Study on the optimum nano-natural pozzolan content in the concrete binder

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Abstract. The objective of this study is to investigate the optimum nano-natural pozzolan (NNP) content in the NNP-based binder concrete. NNP was obtained by grinding a local volcanic scoria for six hours. Twenty-four concrete mixes with four w/b ratios (0.4, 0.5, 0.6 and 0.7) and six-replacement levels of NNP (0%, 1%, 2%, 3%, 4%, and 5%) have been produced. The investigated concrete properties were the compressive strength, the water penetration depth, the concrete porosity and the chloride ion permeability. The efficiency factor (k) of NNP in terms of compressive strength was calculated using the Bolomey equation. Durability indicators have been used to globally evaluate the behavior of NNP-based binder concrete versus control concrete. The results revealed that the efficiency factor (k) decreased to some extent when the NNP content was more than 4%. The calculated durability indicators showed that NNP contents of 3-4% had approximately the highest indicators values. These indicators would be helpful for concrete mix designers. Some correlations between the investigated properties were derived from the analyzed data. The modification of the microstructure of NNP-based cement paste has been observed, as well.

1. Introduction

Although there have been many studies on the use of natural pozzolan in literature, there are still limited works on using volcanic scoria (VS) either at micro or nano-scale. The author think that no or very little number of studies on the use of nano-VS as cement replacement can be found in the literature. Volcanic scoria cones exist in large numbers around the world, like in Syria, Turkey, Iran and others [1-10]. One may find more details on the use of VS as a substitute for Portland cement, in the chapter recently published by the author [11].

One of the main shortcomings associated with using volcanic scoria at a micro-scale is the reduction of strength at early ages. This reduction can be mainly due to the slowness of the pozzolanic reaction between the glassy phase in volcanic scoria and the CH released during cement hydration [12]. However, use of nano-particles could be a solution to overcome this disadvantage. Several types of nano-additives such as nano-SiO₂, nano-clay, nano-Al₂O₃, nano-Fe₂O₃ and carbon nanotubes have recently been used in order to enhance the compressive strength and the concrete durability [13-17]. This enhancement was attributed to the very high fineness and pozzolanic reactivity of the nano-particles [18]. In addition, acting as nucleus, nanoparticles can produce concrete of more compacted microstructure despite of small...
replacement level [14]. However, it is important to mention that nanoparticles have a tendency to agglomerate when using at high dosage (i.e. more 3 wt %) in the mixes [13, 14, 19]. The aggregation forms weak zones and consequently prevents the formation of homogenous hydrate microstructure. Therefore, the optimum dosage of nano-VS should be examined before its exploitation in the field of concrete industry.

A lot of published studies on the use of nano-additives has just investigated the properties of concrete after 7 and 28 days curing [20, 21]. However, properties of concretes containing nano-particles, such as compressive strength, water permeability, chloride penetrability and porosity have not widely been investigated at later ages (i.e. 90 and 180 days). Therefore, the present paper attempts to highlight some different properties of concrete made with binder containing NNP after five curing ages (2, 7, 28, 90 and 180 days). The investigated properties are:

(i) One mechanical property; i.e. the compressive strength (CS).

(ii) Three durability-related properties; i.e. water permeability (WP), porosity (PO) and chloride ion penetrability (CIP).

Six replacement levels of NNP (0%, 1%, 2%, 3%, 4%, and 5%) and four different w/b ratios (0.4, 0.5, 0.6 and 0.7) have been used. The efficiency factor (k) was evaluated considering the compressive strength. On the other hand, the durability indicators were evaluated using the compressive strength and the concrete properties related to its permeability. In addition, some relationships between different properties of concrete have been extracted, and some prediction correlations have been derived.

The outcome of this work, which can be considered the first of its kind in our country, may be useful for the designers of NNP-containing concrete mixes. This optimum content fulfils the best performance of the concrete in terms of compressive strength and durability.

2. Efficiency factor and durability indicators of volcanic scoria

The concept of the efficiency factor, k, was first proposed by Smith [22] as the basis of his rational proportioning approach for fly ash concrete. Originally, the k factor was defined as the mass of a supplementary cementing material that makes the same contribution to the strength of concrete as a unit mass of ordinary Portland cement (OPC). According to Thomas & Matthews’ study [23], 1 kg of fly ash makes the same contribution to the 28-day strength of concrete as 0.32 kg of OPC; i.e. k=0.32. Babu & Rao [24] have suggested that k of fly ash can be suggested as 0.25 for replacements up to 25%. However, studies on silica fume have revealed that k values range from 2 to 4 [25].

Pozzolan can be considered more efficient than OPC when k>1. OPC saving is possible in such a case. On the other hand, pozzolan can be considered less efficient than OPC when k<1. More pozzolan content should be used to achieve the required target strength in such a case. European standard for concrete (EN 206-1:2000) has reported only the efficiency factor, k, for fly ash and silica fume. The maximum percentage of fly ash to be incorporated when the k value is concerned is fly ash/cement ≤ 0.33 by mass. DIN 1045 recommends k value of 0.3 for replacement levels between 10% and 25%. British Code (BC) refers to k value of 0.4 for replacements up to 0.25%. No k value was given for natural pozzolan either at micro- or nano-scale in the European Standard, and little data are available on its efficiency factor at micro-scale in the literature.

Tchamdjou et al. [26] have studied this term in order to evaluate four volcanic scoria samples of different colors (black, dark red, red and yellow). 28-days compressive strength, sorptivity and carbonation were investigated in their study. Their result showed that 15% dark red VS- and 15% red VS-based mortars had a similar durability index versus control mortar when strength, sorptivity and carbonation depth were taken into account. In addition, the mortar with 15% dark red VS was better than control mortar when only strength and carbonation depth were taken into account.
3. Materials and methods

A local natural pozzolan (nano-VS) quarried from the south of Syria was used in the experimental part. The particle size distribution of nano-VS as compared with VS-as received is illustrated in figure 1. SEM micrographs of nano-VS associated with EDX analysis and AFM micrograph of the nano-VS obtained after 6 hours-grinding are shown in figures 2 and 3, respectively. The prolonged grinding may form a highly reactive material on the surface of the mineral particles.

![Figure 1. Particle size distribution of volcanic scoria at different scales.](image1.png)

![Figure 2. SEM (a), EDX (b) and AFM (c) micrographs of nano-VS.](image2.png)
NNP (Nano-VS) has been added at six replacement levels, i.e. (0%, 1%, 2%, 3%, 4% and 5%). Four w/b ratios, i.e. 0.4, 0.5, 0.6 and 0.7 have been adopted in the current work. The method of mixing suggested by Jo et al. [20] was followed, with some minor modification, in the current study. Four properties have been particularly investigated; i.e. compressive strength (CS), water permeability (WP), porosity (PO) and chloride ion penetrability (CIP). These properties have been carried out after five different curing ages i.e. (2, 7, 28, 90 and 180 days) in accordance with ISO 4012, EN 12390-8, RILEM CPC 11.3 and ASTM C1202, respectively.

The concrete compressive strength results and Bolomey strength equation, equation 1, have been employed in determining the efficiency factors of nano-VS. Tchamdjou et al. [26], Pekmezci & Akyuz [27] and Kaid et al. [28] have used the Bolomy equation to determine the efficiency factor of natural pozzolan.

\[ f_c = k_b \left( C + k \times VS - 0.5 \right) \]  

where \( f_c \) is the concrete compressive strength (MPa), \( C \) is the cement content in the concrete (kg/m³), \( w \) is the water content, \( VS \) is the nano-VS content (kg/m³) and \( K_b \) is the Bolomey coefficient. \( K_b \) is calculated from the mixture with zero content of nano-VS, \( k \) is the efficiency factor.

In addition, the durability indicators were calculated using equation 2 [26].

\[ DI = \left( \frac{f_c}{f_{ci}} - 1 \right) - \left( \frac{Per_i}{Per_c} - 1 \right) \]  

where: \( f_{ci}/f_c \) & \( Per_i/Per_c \) are the relative compressive strength and the relative permeability-related property of nano-VS-based binder concretes; \( f_c \) and \( Per_c \) are the compressive strength and permeability-related property of the control concrete. The expression “\(-\left(\frac{Per_i}{Per_c} - 1\right)\)” takes into account the negative effect of permeability-related property on the durability. Concrete with positive \( DI \) is considered better than control concrete in the point of durability’ view.

4. Results and discussion

4.1. Development of concrete compressive strength subsection

Figure 3 illustrates the results of compressive strength development with curing age. As shown in figure 3 all concretes containing nano-VS have higher compressive strengths when compared with the control concrete at all w/b ratios and after all curing ages. In addition, the compressive strength of the concrete incorporating nano-VS was significantly enhanced, particularly at early ages. This improvement can be ascribed to the pozzolanic and filling effects of nano-VS. Further, nano-VS particles were not only acting as a filler, but also as an activator to promote hydration if the nano-particles were uniformly dispersed.

In contract to the results of Hakamy et al. [14] and Oltulu & Sahin [16], the addition of nano-VS beyond 1 wt. % into binder has not adversely affected the compressive strength. This can be due to the adopted mixing method by which the nano-VS particles might be well dispersed and no or limited agglomeration has encountered. The compressive strength of the concretes was found to increase as the nano-VS content increased from 1% to 5%. However, No considerable improvement in strength was observed when nano-VS content increased from 3% to 5%.
4.2. Properties of concrete permeability

Figure 4 shows the results of WP for all percentage of nano-VS, curing ages and w/b ratios. For all types of mixtures WP increased with the increase of w/b ratio. WP moved from low to high when w/b increased from 0.4 to 0.7. According to Neville [29], concrete of “WP≤50 mm” can be considered low permeable concrete. Further, WP was significantly reduced, even at early ages, when nano-VS of content ≥ 3% was used. This can be due to the extremely small size of nano-VS particles which can fill the pores and their very high pozzolanic reactivity which leads to a more compacted matrix with more cementing compounds [30].

Figure 5 shows the correlations among the investigated permeability properties. Definite correlations with regression coefficients (R^2) of more than 0.85, were noted among these properties, such that knowledge of one property can be helpful for estimating the other. According to the Montgomery & Peck [31], the relationship can be labelled excellent when R^2 is equal or bigger than 0.85. More parameters such as concrete aggregate type, volcanic scoria type and other curing conditions could be further incorporated for developing similar relationships.
Figure 4. WP results of the concretes made with different w/b ratios and cured for five different curing ages.

4.3. Efficiency factor & durability indicator

The efficiency factors of nano-VS were calculated for each replacement level using Bolomey equation. Figure 6 illustrates the evolution of efficiency factors, k, of all mixes cured for 28 days. As seen in figure 6, with increasing nano-VS content from 1% to 4%, the efficiency of the nano-VS tends to increase and beyond the replacement level of 4%, k-value tends to significantly decrease. This can be probably attributed to the agglomeration of the nano-VS particles at this level of replacement. In addition, no clear behavior was observed with increasing w/b ratio. This requires further investigation to correlate k values with w/b ratio.

Based on the statistical analysis, an equation to estimate the efficiency factor (k) when considering two variables, i.e. curing age and nano-VS content can be written as follows:

$$k = (\alpha_1 \times NVS + \alpha_2) \times \ln t + \alpha_3 \times NVS + \alpha_4$$

where $k$ is the efficiency factor; $NV$ is the percentage of nano-VS; $t$ is the curing age (day); $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ are constants. Based on the regression analysis of the obtained efficiency factors, the constants have been extracted. The best-fit constants $\alpha_1$, $\alpha_2$, $\alpha_3$ and $\alpha_4$ and the regression coefficients ($R^2$) of the relationship between the experimental and the calculated values are depicted in table 1. The results
indicated significant relationships between the nano-VS efficiency factor and the curing age with different contents of nano-VS. The derived equation for predicting the efficiency factor of VS can be fruitfully employed by the concrete mix designers.

![Figure 5](image.png)

**Figure 5.** Relationships among the permeability properties of the investigated concretes prepared with nano-VS.

| w/b ratio | α₁ | α₂  | α₃   | α₄   | R²  |
|-----------|----|-----|------|------|-----|
| 0.4       | 4.56 | -0.9296 | -31.977 | 6.8028 | 0.893 |
| 0.5       | -0.85 | -0.5963 | -10.652 | 5.4786 | 0.822 |
| 0.6       | 1.9  | -0.7144 | -20.172 | 5.8112 | 0.914 |
| 0.7       | 4.78 | -0.7788 | -33.871 | 5.9765 | 0.962 |

**Table 1.** Constants α₁, α₂, α₃ and α₄ and R² values of the relationship between the experimental and calculated efficiency factors based on the derived equation.

![Figure 6](image.png)

**Figure 6.** Efficiency factors of VS-based binder concretes cured for 28 days at different w/b ratios.
Durability indicator values when all investigated properties were taken into account were calculated according to equation 2 and illustrated in figure 7. Figure 7 shows that almost nano-VS4-based cement concretes with w/b≥0.6 exhibited the highest DI values. This means that these concretes performed the best ones when w/b was equal or more than 0.6, when the compressive strength and all permeability-related properties were taken into consideration. This unexpected result can be explained as follows: Increasing the w/b ratio of a concrete mixture results in a larger inter-particle spacing between cement grains and thus formation of more voids can be expected. In the concrete mix prepared with w/b=0.4, fewer voids can be detected within the cement matrix. On the other hand, the mixture prepared with w/b of 0.6 or more will have higher porosity. Therefore, the authors think that the filling effect of nano-VS might be more obvious in the concretes of relatively high w/b ratios. Nonetheless, further investigation is recommended in this direction. Further, as can be clearly seen in figure 7, the highest positive DI values (i.e. more than 1.7) were recorded when nano-VS content was added either at 3% or 4%.

Figure 7. Durability indicators of concretes containing different volcanic scoria contents cured for 28 days when all investigated properties were taken into account.

4.4. Microstructural analysis
The investigated paste samples were micro structurally examined by Scanning Electron Microscope (SEM, VEGA II TESCAN) after being dried, fragmented and rinsed with acetone. Figure 8 shows the SEM micrographs of the pastes prepared with w/b=0.6 and cured for 7 days. A non-compacted structure with a relatively high porosity can be detected in the control sample as shown in figure 8 (a). On the other hand, more compacted structure with fewer voids is detectable in the nano-VS3-based paste, note figure 8 (b). This significant improvement can be due to the more C-S-H and C-A-S-H compounds, formed through the pozzolanic reaction occurring between the vitrified phase of nano-VS and the portlandite produced during the hydration of cement components, namely C3S and C2S. On the other hand, a lower quantity of CH crystals can be seen in the paste containing nano-VS3 when compared with that of zero nano-VS content.

5. Conclusion
The application of nano-VS can be considered as emerging areas of interest in the countries where a lot of scoria cones are available. This paper points out the following:

- The delay in strength improvement of concrete comprising micro-VS can be overcome by adding small dosages of nano-VS. Hence, study on using both micro and nano-VS is highly recommended.
- The permeability properties of concrete can be significantly reduced by adding nano-VS.
- The binders containing nano-VS content of 3% or 4% performed the best among all other binders taking into account the permeability properties, i.e. water permeability, porosity and chloride penetrability. K-value of about 4.5 (for 4% replacement level irrespective of the w/b ratio) can be considered helpful in a future eco-friendly concrete mix design.
Figure 8. Scanning electron micrographs (×5000) of (a) control paste (nano-VS0) and (b) nano-VS3-containing paste cured for 7 days.

- An attempt to derive a prediction formula for estimating the efficiency factor, i.e. k, was carried out by the authors. The effect of curing age and the volcanic scoria content were considered in this estimation. This formula gives a relatively accurate prediction ($R^2 \geq 0.82$) of the efficiency factor at all w/b ratios.
- SEM analysis showed notable densification in the cement paste containing nano-VS. The microstructure of the cement paste containing nano-VS revealed a dense, compact formation of hydration products and a reduced number of CH crystals.
- Addition of nano-VS can be considered a promising approach in the countries where a lot of scoria cones exists. However, some properties need to be further checked.

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