Some Engineering Properties of Concrete Containing Natural Pozzolana and Silica Fume

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Abstract
Ternary blended cements are often used in cement manufacture using industrial waste and natural resources to produce a low cost and an environment friendly cement. Ternary blended cements also have the advantage of combining the synergic effects of their ingredients, which compensate for their mutual weaknesses. In this paper, the effect of combining a very active mineral addition (silica fume) SF on the mechanical properties and durability of cements containing natural pozzolana NP is analyzed. The optimal couples "natural pozzolana/silica fume" proposal is based on their mechanical properties and durability performance. The results confirm that the use of ternary cements contributes to the improvement of strength at an early stage. Better resistance to sulphate and acid attacks and less chloride ions penetration also enhanced durability.

Keywords: compressive strength; durability; natural pozzolana; silica fume; ternary blended cement

1. Introduction
Cement is responsible for 7% of the world's total emission of CO₂, which is a major greenhouse gas, implicated in global warming. The addition of industrial waste and natural resources such as slag, fly ash, silica fume or natural pozzolana to cement during manufacture contributes to a decrease in energy consumption and the amount of CO₂ released into the air. Hence, low cost environment friendly cement is obtained. Also, when used as a concrete admixture, the amorphous silica present in these additives combines with the calcium hydroxide liberated during the hydration of cement in concrete, to form additional cementitious compound, namely calcium silicate hydrate (CSH). The resultant binder matrix is more chemically resistant, by virtue of its denser microscopic pore structure.

A larger number of studies have shown that different additions, when used as partial cement replacement materials in mortar and concrete have many advantages but also some disadvantages. There is a growing belief that composite ternary and quaternary-blended cements can be optimized to create a synergistic effect, which allows component ingredients to compensate for their mutual shortcomings (Nehdi 2001). In recent years, researchers (Isaia 1999; Khan et al. 2000; Bai et al. 2000 and 2003; Bleszynsky et al. 2002; Shehata and Thomas 2002; Li and Ding 2003; Menendez et al. 2003; Khatib and Hibbert 2005 and Corrasco et al. 2005) have reported that the use of ternary cements, present more advantages compared to both binary cements or OPC.

It should be possible, by the systematic adjustment of the proportions, to produce ternary blended cement (OPC–NP–SF) which utilizes the desirable characteristics of one addition while compensating for the undesirable characteristics of the other. For example, SF increases the low early strength caused by the inclusion of NP and the NP decreases the high water demand of SF. On the other hand, the best combination of these mineral additions, can lead to excellent durability.

The objective of this paper is to present the optimization of the compressive strength in ternary blended cement containing natural pozzolana and silica fume. The durability performance of mortar and concrete containing binary and ternary blended cement (OPC-NP-SF) is also presented.

2. Experimentation

2.1 Materials used
A local ordinary Portland cement with a fineness of 350 m²/kg was used for all the mixes. The natural pozzolana used in this work was from the Beni-Saf quarry in the west of Algeria. The natural pozzolana was ground in a laboratory mill to a specific surface area of 420 m²/kg. The chemical composition of the cement and natural pozzolana are given in Table 1. The
mineralogical composition of the natural pozzolana was determined by X-ray diffraction and is presented in Fig.1. Fig.2. shows the Scanning Electron Microscopic (SEM) of this natural pozzolana. The silica fume used in this study is commercial silica fume called Sikacrete HD of Sika. The sand used in mortar mixes was a standard sand of 2 mm maximum aggregate size. A concrete mix was used only for chloride penetration and sorption tests. Crushed limestone coarse aggregates with a nominal size of 12 mm, and a specific gravity of 2.65, and natural sand with a specific gravity of 2.59 were used for the concrete samples.

Table 1. Chemical Composition (%) of the Cement and Natural Pozzolana

| Element          | Cement | Pozzolana |
|------------------|--------|-----------|
| SiO₂             | 23.7   | 46.9      |
| Al₂O₃            | 6.58   | 16.6      |
| Fe₂O₃            | 4.00   | 9.37      |
| CaO              | 64.9   | 9.38      |
| MgO              | 0.32   | 2.84      |
| CaO(free)        | 0.33   | /         |
| SO₃              | /      | 0.36      |
| IR*              | /      | /         |
| LOI**            | /      | 5.79      |

*) Insoluble residue
**) Loss of ignition

The water to binder (W/B) ratio was kept constant at 0.5. The concrete mix had a total binder content of 400 kg/m³, fine aggregate content of 720 kg/m³ and coarse aggregate content of 1130 kg/m³, while the W/B ratios of 0.4 and 0.6 were used. For the W/B ratio of 0.4, the superplasticizer was added with a dosage of 1 liter per 100 kg of cement to improve workability. Table 2. shows the combination of blended cements studied in the determination of strength of mortars. The durability was conducted only on control cement (OPC) and the cement containing 30% of natural pozzolana (30NP), 10% of silica fume (10SF) and 20% of natural pozzolana with 10% silica fume (20NP10SF).

2.2 Mixes used

The proportions of mortar mix were; one part binder to three parts sand. The binder consisted of cement and one or two additions. For the ternary blended cement (OPC-NP-SF) four total cement replacement levels (NP+SF) of 10%, 20%, 30% and 40% by mass were employed in addition to the control (OPC only) mixtures. The range of replacement levels of NP and SF were from 0% to 40% and from 0% to 10%, respectively. All replacements were made by mass. The water to binder (W/B) ratio was kept constant at 0.5. The concrete mix had a total binder content of 400 kg/m³, fine aggregate content of 720 kg/m³ and coarse aggregate content of 1130 kg/m³, while the W/B ratios of 0.4 and 0.6 were used. For the W/B ratio of 0.4, the superplasticizer was added with a dosage of 1 liter per 100 kg of cement to improve workability. Table 2. shows the combination of blended cements studied in the determination of strength of mortars. The durability was conducted only on control cement (OPC) and the cement containing 30% of natural pozzolana (30NP), 10% of silica fume (10SF) and 20% of natural pozzolana with 10% silica fume (20NP10SF).

2.3 Specimen preparation, curing and casting

The strength of mortars was determined in accordance with the European Standard EN 196-1. The mortar was placed in 40x40x160 mm prismatic steel moulds. After casting, specimens were left covered with a plastic sheet. After removal from the moulds, following a period of 24 hours, mortar specimens were immersed in water saturated with lime at 20°C ± 2 until the time of testing. Compression and three point bending tests were conducted at 2, 7, 28 and 90 days of age. The results reported are the average of six compression tests.

The sorptivity was measured on 70 mm concrete cubic specimens which were oven dried at 105 °C for 24 hs. After mass stabilization, the specimens were coated with epoxy resin on their lateral surfaces only, in order to ensure uniaxial water absorption. A schematic diagram of the water absorption test is given in Fig.3. The masses of the specimens were measured after 1, 4, 9, 16, 36, 49 and 64 minutes of absorption. The sorptivity coefficient (S) was obtained by using the following expression:

\[
\frac{Q}{A} = S \times \sqrt{t}
\]

Where Q is the amount of water adsorbed; A is the cross section of specimen that was in contact with water; t is time; S is the sorptivity coefficient of the specimen (cm/s\(^{1/2}\)).

The rapid chloride permeability test was conducted
in accordance with ASTM C-1202. Two specimens of 100 mm in diameter and 50 mm in thickness conditioned according to the standards were subjected to 60-volt potential for 6 hours. The total charge passed through the concrete specimens was determined and used to evaluate the chloride permeability of each concrete mixture.

For the sulfate attack tests, the mortar specimens were cured in water at $23 \pm 2^\circ C$ for 30 days. After that, the mortar specimens were immersed in 5% sodium sulfate ($Na_2SO_4$) or 5% magnesium sulfate ($MgSO_4$) which was renewed every 30 days. The sulfate attack was evaluated through the measurement of the expansion in accordance with ASTM C-1012 on prismatic specimens measuring $25 \times 25 \times 285$ mm.

The relative acid attack was determined in accordance with ASTM C-267. The mortars specimens were cured in water at $23 \pm 2^\circ C$ for 30 days before being subjected to acid attack. Three specimen of each mortar mix were immersed in 3% sulfuric acid ($H_2SO_4$) or 1% hydrochloric acid ($HCl$). The attacked portions of the mortar specimens were cleaned with de-ionised water and the acid attack then was evaluated through measurement of the weight loss of the specimens and determined as follows:

$$\text{Weight loss(\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

Where $W_1$ is the weight of the specimen before immersion and $W_2$ is the weight of the cleaned specimen after immersion. The solution was renewed every 15 days and the weight loss of the specimens measured.

3. Results and Discussion
3.1 Development of compressive strength

Based on the experimentally obtained results, models were developed at each age. These models are based on the quadratic response surface, where the two experimental variables (the proportion of NP and SF used as partial replacement of cement) have been used. The models are as follows:

$$f_c(t) = a_0 + a_1x_1 + a_2x_2 + a_11x_1^2 + a_22x_2^2 + a_{12}x_1x_2 \quad (3)$$

Where $f_c(t)$ is the compressive strength at t days, $x_1$ is the percentage of NP, $x_2$ is the percentage of SF and $a_0$, $a_1$, $a_2$, $a_{11}$, $a_{22}$ and $a_{12}$ are the coefficients of

| Designation | OPC | Natural Pozzolana | Silica fume | 2 days | 7 days | 28 days | 90 days |
|-------------|-----|-------------------|-------------|--------|--------|---------|---------|
| OPC         | 100 | 0.00              | 0.00        | 17.6   | 15.7   | 14.2    | 13.8    |
| 2.5SF       | 97.5| 0.00              | 0.25        | 15.8   | 15.7   | 14.2    | 13.8    |
| 5.0SF       | 95.0| 0.00              | 0.50        | 16.5   | 14.3   | 13.8    | 13.5    |
| 7.5SF       | 92.5| 0.00              | 0.75        | 15.8   | 15.7   | 14.2    | 13.8    |
| 10SF        | 90.0| 0.00              | 0.00        | 15.8   | 15.7   | 14.2    | 13.8    |
| 10NP        | 90.0| 10.0              | 0.00        | 15.8   | 15.7   | 14.2    | 13.8    |
| 7.5NP2.5SF  | 90.0| 0.75              | 0.25        | 16.5   | 14.3   | 13.8    | 13.5    |
| 5.0NP5.0SF  | 90.0| 0.50              | 0.50        | 16.5   | 14.3   | 13.8    | 13.5    |
| 2.5NP7.5SF  | 90.0| 0.25              | 0.75        | 16.5   | 14.3   | 13.8    | 13.5    |
| 20NP        | 80.0| 0.00              | 0.00        | 16.5   | 14.3   | 13.8    | 13.5    |
| 17.5NP2.5SF | 80.0| 17.5              | 0.25        | 16.5   | 14.3   | 13.8    | 13.5    |
| 15.0NP5.0SF | 80.0| 15.0              | 0.50        | 16.5   | 14.3   | 13.8    | 13.5    |
| 12.5NP7.5SF | 80.0| 12.5              | 0.75        | 16.5   | 14.3   | 13.8    | 13.5    |
| 10NP10SF    | 80.0| 10.0              | 10.0        | 16.5   | 14.3   | 13.8    | 13.5    |
| 30NP        | 70.0| 30.0              | 0.00        | 16.5   | 14.3   | 13.8    | 13.5    |
| 27.5NP2.5SF | 70.0| 27.5              | 0.25        | 16.5   | 14.3   | 13.8    | 13.5    |
| 25.0NP5.0SF | 70.0| 25.5              | 0.50        | 16.5   | 14.3   | 13.8    | 13.5    |
| 22.5NP7.5SF | 70.0| 22.5              | 0.75        | 16.5   | 14.3   | 13.8    | 13.5    |
| 20NP10SF    | 70.0| 20.0              | 10.0        | 16.5   | 14.3   | 13.8    | 13.5    |
| 40NP        | 60.0| 40.0              | 0.00        | 16.5   | 14.3   | 13.8    | 13.5    |
| 37.5NP2.5SF | 60.0| 37.5              | 0.25        | 16.5   | 14.3   | 13.8    | 13.5    |
| 35.0NP5.0SF | 60.0| 35.5              | 0.50        | 16.5   | 14.3   | 13.8    | 13.5    |
| 32.5NP7.5SF | 60.0| 32.5              | 0.75        | 16.5   | 14.3   | 13.8    | 13.5    |
| 30NP10SF    | 60.0| 30.0              | 10.0        | 16.5   | 14.3   | 13.8    | 13.5    |
the model. The coefficients for the equation at 2, 7, 28 and 90 days are shown in Table 3., where $R$ is the coefficient of correlation.

Fig.4. illustrates the isoresponse curves of compressive strength showing the interaction effect of NP and SF for the domain studied in the ternary system. It can be seen that the compressive strength decreased with the increase in NP content at early ages. After 28 days, the addition of SF increased the strength for all levels of NP replacements.

In summary, the point of maximum strength is less than 10% of the SF replacement level at the early ages. But at 90 days, this point moves toward the 20% level of NP replacement and 10% of SF content.

### 3.2 Sorption

Fig.5. shows the influence of the W/B ratio on the sorptivity of concretes containing different amounts of addition at the age of 28 and 90 days. As is evident, the diminution of the W/B ratio reduces the sorptivity.

At 90 days of age, with regard to the plain concrete, the sorptivity coefficient of concrete containing 30% of natural pozzolana and 10% of silica fume diminished by 32% and 58%, respectively, for W/B of 0.6. While, 20%NP+10%SF mixture diminished the sorptivity coefficient by 38% and 43% for a W/B ratio of 0.4 and 0.6, respectively. In this case, pores in the bulk paste or in the interfaces between aggregates and cement paste is filled by these mineral admixtures, hence, the capillary pores are reduced by the formation of secondary CSH gel due to the pozzolanic reaction, which results in a reduction of the capillary sorption of concrete.

![Fig.4. Compressive Strength (in MPa) Isoresponse Curves for the Ternary System (OPC-NP-SF) at Different Ages](image)

![Table 3. Coefficients Model for the Compressive Strength Age](image)

| Age  | Coefficients | a₀   | a₁   | a₂   | a₁₁  | a₂₂  | a₁₂  |
|------|--------------|------|------|------|------|------|------|
| 2    | 17.69        | -2.78| -6.16| 0.1  | 1.8  | 0.4  | 0.97 |
| 7    | 39.94        | -0.93| -0.62| 0.4  | 4.1  | -2.5 | 0.93 |
| 28   | 49.72        | 2.25 | 3.67 | -1.1 | 0.5  | -1.8 | 0.85 |
| 90   | 49.32        | 2.09 | 13.43| -0.7 | -8.8 | -0.7 | 0.78 |

![Fig.5. Sorptivity Coefficients of Concrete at 28 and 90 Days](image)
3.3 Rapid chloride ion permeability

The rapid chloride ion permeability of concrete, measured in terms of the electric charge passed through the specimens in coulombs, is shown in Fig. 6. It can be seen that, the diminution of the W/B ratio from 0.6 to 0.4 reduces significantly the rapid chloride ion permeability. Also, the rapid chloride ion permeability of concrete containing pozzolanic materials was lower than the permeability of plain concrete. This may be related to the refined pore structure of these concretes and their reduced electrical conductivity (Talbot et al. 1995).

The (20% NP+10% SF) mixture yielded the lowest chloride permeability for the high W/B ratio of 0.6. However, it seems that the ternary blend concrete exhibits better chloride ion permeability performance than plain concrete and concrete with single addition replacements. This trend in results has also been reported by other researchers (Bleszynsky et al. 2002; Bai et al. 2003).

3.4 Sulfate attack

Fig. 7. shows the expansion of mortars exposed to 5% Na_2SO_4 (NS) and 5% MgSO_4 (MS). Higher expansion in specimens placed in an (NS) environment compared to those placed in an (MS) environment are observed. Also, higher expansion was observed for OPC mortar prisms.

After 32 weeks of exposure to (NS) or (MS) solution, the addition of 10% silica fume produces an important reduction in expansion of 83% and 63%, respectively, compared to the corresponding expansion of OPC mortar, and the addition of 30% of natural pozzolana produces a reduction of 54% in the (NS) solution and 44% in the (MS) solution. The higher expansion observed in plain mortar may be attributed to the formation of secondary ettringite, which is characterized by expansion and cracking. In mortar containing pozzolanic materials, pozzolanic reaction consumes part of the Ca(OH)₂ produced by the hydration of cement. Hence, the quantity of gypsum formed in the reaction between sulfates and Ca(OH)₂, which is responsible for the formation of secondary ettringite, will be smaller in pozzolanic cement than in plain cements. Further, the pozzolanic reaction produces a secondary CSH gel that also results in the densification of the hardened cement paste, since it is deposited in the pores and enhances the paste-aggregate interface. These effects reduce significantly the diffusion of SO_4²⁻ ions and explain the lower expansion observed in pozzolanic cements as compared to plain cement. However, the silica fume improves significantly the sulfate resistance of natural pozzolana cements.

3.5 Acid attack

Fig. 8. shows the test results of weight change versus time for mortar specimens exposed to 1% HCl and 3% H_2SO_4 solutions for 180 days.

After 180 days exposure to 3% H_2SO_4 solutions, the total loss in weight of OPC mortar was 75%. When the replacement level of cement is 30% of natural pozzolana, there is no effectiveness in reducing the total loss in weight of OPC; and for 10% of silica fume the loss in weight is lower than the corresponding OPC mortar by 40%. However, the 20%NP+10%SF mixture reduces the total loss in weight of both OPC and cement with 30% of natural pozzolana by 20%.

After 180 days exposure to 1% HCl solutions, the total loss in weight of OPC mortar was about 35%. When the replacement level of cement is
either 10% silica fume or 30% natural pozzolana, the loss in weight is lower than the corresponding OPC mortar by 26% and 16%, respectively. However, the 20%NP+10%SF mixture reduces the total loss in weight of OPC by 26.5%.

Therefore, it can be concluded from the results that silica fume can be used to improve both hydrochloric acid (HCl) resistance and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) resistances of the OPC and the cement containing natural pozzolana.

### 4. Conclusions

This study was conducted to assess the effect of the interaction between Natural pozzolana and silica fume on the properties of mortar and concrete. The following conclusions can be drawn from the present study:

- The point of maximum strengths is around 7.5% of SF and low NP replacement level at the early ages. After 28 days, this point moves toward the high level of NP replacement and low SF content.
- The partial replacement of cement with additions reduces the sorption of concrete. Also, the sorption decreases with the duration of curing.
- Chloride ion permeability of concrete is decreased considerably with the lowering of W/B ratio. The ternary blend concrete exhibits better chloride ion permeability performance than plain concrete and concrete with single addition replacements.
- Lower expansion is observed with natural pozzolana cements under sulfate attack and the addition of silica fume reduces further the expansion of natural pozzolana cement.
- It can be concluded from the results that NP can only be used to improve hydrochloric acid (HCl) resistance of the OPC mortar, while SF can be used to improve both the hydrochloric acid (HCl) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) resistances of the OPC mortar and the mortar containing NP.

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