00	145	240
80:20	145	240
70:30	167	265
60:40	180	290
100:001	155	255
80:201	170	259
70:301	190	278
60:401	200	300

Table 3
Water to Portland cement plus natural pozzolan ratios of plain and blended Portland cement pastes

Composition of blend	Water/Portland cement plus natural pozzolan ratio (%)
100:00	34.00
80:20	35.50
70:30	35.56
60:40	38.33
100:001	27.78
80:201	30.00
70:301	32.56
60:401	34.00

in the mixture. It is well known that the strength of blended Portland cement pastes in which natural pozzolan is partially substitutes for Portland cement is considerably less than that of Portland cement pastes at early stage of hydration [6]. This has been explained by the slowness of the pozzolanic reactions. The glassy particles in the natural pozzolan react with the calcium hydroxide released during cement hydration to form additional calcium silicate hydrate. This is supported by the pozzolanic activity test results. Since these are discussed in some depth in Chapter 2, they will not be mentioned further here. This reaction causes the strength of blended Portland cement pastes to increase with time. However, some controversy still exists regarding the time at which the pozzolanic reaction begins. The studies conducted have demonstrated that the reaction rate depends on the reactivity of the pozzolan and the reaction becomes significant after several days of curing when the pozzolan is highly reactive [3–5].

Table 4 shows the influence of natural pozzolan content on the compressive strength of Portland cement–natural pozzolan blends with and without superplasticiser. Much more detailed information concerning the cure times as well as the conditions occurring during the compressive strength tests is also given in this table. The compressive strengths of wet samples without superplasticizer at 7 days of curing decrease from 68.81 to 43.13 MPa, as natural pozzolan content increases from 0% to 40%. For the blends made using the superplasticizer, the decrease is from 69.03 to 46.56 MPa. This is found to be the case for wet samples with curing periods between 28 and 180 days. It is apparent that the predicting the mechanical performance of blended Portland cement with natural pozzolan from these findings may give misleading results due to differences in water to Portland cement plus natural pozzolan ratios. However, the precise mechanisms responsible for the observed reductions in compressive strengths can be found by comparing the test results obtained for the plain Portland cement paste without superplasticizer with those of natural pozzolan blended Portland cement pastes with compositions of 60:40 and 60:401. Since the water to Portland cement plus natural pozzolan ratio of the blend with a composition of 60:401 is the same as that of Portland cement paste, the decrease in the 28-day compressive strength is a consequence of the higher natural pozzolan content in this blend. When the natural pozzolan blended Portland cement pastes with compositions of 60:40 and 60:401 are compared, the reason for the reduction in the 28-day compressive strength is found to be related to the increase in water content. From these findings, it can be concluded that two mechanisms are responsible for the strength reduction in the blended Portland cement with natural pozzolan, i.e., the increase in water and natural pozzolan contents. The similar behaviour is also observed for the compressive strengths of dry samples with and without superplasticizer. However, these samples provide slightly lower strength characteristics in comparison to their moist counterparts. This can be explained by the fact that high drying temperature causes a damage in the microstructure of hardened Portland cement–natural pozzolan blends. The use of natural pozzolan to partially replace Portland cement is found to reduce the compressive strengths of blended Portland cement pastes with age between 7 and 180 days. Despite of this fact, the test results obtained for the blended Portland cements containing varying proportions of natural pozzolan suggest an optimum natural pozzolan content of about 20% from the standpoint of strength. At 28 days of curing, the decrease in compressive strength of this blend in comparison to Portland cement paste is 7.81 MPa for wet sample and 11.03 MPa for dry sample. Even after 180 days of curing, this blend containing 80% Portland cement and 20% natural pozzolan clearly exhibit somewhat lower compressive strength values than Portland cement pastes. However, the level of reduction in strength encountered on cure can be greatly diminished through the incorporation of the superplasticizer. Experimental evidence clearly show that the use of superplasticizer in the appropriate concentration reduces the water requirement and results in a quite dramatic improvement in compressive strength. On the other hand, the degree of enhancement in mechanical properties depends on the natural pozzolan content in the

Table 4
The effect of natural pozzolan content and cure time on the wet and dry compressive strengths of blended Portland cement pastes with and without superplasticizer (MPa)

Composition of blend	Cure times (days)									
	7		28		56		90		180	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
100:00	68.81	62.69	76.56	75.56	81.88	77.81	93.13	77.81	94.38	85.62
80:20	53.13	51.28	68.75	64.53	69.38	65.00	76.25	71.25	77.81	72.81
70:30	52.19	45.31	64.06	62.50	64.38	64.38	67.50	64.43	71.88	67.71
60:40	43.13	45.31	56.88	53.21	64.38	54.32	64.69	56.88	67.81	57.50
100:001	69.03	61.56	78.56	76.45	83.13	80.98	95.44	92.65	96.94	93.34
80:201	59.19	56.25	74.38	74.38	79.06	75.47	81.41	78.42	91.88	84.69
70:301	56.88	49.38	67.19	59.06	69.78	64.06	73.91	64.69	78.13	69.69
60:401	46.56	45.63	58.13	55.38	64.56	61.41	69.50	62.58	71.09	63.40

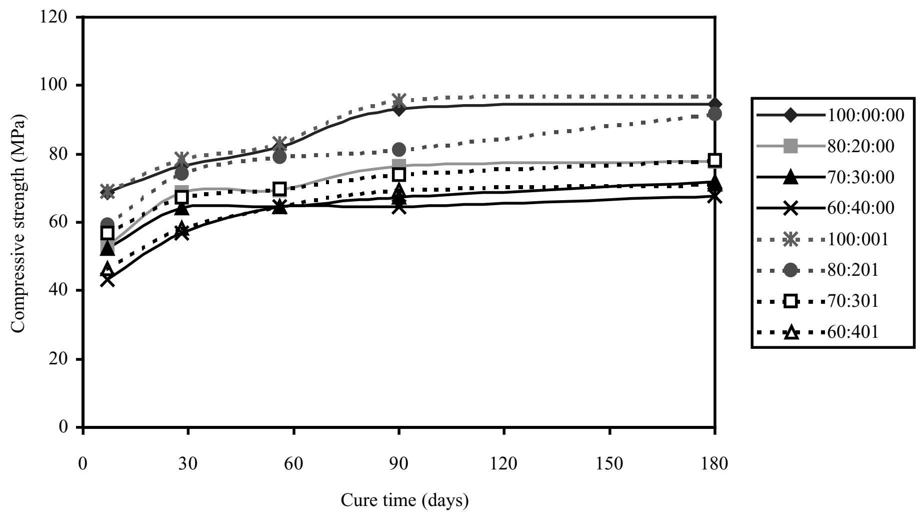

Fig. 1. Development of strengths of plain and natural pozzolan blended Portland cement pastes with or without superplasticizer with cure time.

mixture. At high contents of natural pozzolan, the contribution of superplasticizer to strength begins to decrease progressively since there is no significant difference in water to Portland cement plus natural pozzolan ratios of these blends. The compressive strengths of natural pozzolan blended Portland cement pastes with and without superplasticizer increase with cure time. This is presented in Fig. 1, which shows the change in compressive strength of wet samples as a function time and natural pozzolan replacement level. From this figure, it can be seen that the development of strength of these blends is influenced by the proportions of natural pozzolan and Portland cement. These blends gain a considerable part of their strengths at 7 days of curing. However, the rate of increase in compressive strength of blended Portland cement with natural pozzolan beyond the 28 days of curing decreases substantially. There is no significant difference between the 90- and 180-day compressive strength of these blends with and without superplasticizer.

A mathematical model is developed experimentally to predict the effect of cure time and natural pozzolan replacement level on the compressive strength of blended Portland cement pastes.

$$\sigma = \sigma_o/[1 + \exp(a + bp + cp^2)]^n \quad (1)$$

where σ is the compressive strength of natural pozzolan blended Portland cement paste at a given cure time and natural pozzolan replacement level (MPa); p is the natural pozzolan replacement level (%); σ_o is the compressive strength of plain Portland cement paste with or without superplasticizer at a given cure time (MPa); a, b, c, n are the empirical constants depending on the cure time of blended Portland cement pastes.

The material constant and correlation coefficients are given in Table 5. The value of correlation coefficients is equal to 1. This value suggests that there is a very good

Table 5
Material constants and correlation coefficients for wet samples

	Cure time (days)	σ_0	Material constants				Correlation coefficient (r)
			a	b	c	d	
The blends without superplasticizer	7	68.81	0.088	109.94	− 6.04	0.01	1
	28	76.56	− 0.94	41	120.36	0.0084	1
	56	81.88	− 4.47	55.01	− 78.60	0.048	1
	90	93.13	− 4.83	53.78	− 66.81	0.061	1
	180	94.38	− 15.58	721.95	− 574.99	0.0018	1
The blends with superplasticizer	7	69.03	0.1167	39.87	173.44	0.0085	1
	28	78.56	− 2.67	− 0.87	206.43	0.01	1
	56	83.13	− 7.93	50.01	− 57.13	0.085	1
	90	95.44	− 4.29	56.23	− 53.72	0.033	1
	180	96.94	− 10.25	67.31	− 76.04	0.069	1

agreement between these compressive strength data and those calculated with the proposed equation.

This mathematical model was also tested on relative compressive strength data reported by Massazza and Costa [7] for natural pozzolan blended Portland cement mortars. However, in this case, Eq. (1) must be rearranged as:

$$\sigma/\sigma_{28} = 1/[1+\exp[f(p)]]^{n} \quad (2)$$

where $f(p)$ is a polynomial of second or higher order; σ_{28} is the 28-day compressive strength of plain Portland cement mortar (MPa); σ is the compressive strength of natural pozzolan blended Portland cement mortar at a given cure time and natural pozzolan replacement level (MPa). Meanwhile, it can be noted that, at a given cure time, σ represents also the compressive strength of plain Portland cement mortar when p equals to 0.

In the regression analysis, the degrees of polynomials were found to be 3 for the 7 days of curing period and 4 for the 28 days, 3 and 6 months, and 1 year of curing periods. The value of material constant n in the equation lies between -0.011 and 0.38. For short curing periods of up to 28 days, the predicted relative compressive strength values are in excellent agreement with those measured by Massazza and Costa, with correlation coefficient 1. The same trend is also observed for higher curing periods, but deviations from this model generally arise as a consequence of the higher level of Portland cement replacement by natural pozzolan. The deviation becomes greater for p>40%. Although this model does not include any effects for aggregate, it yields sufficient information concerning the compressive strength of mortars containing natural pozzolan as partial replacement for Portland cement. Therefore, this relation can be applied to natural pozzolan blended Portland cement pastes and mortars. It is also to be noted that the model representation used in the analysis is valid for Portland cement replacement levels of up to 40% by natural pozzolan.

3.4. Porosity

The water content of the blends and the extent of hydration and pozzolanic reactions is believed to be the major causes of the variation in porosity. The use of an appropriate superplasticizer provides a better distribution of cement particles and reduces the water content [1]. The decrease in water content is known to play a more important role in decreasing the porosity. The Portland cement hydration and pozzolanic reactions cause the porosity of blended Portland cement pastes to decrease progressively. However, the contribution of pozzolanic reactions to space-filling process becomes significant at advanced stage of hydration [3]. The filling of these gaps with hydration products increases the strength and durability characteristics of blended Portland cement pastes. The reaction products of natural pozzolan blended Portland cement paste are nearly the same as those found in Portland cements. These are calcium silicate hydrate, calcium hydroxide, ettringite, tetracalcium aluminate hydrate and monosulphoaluminate [5].

The effect of cure time on the porosity of Portland cement and natural pozzolan blended Portland cement pastes with and without superplasticizer is shown in Fig. 2. The porosity of Portland cement pastes at 7 days is found to be about 32.85%. The value of this ratio decreases from 32.85% up to about 19.86%, as the cure time increases from 7 to 180 days. This result confirms the assumption that the porosity of Portland cement paste decreases with increasing cure time. The same is found to be true for natural pozzolan blended Portland cement pastes. For example, the porosity of blend with a composition of 60% Portland cement and 40% natural pozzolan decreases to about 37.92% in 7 days and to about 27.19% in 180 days. For the superplasticized blend having the same composition, the porosity decreases from 37.09% to 23.89% in 7–180 days. These results suggest that the porosity of natural pozzolan blended Portland cement paste with superplasticizer is lower than that of

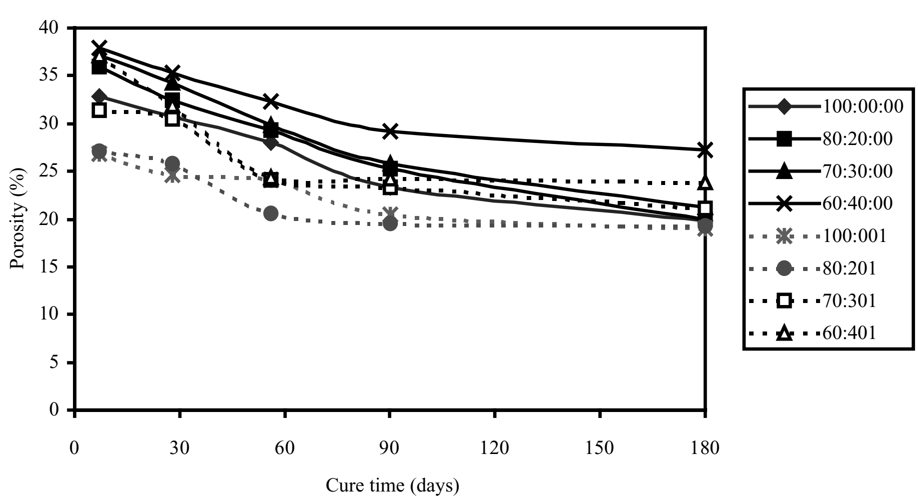

Fig. 2. The variation of porosities of plain and blended Portland cement pastes with or without superplasticizer with cure time.

the pastes without superplasticizer during the cure period. This arises from the fact that the superplasticizer is capable of providing a decrease in water contents of these blends.

In general, the porosity of natural pozzolan–Portland cement blends with and without superplasticizer increases with an increase in natural pozzolan content. The increase in porosity due to natural pozzolan replacement is more pronounced in the blends without superplasticizer. This may be attributed to the porous structure of natural pozzolan. The same explanation for the increase in porosity of blended Portland cement with fly ash is also made by Helmuth [3]. Up to 56 days of curing, the natural pozzolan blended cement pastes with and without superplasticizer tend to form a family of parallel curves. However, relatively minor changes in porosity curves of the blends with superplasticizer are observed with increasing cure time. This may be due to a relatively more uniform microstructure of these blends. This modification of the microstructure is to be expected suppose that the superplasticizer causes a better hydration of natural pozzolan blended Portland cement pastes [1].

3.5. Freeze thaw resistance

It is well known that the resistance of blended Portland cement pastes to freezing and thawing depends on a number of parameters of which the strength of blended Portland cement pastes as well as degree of saturation and pore system are among the most important. The latter is thought to be especially important in causing a damage of blended Portland cement paste. The nature, level and reactivity of the pozzolan is also of considerable importance in determining the durability performance of the blended Portland cement pastes [5]. Fig. 3 shows variations of relative dynamic modulus with respect to the number of freeze–thaw cycles. The tests results demonstrate that the blends with a composition of 80% Portland cement, 20% natural pozzolan and 1% superplasticizer can withstand 192 cycles of freezing and thawing without substantially losing its mechanical strength. This is evident from the relative dynamic modulus of elasticity and the compressive strength test results obtained after 192 cycles of freezing and thawing (Table 6). The ability of this composite retain a considerable part of its strength after aging can be an indication of its high degree of resistance to freeze–thaw cycles. Meanwhile, the compressive strength of this mix after 192 freezing and thawing cycles is quite similar to that of the plain Portland cement pastes with superplasticizer, which exhibit good resistance to freezing and thawing. However, increasing the Portland cement replacement by natural pozzolan from 20% to 30% makes the freezing and thawing resistance decrease. This conclusion is confirmed with the comparison of characteristics of natural pozzolan blended Portland cement pastes with compositions of 80:20 and 70:301. Since the 28-day compressive strength values of these pastes are almost the same, the reduction in freeze–thaw resistance of latter composition is a result of the increase of natural pozzolan content. For the natural pozzolan replacement of 40%, the loss of strength observed during cycling appears to be relatively high. This blend shows pronounced deterioration after completion of 60 freezing and thawing cycles, with less than 80% of its original compressive strength being retained. These results point out that a lower level of

Table 6
The compressive strengths of plain and blended Portland cement pastes after and before freeze–thaw cycling (MPa)

Composition of blend	Number of cycles						
	0	28	60	67	125	145	192
100:00	76.56					74.32	
80:20	68.75				52.5		
70:30	64.06	48.44					
60:40	56.88	25.12					
100:001	78.56						74.38
80:201	74.38						71.89
70:301	67.19			47.56			
60:401	58.13		45.94				

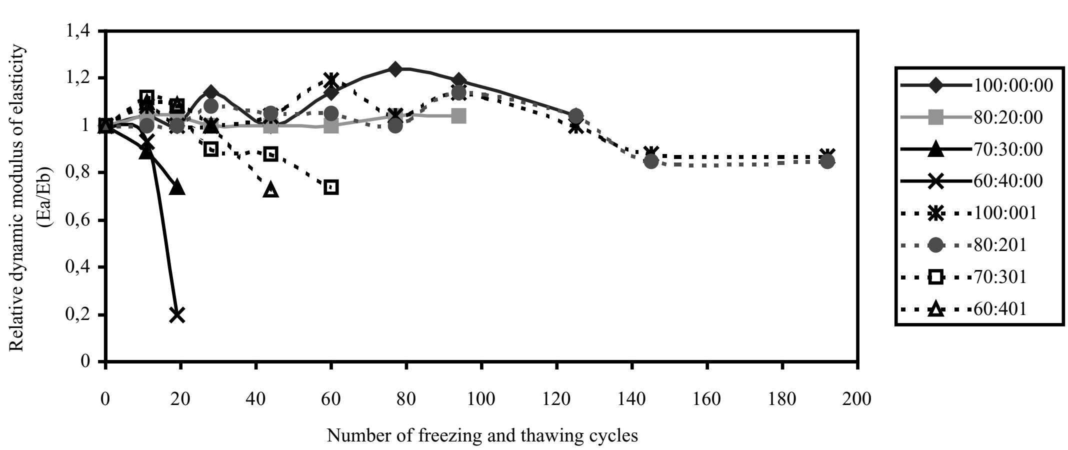

Fig. 3. The variation of relative dynamic modulus of elasticity with number of freezing and thawing cycles. E_a/E_b is the ratio of dynamic modulus of elasticities after and before cycling.

Portland cement replacement by natural pozzolan is necessary from the standpoint of freeze–thaw durability. The durability performance of plain and natural pozzolan blended Portland cement pastes without superplasticizer is considerably lower than that of the superplasticized counterparts. These blends tend to disintegrate before 192 freeze–thaw cycles. Plain Portland cement paste without superplasticizer and the blend with a composition of 80:20 deteriorate at almost the same rate up to 125 freezing and thawing cycles at which the latter disintegrates. But the former shows a slightly better performance and undergoes a pronounced deterioration at 145 freezing and thawing cycles. The replacement of Portland cement by increasing proportions of natural pozzolan leads to a decrease in durability performance. The blended Portland cements with 30% and 40% natural pozzolan are shown to suffer serious degradation when subjected to repeated cycles of freezing and thawing. The durability performance of these blend is limited to the freeze–thaw cycling of approximately 30. The poor performance of these blends to freezing and thawing is consistent with their higher porosities.

3.6. Sodium sulfate attack

Tricalcium aluminate (C_3A) and tetracalcium alumino ferrite (C_4AF) contents in Portland cement is thought to be particularly important in determining the sulfate resistance [1–5]. These phases tend to react with sulfates to form ettringite. The formation of ettringite causes an expansion and disintegration of hardened Portland cement pastes. Fig. 4 shows variations of relative dynamic modulus with respect to the number of wetting and drying cycles. In general, plain Portland cement pastes with and without superplasticiser does not show any signs of attack up to 40 days. This is supported by the relative dynamic modulus of elasticity and the compressive strength test results (Table 7), which remain constant during sulfate attack. However, there is a strong tendency of decrease in relative dynamic modulus of elasticity of the blend containing 80% Portland cement and 20% natural pozzolan and 1% superplasticizer. This blend retains in excess of 40% of its original strength after 14 days of exposure to sodium sulfate solution. The resistance to chemical attack caused by sodium sulfate decreases considerably with increasing natural pozzolan content in the blend. Increasing the Portland cement replacement by natural pozzolan from 20% to 40% leads to a decrease of time to failure from 14 to 7 days. This is because the reaction of calcium hydroxide released during Portland cement hydration with aluminates from both the Portland cement and natural pozzolan and sulfates in solution produce ettringite. The expansion caused by ettringite formation causes a damage in the blended Portland cement pastes. The increase of the degree of deterioration with increasing natural pozzolan content may be related to the high alumina concentration in solution. Sodium sulfate is also shown to have a strong influence on the compressive strength of natural pozzolan blended Portland cement paste without superplasticizer. Sulfate resistance of these blends is considerably lower than that of superplasticized counterparts. For example, seven cycles of wetting and drying with sodium sulfate solution results in about 20% retention of strength. The decreased sulfate resistance, in this case, can possibly be attributed to the higher porosity of blended Portland cement pastes without superplasticizer.

Table 7
The compressive strengths of plain and Portland cement pastes after and before wetting and drying cycles with sodium sulfate solution (MPa)

Composition of blend	Number of cycles				
	0	7	11	14	40
100:00	76.56				71.25
80:20	68.75	29.38			
70:30	64.06	22.5			
60:40	56.88	21.25			
100:001	78.56				75.53
80:201	74.38			30.94	
70:301	67.19		20.94		
60:401	58.13	23.44			

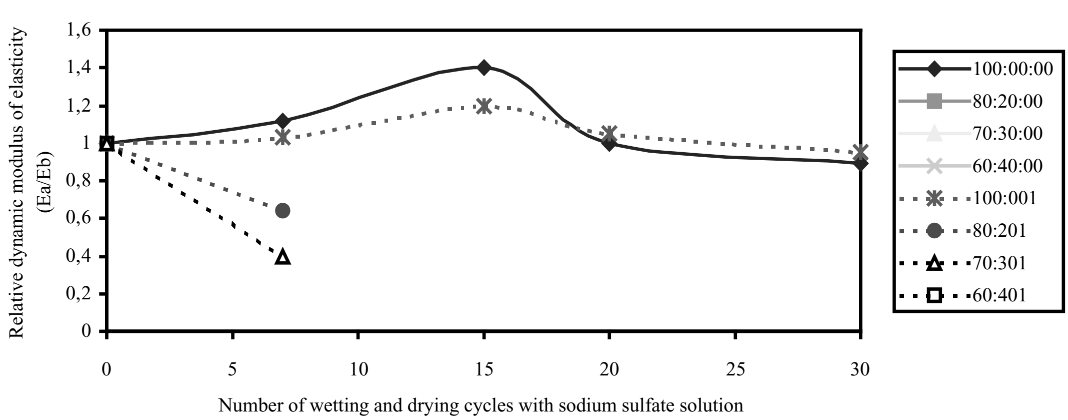

Fig. 4. The variation of relative dynamic modulus of elasticity with number of wetting and drying cycles.

4. Conclusions

From these data obtained is possible to draw some conclusions of great importance.

1. The replacement of Portland cement by natural pozzolan causes an increase in the water content required for obtaining a constant workability. The naphthalene-type superplasticizer allows a significant reduction in the water to Portland cement plus natural pozzolan ratio. However, at large natural pozzolan replacements, the effectiveness of superplasticizer with regard to decreasing water content is observed to be impaired.

2. There appears to be a clear evidence that the naphthalene-type superplasticizer affects the initial and final setting times of plain Portland cement pastes. This organic admixture retards the initial and final setting times of plain Portland cement pastes by at least 10 and 15 min, respectively. Similar effect is seen when the 1% superplasticizer is added to the natural pozzolan blended Portland cement paste. However, the major factor affecting the initial and final setting times is the large replacement of Portland cement with natural pozzolan. For example, the 40% substitution of Portland cement by natural pozzolan increases the final setting time from 4 to about 5 h.

3. The equation developed in this study permits the compressive strengths of natural pozzolan blended Portland cement pastes to be predicted with a high degree of accuracy.

4. The porosity of blended Portland cement pastes increases with increasing natural pozzolan content. However, the higher porosity due to replacement of Portland cement with natural pozzolan can be reduced by the application of longer periods of curing. Further curing increases the extent to which the pores in hydrated paste are filled with hydration products, thereby decreasing porosity. The reduction in porosity also arise with the use of superplasticizer, which leads to a decrease in the water to Portland cement plus natural pozzolan ratio.

5. At the initial stage hydration, a blend of Portland cement and natural pozzolan has a compressive strength less than Portland cement. However, after 180 days of curing, the compressive strength of the blends containing 80% Portland cement and 20% natural pozzolan and 1% superplasticizer is very close to that of plain Portland cement pastes. The increase in strength observed at later ages appears to be a result of the reaction of natural pozzolan with calcium hydroxide produced by hydration of Portland cement.

6. The high rate of increase in compressive strength of plain and blended Portland cement pastes up to 7 days decreases substantially beyond the age of 28 days.

7. It is found that freeze–thaw resistance shows a strong dependence on the natural pozzolan content. In general, the natural pozzolan has a detrimental effect on the resistance of blended Portland cement pastes to freezing and thawing. Nevertheless, successful results are obtained with the blends having a lower level of Portland cement replacement by natural pozzolan. For example, at water to Portland cement plus natural pozzolan ratio of 30%, natural pozzolan blended Portland cement pastes with a composition of 80:201 exhibit good resistance to freezing and thawing.

8. Sulphate attack on blended Portland cement with natural pozzolan is found to be related to the composition and the porosity of hardened blends. Highly concentrated solution of sodium sulfate is quite effective in reducing the strength of blended Portland cement pastes. This is likely due to formation of ettringite, which causes expansion and deterioration of blended Portland cement pastes. Although the natural pozzolan blended Portland cement paste with a composition of 80:201 provides a significant strength retention after 14 cycles of wetting and drying with sodium sulfate solution, its sulfate resistance is considerably lower than that of plain Portland cement pastes with and without superplasticizer. On the other hand, the adverse effect of sodium sulfate on the compressive strength is much more pronounced in the blended cement pastes without superplasticizer. The time to failure of these samples is much less than the superplasticized counterparts. This seems to be true for natural pozzolan replacements of less than 40%. At the 40% substitution, there is no pronounced difference between the blends with and without superplasticizer in terms of the time to failure.

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