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# The long-term durability performance of gypsum–Portland cement–natural pozzolan blends

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**Abstract**

The density, workability, porosity, strength development, and durability of gypsum–Portland cement–natural pozzolan blends are discussed in this paper. The results indicate that the variation in proportions of the mix constituents causes changes in the density. The effects of adding a superplasticizer depend on the amount of added. The higher dosages of a naphthalene-based superplasticizer permit a much greater increase of workability. This improvement in workability can be used to produce mixes with a lower water/binder ratio while maintaining constant workability. The gypsum–Portland cement–natural pozzolan blend gives lower strength than gypsum at age of 1 day. However, its strength continues to increase from 1 day onward and exceeds that of gypsum at 28 days. The effect of porosity on the strength can be described with a quadratic exponent for gypsum–Portland cement–natural pozzolan blends. The porosity tends to decrease significantly with the curing period. The rate of reduction is high for curing periods up to 28 days. However, above this period, the rate is much reduced. The durability assessments are made by examining the behaviour of gypsum–Portland cement–natural pozzolan blends in water and freezing and thawing cycles. The blends with compositions of 41:41:18 (gypsum/Portland cement/natural pozzolan) and 41:41:18S1 (gypsum/Portland cement/natural pozzolan/1% superplasticizer) give excellent property retention after ageing in water at 20 °C for 95 days. An exponential equation $\sigma = \sigma_0[1+(1-e^{-bt})/a]$, where $\sigma_0$ is the initial strength of gypsum–Portland cement–natural pozzolan blend, $\sigma$ is the strength of the gypsum–Portland cement–natural pozzolan blend after exposure to the water for time *t*, *t* is the duration of exposure to the water, and *a* and *b* are the material constants to be determined, is proposed to predict the variation of compressive strength of these blends immersed in water with time. This equation shows excellent agreement with the data on 41:41:18 and 41:41:18S1 in a period of 95 days. These blends perform very well during the freezing and thawing test. They do not show any deterioration up to 20 cycles of freezing and thawing. However, the test results after 30 cycles show that the scaling resistance of 41:41:18S1 is somewhat better than that of 41:41:18.


*Keywords:* Gypsum–Portland cement–natural pozzolan blends; Long-term performance; Ageing in water; Freezing and thawing

## 1. Introduction

The single most important factor likely to influence the strength of the gypsum binder is the water. The presence of atmospheric moisture even at low relative humidity (RH) is sufficient to bring about a dramatic reduction in strength of gypsum binder. For this reason, gypsum products are generally used in the building industry as a surface finish on interior walls. In recent years, considerable amount of work has been undertaken in an attempt to enhance the water resistance of this material. Epoxy impregnation [1,2] made it possible to produce gypsum products with improved water resistance. Epoxy formulation employed in impregnation process was prepared from a diglycidylether of bisphenol A cured using an alkylenediamine curing agent. Epoxy-impregnated gypsum specimens exhibited water absorption values approximately equal to zero after 7 days water immersion at 20 °C. Therefore, these composites can be considered as substantial improvements over the gypsum with regard to hydrophobic character. However, the use of impregnation process in the production of gypsum products is limited by its very high cost. For this reason, the water-resistant gypsum binders have been developed by blending the gypsum with Portland cement and pozzolan. In a study [3], resistance of gypsum-based materials to humid environment was improved by the use of blends containing 75% gypsum, 20% Portland cement, and 5% silica fume. Similar

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results have also been obtained for the gypsum–Portland cement blends containing flay ash [4] or granulated blast furnace slag [5,6] or natural pozzolan [7]. The recent study [7] indicated that the gypsum–Portland cement–natural pozzolan blends with compositions of 41:41:18 and 41:41:18S1 (with 1% superplasticizer) give excellent properties retention after ageing in water at 20 °C for 95 days. One of the significant features that distinguishes gypsum–Portland cement–natural pozzolan blends from gypsum is the curing procedure. To produce an optimum cure, the short period of moisture curing must be followed by a water curing for a period of 28 days [7]. However, longer curing periods may be required for obtaining higher strengths. The setting times of these pastes range from 8 to 11 min. The addition of a naphthalene-based superplasticizer to these pastes increases the setting time from approximately 11 to 35 min [7]. In this study, density, porosity, workability, strength development, and durability characteristics of gypsum–Portland cement–natural pozzolan blends were investigated. The long-term durability performance of these blends was studied by ageing the 28-day-hardened cubes of the blends in water or by subjecting them to alternate freeze–thaw cycles.

## 2. Materials and method

Calcium sulphate hemihydrate (β-hemihydrate) was blended with ordinary Portland cement and natural pozzolan. This blend was ground in a ball mill to fineness similar to Portland cement. The chemical composition of the natural pozzolan is given in Table 1. To effectively counteract the loss of workability and rapid setting caused by high gypsum content, a naphthalene-based superplasticizer was incorporated into the mixtures. The addition of superplasticizer allows the same workability to be obtained with a lower water/binder ratios. The water/binder ratio was 50% by weight except in the mixtures containing superplasticizer where water/binder ratio ranges from 40% to 45%. The consistency of all the pastes was the same, namely plastic. Each mix was designated by the mixing proportions of the materials. For example, 41:41:18 identifies a mix with a composition of 41% gypsum, 41% Portland cement, and 18% natural pozzolan. Similarly, 41:41:18S1 represents the same mix with 1% superplasticizer. The composition of gypsum–Portland cement–natural pozzolan blends was modified by the addition of gypsum and superplasticizer. The effects of variations in binder composition on the physical, mechanical, and durability performance of the composites were investigated. Test results pertaining to gypsum–Portland cement–natural pozzolan blends were compared with the data obtained for gypsum, Portland cement, gypsum–Portland cement, and Portland cement–natural pozzolan systems. The pastes were mixed by hand for 1 min, cast into 4 × 4 × 4-cm moulds, and then compacted by jolting. The samples were stored in a fog room at about 95% RH and a temperature of 20 ± 2 °C for 1 h. At the end of this period, they were demoulded and cured in the fog room conditions (20 ± 2 °C and 95% RH) for 28 days followed by drying in an oven at 40 °C to constant weight. Density was calculated from the mass and volume of the sample. The porosity of samples was determined by the water-replacement method (Archimedes method) and the weight of the dry and wet specimen and its weight in water were measured (apparent porosity). The effect of curing period on the porosity were also determined. The gypsum–Portland cement–natural pozzolan blend that yields the maximum strength was used for strength development test. In the test of ageing in water, the specimens were immersed into water to measure their compressive strength after different periods. Freeze–thaw test was conducted according to TS 699 (methods of testing for natural building stones). A cycle consists of thawing the sample for 4 h in water at 20 °C followed by 4 h freezing at −20 °C.

Table 1
Chemical composition of natural pozzolan (%)

| | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $Na_2O$ | $TiO_2$ | $K_2O$ | $SO_3$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|
| Natural pozzolan | 68.4 | 11.15 | 2.05 | 0.35 | 0.03 | 0.28 | 0.37 | 2.2 | 4.58 | 10.5 |

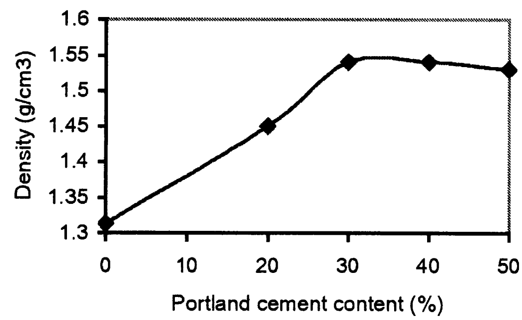


Fig. 1. The effect of Portland cement content on the density of gypsum–Portland cement blends.

## 3. Results and discussion

### 3.1. Density

Fig. 1 shows the density of gypsum–Portland cement blends. A general increase in the density of gypsum–Portland cement blends is observed compared to gypsum. This increase is much more pronounced on the blends with a Portland cement content higher than 20%. On the other hand, the density of gypsum–Portland cement blends with compositions of 50:50, 60:40, and 70:30 is hardly affected by variation of Portland cement content. This result indicates that a relatively uniform density can be obtained for mix proportions in a given size range. The effect of natural

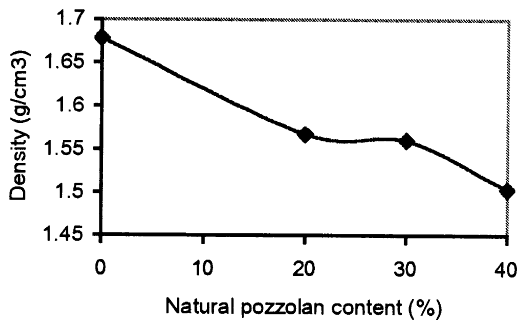


Fig. 2. The effect of natural pozzolan content on the density of Portland cement–natural pozzolan blends.

pozzolan content on the density of Portland cement–natural pozzolan blends is shown in Fig. 2. The different trend is observed for the Portland cement–natural pozzolan blends. The density of these blends decreases with rising natural pozzolan content and becomes nearly constant at natural pozzolan contents of 20% and 30%. The density of gypsum–Portland cement–natural pozzolan blends is illustrated in Fig. 3. There is no change in the density of these blends with gypsum contents of 41% and 44%. However, the increase in the gypsum content from 44% to 50% leads to a decrease in the density. Moreover, it is found that the gypsum contents between 50% and 75% does not provide a reduction in the density. This is to be expected since the amount of natural pozzolan in these gypsum–Portland cement–natural pozzolan blends (50:40:10, 62.5:30:7.5, and 75:20:5) is of less importance.

### 3.2. Workability

Fig. 4. shows the effect of superplasticizer on the water requirement of gypsum–Portland cement–natural pozzolan blends with a composition of 41:41:18. The increased content of gypsum increases the rate of the loss of workability with time of gypsum–Portland cement–natural pozzolan blends. This effect is counteracted by the addition of a naphthalene-based superplasticizer. The higher dosage of superplasticizer permits a greater water reduction. The amount of water reduction varies between 10% and 20%. However, these values may change depending on physical

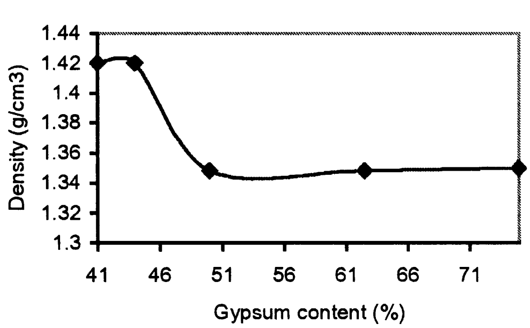


Fig. 3. The effect of gypsum content on the density of gypsum–Portland cement–natural pozzolan blends.

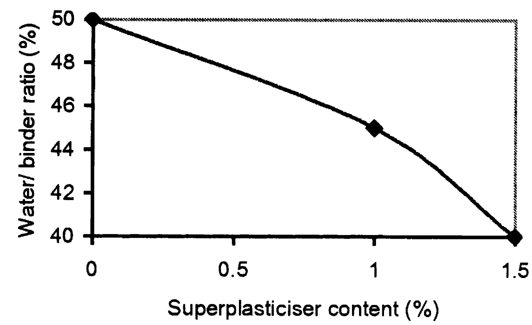


Fig. 4. The effect of superplasticizer on the water requirement of gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18.

properties of each of the ingredients entering into the mixture, and especially on the level of workability, which is to be maintained.

### 3.3. Strength development

It is well known that water curing is essential for the development of the compressive strengths of gypsum–Portland cement–natural pozzolan blends. However, the rates of increase in compressive strengths of these blends up to 28 days are not evident. In order to provide this information, the compressive strengths of water-cured gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18 are determined at the ages of between 1 h and 28 days. For a comparison purpose, tests are also made on gypsum and water-cured Portland cement binders. Gypsum binder is cured in the laboratory conditions at 20 °C and 65% RH due to the potentially adverse effect of water on calcium sulphate-based materials. The changes in gain of strength of binders with age between 0 and 28 days are shown in Fig. 5.

As can be seen, the gypsum has a high rate of strength gain. Therefore, the Portland cement–natural pozzolan blends that contain gypsum have the ability to provide high early strengths at normal temperature. Rapid strength development of these blends occurs during the first hour (about 4 MPa), followed by a period of high strength gain to 1 day, and a slow increase in the rate at ages greater than 1 day. Compressive strengths of gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18 up to 7 days are not higher than that of gypsum. However, after 28 days, its strength exceeds that of gypsum. Whereas gypsum maintains a relatively constant mechanical strength during this period of time. From these results, it can be concluded that a very quick hardening blend can be obtained by adding gypsum to the Portland cement–natural pozzolan blend, but always with a reduction of strength below that of the Portland cement.

### 3.4. Porosity

The porosity of gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18 is adjusted by

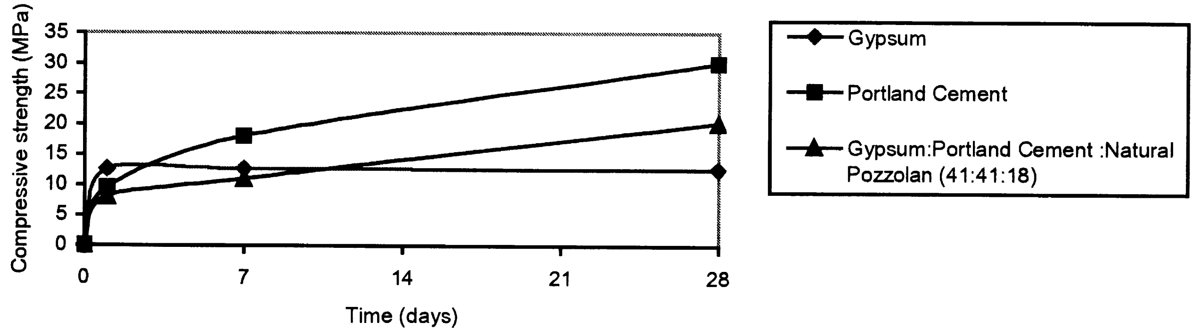


Fig. 5. Strength development curves for binders.

the addition of different amounts of superplasticizer to binder. Porosity changes from 18% to 30% when the ratio of water to binder varies from 40% to 50%.

As can be seen in Fig. 6, the strength of gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18 decreases with increasing porosity. The dependence of the strength of the blend on its porosity is apparent. However, a relation between the gypsum contents of these blends and their porosities can be considered. Since gypsum affects the progress of hydration of Portland cement, the porosity within the hydrated portland cement paste is also affected. The increase in gypsum content from 41% to 44% causes a reduction in porosity. However, the porosity of the blends increases and remains almost constant with further increase in gypsum content [7]. The effect of the porosity on strength can be expressed by a quadratic exponent:

$$\sigma = \sigma_0 e^{-(a.p+b.p^2)} \quad (1)$$

where $p$ is the porosity, $\sigma_0$ is the strength of gypsum–Portland cement–natural pozzolan blend at zero porosity, $\sigma$ is the strength of gypsum–Portland cement–natural pozzolan blend with porosity $p$, and $a$ and $b$ are the material constants.

Eq. (1) shows excellent agreement with the data on gypsum–Portland cement–natural pozzolan blend over a narrow range of porosity only at the lower end (0–30%).

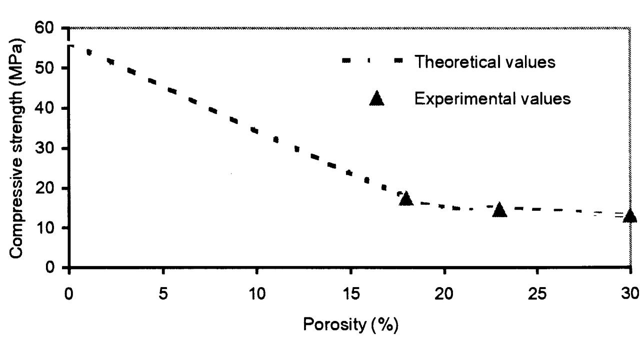


Fig. 6. The effect of porosity on the compressive strength of gypsum–Portland cement–natural pozzolan blend with a composition of 41:41:18, $\sigma_0 = 56.26$, $a = 8.67$, $b = -12.67$, correlation coefficient ($R$) = .99.

The values of parameters $\sigma_0$, $a$, and $b$ are given in Fig. 6 also with the correlation coefficient. The nonlinear least square method was used to calculate the material parameters in the proposed equation. The value of $\sigma_0$ obtained from Eq. (1) is 56.26 MPa. However, Eq. (1) fails to provide any specific information regarding the porosity value at which the strength of the blend becomes zero. The effect of curing period on porosity of the gypsum–Portland cement–natural pozzolan blends is also assessed. Porosity changes were determined at intervals from 7 to 95 days of soaking in water at a temperature of 20 °C. Fig. 7 shows the influence of curing period on the porosity of gypsum–Portland cement–natural pozzolan blends with a composition of 41:41:18 and 41:41:18S1. It can be seen that the porosity of the blends decreases with an increase in curing period. The reduction in porosity may be due to filling of pore space with hydration products. The high rate of decrease in porosity up to 28 days of hydration is apparent. However, the rate of decrease in porosity beyond the 28 days of hydration is much reduced.

### 3.5. Effect of ageing in water

The main deterioration agent to be considered for gypsum used in buildings is water. Even a small amount of water produce severe strength reduction. It can be seen in Fig. 8 that the compressive strengths of gypsum and gypsum–Portland cement–natural pozzolan blend with a composition of 75:20:5 measured after immersion in water

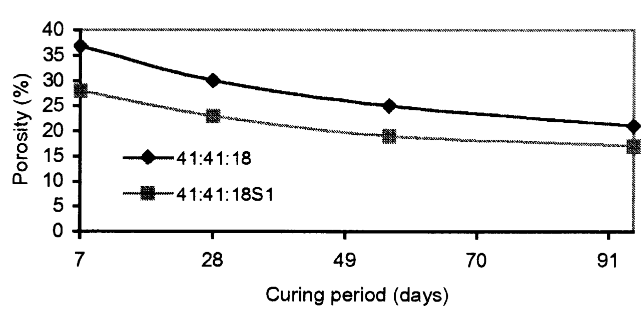


Fig. 7. The effect of curing period on the porosity of gypsum–Portland cement–natural pozzolan blends with and without superplasticizer.

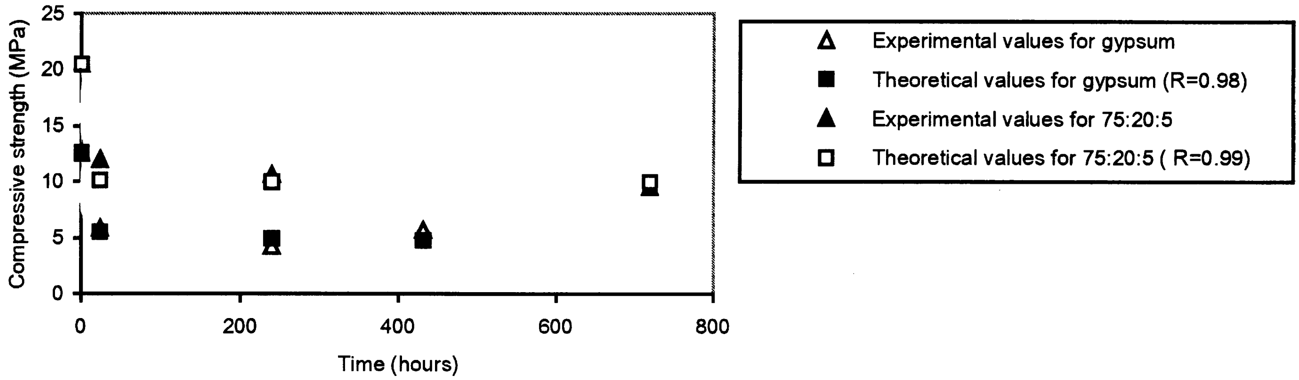


Fig. 8. The effect of ageing in water on the compressive strengths of gypsum and gypsum–Portland cement–natural pozzolan blend with a composition of 75:20:5.

decrease sharply after different periods of ageing time. The strength variations of these binders in relation to the duration of exposure to water can be represented as

$$\sigma = \sigma_0/(1 + t^a) \quad (2)$$

where $\sigma_0$ is the initial strength of binder (MPa), $t$ is the duration of exposure to the water (h), $a$ is a constant depending on the type of binder, and $\sigma$ is the strength of binder after exposure to the water for time $t$ (MPa).

This model may be perfectly applicable to gypsum and gypsum–Portland cement–natural pozzolan blend with a composition of 75:20:5. However, it may be noted that Eq. (2) is applicable at $t \leq 720$ h. The value of a constant is 0.08 for gypsum and 0.01 for gypsum–Portland cement–natural pozzolan blend with a gypsum content of 75%.

The long-term durability properties of gypsum–Portland cement–natural pozzolan blends are influenced by the amount of gypsum in the mixture. The high proportioning of gypsum in the blend causes a rise in the sensitivity to water. Whereas, the 41:41:18 and 41:41:18S1 systems clearly exhibiting substantially less gypsum content than the other system demonstrated above are relatively unaffected by moist environment. The strengths of these blends exhibit a slight increase (probably due to cure) during ageing in water. The attempts to find a mathematical relationship between strength and time of exposure are based on simple curve-fitting procedures. It is proposed that the curves approach asymptotically a minimum strength increase rate so that the strength can be expressed by the relation

$$\sigma = \sigma_0[1 + (1 - e^{-b,t})/a] \quad (3)$$

where $\sigma_0$ is the initial strength of gypsum–Portland cement–natural pozzolan blend (MPa), $t$ is the duration of exposure to the water (h), $\sigma$ is the strength of gypsum–Portland cement–natural pozzolan blend after exposure to the water for time $t$ (MPa), and $a$ and $b$ are the material constants.

The values of $a$ and $b$ are found to be 1.68 and 0.02 for 41:41:18 and 1.79 and 0.01 for 41:41:18S1. Predicted strengths are generally about 2–7% lower than test values. Eq. (3) can be used successfully to describe the long-term durability performance of gypsum–Portland cement–natural pozzolan blends but it is not applicable to gypsum–Portland cement–natural pozzolan blends with a high gypsum content. On the other hand, the proposed equation is valid for 95 days and may give erroneous predictions for periods of time longer than 95 days.

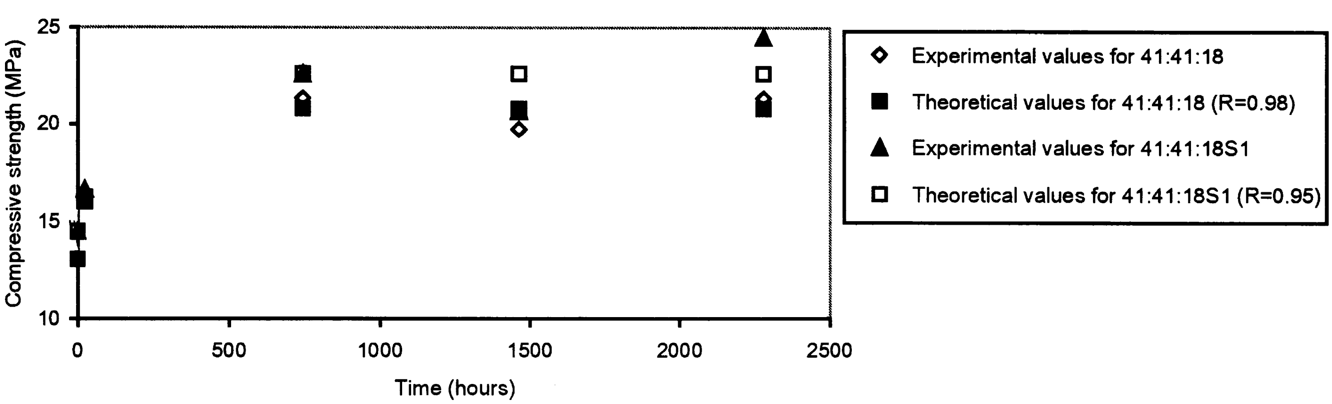


Fig. 9. Effect of ageing in water on the compressive strengths of gypsum–Portland cement–natural pozzolan blends with and without superplasticizer.

The long-term strength of gypsum–Portland cement–natural pozzolan blends under the action of water is dependent on the mix composition. The change in the mix composition makes the development of a common theory and method for calculating the long-term strength difficult. An extremely important conclusion from this study is that the long-term strength of these blends is characterised by two equations. Correlation analysis of the test results given in Figs. 8 and 9 shows that the correlation coefficients ($R$) range from .95 to .99. These values are close to 1. Therefore, the proposed equations are a reliable and practically convenient method of evaluating the long-term durability performance of gypsum–Portland cement–natural pozzolan blends aged in water up over the periods of time considered in this study.

### 3.6. Freeze–thaw resistance

Considerable information concerning the cause of fracture as well as the damage mechanisms occurring during the freeze–thaw tests can be obtained from a visual examination of the samples. Therefore, the samples were examined after about every five freeze–thaw cycles. The scaled-off particles and internal cracking clearly visible on the surface were noted. The test was terminated after 30 freeze–thaw cycles. The effect of freezing and thawing was also assessed from measurements of the loss of compressive strength. The reduction in the strength after a number of cycles of freezing and thawing shows the deterioration of the material. The results of these tests are given in Tables 2 and 3. These data are presented only for the purpose of giving a general picture of the direction and magnitude of the property changes. The values may vary depending on the test method used, the test conditions, and the specific composition of the material.

As would be expected, the strengths of gypsum and gypsum–Portland cement blend decrease very rapidly during cyclic. The extent of damage varies from internal cracking to severe disintegration of the matrix as the freeze–thaw cycle progress. The decreased strength can be caused by a combination of factors, an increase in the solubility of gypsum during thawing in water and also an increase in the number of microfissures in the matrix during freezing in air. This later phenomenon possibly makes a major contribution to the decreased strength of the gypsum–Portland cement blends.

Table 2
Scaling resistance of binders

| Gypsum/Portland cement/natural pozzolan | Number of cycles | | | | | |
|---|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 25 | 30 |
| 100:00:00 | – | * | 0 | ϕ | ϕ | ϕ |
| 50:50:00 | + | + | – | * | 0 | ϕ |
| 00:70:30 | + | + | + | + | + | + |
| 50:40:10 | + | + | + | – | * | 0 |
| 41:41:18 | + | + | + | + | – | * |
| 41:41:18S1 | + | + | + | + | + | – |

+ Sound; – internal cracking; * internal cracking and scaling; 0 scaling; ϕ crumbling.

Table 3
Relative strengths ($\sigma_a/\sigma_b$) of the binders

| Gypsum/Portland cement/natural pozzolan | Number of cycles | | | | | |
|---|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 25 | 30 |
| 100:00:00 | 0.10 | | | | | |
| 50:50:00 | | | 0.19 | | | |
| 00:70:30 | | | | | | 0.92 |
| 50:40:10 | | | | 0.51 | | |
| 41:41:18 | | | | | 0.74 | |
| 41:41:18S1 | | | | | | 0.78 |

$\sigma_a/\sigma_b$ express the ratio of strengths after and before freeze and thaw cycles.

Portland cement–natural pozzolan blend with a composition of 70:30 perform very well during the scaling test. This blend does not show any deterioration after 30 cycles of freezing and thawing. However, strength test done after exposure indicate that there is a 8% reduction in compressive strength. On the other hand, the scaling resistance of gypsum–Portland cement–natural pozzolan blend with superplasticizer (41:41:18S1) is very close to that of Portland cement–natural pozzolan blend. This blend retains in excess of 75% of its compressive strength at the end of 30 cycles. Moreover, it offers much better durability performance than the 41:41:18 system. The increase in the performance is found to be due to a reduction in water/binder ratio with superplasticizer addition. The 41:41:18 system shows signs of internal cracking at 25 cycles. At 20 cycles, significant deterioration is observed in the blend with a composition of 50:40:10. This is clear from the test results given in Table 3. From these considerations, it can be concluded that improved resistance to freezing and thawing is obtained by reducing the amount of gypsum or the water/binder ratio in the gypsum–Portland cement–natural pozzolan blends.

## 4. Conclusions

The findings from this investigation are summarised as follows:

1. The density of gypsum–Portland cement–natural pozzolan blends ranges from about 1.34 to 1.42 g/cm$^3$. Density variations are generally caused by the changes in mix composition. Lower densities can be obtained by increasing the gypsum or natural pozzolan content in the mix.
2. Workability of the gypsum–Portland cement–natural pozzolan pastes can be adjusted by a naphthalene-based superplasticizer. Adding 1% to 1.5% superplasticizer by weight of binder dramatically reduces the water demand when compared to paste without superplasticizer.
3. Experimental evidence appears to indicate that the apparent porosity of the gypsum–Portland cement and natural pozzolan blends can be predicted to a good approx-

imation using quadratic exponent function. There is a strong trend for porosity values to decrease with increasing cure time.

4. It is possible to produce gypsum–Portland cement–natural pozzolan blends to have strengths exceeding that of gypsum at ages of 28 days.

5. Adding natural pozzolan is an effective way of improving the resistance of gypsum–Portland cement blends to water. The gypsum content and the water/binder ratio play a very important role in determining the response of the gypsum–Portland cement–natural pozzolan blends to water and freezing and thawing. The 41:41:18 and 41:41:18S1 composites exposed to water retain their initial appearance and show no indications of damage. They offer modest compressive strength improvement and much better durability performance than the gypsum. The strength variations of these blends under the action of water can be predicted accurately by using an exponential function. However, this equation is not applicable to gypsum–Portland cement–natural pozzolan blends with a high gypsum content. Freeze–thaw cycling is more damaging than continuous exposure to water. But the 41:41:18S1 system maintains a relatively high mechanical strength up to 30 cycles.

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